

Impurity proton NMR signals from common “proton-free” laboratory materials

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Abstract

For the study of small samples (tens of microns cubed) by NMR, impurities from the environment and construction materials (Teflon, Kel-F, glass NMR tubes, etc.) can dominate the signal, in particular for proton NMR. Using pulsed NMR with a resolution of several microseconds, we have studied a number of common construction materials considered to be proton-free and find considerable proton impurity. We present results in terms of impurity proton spins per milligram and discuss procedures to minimize the effects of impurity signal.

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1. Introduction

In an era of the study of nanoscopic, mesoscopic, and microscopic samples, great care must be taken to isolate NMR signals from impurity or unwanted signals arising from the experimental environment, including construction materials. This is a particularly challenging problem for proton NMR, as protons seem to be ubiquitous. We have studied a number of common laboratory materials at liquid nitrogen temperatures, including glass NMR tubes, Teflon, Kel-F, etc., and found that all of these contain protons. Signals from these materials are compared to proton signals in water and epoxies.

Sample sizes for most solid-state NMR experiments are limited only by the region of homogeneity of the static magnet field and RF pulse fields. However, it is becoming more common to study mesoscopic or biological materials in which the size of the sample can be microscopic, presenting a challenge for a generally low sensitivity technique such as NMR. In our case we have been studying samples of solid hydrogen prepared and pressurized in a diamond anvil cell (DAC). Such sam-

ples are limited by the size of the diamond flat: the higher the desired pressure, the smaller the flat. Experiments aiming for the megabar regime might have a nanoliter-scale volume ($\sim 100\text{-}\mu\text{m}$ diameter, $\sim 10\text{-}\mu\text{m}$ thick) at ambient pressure, containing $\sim 10^{16}\text{--}10^{17}$ spins. Despite their small size such samples can be studied by NMR [1,2]. Signals from such samples can be observed without problem using a sensitive NMR spectrometer, however the limiting factors are proton impurity signals in or near the coil and the filling factor. In our research we have been confronted by such challenges for some time. In this article we describe some of the observations and methods that may be useful to the NMR community, as well as quantitative measurements of proton concentrations in a number of laboratory materials.

The first line of defense against impurity signals is to avoid hydrogen-bearing materials and to follow a rigorous cleaning and handling procedure throughout the experiment. But as we report in this work, high sensitivity measurements of ^1H NMR in solid samples can also be compromised by surprising sources of impurities such as so-called “proton-free” insulators and even NMR-grade Pyrex sample holders. Hydrogen impurities are found in many “proton-free” insulating materials.

A second consideration is the RF circuit design which should optimize the filling factor. The desired NMR

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signal is proportional to the sample filling factor defined as

$$\eta = \frac{\int_{\text{sample}} B^2 dV}{\int_{\text{all space}} B^2 dV}, \quad (1)$$

where B is the amplitude of the RF field and the integration is over volume. Clearly if the filling factor has a value of 1, then the RF field will not couple to impurities outside of the sample (in this paper we consider the sample itself to be pure, containing no impurities). However, from the form of the filling factor it is clear that if η is small, then the RF field in the space outside of the sample can contribute to the impurity signal if the static field is reasonably uniform or if the resonance condition is satisfied. For diamond anvil cells Pravica and Silvera [3] improved the filling factor by about a factor of 50 to 0.16, compared to the geometry of Lee et al. [4]. Recent efforts to optimize filling factor with microcoils have achieved substantially higher values and reported absolute sensitivities to $\sim 10^{12}$ spins at room temperature [5].

Stray inductance is an important concern as the coil size diminishes. In a DAC experiment the proximity of the tuning capacitor, and thus the decrease of stray inductance, is limited by diamonds and diamond-mounting hardware required since we cannot use proton-bearing epoxy or cement, as is traditional. Thus for our single-turn coils, stray inductance is comparable to, or larger than, the coil inductance. Further, the leads extend the region of RF pulsing away from the sample, thus allowing a greater chance for resonance of unwanted impurity spins, as discussed generally for the filling factor.

