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Communication

Spectral editing in solid-state MAS NMR of quadrupolar nuclei using selective satellite inversion

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Abstract

A sensitivity enhancement method based on selective adiabatic inversion of a satellite transition has been employed in a $(\pi/2)_{CT}$–$(\pi)_{ST_1}$–$(\pi/2)_{CT}$ spectral editing sequence to both enhance and resolve multisite NMR spectra of quadrupolar nuclei. In addition to a total enhancement of 2.5 times for spin 3/2 nuclei, enhancements up to 2.0 times is reported for the edited sites in a mixture of rubidium salts.
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Keywords: Quadrupolar nuclei; Sensitivity enhancement; Inversion; Spectral editing; Satellite inversion

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Rotor assisted population transfer (RAPT) is a method [1,2] for enhancing the solid-state NMR central transition (CT) sensitivity of half-integer quadrupolar nuclei by transferring populations from the (unobserved) satellite transitions (ST) through selective saturation of the satellite transitions. An improved RAPT sequence using Frequency-Switched Gaussian pulses (FSG-RAPT) was later designed [3] to provide not only a more robust experimental enhancement but also the ability to measure quadrupolar coupling constants, C_q. This approach combines the sensitivity advantage of the central transition with the C_q measurement precision advantage of the satellites. The dependence of the FSG-RAPT enhancement on offset frequency for nuclei with different C_q values was also exploited to design the $(\pi/2)_{CT}$–RAPT–$(\pi/2)_{CT}$ and RAPT–$(\pi)_{CT}$–RAPT–$(\pi/2)_{CT}$ schemes, for the selective excitation or suppression, respectively, of nuclei with large quadrupolar couplings [4]. These methods, specifically $(\pi/2)_{CT}$–RAPT–$(\pi/2)_{CT}$, have been successfully utilized to understand the complex structure of Pyrex® by ^{11}B NMR [5]. More recently, Smith and Seith [6] used $(\pi/2)_{CT}$–RAPT–$(\pi/2)_{CT}$ to simplify a complex ^{93}Nb spectrum in a layered perovskite, and, additionally, added the $(\pi/2)_{CT}$–RAPT scheme to QPASS [7] to edit ^{93}Nb NMR spectrum of $KCa_2Nb_3O_{10}$ that contains two overlapping niobium sites. Also, the RAPT editing schemes have been applied to selective ^{23}Na–^{1}H cross-polarization experiments, and to simplify heteronuclear correlation spectra in various Na salts [8].

Recently, Wasylishen and coworkers [9] demonstrated that a hyperbolic secant pulse [10] can provide even greater central transition enhancements through a selective inversion of the satellite transitions during magic-angle spinning [11]. Many theoretical details behind this approach have yet to be worked out, but the successful use of a hyperbolic secant pulse to invert the full manifold of satellite spinning sidebands represents an exciting possibility for central transition sensitivity enhancements, selective excitation or suppression of sites, and C_q measurements, as was the case for RAPT.

In this communication, we report a new scheme for spectral editing based on the selective inversion obtained using the WURST pulse shape for adiabatic inversion [12,13]. WURST stands for Wideband, Uniform rate, Smooth Truncation: WURST operates at a lower peak radiofrequency field level than a hyperbolic secant pulse

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[10], prevents out-of-band excitation and inverts uniformly on a wide frequency range. The amplitude, phase and the excitation profile for the shaped pulse are shown in Fig. 1. We show that (1) a single WURST inversion pulse applied to single satellite transition spinning sideband can invert the full manifold of satellite spinning sidebands, and (2) selective inversion of resolved satellite spinning sidebands can be used to perform spectral editing of overlapping sites in a central transition spectrum. At the same time, substantial sensitivity enhancements of up to 2.0 times for the edited sites are reported.

