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Composite pulses for efficient excitation of half-integer quadrupolar nuclei in NMR of static and spinning solid samples

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ABSTRACT

Composite pulses of the type $(\tau_p)_x(2\tau_p)_{-x}(3\tau_p)_x$ allow one to excite the central transition of nuclei with half-integer spin with enhanced efficiency compared to a simple $(\tau_p^{sp})_x$ pulse. The method has been tested on solid samples containing sodium-23 ($I = 3/2$), aluminium-27 ($I = 5/2$) and scandium-45 ($I = 7/2$) under both static and magic-angle spinning conditions. Numerical simulations for $I = 3/2$ indicate that the enhancement is due to a more efficient conversion of Zeeman population differences associated with the satellite transitions to the central transition.

1. Introduction

Sensitivity is no doubt the Achilles' heel of NMR spectroscopy. This is inevitably due to the small population differences between the Zeeman energy levels when an external magnetic field lifts their degeneracy [1]. In the solid state, the resulting weak signals may be further compromised by the dispersion of frequencies caused by anisotropic interactions [2]. This is particularly true for quadrupolar nuclei, which represent the vast majority of NMR-active spins. The quadrupolar interaction, which cannot be fully removed by magic-angle spinning (MAS) because of second-order terms, is often very large and results in a severe lack of spectral resolution and, consequently, in weak signal-to-noise ratios [3]. Several methods have been proposed to partially overcome these intrinsic limitations that affect the acquisition of NMR spectra of quadrupolar nuclei in the solid state. Most proposed approaches achieve signal enhancement of the central transition (CT) $m_I = +1/2 \leftrightarrow m_I = -1/2$ of nuclei with half-integer spin ($I \geqslant 3/2$) through the selective *rf*-manipulation of the populations of the Zeeman eigenstates [4–23]. This *preparation* step is then usually followed by a *selective excitation* of the CT. Clearly, if the populations of the satellite transitions (STs) $m_I = \pm 1/2 \leftrightarrow m_I = \pm 3/2$ can be driven away from their equilibrium values, an enhanced population difference across the CT can be obtained. These population-transfer techniques achieve signal enhancement of the CT via inversion or saturation of the STs [24]. In contrast to these earlier approaches, this Letter focuses on an *excitation* process that does *not* require any preparation step. We present a new recursive composite scheme [25] comprising non-selective 'hard' pulses of the form $(\tau_p)_x(2\tau_p)_{-x}(3\tau_p)_x \ldots (n\tau_p)_{\pm x}$, where τ_p is the time length of the first pulse, $3 \leqslant n \leqslant 7$, and the phase of the last pulse is $+x$ or $-x$, for odd or even values of n, respectively. This may be regarded as an unusual form of time-dependent amplitude modulation where the modulation frequency decreases with time. A regular phase alternation $\pm x$ at intervals τ_p would generate sidebands at $\omega = \omega_{rf} \pm 1/\tau_p$, and larger intervals $n\tau_p$ would cause the sidebands to move closer together to $\omega = \omega_{rf} \pm 1/(n\tau_p)$. Neither picture applies to our excitation scheme, where the *rf* phase oscillates with increasing time steps. This achieves signal enhancement of the CT without *preliminary* manipulation of the populations of the ST. Our method achieves an efficient excitation of the CT single-quantum coherence (SQC) and minimizes ST SQC as well as spurious coherences of higher orders which necessarily occur during a single pulse. Given that the *rf*-manipulations are much shorter than in previous approaches (μs instead of ms), we refer to our excitation scheme as COMPACT-*n* (Composite Pulses Adapted for Central Transitions), *n* being the number of pulses.

2. Simulations

In order to explore the excitation profile of the various populations and coherences during a composite pulse, numerical simulations have been carried out for a quadrupolar spin $I = 3/2$ with the SIMPSON program [26]. We make use of irreducible spherical tensor operators $T_{l,p}$ [27], of rank l and coherence order

Abbreviations: CT, central transition; ST, satellite transition; SQC, single-quantum coherence; TQC, triple-quantum coherence.

