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Dynamic Nuclear Polarization Enhanced Natural Abundance ^{17}O Spectroscopy

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Supporting Information

ABSTRACT: We show that natural abundance oxygen-17 NMR of solids could be obtained in minutes at a moderate magnetic field strength by using dynamic nuclear polarization (DNP). Electron spin polarization could be transferred either directly to ^{17}O spins or indirectly via ^{1}H spins in inorganic oxides and hydroxides using an oxygen-free solution containing a biradical polarization agent (bTbK). The results open up a powerful method for rapidly acquiring high signal-to-noise ratio solid-state NMR spectra of ^{17}O nuclear spins and to probe sites on or near the surface, without the need for isotope labeling.

As one of the most abundant elements on Earth and in the human body, oxygen is ubiquitous in minerals and is a major component in biologically relevant compounds such as organic molecules, peptides and biomolecules. Oxygen-based materials and molecules are of considerable importance in a wide range of technologically relevant areas including ceramics, catalysts and polymers, being intimately involved in bonding and controlling structure and physical properties. As such, the development of methods for their characterization is of fundamental importance.

Solid-state nuclear magnetic resonance (NMR) spectroscopy is one of most powerful analytical techniques available today to investigate the local structure of powdered solids due to its sensitivity at the atomic lengthscale through the interactions of the nuclear spins with their surroundings.[1] Commonly studied nuclei in solid-state NMR include spin $I = 1/2$ nuclei such as ^{1}H, ^{13}C, ^{15}N, ^{29}Si, ^{31}P but also nuclei having a spin larger than 1/2 (quadrupolar nuclei) such as ^{2}H, ^{14}N or ^{27}Al. Oxygen NMR investigations are, however, relatively scarce, because the only NMR-active isotope of oxygen, ^{17}O, is also the least abundant (0.037%) of all of the three isotopes (^{16}O - 99.76%, ^{18}O - 0.2%), making ^{17}O one of the more challenging nuclei to observe by NMR spectroscopy.[2] The quadrupolar nature of this nucleus ($I = 5/2$) also adds to the complexity, as the well-established magic angle spinning (MAS) technique fails to completely remove the second-order quadrupolar broadening,[3] leading to low-resolution spectra. Natural abundance solid-state NMR spectra of ^{17}O are therefore rare and are often associated with poor signal-to-noise (S/N) ratios even when a combination of very high fields, large sample volume, and/or extended acquisition times are used.[2d,h] Isotopic enrichment in ^{17}O is thus required, and samples have to be prepared from extremely expensive ^{17}O-labeled chemicals such as O_2 and H_2O, with often extensive and challenging synthesis procedures, undoubtedly limiting the use of ^{17}O NMR.

High-field dynamic nuclear polarization (DNP)[4] is currently revolutionizing solid-state NMR by enhancing NMR sensitivity by multiple orders of magnitude, using a microwave-induced transfer of polarization from electron to nuclear spins at cryogenic temperatures (4−110 K).[4c,5] Stable radicals such as TEMPO[6] or biradicals, TOTAPOL,[7] bTbK[8] or tCTbK[9] are used as a source of the electrons under aqueous[4c,6] or nonaqueous conditions.[10] Saturation of the electron paramagnetic resonance (EPR) transitions of the radicals results in either polarization enhancement of the abundant ^{1}H spins, which is subsequently transferred to lower γ nuclei such as ^{13}C or ^{15}N by cross-polarization (a process called indirect DNP)[11] or direct polarization of the heteronuclei (direct DNP).[12] Following the pioneering work of Griffin et al.,[4c] DNP NMR has been successfully applied to biologically relevant molecules[13] and more recently in materials science[14] to an increasingly large range of nuclei,[4c,12a,14b,c,15,16] with ^{17}O indirect DNP having only been successfully performed very recently on the simple case of ^{17}O-labeled H_2O.[16] Here we show that natural abundance ^{17}O NMR spectra of inorganic solids can be easily obtained in minutes using either indirect or direct DNP enhanced NMR, solving the intrinsically poor sensitivity of ^{17}O nuclear spins.