In Fig. 2a is the CT resonance and part of the ST spinning sideband resonances for the three crystallographically distinct ^{87}Rb sites in $RbNO_3$. With similar quadrupolar coupling constants [15], all three sites are overlapping in the CT and ST resonances. As shown in Fig. 2b, by applying a WURST inversion pulse on a single ST spinning sideband, which contains all three sites, an enhancement of all three sites in the central transition spectrum is obtained. The enhanced spectrum was obtained by applying a 5 ms inversion pulse on the $n = 6$ ST spinning sideband, located at an offset of 122.3 kHz from the CT. An enhancement of 2.5 times is observed, and equally as important, the enhancement is uniform though out the line shape. The enhancement factor was identical when applied to individual spinning sidebands ranging from $n = 5$ to 17 (offset range 100–300 kHz). Again, we emphasize that the adiabatic WURST inversion pulse was applied to a single spinning sideband. This method differs from that of Siegel et al. [9,16] who applied double frequency adiabatic inversion pulses at frequencies far off resonance with single site systems such as $^{87}RbClO_4$, $^{27}Al(acac)_3$ and $^{55}Mn_2(CO)_{10}$ [9,16].

The $(\pi/2)_{CT}$–RAPT–$(\pi/2)_{CT}$ approach [3,4] for selective excitation of resonances with the largest C_q values also exists with adiabatic inversion pulses. However, there is an additional possibility with adiabatic inversion pulses, not available with RAPT, for selective excitation amongst sites with similar C_q values, provided the satellite transitions resonances of different sites are resolved. In fact, this possibility is enhanced for higher spin nuclei where the second-order anisotropic width of the innermost satellite is narrower than the central transition under MAS (assuming the rotor angle is accurately set). To illustrate this aspect, simulated spectra of central and satellite transitions as a function of nuclear spin I are shown in Fig. 3. The spectra were simulated with a spinning frequency of 10 kHz and using a dwell time of half a rotor period in order to separate the even and odd spinning sidebands. The odd sidebands contain little to no contribution from the central transition. For spin $I = 3/2$ one can see that the second-order anisotropic broadening of the satellites are slightly narrower than the central transition. For spin $I = 5/2$ the inner satellite pair is significantly narrower, whereas for spins $I = 7/2$ and 9/2 it is the 2nd inner satellite pair, $\langle \pm 5/2, \pm 3/2 \rangle$ that is narrowest. This well-known narrowing [17–22], can be readily exploited with adiabatic inversion pulses to perform spectral editing of the central transition region. Thus, our approach is to use a $(\pi/2)_{CT}$–$(\pi)_{ST_1}$–$(\pi/2)_{CT}$ sequence, where the central transition of all sites are pre-saturated by a $(\pi/2)_{CT}$ pulse, followed by restoration of the desired site's central transition

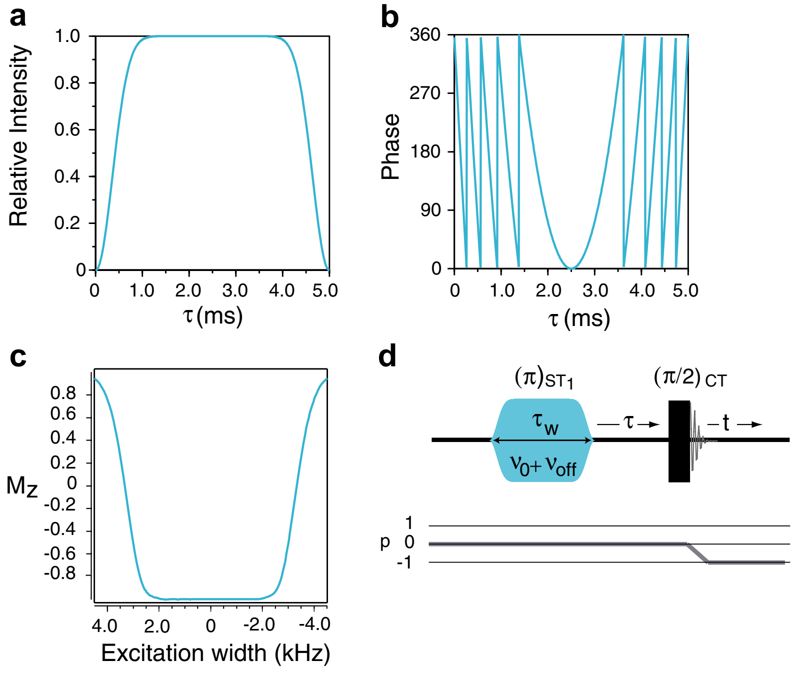

Fig. 1. (a) Amplitude and (b) phase as a function of the pulse length of the WURST pulse. (c) Magnetization profile as a function of frequency offset. The pulse length and the excitation width are as shown. (d) The $(\pi)_{ST_1}$–$(\pi/2)_{CT}$ sequence, where the selective π rotation of the innermost satellite is accomplished by adiabatic inversion using the WURST pulse.

