



## High-field QCPMG NMR of large quadrupolar patterns using resistive magnets

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### ABSTRACT

Spectroscopy in a high magnetic field reduces second-order quadrupolar shift while increasing chemical shift. It changes the scale between quadrupolar and chemical shift of half-integer quadrupolar spins. The application of QCPMG multiple echo for acquiring large quadrupolar pattern under the high magnetic field of a 25 T resistive magnet is presented for acquiring large quadrupolar patterns. It shows that temporal field fluctuations and spatial homogeneity of the Keck magnet at the NHMFL contribute about  $\pm 20$  ppm in line broadening. NMR patterns which have breadths of hundreds to thousands of kilohertz can be efficiently recorded using a combination of QCPMG and magnetic field stepping with negligible hindrance from the inhomogeneity and field fluctuations of powered magnets.

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### 1. Introduction

The application of high magnetic fields in NMR is well known to enhance both sensitivity and resolution. Given that present day Nb<sub>3</sub>Sn superconducting magnets are approaching a limit of about 22 T, the viability of performing NMR experiments with resistive and hybrid resistive/superconducting magnets which can generate higher magnetic fields is of great interest. Magnetic field inhomogeneity and temporal fluctuations present the major obstacles to using these powered magnets and tend to cause line broadening on the order of kilohertz, which prohibits most attempts at acquiring high-resolution NMR spectra. Nonetheless, a number of studies have been reported using Bitter resistive magnets and hybrid resistive/superconducting magnets with magnetic fields of up to 45 T [10,43,39,47,52,24,41] and pulsed magnets reaching up to 70 T [21,15]. Most recently, <sup>1</sup>H line widths of < 40 ppb have been achieved using a 25 T resistive magnet [13], showing great promise for future high-resolution applications.

There is growing interest in the investigation of quadrupolar nuclei in non-spherically symmetric chemical sites which give rise to NMR patterns spanning hundreds to thousands of kHz, so called wideline spectra. This interest stems largely from the sheer ubiquity of quadrupolar nuclei, which represent ~75% of the NMR-active nuclei in the periodic table and hence constitute integral components of many industrially and biologically

relevant substances [31,32,51,37,27,26,12,11,9,44]. Many quadrupolar nuclei (nuclei with spin quantum numbers > 1/2) tend to exhibit poor sensitivity due to their low gyromagnetic ratios and natural abundances. Additionally, quadrupolar nuclei possess electric quadrupole moments which interact with electric field gradients causing distribution of the signal over a large frequency range. In this context, the major disadvantage of using powered magnets can be negligible, since line broadening due to the external field inhomogeneity and fluctuations is minor compared to the broadening due to the internal quadrupolar interaction. Instead the high magnetic field narrows the wide quadrupolar pattern making it easier for acquisition. The high fields also increase the chemical shift anisotropy if that is the parameter of interest.

The CPMG sequence [7,33] has been adapted for signal enhancement of quadrupolar nuclei resulting in the so-called quadrupolar Carr–Purcell Meiboom–Gill (QCPMG) experiment [23]. Using the QCPMG sequence, the magnetization is refocused repetitively giving rise to a train of echoes, which when Fourier transformed yields a set of spikelets with a manifold resembling the conventional powder pattern. Since all the intensity is allocated into sharp spikelets, a large gain in signal is obtained at the expense of some resolution, which is dictated by the spikelet separation. The QCPMG pulse sequence has been applied on numerous occasions to facilitate the acquisition of highly unresponsive nuclei [17,48,45,25,36,28]. The rapid cyclical refocusing of the CPMG sequence makes it an ideal experiment for application in powered magnets due to its reduced sensitivity to field inhomogeneity and temporal fluctuations. Indeed, the

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robustness of the CPMG sequence is evidenced by its application in the field of well-logging, where magnetic field gradients are severe due to the nature of sampled environments and their position outside the magnet [14,18]. Furthermore, acquisition of high-resolution solution NMR spectra using the CPMG sequence in inhomogeneous fields has previously been shown [24].