The experimental conditions required to observe DNP enhancement are essential to the increase in sensitivity, and we have used an already well-established and robust approach[14a,b] for sample preparation using a solution of biradical bTbK[8] in water-free and oxygen-free 1,1,2,2-tetrachloroethane ($C_2Cl_4H_2$) solvent[10] to wet the inorganic solids (see the Supporting Information [SI]) for details of all samples preparation.

Figure 1a shows the remarkable effect of DNP on the ^{1}H ^{17}O selective CP[17] MAS spectra of Mg(^{17}OH)$_2$ where we observed

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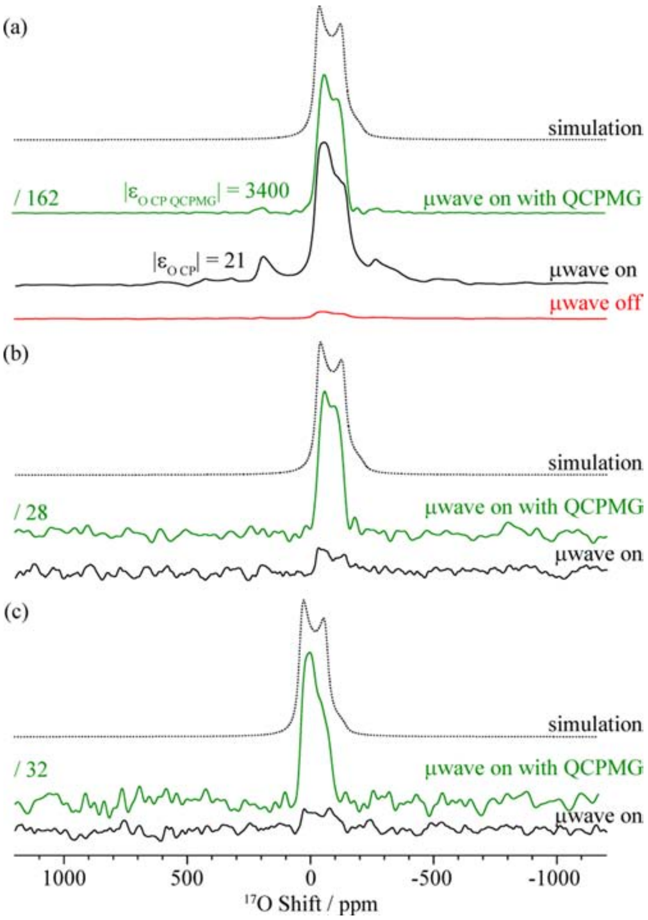

Figure 1. ^{1}H ^{17}O selective CP[17] (full black lines) and CP QCPMG[19] (green lines) MAS spectra of (a) ^{17}O-enriched Mg(^{17}OH)$_2$, (b) natural abundance Mg(OH)$_2$ and (c) natural abundance Ca(OH)$_2$ recorded with microwave irradiation at $\nu_0(e^-)$ = 263.7 GHz. The ^{1}H ^{17}O selective CP MAS spectrum of ^{17}O-enriched Mg(^{17}OH)$_2$ recorded without microwave irradiation is shown in red. All the spectra were recorded at ∼105 K with $\nu_0(^1H)$ = 400.430 MHz and $\nu_0(^{17}O)$ = 54.280 MHz under ν_{rot} = 12.5 kHz and SPINAL-64 ^{1}H heteronuclear decoupling[21] with $\nu_1(^1H)$ = 100 kHz. Sixty-four scans with a 10 s recycle delay were averaged (experimental time = 10 min). The QCPMG spectra shown were processed by first adding all the 60 echoes together followed by Fourier transformation (see SI), and the intensities are scaled as indicated. Samples were wet with 20 mM bTbK[8] $C_2Cl_4H_2$ solution.[10] ε_H, $\varepsilon_{O\ CP}$ and $\varepsilon_{O\ CP\ QCPMG}$ were determined on the ^{17}O labeled samples and were 24, 21, 3400 for Mg(^{17}OH)$_2$ and 17, 17, 4000 for Ca(^{17}OH)$_2$ (see SI), respectively. Central transition simulations for Mg(OH)$_2$[2g] and Ca(OH)$_2$[2e] are shown in black dashed lines (see Figure S3 in SI).