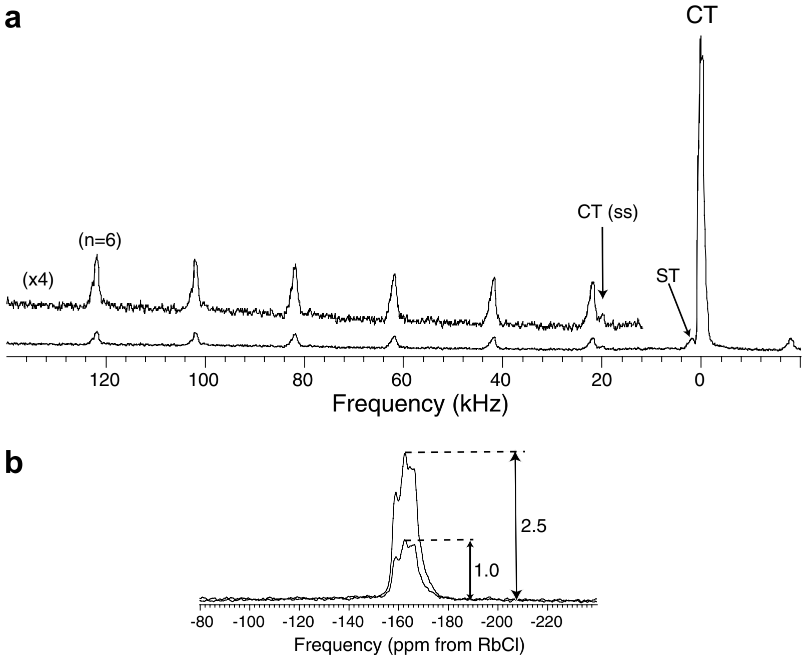

Fig. 2. (a) ^{87}Rb spectrum of RbNO$_3$ (10 k scans) acquired at a spinning rate of 20 kHz showing CT and ST signals. Only one side of the spinning sideband envelope is shown. (b) Comparison of CT intensity obtained from WURST [12,13] adiabatic inversion pulse ($\tau = 5$ ms, excitation width = 3 kHz, $\nu_{rf} = 5.5$ kHz) with no enhancement (512 scans). All experiments were performed on a Bruker DMX 400 spectrometer using a Bruker 2.5 mm MAS probehead. The magic-angle was set using K^{79}Br, and further calibrated by maximizing the ST-CT echo intensity in ^{87}RbNO$_3$ [14]. Solid RbCl was used to calibrate the rf-field strengths and used as chemical shift reference. The equilibrium magnetization recovery delay used was approximately 500 ms. Typically, the WURST excitation widths used were slightly larger than the anisotropic linewidth of the satellite spinning sidebands. For creating a WURST pulse, the Bruker ShapeTool® was used.

