



Communication

Magic-angle spinning solid-state multinuclear NMR on low-field instrumentation



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ABSTRACT

Mobile and cost-effective NMR spectroscopy exploiting low-field permanent magnets is a field of tremendous development with obvious applications for arrayed large scale analysis, field work, and industrial screening. So far such demonstrations have concentrated on relaxation measurements and lately high-resolution liquid-state NMR applications. With high-resolution solid-state NMR spectroscopy being increasingly important in a broad variety of applications, we here introduce low-field magic-angle spinning (MAS) solid-state multinuclear NMR based on a commercial ACT 0.45 T 62 mm bore Halbach magnet along with a homebuilt FPGA digital NMR console, amplifiers, and a modified standard 45 mm wide MAS probe for 7 mm rotors. To illustrate the performance of the instrument and address cases where the low magnetic field may offer complementarity to high-field NMR experiments, we demonstrate applications for ²³Na MAS NMR with enhanced second-order quadrupolar coupling effects and ³¹P MAS NMR where reduced influence from chemical shift anisotropy at low field may facilitate determination of heteronuclear dipole–dipole couplings.

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1. Introduction

Along with maintained strong focus on high-field NMR spectroscopy, the past few years have witnessed a considerable interest in the development of low-field NMR instrumentation for low-cost, mobile, and screening NMR applications [1,2]. A variety of low-field NMR instruments have recently been developed for relaxation measurements [3–7], magnetic resonance imaging [8–11], and lately also high-resolution liquid-state NMR spectroscopy [1,11–14]. The instrumentation involves many different sources to the fundamental magnetic field, including earth field devices [15–17], low-field permanent magnets in single-sided setups [4,12,18–20], arrays of cubic magnets [21,22], and cylindrical Halbach [11,14,23–25] geometries. In combination with advanced digital FPGA (Field Programmable Gate Array) based rf consoles [26–29], such instrumentation has found applications in diverse areas such as geology, mining, and cement chemistry [5,30–34], food science and control [35–38], chemical synthesis [39,40], as well as clinical-oriented disease screening [7,41–43]. The obvious advantage of low-field NMR is instrumentation cost, mobility and

robustness, while spectral resolution/dispersion and sensitivity are remaining challenges. The sensitivity challenge has recently been addressed through combination with dynamic nuclear polarization [44] and parahydrogen [45] hyperpolarization technology.

In this paper, we demonstrate that a simple combination of a commercial low-field Halbach magnet with a homebuilt FPGA digital rf console, amplifiers, and a standard MAS probe offers the possibility to perform low-field high-resolution solid-state multinuclear MAS NMR spectroscopy. Such instrumentation may have interesting industrial applications, as well as scientific applications where different scaling of field-dependent nuclear spin interactions may offer complementary insight to that obtained using standard instrumentation at higher magnetic field strengths. The latter applies to chemical shift (isotropic and anisotropic) interactions, which scale linearly with the magnetic field, and to second-order quadrupolar couplings which scale inversely to the field, while dipole–dipole couplings and quadrupolar coupling interactions to first order remain invariant with respect to the external field. Such aspects are here illustrated by determination of the ²³Na quadrupolar coupling parameters for NaNO₃ from the second-order MAS NMR powder pattern for the central transition (CT) and by determination of the ³¹P–¹⁹F dipole–dipole coupling

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for $\text{K}_2\text{PO}_3\text{F}$ using ^{31}P MAS NMR, taking advantage of the reduced influence from the ^{31}P chemical shift anisotropy (CSA) at low field.

2. Methods

The low-field solid-state NMR spectrometer (illustrated in Fig. 1a) was assembled using the components listed in (i)–(vi) below. (i) A commercial 0.45 T (19 MHz ^1H frequency) tomograph Halbach magnet (Fig. 1a) was purchased from ACT (Aachen, Germany). The magnet material SmCo has a temperature coefficient of -300 ppm/K (see also Fig. 1f) and is arranged in a cylindrical Halbach type design with a horizontal bore of 62 mm, and the direction of the magnetic field perpendicular to the bore axis. In the present applications the magnet was operated without additional shims beyond the native configuration of the magnet. In this configuration, the MAS probe with its 7 mm o.d./5 mm i.d. rotor (sample volume of 220 μl) produces a line width (Full Width at Half Maximum) of $\text{FWHM} = 1$ ppm for a single-scan ^1H spectrum of H_2O (i.e., $\text{FWHM} = 19$ Hz) in a rotating sample. (ii) A Nanonord (Aalborg, Denmark) broadband, single channel, digital rf console with FPGA and Digital Signal Processing (DSP) units on a 10×16 cm² board, which operates at a sampling frequency of 25 MHz. (iii) A high-power amplifier (400 W, $10 \times 22 \times 4.5$ cm³) and a preamplifier have both been designed and built in-house and the latter implemented on the console board. (iv) Crossed diodes and quarter lambda stubs for simple passive transmit/receive switching are also homebuilt. (v) A PC with interface for data processing and user-friendly control of the spectrometer has been programmed in MATLAB[®] for these purposes. (vi) An old prototype 7 mm Varian 400 MHz narrow-bore (45 mm) MAS probe, which was modified years ago in our lab with an improved homebuilt 7 mm ceramic MAS stator and a double-tuned rf coil for high-field CP/MAS NMR, has been brought into use again. To achieve the low-field operation of 19 MHz for ^1H NMR and additional lower-field X-nuclei operations, the probe has now been further modified by introducing a new double-tuned rf coil wound on a PEEK (Poly-Ether Ether Ketone) support with a 0.5 mm thread pitch and 20 turns of 0.25 mm copper wire (Fig. 1b). With this setup quality factors of 39 and 52 are obtained for ^{31}P (7.7 MHz) and ^1H (19 MHz) on the low- and high-field rf channel, respectively. The probe is tunable for other frequencies, e.g. ^{79}Br (4.77 MHz), by inserting chip capacitors.