an ^{17}O signal DNP enhancement factor of $\varepsilon_{O\ CP}$ = 21 (determined as $\varepsilon = (I_{DNP} - I_{Boltzmann})/I_{Boltzmann}$ where I_{DNP} and $I_{Boltzmann}$ are the signal intensities with and without microwave irradiation, respectively), demonstrating that the direct ^{1}H polarization enhancement ε_H = 24 (see SI) is efficiently transferred from the solvent to the hydroxide groups of the solid. The observed ^{17}O second-order quadrupolar line shape can be fitted with reasonable agreement to the previously determined quadrupolar parameters of Mg(OH)$_2$.[2g] We also note that the quadrupolar coupling constant in Mg(OH)$_2$ (C_Q = 7.0(2) MHz) is among the largest for ^{17}O,[2a] demonstrating that ^{17}O indirect DNP could be widely applied with the experimental conditions used here (B_0 = 9.4 T and ν_{rot} = 12.5 kHz). It was recently demonstrated that the combination of the CPMG pulse sequence with DNP yields dramatic further improvements of sensitivity.[18] CPMG sequences involving quadrupolar nuclei (QCPMG)[19] are routinely used in solids and make use of the much longer T_2' observed for the typically broad NMR resonances of nuclear spins greater than 1/2. Here, a further signal enhancement of a factor ≈ 160 is obtained (Figure 1a), showing that this is a powerful way to detect the broad signals of insensitive nuclei such as ^{17}O at natural abundance. Under static conditions,[16] dramatic similar enhancements were also observed (Figure S5 in SI), an important finding for quadrupolar nuclei which often give rise to spectra whose line width frequently exceeds the available MAS frequency.

The sensitivity of ^{17}O indirect DNP observed on ^{17}O enriched materials clearly opens the way to collect ^{17}O spectra at natural abundance. Figures 1b and c show the ^{1}H ^{17}O CP and QCPMG MAS spectra of both Mg(OH)$_2$ and Ca(OH)$_2$ at natural abundance, prepared in a similar manner to Mg(^{17}OH)$_2$ discussed above. Each DNP spectrum was acquired in only 10 min with 64 scans and a recycle delay of 10 s. Although ^{1}H ^{17}O CP MAS spectra acquired under microwave irradiation yield barely visible ^{17}O signals (which are not visible above the noise without DNP), the combination with QCPMG produces very intense natural abundance ^{17}O signals.

The fast acquisition of indirect DNP ^{1}H ^{17}O CP QCPMG spectra allows us to collect multidimensional correlation spectroscopy spectra and establish nuclear spin connectivities. Figure 2 shows the 2D ^{1}H ^{17}O CP HETCOR spectrum of Mg(OH)$_2$ at natural abundance (with a 20 mM solution of bTbK[8] in $C_2Cl_4H_2$[10]) using QCPMG trains during signal acquisitions and under microwave irradiation. This spectrum was acquired in less than 30 min with 16 scans and clearly shows that the ^{17}O site in Mg(OH)$_2$ is connected with a ^{1}H signal at about 1 ppm in agreement with the expected shift for an isolated OH$^-$ group.[20] This peak was also observed as a shoulder in the ^{1}H MAS spectrum (Figure 2a), the more intense signal being attributed to the $C_2Cl_4H_2$ solvent.

