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Revisiting NMR composite pulses for broadband ^2H excitation

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Abstract

Quadrupolar echo NMR spectroscopy of static solids often requires RF excitation that covers spectral widths exceeding 100 kHz, which is difficult to obtain due to instrumental limitations. In this work we revisit four well-known composite pulses (COM-I, II, III and IV) for broadband excitation in deuterium quadrupolar echo spectroscopy. These composite pulses are combined with several phase cycling schemes that were previously shown to decrease finite pulse width distortions in deuterium solid-echo experiments performed with two single pulses. The simulations and experiments show that COM-II and IV composite pulses combined with an 8-step phase cycling aid in achieving broadband excitation with limited pulse width distortions.

Keywords

Quadrupolar Echo; Deuterium; Composite pulses; Phase cycling

1. Introduction

In solid-state Nuclear Magnetic Resonance (NMR), deuterium quadrupolar echo spectroscopy is a powerful tool for investigating structure and dynamics. This method allows for measuring quadrupolar coupling parameters from static powder patterns facilitating the study of dynamics, hydrogen bonding, ligand identification and chemical exchange in a variety of systems.^[1-4]

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Although the quadrupolar couplings of spin-1 ^2H nuclei are far smaller than those of most half-integer spin nuclei, their values (typically in the range of $C_Q = e^2qQ = 50\text{--}180\text{ kHz}$)^[5,6] are comparable with the maximum RF field strength that can be achieved by modern NMR probes. Therefore, high RF fields for efficient excitation are strongly desired to cover the wide spectral widths encountered in deuterium experiments. To uniformly excite the wide spectral widths, several composite pulses have been developed.^[7-11] Siminovitch et al. have also adapted a composite pulse approach to reduce the RF field requirements in the deuterium quadrupolar echo experiments.^[12] In their study, four different composite 90° pulses (COM-I, II, III and IV) were compared and analyzed. In addition, T.M. Barbara has shown how phase distortions may be manifested in composite pulses due to finite pulse width effects.^[13]

However, the issue of phase cycling was not addressed in these two works.^{[12] [13]} Recently, a new analysis showed the importance of phase cycling both the pulses and the receiver for suppressing spectral artifacts due to finite pulse widths.^[14] Indeed, in the case of quadrupolar echo using two single pulses, the evolution of the spin system under both RF and quadrupolar interactions was shown to give rise to spectral distortions that may be decreased by phase cycling.

In this paper, we revisit the previous four composite pulses (COM-I, II, III and IV) and we combine them with the 8-step phase cycle developed for deuterium quadrupolar echo experiments.^[14] Numerical simulations and experiments were performed to investigate the performances of these composite pulses with a 2-, 4- or 8-step phase cycling scheme. It is shown that the 8-step phase cycling minimizes the distortions, which allows for accurate line-shape measurements.

2. Simulations

The basic principle of the conventional two-pulse quadrupolar echo sequence is shown in Fig.1. The quadrupolar interaction is refocused by the two 90° pulses and an echo is formed at time τ_2' after the second pulse (Fig.1a). As the signal does not need being recorded immediately after the second pulse, the instrumental limitation imposed by the finite recovery time of the receiver and probe ringing effects may be overcome. In this sequence, the nuclear spins evolve under both the RF and the quadrupolar interaction, which are often of comparable sizes, hence leading to a distorted echo occurring at τ_2' , which is often different from the delay τ_1' in between the two pulses.^[15] In practice, the signal is sampled after the second pulse, before the echo peak, and is then left shifted in order to place the first data point at the peak of the echo before Fourier transformation.

The composite 90° pulses studied in this paper, denoted as COM-i ($i = \text{I-IV}$), are shown in Table 1. Here, we have always used two identical composite pulses in each sequence. The origin of the quadrupolar dephasing is always close to the center of each RF excitation period. Since the durations of these composite pulses are different, the echo spacings τ_1' and τ_2' have to be calculated to retain the same magnetisation evolution time, τ_1 , for each composite pulse which can be expressed as

$$\tau_1' = \tau_1 - t_p^{tot} \quad (1)$$

$$\tau_2' \approx \tau_1' + t_p^{tot}/2 = \tau_1 - t_p^{tot}/2 \quad (2)$$

In the above expression τ_1 is fixed in each experiment and t_p^{tot} is the total length of single or composite 90° pulses. Under these conditions the echo delay τ_1' is shortest in the case of COM-III due to the fact that the total length of this composite pulse lasts for $t_p^{tot} = 12t_{90}$, where t_{90} corresponds to the nominal 90° pulse length for the quadrupolar echo sequence with single 90° pulse (referred as SP). The other composite pulses lasts $t_p^{tot} = 3t_{90}$, $6t_{90}$, and $6t_{90}$ for COM-I, COM-II, and COM-IV, respectively.