A third consideration is the T_1 and T_2 of the impurities relative to that of the sample. Solid hydrogen relaxes extremely quickly in the transverse direction ($\sim 7 \mu\text{s}$ at liquid helium temperatures). The hydrogen signal decays on a time scale equal to or faster than most impurity signals. Liquid NMR spectroscopy rarely suffers from impurities in solid materials because the T_2 's of liquids are generally much longer than those of impurities. A striking example of this effect can be demonstrated in any typical MRI system optimized for imaging hydrogen in tissue: place an NMR tube filled with Stycast 1266 epoxy in the system. The epoxy with a short T_2 will show practically no signal, and thus no discernible image of the tube. On the other hand, liquid water with a $T_2 \sim 2\text{s}$ will show a clear image of the tube boundary. This occurs because of the fast decay time of the epoxy signal, despite the fact that Stycast 1266 epoxy contains an order of magnitude more hydrogen per unit mass than water. In general, glues, epoxies, and even ceramic adhesives contain substantial densities of hydrogen and should be avoided when the characteristic relaxation time of the sample of interest is short. If the impurity has a T_1 substantially longer than that of the sample, the

influence of the impurity can be suppressed by saturating this contribution.

Given these considerations, it is very useful to know the hydrogen impurity content and relaxation times of “proton-free” materials for use in high sensitivity, fast relaxation NMR experiments, thus the motivation for this work. In the case of DAC experiments, FEP Teflon or Kel-F (polychlorotrifluoroethylene or fluoroethene) are typical construction materials for use near the coil region to insulate the coil windings or to guard against voltage arcing of the coil to the nearby mounting hardware. But to what level are they suitable choices? We have found, for example, that FEP Teflon has measurable impurities, but fewer than “spaghetti tube” Teflon (wire insulation). Kel-F appears to be one of the best choices [6]. Alumina, containing waters of hydration, showed measurable impurity signal, as previously discussed by Pravica and Silvera [3]. NaCl is of interest because it has been used as a gasket insulator [2], with the successful use of NaCl mixed with diamond powder to fill a slit in the sealing gasket, adjacent to the sample and part of the coil.

Proton-free adhesives would be very useful as construction materials. Epoxies are loaded with protons, but ceramic adhesives might be possible proton-free bonding agents. Typically the binders for such adhesives are proton-bearing, and even if not, the ceramic powder itself may contain waters of hydration, such as in Cotronics' Resbond 919 adhesive. Surprisingly, pyrex NMR tubes themselves, commonly used as NMR sample holders show measurable impurity signals. Capacitors, too, deserve a closer look as they are frequently soldered very close to the coil in high sensitivity NMR experiments and likely contain waters of hydration. Lastly, for interest, we measured both Stycast 1266 and Lord 305 epoxies, confirming a high density of hydrogens that is greater even than that in water.

Methods of preparation of some of these materials can play an important role in reducing the level of impurities. For example, baking a ceramic adhesive after curing drives off hydrogen impurities. Where water is called for to cure a ceramic adhesive, D_2O can be used instead to try to produce a suitable proton-free epoxy.

2. Experimental setup and procedures

We tested various insulators at liquid nitrogen (LN_2) temperature using a 27.5 mg H_2O (ice) sample as a standard for comparison. Samples were loaded into an NMR tube of 5-mm diameter and sample volumes were kept constant at $\sim 50\text{mm}^3$ to minimize variations in filling factor. Each new sample was placed in the cryogenic environment with care not to introduce impurities from the air. In all cases the procedure was to measure the dipolar spin echo [7]. The peak of any given echo is

proportional to the number of spins in the sample, but transverse and longitudinal relaxation variations must be accounted for between samples. We varied the pulse delay time τ to extrapolate the signal to zero time, essentially a T_2 measurement. Owing to the typical 1 s longitudinal relaxation times, and for efficiency's sake, some samples were measured at times faster than T_1 to obtain T_2 and then later corrected by means of a T_1 measurement. This also had the useful effect of partially saturating the pyrex tube signal ($T_1 \sim 10$ s) for most sample measurements. Some systematic error was introduced by this procedure, for which we have accounted with our reported errors. Our philosophy was to measure many samples to see if they had impurity proton signal, rather than to measure a few with timely high precision measurements of T_1 and T_2 , ultimately required to determine the impurity concentration with high precision. This is based on the observation that precision is not useful when the content of proton impurity can vary from sample to sample of say Teflon, depending on the source, type, etc.