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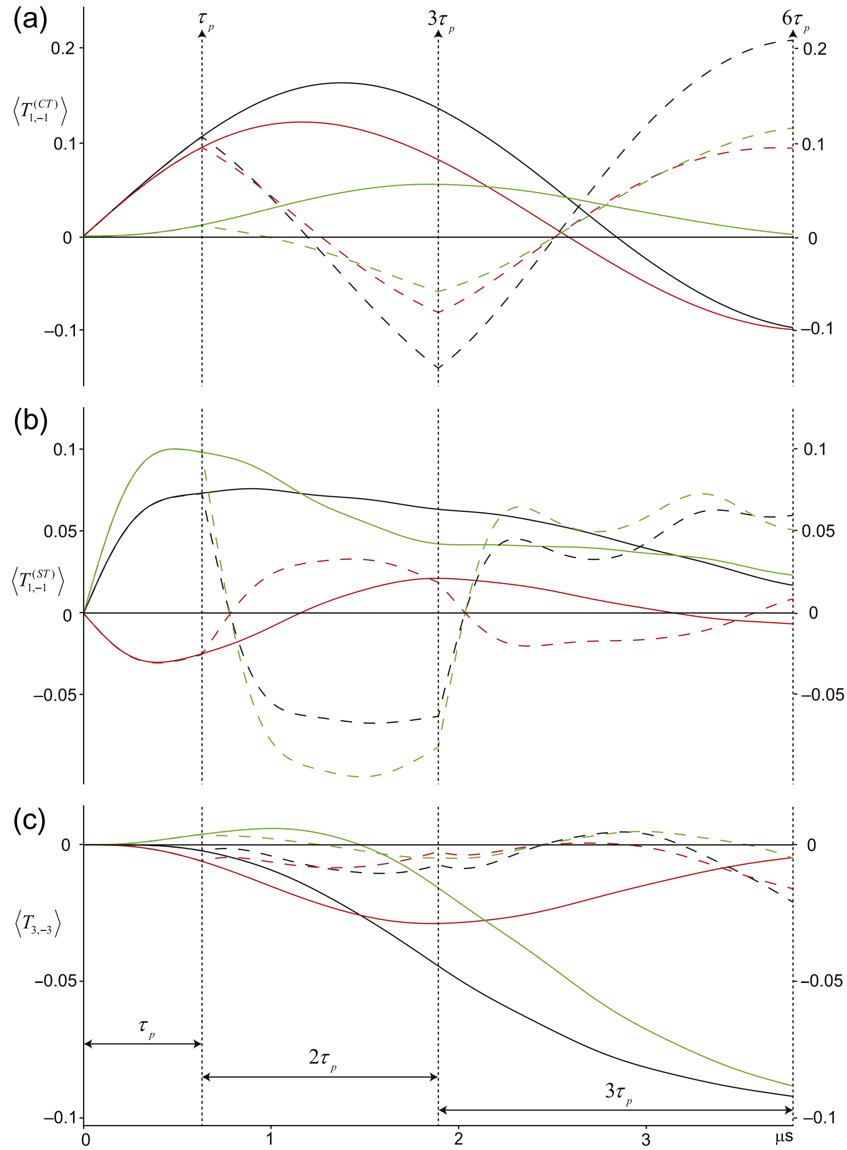

Figure 1. Numerical simulations of the expectation values of the single-quantum coherences (SQC) associated with the central transition (CT) and the satellite transitions (ST) of a spin I = 3/2: (a) $T_{1,-1}^{(CT)}$, (b) $T_{1,-1}^{(ST)}$ and (c) the triple-quantum coherences (TQC) $T_{3,-3}$ during a single pulse of duration τ_p^{sp} (continuous lines) and during a composite COMPACT pulse with $n = 3$ (dashed lines) for $0 < t < 6\tau_p$. In black, red and green, different initial states $T_{1,0}$, $T_{1,0}^{(CT)}$ and $T_{1,0}^{(ST)}$, respectively, were considered. The vertical lines indicate the phase reversals during the composite pulse. The length of the first pulse was $\tau_p = 0.63$ µs. The *rf* field strength was $\omega_1/(2\pi) = 100$ kHz. The offset or chemical shift was $\omega_I/(2\pi) = 0$ Hz, the quadrupole coupling constant $C_Q = 3$ MHz and the asymmetry parameter $\eta_Q = 0.5$. The spinning frequency was $\omega_R/(2\pi) = 10$ kHz. Simulations were run for 256 crystallite orientations and 3 γ angles.

Table 1
Expectation values of $T_{1,-1}^{(CT)}$, $T_{1,-1}^{(ST)}$ and $T_{3,-3}$ at the end of a single pulse and after a composite COMPACT-3 pulse. In the case of the single pulse, the expectation values of the three operators shown in bold indicate the maxima that are achieved at the corresponding pulse widths.

Pulse length (µs)	$\langle T_{1,-1}^{(CT)} \rangle$	$\langle T_{1,-1}^{(ST)} \rangle$	$\langle T_{3,-3} \rangle$
Single pulse			
$\tau_p^{sp} = 0.89$	0.138	**0.076**	−0.007
$\tau_p^{sp} = 1.39$	**0.163**	0.071	−0.022
$\tau_p^{sp} = 3.78$	−0.097	0.017	**−0.092**
COMPACT-3			
$6\tau_p = 3.78$	**0.208**	0.060	−0.021

p. The operator $T_{1,-1}$ corresponds to observable (in-phase) single-quantum coherence (SQC), and $T_{3,-3}$ describes triple-quantum coherence (TQC). It is convenient to decompose the single-quantum operator $T_{1,-1}$ into $T_{1,-1} = T_{1,-1}^{(CT)} + T_{1,-1}^{(ST)}$, where $T_{1,-1}^{(CT)}$ corresponds to the CT and $T_{1,-1}^{(ST)}$ to the sum of the STs. Furthermore, we decompose the Zeeman order $T_{1,0}$ into $T_{1,0} = T_{1,0}^{(CT)} + T_{1,0}^{(ST)}$ and consider these two terms separately as initial operators, so as to monitor how the populations of the Zeeman eigenstates contribute to the creation of coherences (off-diagonal elements). The following tensor operators can be detected if the signal is defined to be $s(t) = \mathrm{Tr}[T_{l,p}\sigma(t)]$ with $l = 1$ and $p = -1$:

$$T_{1,-1}^{(CT)} = \frac{1}{\sqrt{10}}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad T_{1,-1}^{(ST)} = \frac{1}{\sqrt{10}}\begin{pmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix} \tag{1a}$$