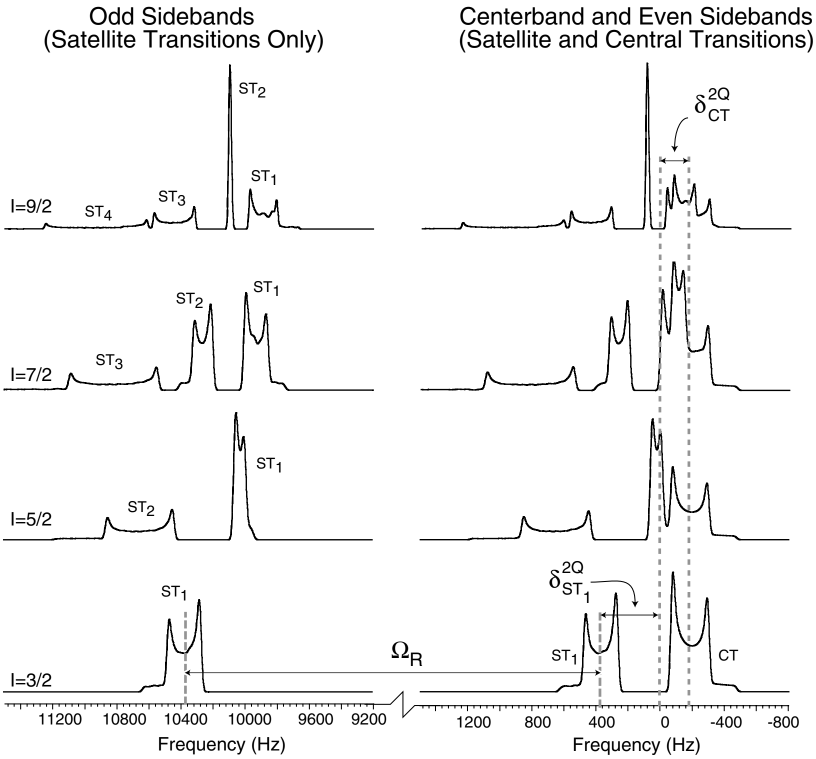

Fig. 3. Simulated central and satellite transitions spectra for spin $I = 3/2$, $5/2$, $7/2$, and $9/2$ nuclei with C_q values of 1.0, 2.04, 3.13, and 4.24 MHz, respectively, using half-rotor synchronized acquisitions to separate even and odd sidebands. The C_q value for each spin I was adjusted for constant central transition line widths ($\eta_q = 0.0$ and $\nu_L = 131.45$ MHz). The second-order shifts [17] of the central (δ^{2Q}_{CT}) and satellite transitions (δ^{2Q}_{ST}) are given by $\delta^{2Q}_{m,m-1} = \frac{-3[I(I+1) - 9\,m(m-1) - 3]}{40\nu_L^2 I^2 (2I-1)^2} C_q^2 (1 + \frac{\eta_q^2}{3}) \times 10^6$(ppm). For spin 7/2 and 9/2 nuclei, the central and the inner satellite transitions (ST$_1$) overlap.

polarization by selective inversion of its innermost satellite transition prior to detection with a central transition selective π/2 pulse. An additional advantage of this approach over $(\pi/2)_{CT}$–RAPT–$(\pi/2)_{CT}$ is that the edited spectrum is enhanced compared to both the conventional Bloch decay experiment and the edited $(\pi/2)_{CT}$–RAPT–$(\pi/2)_{CT}$ experiment [3,4,6,8] due to the use of selective inversion rather than selective saturation.

As an example we use the ^{87}Rb spectrum of a mixture of Rb_2SO_4 and $RbClO_4$, shown in Fig. 4. Rb_2SO_4 contains two Rb sites, while $RbClO_4$ contains one (see Table 1). In the mixture spectrum, the CT resonance of Rb_2SO_4-II overlaps with the CT resonance of the $RbClO_4$ site. In contrast, the ST resonances of all three sites are better resolved, although there still is partial overlap of the Rb_2SO_4-I and Rb_2SO_4-II ST resonances. Using the $(\pi/2)_{CT}$–$(\pi)_{ST_1}$–$(\pi/2)_{CT}$ sequence we obtained the edited spectra shown in Fig. 4c–e for each site, with edited site enhancements of 2.0, 1.8, and 1.2 for Rb_2SO_4-I, $RbClO_4$ and Rb_2SO_4-II, respectively. The approach works well for two of the three sites, with the inversion being more efficient for smaller C_q sites. Some residual Rb_2SO_4-I resonance is obtained in the Rb_2SO_4-II edited spectrum

Table 1
Quadrupolar parameters and relative second-order quadrupolar shifts of rubidium salts

Site	C_q (MHz)	η_q (—)	δ_{CT}^{2Q}[a] (Hz)	δ_{ST}^{2Q}[a] (Hz)
Rb_2SO_4-I	2.67	0.89	−1718	3436
$RbClO_4$	3.2	0.21	−1979	3959
Rb_2SO_4-II	5.28	0.13	−5343	10686

[a] Second-order shifts for the CT and ST, respectively.