Data were taken in a 5.2-T modest-homogeneity superconducting magnet, with ^1H resonance frequency at 221.7 MHz. The experiment was performed at ~ 80 K to enhance sensitivity relative to room temperature. Samples were cooled by LN_2 boiloff from an LN_2 bath filling the bottom of the cryostat and the temperature was monitored. Temperature variations were small for most samples, but were accounted for in all cases by normalizing to 80 K in the analysis.

The NMR spectrometer is homebuilt with high sensitivity quadrature detection. Digitization and signal averaging were performed with a Tektronix 520 TDS oscilloscope. The pulse sequence used in all cases was the $\pi/2(x) - \tau - \pi/2(y)$ dipolar echo. The maximum echo was determined for the test H_2O sample and resulted in $\pi/2 = 1 \mu\text{s}$, indicating $H_1 \sim 60$ G. The receiver bandwidth was set to ± 500 kHz and maintained throughout the experiment. Pulse power was maintained constant to within 5% or better for the duration of the experiment and pulses were kept constant at $1 \mu\text{s}$. Samples were not temperature controlled, but were monitored with a thermometer. To increase sensitivity and maintain the shortest leads possible to the coil, only fixed ceramic capacitors were used to make the circuit resonance. The experiment was designed for only LN_2 temperature, and thus the magnetic field could be ramped to match the Larmor condition once the temperature and circuit resonance were stable. The circuit resonance shifted by less than 200 kHz over the duration of the entire experiment, which was well within the intrinsic circuit and receiver bandwidths. The tank circuit had a $Q = 100$ and receiver ringing decreased to the level of the spectrometer noise at $\sim 10 \mu\text{s}$ after a pulse. Values of 2τ were varied typically from 20 to 200 μs , and repetition times for spin-lattice relaxation measurements

varied from 50 ms to 10 s. H_2O , with a T_1 of 10 min, required longer delays. All spin-lattice relaxation values were obtained by progressive saturation where at least three repetitions were performed to set up a steady-state signal prior to signal averaging and acquisition.

The sample probe was a leak-tight stainless steel tube that fit through an ultra-torr seal in the flange at the top of the cryostat. As shown in Fig. 1, at the end of the stainless steel tube was a connecting brass rod and a Teflon cap designed to accept a standard 5-mm NMR pyrex tube. The insert could be simply and reproducibly inserted into the cryostat without disturbing the RF circuit, therefore greatly increasing the efficiency and reliability of the measurements. During all insertions and removals, a steady overpressure of N_2 gas was maintained inside the cryostat, preventing water or other impurities from entering the sample region. The NMR tube was cut to a length of 22 mm, long enough so that any suspected ^1H impurities in the Teflon sleeve were well outside the coil region. This was verified by measuring the circuit background signal when the insert was in place but without the NMR tube. No increase in signal above the circuit background was measured. The entire tank circuit was ultrasonically cleaned *in situ* with acetone, hexanes, and methanol, sequentially.

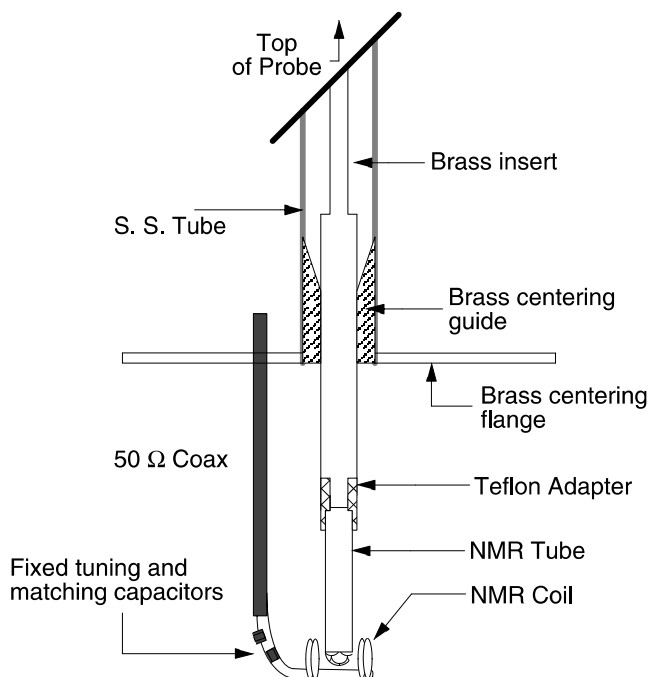


Fig. 1. Assembly for making consistent measurements of multiple samples at liquid nitrogen temperature. Note that only the NMR tube and sample are removed and reinserted between measurements, guaranteeing the same coil geometry and placement for each measurement. The insertion rods and NMR tube were fully warmed by heat gun to room temperature before re-insertion to eliminate any condensation.