The excitation bandwidth of rf pulses is usually limited to a range of approximately a couple of hundred kHz by currently achievable rf amplitudes and the Q factor of NMR probes. Therefore, for patterns with breadths greater than the excitation bandwidth, the full spectrum must be reconstructed from segments acquired at different offset frequencies [31,32,17,45,19,1,29]. Recently, attempts at overcoming excitation bandwidth limitations for quadrupolar nuclei have been reported which include the use of microcoils [53,38,46] or frequency-swept pulses [46,34,35,2]. In particular, the combination of either of these techniques with QCPMG seems to hold much potential [46]. A distinct advantage of employing powered magnets for the acquisition of wide-line spectra is the ability to change magnetic field rapidly providing the convenience of field stepping rather than frequency stepping, which requires re-tuning of the probe circuitry.

Solid-state  $^{35}\text{Cl}$  NMR is a powerful structural characterization tool which yields patterns very sensitive to even slight changes in the  $^{35}\text{Cl}$  environment [37,4,8,3,5,6,16]. Indeed, in combination with quantum chemical calculations, the sensitivity of  $^{35}\text{Cl}$  NMR to hydrogen-bonding networks [4,8] can even aid the refinement of proton positions in the crystal structure [5]. Furthermore, different pseudopolymorphs and polymorphs of  $\text{SrCl}_2$  [3] and various HCl salts of local anesthetics [16] show very distinct differences and can be identified with  $^{35}\text{Cl}$  NMR. Recently, the study of metallocene chloride samples have helped deduce the structure of Schwartz's reagent ( $(\text{C}_5\text{H}_5)_2\text{ZrHCl}$ ) for which a diffraction structure has not been obtained [37]. In this work, we use a series of metallocene dichloride samples  $\text{Cp}_2\text{MCl}_2$  {M=Ti, Zr, Mo, W; Cp= $\text{C}_5\text{H}_5$ } to demonstrate the viability of investigating samples with spectra spanning very broad frequency ranges using powered magnets.

## 2. Experimental

Samples of  $\text{Cp}_2\text{MCl}_2$  {M=Ti, Zr, Mo, W; Cp= $\text{C}_5\text{H}_5$ } were purchased from Strem Chemicals, Inc. and used without further purification. NMR experiments at 25 T were carried out on the Keck resistive magnet at the NRMFL described previously [41,13] using a Tecmag Discovery console. A 830 MHz narrow bore magnet equipped with a Bruker DRX console was used to acquire spectra at 19.6 T. The Larmor frequency of  $^{35}\text{Cl}$  is 81.6 MHz at 19.6 T and 104.0 MHz at 25 T. A single-resonance home-built probe using a 4.0 mm Samoson MAS stator was used for all experiments. Parafilm plugs were used to restrict the sample volume to approximately the middle 5 mm of the rotor, as well as to minimize the exposure of samples to air and moisture.

Experiments were recorded using a modified QCPMG sequence  $\{p1_{(\varphi_1)} - \tau_1 - [\tau_2 - p2_{(\varphi_2)} - \tau_2 - \tau_{a(Rx)}]_n\}$  with pulse phases  $\varphi_1 = Rx = \{+x, -x\}$  and  $\varphi_2 = \{+y\}$  [23,2], for which acquisition begins from the first full-echo rather than the top of the first echo. For experiments at 25 T on the  $\text{Cp}_2\text{MCl}_2$  samples,  $\tau_1$  was set to half of  $\tau_a$  ( $=112 \mu\text{s}$ ) to position the echoes in the middle of each acquisition period, and  $\tau_2$  was set to  $16 \mu\text{s}$  to minimize the effects of probe ringing. Pulse widths of  $p1=2.7 \mu\text{s}$  and  $p2=3.4 \mu\text{s}$  were employed (corresponding to pulses selective for the central-transition with flip angles of  $90^\circ$  and  $113^\circ$  to obtain a broader excitation bandwidth) with a rf nutation frequency of 46.3 kHz and spectral width of 1.0 MHz for all samples. The complete

powder patterns were obtained by summation of segments acquired by stepping the external magnetic field in intervals of 0.048 T, which correspond to 200 kHz steps in frequency. The number of echoes  $\times$  transients acquired for each segment of the  $\text{Cp}_2\text{MCl}_2$  {M=Ti, Zr, Mo, W} spectra was  $163 \times 256$ ,  $327 \times 256$ ,  $81 \times 2048$  and  $81 \times 2048$ , respectively. A 1.0 s recycle delay was used for  $\text{Cp}_2\text{ZrCl}_2$  and 0.5 s for the rest of the samples.