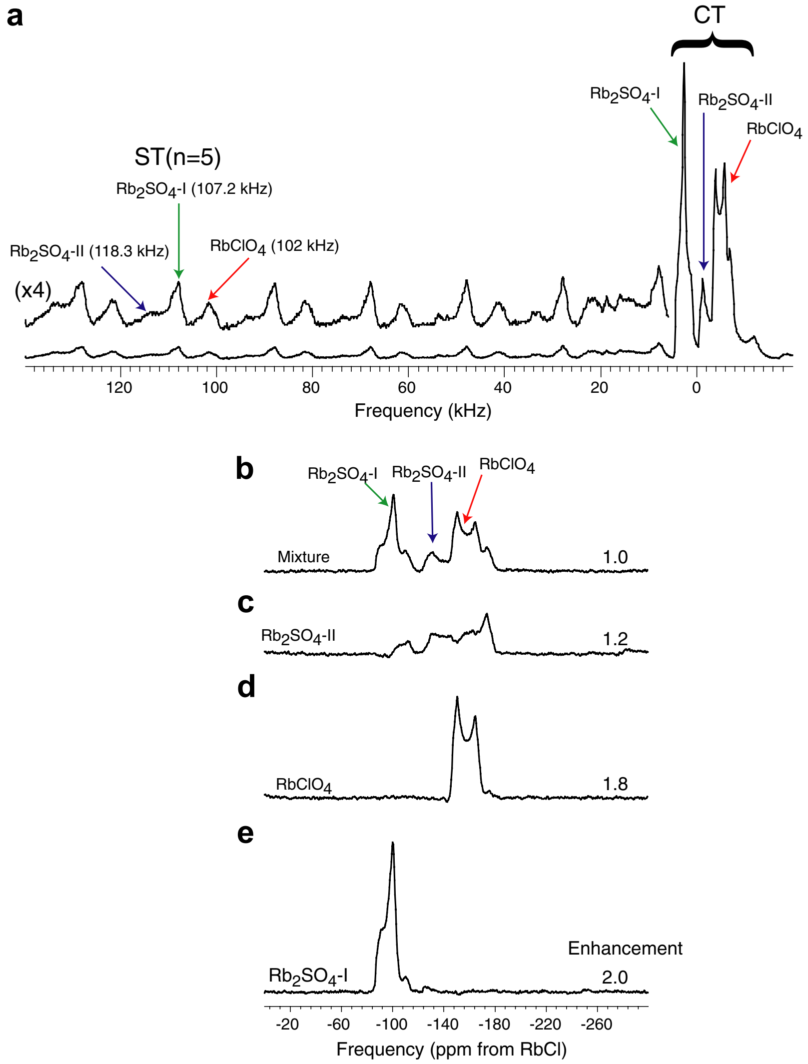

Fig. 4. (a) ^{87}Rb spectrum of a 1:1 mixture of polycrystalline $RbClO_4$ and Rb_2SO_4 [15,23] (40 k scans) acquired at a spinning rate of 20 kHz showing CT and ST signals. Only one side of the spinning sideband envelope is shown. (b) Single pulse spectrum (512 scans) and (c–e) $(\pi/2)_{CT}$–$(\pi)_{ST_1}$–$(\pi/2)_{CT}$ edited spectra (512 scans) for each site (CT region only). In each case, the inversion pulse was applied on one spinning sideband at the chosen offset as shown in (a). The adiabatic pulse parameters for the different sites are as follows: (c) $\tau = 2$ ms, excitation width = 8 kHz, $\nu_{rf} = 8.5$ kHz. (d) $\tau = 5$ ms, excitation width = 3 kHz, $\nu_{rf} = 5.5$ kHz. (e) $\tau = 5$ ms, excitation width = 3 kHz, $\nu_{rf} = 5.5$ kHz. The spectrometer offset was placed at the middle of the CT resonances to minimize the off-resonance effects that are caused by the low power read pulse.

because slight spectral overlap of ST resonances prevents the inversion pulse from being completely selective on the Rb_2SO_4-II ST resonance. A lower than expected CT enhancement may arise from the $(\pi/2)_{CT}$ pulse not being completely CT selective, thus affecting the ST populations to some small degree. The spectral editing based on selective inversion is not limited to spin 3/2 nuclei; significant signal enhancements of the edited sites could be achieved for higher spin systems.

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