The tank circuit was mounted for low temperature operation in the superconducting magnet bore. A helmholtz coil allowed the NMR sample tube to fit between the two halves of the coil. The sample was guided into the exact center of the coil by means of tapered guides inside a stainless steel shaft (see Fig. 1). The height was maximized by the signal from the H₂O sample, both for homogeneity in the magnetic field and for the best location of the sample within the coil. This height was then marked and used as the location for all the test samples. The 6-turn, 1/8-in. diameter coil had a calculated inductance of $\leq 0.05 \mu\text{H}$, and the room-temperature circuit resonance was achieved at 222.5 MHz with fixed matching and tuning capacitors in a parallel-tuned, series-matched arrangement. All tank circuit components were within 5 cm of the coil to minimize power loss into the leads, but separated from the coil by at least 2 cm to avoid the possibility of impurity ¹H contamination. Based on matching and tuning capacitance of ~ 0.5 and 5.0 pF respectively, we calculate an additional stray inductance of $\sim 0.05 \mu\text{H}$ as the result of lead lengths required to keep impurity-bearing capacitors away from the coil. Variable tuning and matching were unnecessary for this experiment as all measurements were carried out at fixed temperature. Circuit tuning shifted down by $\sim 1 \text{ MHz}$ at LN₂ temperature compared to room temperature, while circuit matching changed only minimally. Tuning was monitored throughout the experiment and seen to change by less than 200 kHz over the duration of the experiment. A 50- Ω resistor near the sample region, but far enough away to avoid introducing impurities, was used as a pickup antenna to monitor pulse power to the coil. No breakdown voltage (arcing) was ever encountered, and pulse power to the coil varied by less than 5% over the duration of the experiment.

3. Results and analysis

The preparation and quantity of the various samples studied are given in Table 1. There was a measurable circuit background signal (with no sample or NMR tube in place) despite in situ ultrasonic cleaning with hexanes, acetone, and methanol. In addition it was found during the course of the experiment that the NMR tube itself contained a measurable impurity signal. For all samples, the results were corrected for the NMR tube background signal. The circuit background had negligibly small effect owing to its extremely fast T_2 ($\leq 15 \mu\text{s}$). Only the alumina and Lord 305 had similar T_2 values, in which case the magnitude of signal from those samples was much larger than the background, even for the longest 2τ values. Examples of the spin echo decay times for selected samples are shown in Fig. 2.

After correcting for T_1 , slight temperature variations, and the NMR tube background, the zero-time extrapolations of the T_2 decays were normalized to the mass and magnitude of the zero-time signal of water, resulting in a measure for the number of ¹H spins per milligram of sample for each insulator. This is represented in Fig. 3, where we show the measured signal (top), and the resulting spins/mass (middle). In the bottom panel of Fig. 3 we show for interest the “effective” spins per milligram for a given delay time between the RF pulses, taking into account the T_2 's we measured. It is instructive to see that for all samples even a delay time of $300 \mu\text{s}$, and certainly for $1000 \mu\text{s}$, the effect of the hydrogen impurities measured here are negligible by many orders of magnitude. Most samples do not even appear on the graph for $2\tau = 1000 \mu\text{s}$. We have indicated with dotted lines the region between 3×10^{16} and 3×10^{22} to show the “window” of total number of spins for most NMR experiments.