The 8-step phase cycling scheme developed for spin-1 quadrupolar echo spectroscopy,^[14] shown in Table 2, has been used for the current study. We have also compared the results obtained with this full 8-step phase cycling with those achieved with the 2- and 4-step phase cycling consisting of the first 2 and 4 steps shown in Table 2.

Simulations of powder sample spectra were carried out using the Spin-Evolution software^[16] with 501,500 (α_{CL} , β_{CL}) polar angles defining the quadrupolar tensors with respect to the laboratory frame, which were selected according to the ASG algorithm to profit of its interpolation procedure.^[17] In the simulations, we have introduced a static field of 9.395 T (61.402 MHz for ^2H) and two deuterium atoms with $\eta_Q = 0$, $C_Q = 48$ or 160 kHz, and the same orientation of the quadrupolar tensor. Both 1st- and 2nd-order quadrupolar terms were always taken into account, except in Fig.1b where the spectrum was simulated with 1st-order only to be shown as a reference. Dipolar coupling and chemical shift anisotropy were ignored in these simulations, as they are much smaller than the dominating quadrupolar coupling. For each simulated spectrum, the signal was sampled with a dwell time of $3\mu\text{s}$ directly after the second single or composite 90° pulse, and then left-shifted to place the first data point at the top of the echo before Fourier transformation.

We show in Fig.1b the spectrum simulated using two ideal 90° pulses with only the 1st-order quadrupolar interaction taken into account; both pairs of horns are then equally intense. For each pair, the separation is equal to $0.75C_Q(1 - \eta_Q)$, thus leading to 36 and 120 kHz in the figure.^[18] However, when the 2nd-order quadrupolar terms are taken into account, the spectrum becomes asymmetric (Fig.1c), as always observed experimentally, especially at low magnetic fields.

Fig.2 shows the echo spectra simulated using two composite or single 90° pulses with $\nu_1 = 40$ kHz and with (Fig.2a) or without (Fig.2b) the 8-step phase cycling. The figure shows that the peaks of all the spectra obtained with this 8-step phase cycling scheme are more symmetric than those without phase cycling, due to the fact that the finite pulse width effect is better suppressed. COM-II and -IV yield spectra with a flat baseline, and the feature of the left outer edge (as indicated by an arrow) is more apparent with COM-II. We also note that using two 90° single pulses (SP) leads to poor excitation of the deuterons having a large C_Q value, as the intensities of the outer horns at ± 60 kHz are then almost three times smaller

than with composite pulses. These results indicate that proper phase cycling is important to suppress the finite pulse width effects in quadrupolar echo experiments with both composite and single pulses, and that moderate RF fields may achieve efficient excitation with the composite pulses.

3. Experimental

Experiments were performed at room temperature on a Bruker Avance III 7.046 T spectrometer operating at a ^2H Larmor frequency of 46.051 MHz. Perpetuated palmitic acid ($\text{PA-}d_{31}$) sample was purchased from Cambridge Isotopes and was packed into a 4 mm rotor, but experiments were performed with a static sample. The spectra were collected by accumulating 1000 scans with a recycle delay of 16 s and a dwell time of 1.6 μs . The RF amplitude (ν_1) and magnetisation evolution time (τ_1) are indicated in the figure captions. Suitable left shifting was applied before Fourier transformation.

The choice of the phase cycling was analyzed by comparing the spectra recorded with an incomplete 2- or 4-step phase cycling and the complete 8-step phase cycling scheme (Fig.3) using the moderate RF field of $\nu_1 = 35.7$ kHz. Two overlapping powder patterns are observable, with $\eta_Q = 0$ and a splitting of 41 and 125 kHz. These two deuteron sites correspond (i) to the methyl group associated with motional averaging and (ii) to the chain species experiencing the largest quadrupolar interaction, respectively. Based on these splitting values the quadrupolar couplings for the two sites were determined to be $C_Q = 55$ and 167 kHz, respectively.

We found that the resulting powder patterns are more symmetric using the 8-step phase cycling rather than the two incomplete phase-cycling schemes. However, this improvement is less apparent in the case of COM-II and -IV. Comparing these two composite pulses, the symmetry of the outer horns is slightly better with COM-II. With COM-III, both horns are distorted which may be related to larger finite pulse width effects related to the longer composite pulse duration. We note that with COM-I, the signal corresponding to $C_Q = 55$ kHz is reduced in the center of the spectra compared with the echo signal recorded with two single pulses, which has also been observed in a previous study.^[12] We also note that the single pulses lead to poor excitation of the spins having the largest quadrupolar coupling constant, as the intensity of the outer horns at ± 60 kHz is almost three times smaller than with composite pulses, which is consistent with our simulations.