Experiments acquired at 19.6 T for  $\text{Cp}_2\text{ZrCl}_2$  and  $\text{Cp}_2\text{TiCl}_2$  employed parameters similar to those employed at 25 T, with the major exception being that spectral segments were acquired by stepping the transmitter frequency instead of the applied magnetic field. Frequency stepping was also used for  $\text{Cp}_2\text{MoCl}_2$  and  $\text{Cp}_2\text{WCl}_2$ ; however, acquisition was performed using the recently reported WURST-QCPMG pulse sequence [35] to reduce the number of spectral segments required. WURST-80 pulses [22] of  $50 \mu\text{s}$  with sweeps of 900 kHz and a rf nutation frequency of 17.3 kHz were employed. WURST-QCPMG was not applied at the higher magnetic field due to the inability of the pulse programmer to generate the fast phase modulation necessary for the shaped pulses. All spectra were externally referenced by setting the  $^{35}\text{Cl}$  resonance of a  $\text{NaCl}(\text{aq})$  solution to  $\delta_{\text{iso}}=0.0$  ppm. During processing, each of the echoes in the QCPMG fid was reduced to 100 complex points prior to Fourier transformation, resulting in a 10 kHz separation between spikelets. The transverse relaxation decay was sufficiently long in all cases to yield considerable signal enhancement using the QCPMG experiment even without heteronuclear  $^1\text{H}$  decoupling.

## 3. Magnetic field temporal fluctuations and spatial homogeneity

The temporal fluctuation and spatial homogeneity of the Keck magnet is expected to be the major hindrance to performing routine solid-state NMR experiments. Fig. 1 shows the  $^{35}\text{Cl}$  NMR signal of  $\text{NaCl}(\text{aq})$  at 10 s intervals. The line width is broadened to about 3 ppm by a combination of static inhomogeneity and power supply noise and hum. Previous studies have reported that the field also fluctuates at the line frequency of 60 Hz and its lower harmonics, and a 1440 Hz component from the pulsed rectifier used in the power supply. The resonance frequency is also seen to vary over a range of approximately  $\pm 20$  ppm over the course of

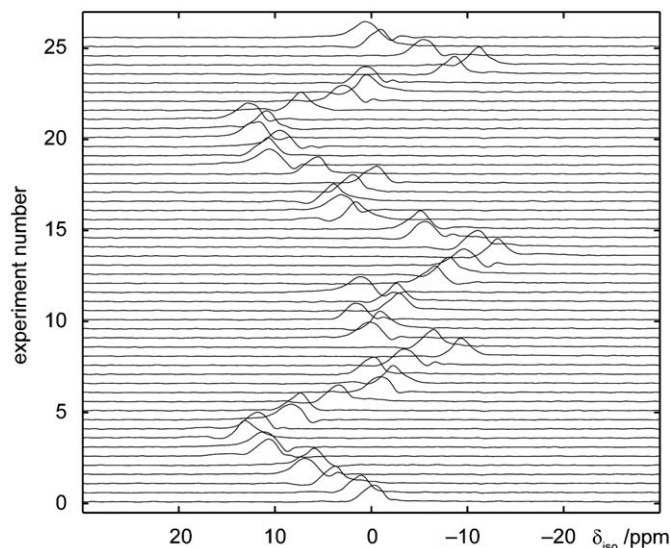


Fig. 1. Array of  $^{35}\text{Cl}$  NMR spectra of a  $\text{NaCl}$  aqueous solution acquired at 10 s intervals, illustrating variation of the applied magnetic field over a time frame of approximately 260 s.

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