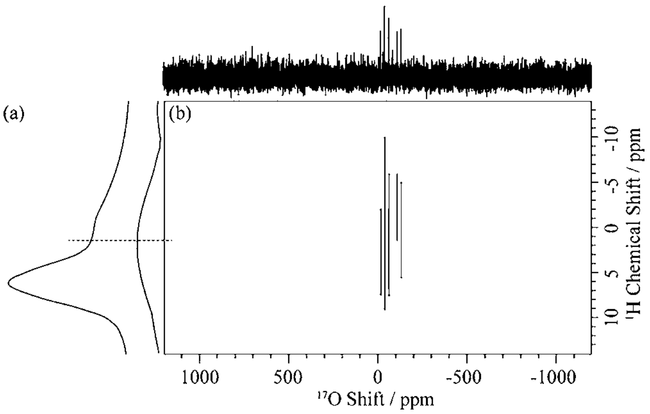

Figure 2. Contour plot of the two-dimensional (2D) ^{1}H ^{17}O CP QCPMG HETCOR spectra of Mg(OH)$_2$ at natural abundance under microwave irradiation at $\nu_0(e^-)$ = 263.7 GHz.[5a] All the others acquisition parameters and sample details are identical to those of Figure 1. A total of 9 t_1 increments of 80 μs with 16 scans and a 10 s recycle delay were averaged (experimental time = 24 min). (a) ^{1}H MAS spectrum. (b) 2D spectrum. Near left: ^{1}H F_1 sum projection of the 2D spectrum. Top: ^{17}O F_2 sum projection.

Many oxides in mineralogy, geochemistry, materials science, and solid-state chemistry are proton free and therefore direct e$^-$ to ^{17}O polarization is desirable. Figure 3a shows the DNP enhancement profile recorded on the ^{17}O-enriched Mg^{17}O sample, wet with a 20 mM solution of bTbK[8] in $C_2Cl_4H_2$,[10] obtained by sweeping the NMR magnetic field strength. The profile has the typical EPR line shape of the bTbK polarizing agent,[8] with a maximum positive and negative enhancement at $\nu_0(^{17}O) = 54.256$ MHz (DNP(+)) and $\nu_0(^{17}O) = 54.143$ MHz (DNP(−)), respectively. The DNP(−) position (corresponding to the low-field side of the EPR line shape) gives a better enhancement than DNP(+) as often observed for direct DNP with biradicals for a cross-effect (CE) mechanism transfer to non-protonic spins.[12,14c] Figure 3b displays the resulting ^{17}O MAS NMR spectra of natural abundance MgO at DNP(−) with and without microwave irradiation recorded in only 8 scans and 16 min. A direct enhancement of $\varepsilon_O = -43$ was observed, and the oxygen signals of MgO are clearly visible. Two signals are detected at 47 and 42 ppm, corresponding to bulk MgO and surface MgO,[2f] respectively, in agreement with the moderately high surface-to-bulk ratio of the small nano particles used here. (The particles were prepared by calcination of $Mg(OH)_2$ leading to MgO particles with a coherence length of ~8(1) nm, as determined from the Debye−Scherer analysis of the XRD patterns; TEM images indicate that the primary particles are 200−400 nm across and 50 nm thick but contain small pores of 5−10 nm in diameter, accounting for the shorter XRD coherence length; see SI for full details). We also note that both bulk and surface sites are enhanced identically (Figure S7 in SI) consistent with the presence of small particles.[22] It is also important to note that the surface site has a larger quadrupolar coupling constant than the bulk MgO site, but this does not appear to affect the enhancement.[2f] One of the advantages of direct DNP is that it could also be potentially combined with sensitivity enhancement methods available for half-integer spins and involving population inversion of the satellite transitions.[23] Using double frequency sweep (DFS),[23b] a further sensitivity of a factor of 4 (out of the theoretical $2I = 5$ for ^{17}O) could be obtained (Figure 3b), yielding high S/N ratio ^{17}O solid-state NMR spectra of natural abundance oxide in a few minutes, that would take more than half a year of experimental time without DNP and DFS.