Because the direction of the magnetic field is orthogonal to the bore direction, the standard magic-angle adjustment is supplemented with an additional device for angle adjustment, which controls the rotation of the probe (see Fig. 1c and d). Rotation of the probe is important because the range of the original angle-setting mechanism is insufficient for the probe and its rotor sample to be aligned in a plane, which includes the directions of both the magnet bore and the magnetic field axes. Thus, adjustment of the exact magic-angle is performed by rotation of the original MAS-angle setting for the probe by $\sim 45^\circ$. The MAS probe employed 7 mm PSZ (Partially Stabilized Zirconia) rotors, as mentioned above with a wall thickness of 1 mm for the present applications, and spinning frequencies (ν_r) within the range $\nu_r = 4.3$ – 4.8 kHz (stable within ± 20 Hz without rotor control) using air pressures of 2.6 and 1.25–1.5 bar for the air-bearing and -drive, respectively. The magic angle has been set employing ^{79}Br MAS NMR for a sample of KBr [46], primarily by a $\sim 45^\circ$ rotational adjustment of the probe, followed by minor touches of the ordinary, homebuilt precise MAS-angle adjustment device in the probe. This procedure results in a $\text{FWHM} = 157$ Hz (incl. 20 Hz of Lorentzian line broadening) for the centerband in the ^{79}Br spectrum shown in Fig. 1e and f. Considering the “additional non-shimmed” B_0 inhomogeneity of the ACT Halbach permanent magnet, this value agrees well with the typical

value of ~ 140 Hz observed at higher fields of 7–14 T in our laboratories.

To account for the temperature dependence of the field drift for the permanent magnet, scans are averaged with correction for the drift. An algorithm that performs two separated post-processing schemes of the same data is applied to the averaged data, collected in blocks of 1–10 min, where the time period depends on the stability of the local temperature and the intrinsic line width of the resonances. First, a drift curve, representing the drift for the time of each block, is obtained through peak positions of the Fourier transform of an average of several blocks around the block and with a large line broadening (100–500 Hz for the cases presented here) to achieve a sufficient SNR. The obtained drift curve from this moving average is then smoothened. Second, the original blocks are Fourier transformed with low (or no) line broadening and summed employing the shifts from the drift curve, whereby the final spectrum is achieved.

To account for a severe probe ringing with a ring-down time ($T_{\text{ring-down}}$) of about 100 μs (as determined from an experimental FID without a sample according to the expression $A \cdot \exp(-t/T_{\text{ring-down}})$) caused by the low resonance frequencies, we applied either: (i) a rotor-synchronized Hahn echo [47] experiment with suppression of ringing from both rf pulses by a 4-step phase cycle (phase of first pulse: $x, -x, x, -x$, second pulse: x, x, y, y , and receiver: $x, -x, -x, x$) or (ii) a single-pulse experiment with subtraction of the first 960 μs of the FID for a data set obtained without a sample in order to eliminate effects of the ring-down in the spectral FIDs. We note that there is still visible ringing in the FID (without a sample) after about 500 μs , which is comparable in size to the low-intensity NMR signal.

All simulations were performed using the open-source simulation program SIMPSON [48,49], where also the definition of the internal interaction parameters ($C_Q, \eta_Q, \delta_{\text{aniso}}, \eta_{\text{CS}}, b/2\pi$) used in this work can be found. We note, using this approach, that the internal nuclear spin interactions are formulated in the high-field approximation which is valid here considering the field and the spin systems studied. For the ^{31}P simulations we used powder averaging of 30–168 sets of REPULSION [50] α, β crystal angles and 8–16 γ angles, whereas 232 ZCW [48] angle pairs and up to 128 γ angles were used for the ^{23}Na simulations.

3. Results and discussion

Fig. 2a shows the low-field 5.03 MHz ^{23}Na MAS spectrum for $\nu_r = 4.5$ kHz of the CT for a powder sample of NaNO_3 which exhibits a clearly visible second-order quadrupolar line shape. Fig. 2b illustrates a simulation of the ^{23}Na second-order line shape for the CT using the earlier reported parameters, $C_Q = 337$ kHz, $\eta_Q = 0.0$, determined from a satellite transition (ST) spectrum [51]. An excellent agreement between the experimental and simulated spectrum is observed. Fig. 2c shows an expansion for the CT, as obtained from a simulation of the complete ^{23}Na MAS spectrum (CT and STs) at 105.8 MHz (9.4 T), and it is noted that the second-order line shape is not resolved at high field strength. The inset in Fig. 2d shows a simulation of the complete ^{23}Na MAS spectrum (with a cut-off of the CT). It is evident that low-field applications are particularly interesting in cases where the line shapes or spinning sideband (ssb) patterns are influenced by other interactions such as chemical shift anisotropy (CSA) or as a supplement to high-field measurements through exploitation of the field-dependent scaling of different interactions.

As an example of the reduced influence on the CSA interaction at low field, Fig. 3 shows experimental and simulated low/high-field ^{31}P MAS NMR spectra of Brushite (calcium hydrogen phosphate dihydrate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) considering the CSA parameters

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