Table 1
Samples studied, preparation details, and sample quantities

Sample	Preparation	Mass (mg)	Spins/mg
H ₂ O	Tap water	27.5	$6.7\text{e} + 19$
Circuit impurities	Ultrasonic clean		
Pyrex 5-mm NMR tube (superior brand)	Cut to 22-mm length; Ultrasonic clean	55 (estimated mass in coil)	$2.2\text{e} + 17$
NaCl 1	Crystals; no bake	38	$4.8\text{e} + 17$
NaCl 2	Crystals; baked to 500 °C	54	$4.4\text{e} + 17$
KEL-F	Flakes	30	$6.4\text{e} + 17$
FEP Teflon	Flakes	54.5	$4.5\text{e} + 17$
Spaghetti Teflon	Flakes	40.5	$1.3\text{e} + 18$
Teflon sheet 0.005 in. thick	Flakes	23	$1.6\text{e} + 18$
Resbond 919 ceramic adhesive, Cotronix	Powder, baked to 500 °C; prepared with heavy water (D ₂ O)	34.5	$2.4\text{e} + 18$
Al ₂ O ₃	Powder	10	$1.0\text{e} + 19$
PTFE Teflon	Flakes	54.5	$6.8\text{e} + 17$
Lord 305 epoxy	1:1 mix by weight; 1-mm size pieces	21	$4.9\text{e} + 21$
ATC chip capacitors	Chip capacitors	57	$1.0\text{e} + 18$
Stycast 1266 epoxy, Emerson and Cummings	100:28 mix by weight; 1-mm size pieces	19.5	$1.8\text{e} + 21$

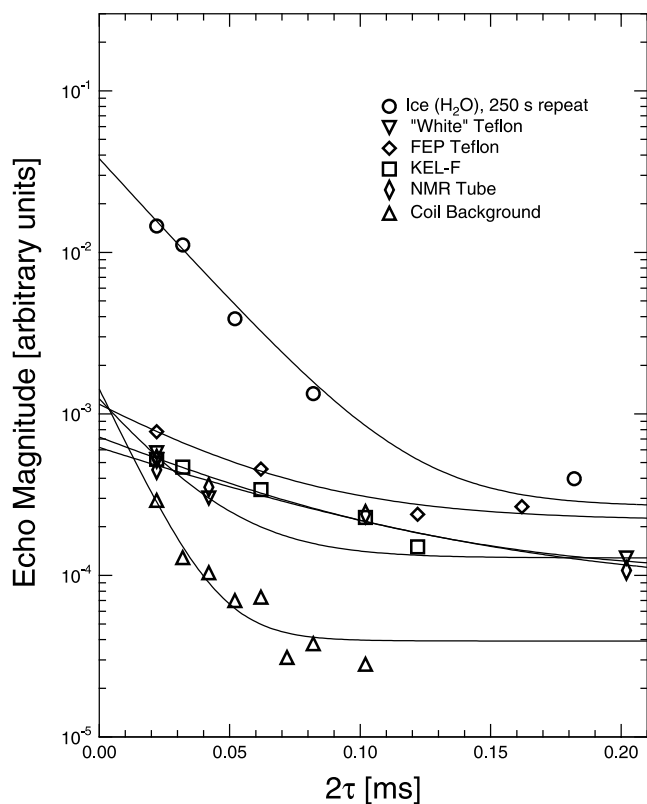


Fig. 2. Spin-echo decays for selected samples, including the NMR tube and water calibration sample. The measured T_2 allow extrapolation of signal to zero time and determination of the spin concentration shown in Fig. 3. Note the circuit background signal decays to negligible values at short time values. The NMR pyrex tube exhibited a surprisingly large background signal and longer transverse relaxation, requiring its subtraction from the rest of the data. Curvature of exponential fits on the log plot is the result of allowing a nonzero baseline parameter.

The transverse relaxation times of all the samples here are $\leq 100 \mu\text{s}$, (aside from the NMR tube, which was $\sim 200 \mu\text{s}$), explaining why they have been successfully used as “proton-free” materials for decades in standard proton NMR experiments. Most chemistry and life science applications of proton resonance allow for millisecond relaxation times or longer, placing the signal from these hydrogens well below the sample of interest. The materials studied here were chosen expressly for their generally accepted proton-free reputation, which may or may not be true, as we have shown. For example, in [5], epoxy was used to mount the microcoils, yet they did not suffer from problems of impurity signals.