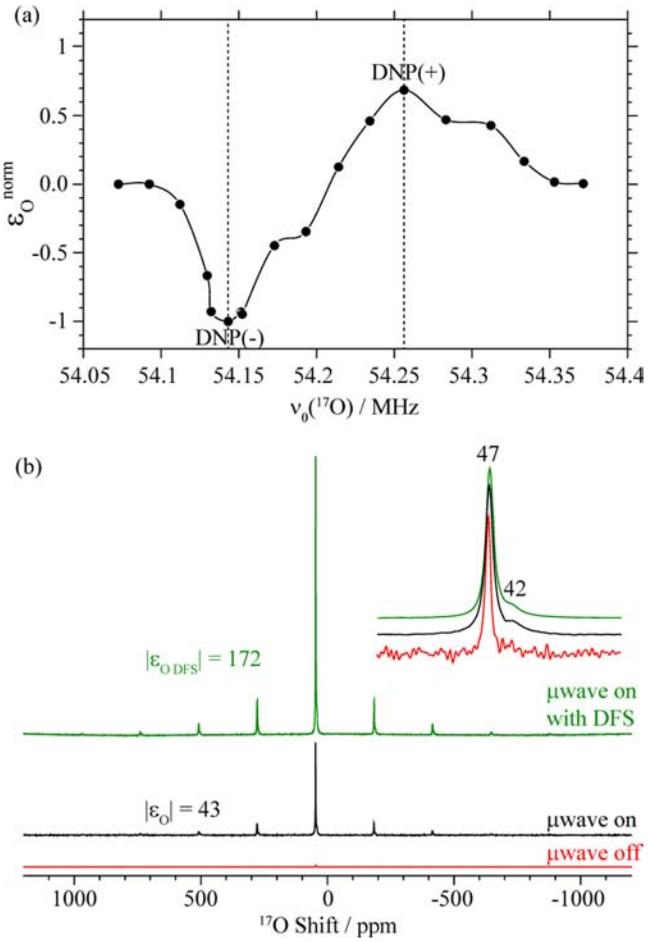

Figure 3. (a) Field-dependent direct ^{17}O DNP enhancement profiles of ^{17}O-enriched Mg^{17}O recorded at ~105 K. Mg^{17}O was wetted with 20 mM bTbK $C_2Cl_4H_2$ solution. The equilibrium Boltzmann ^{17}O polarization was eliminated by presaturation with a train of 100 $\pi/2$ ^{17}O selective pulse separated by 20 μs. ^{17}O rotor synchronized Hahn echo spectra were recorded after a microwave polarization time of 30 s. The DNP enhancements are normalized to $\varepsilon_O^{norm} = \varepsilon_O/|\varepsilon_O^{max}|$, where ε_O and $|\varepsilon_O^{max}|$ are the direct ^{17}O enhancement at each $\nu_0(^{17}O)$ and the maximum direct enhancement, respectively. The optimal positive and negative DNP enhancement positions are given as DNP(+) and DNP(−), respectively. (b) Comparison of the ^{17}O spectra of MgO at natural abundance obtained without DNP (red), with direct DNP (black) and with direct DNP and DFS[23b] enhanced scheme (green), shown at $\nu_0(^{17}O) = 54.143$ MHz (DNP(−) position). Eight scans were averaged with a microwave polarization time of 120 s (experimental time = 16 min). Inset between 70 and 20 ppm shows the MgO central transitions (scaled so that the intensities of the 47 ppm resonances are similar).

In conclusion, we have demonstrated that ^{17}O NMR spectra of oxides and hydroxides at natural abundance (0.037%) can be acquired quickly using DNP. Direct e$^-$ to ^{17}O polarization transfer or indirectly by means of ^{1}H were obtained showing that NMR spectroscopy can be performed on highly insensitive nuclei such as ^{17}O. The application of the approach to examine a wide range of technologically relevant materials can be readily envisaged to examine surface, subsurface and bulk sites.

■ ASSOCIATED CONTENT

Supporting Information

Details of all synthesis, samples preparation, experimental methods, DNP on ^{17}O-enriched materials, XRD patterns, TGA curve, TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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