Referring to Fig.3a and 3b with the 2- and 4-step phase cycling (first 2 and 4 steps of Table 2, respectively), a pair of artifacts is introduced for COM-II, -III and -IV at the frequency of ± 85 kHz (as indicated by an arrow for COM-III), and several burs in the center of the spectra are also present. These artifacts and small dips are removed by employing the 8-step phase cycling (Fig.3c), resulting in spectra with much smoother inner horn and baseline without artifacts. All these results confirm that adapting the 8-step phase cycling results in undistorted composite pulse quadrupolar echo spectra. Globally, we found that COM-II and -IV, with a slight advantage for COM-II, performed the best among the four different composite pulses investigated.

To analyze in more details the efficiency of composite pulse excitation, we implemented the quadrupolar echo sequence with COM-II and -IV and with single 90° excitations, using the 8-step phase cycling scheme under different RF fields, as shown in Fig.4.

With the weak RF field of $\nu_1 = 18$ kHz, only one species can be observed using two single pulses (Fig.4a). However, the signal arising from the large quadrupolar interaction related to chain deuterons may be also observed using COM-II and -IV. Although the powder pattern is then distorted, this weak RF field may facilitate the analysis of temperature sensible protein systems, since it is possible to estimate the C_Q values from these distorted spectra.

With the moderate RF field of $\nu_1 = 35.7$ kHz, the signal of the outer horns is still weak using two single pulses (Fig.4b). The central part of the powder pattern is smoother with COM-II and -IV, while it looks flat with the single pulses (as indicated by an arrow).

With the large RF field of $\nu_1 = 62.5$ kHz, artifacts are encountered as shown in the dashed box of Fig.4c. These additional artifacts might be due to higher phase transients and probe ring-down effects associated with higher RF field, which may be only partially compensated by the 8-step phase cycling.

4. Conclusions

In this work we have reported on the performance of composite pulses in deuterium quadrupolar echo experiments. Simulations and experiments have confirmed that finite pulse width effects are partially removed by proper phase cycling. It is shown that COM-II and -IV are superior to the other composite 90° pulses studied as they reduce the requisite RF fields for uniform excitation, but also give undistorted spectra without baseline artifacts. COM-III was found to yield a distorted powder pattern due to its much longer pulse duration. Our results show that the full 8-step phase cycling is robust in cancelling undesired terms that contribute to spectral distortions and should be applicable for quadrupolar echo spectroscopy based on composite pulses.

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Fig.1.

(a) The quadrupolar echo pulse sequence investigated in this work. In the experiment, the echo is formed at τ_2' after the second 90° pulse. Simulated ^2H quadrupolar echo using two ideal 90° pulses with 1st- only (b) or with both 1st - and 2nd-order (c) quadrupolar interactions taken into account are shown as references for the simulation section. In the ideal case of (b), the echo is not distorted and is formed at $\tau_2' = \tau_1'$ after the second 90° pulse.

Fig.2.

Quadrupolar echo spectra simulated with two single (SP, black), COM-I (red), COM-II (green), COM-III (blue), and COM-IV (purple) 90° pulses using either an 8-step phase cycling scheme (a) or without phase cycling (b). In these simulations, the RF field amplitude was set to $\nu_1 = 40$ kHz, with $\tau_1 = 100$ μ s.

Fig.3.

Quadrupolar echo spectra of PA- d_{31} acquired using 2- (a), 4- (b) and 8-step (c) phase cycling scheme with two single (SP, black), COM-I (red), COM-II (green), COM-III (blue), and COM-IV (purple) 90° pulses. The RF field was $\nu_1 = 35.7$ kHz and $\tau_1 = 100$ μ s. δ_{2H} denotes the isotropic chemical shift in the unit of kHz.

Fig.4.

Quadrupolar echo spectra of PA- d_{31} acquired using 8-step phase cycling scheme with two single (SP, black), COM-II (green) and COM-IV (purple) pulses. The RF field was $\nu_1 = 18$ (a), 35.7 (b), 62.5 (c) kHz, and $\tau_1 = 180$ (a), 100 (b), 60 (c) μs , respectively. When decreasing the rf field (ν_1), the delays were adjusted to ensure that $\tau_1' = \tau_1 - t_p^{\text{tot}} > 0$.

Table 1

The four composite 90° pulses used to replace the two single 90° pulses in the quadrupolar echo sequence in Fig.1. Nominal pulse flip angles are given in degrees and a bar denotes a 180° phase shift. The total pulse length, t_p^{tot} , is given as a function of the nominal 90° pulse length, t_{90} .

Sequence	Composite 90° pulse	t_p^{tot}
COM-I	$135\ 90\ 45$	$3t_{90}$
COM-II	$90\ 180\ 90\ 135\ 45$	$6t_{90}$
COM-III	$135\ 180\ 90\ 135\ 45\ 90\ 180\ 90\ 135$	$12t_{90}$
COM-IV	$135\ 180\ 90\ 135$	$6t_{90}$