In all cases the signal resonated at the same location in frequency as the water signal with typical broad linewidths consistent with T_2 being $\leq 100 \mu\text{s}$. The NMR tube signal was narrower ($\sim 20 \text{ kHz}$) compared to the other samples, a result of its longer T_2 . The T_2 of water was measured to be $25 \mu\text{s}$, consistent with the linewidth of ice at 77 K previously reported [8,9]. In addition to its fast T_2 relaxation, the circuit background signal had a faster T_1 than our fastest repeat times of 50 ms, thus eliminating

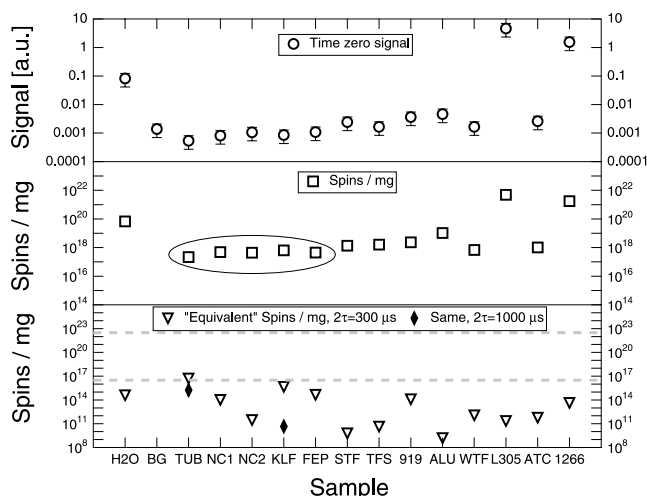


Fig. 3. (top) Absolute signal, not normalized, from hydrogen impurities in arbitrary units. Note measurable background (BG) for the NMR coil alone. (middle) Number of ^1H impurity spins per milligram (square symbols) of common laboratory insulators, measured at 80 K (bottom). “Effective” spins per mg at $2\tau = 300 \mu\text{s}$ (triangles) and $1000 \mu\text{s}$ (diamonds). For the latter only values above the 10^8 level are shown; all others are lower. Dotted lines indicate, in absolute spin count (not spins per milligram) the typical sample sizes of most high resolution chemical or biological samples (upper dotted line) as compared to the sample sizes we measure in a DAC experiment (lower dotted line). The circuit background source is unknown, therefore no mass measurement applicable. The mass of the NMR tube was estimated from the fraction located within the coil volume. From left to right: H_2O tap water; NMR coil (background); NMR pyrex tube; NaCl crystals without high temperature bake; NaCl baked at 500°C ; KEL-F (polychlorotrifluoroethylene); FEP Teflon; Teflon insulating tube (“spaghetti” Teflon); Teflon sheet (0.005 in. thick); Resbond 919 ceramic adhesive, baked at 500°C and activated with heavy water (D_2O) and subsequently baked at 500°C ; Al_2O_3 baked at 500°C ; Polytetra-fluoro-ethylene (PTFE) Teflon (standard “white Teflon”); Lord 305 two-part epoxy (mixed 1:1 by weight); American Technical Ceramics (ATC) ceramic chip capacitors; and Stycast 1266 epoxy by Emerson and Cummings, two-part epoxy 100:28 mix of parts A to B by weight. The best choices for low spin impurity count are circled, although we emphasize the effect of the long T_2 in the NMR tube.

water (ice) condensation as the origin of the impurity signal. As discussed above, our experimental procedures were quite rigorous to prevent water vapor from entering the cryostat; nonetheless liquid nitrogen dewars are known to collect ice buildup that could enter during a nitrogen transfer, a possibility that we have ruled out based on the background signal’s T_1 . Last, we note that the circuit background signal had a T_2 of $\sim 13 \mu\text{s}$ with a larger frequency spread of $\sim 150 \text{ kHz}$. This points to the possibility we were measuring impurities from several monolayers of residue, perhaps left from the ultrasonic bath on the coil itself, resulting in fast relaxation at the surface. From Fig. 2 we see only one component of relaxation, so multiple sources of impurities are ruled out to within the accuracy of the data. In any case, the coil background signal relaxation time combined with the overall low signal magnitude made its effect negligible for most samples.

4. Conclusions

We find that all the insulators chosen for this study, comprising a reasonable representation of “proton-free” materials, contain nontrivial amounts of hydrogen impurities. Only three of our samples, KEL-F, FEP Teflon, and NaCl are suitable for use in and around the coil region for ^1H NMR experiments on small solids with short relaxation times. Even those insulators contain $\sim 10^{17}$ ^1H spins/mg, which puts constraints on the amount and location of such a material that can be used in the sample region. Other materials, such as standard PTFE Teflon in sheet or rod form, epoxies, and ceramics are only suitable if the experiment dynamics allow for characteristic sample spin echo times much longer than the ≤ 100 μs time scales reported here for the impurities.

Acknowledgments

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