

Short communication

Optimizing magic-angle spinning sideband suppression

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Abstract

A generalized description of sideband suppression with inversion pulses is presented. As an example of optimization, a sequence with three inversion pulses is demonstrated.

Keywords: Nuclear magnetic resonance; Magic-angle spinning; Sideband suppression

1. Introduction

A variety of methods has been proposed to eliminate sidebands in the solid-state magic-angle spinning (MAS) spectra. Most of them use four [1] or more [2] inversion pulses to create the desired phase shift in the signal modulation terms.

Application of long pulse sequences may occasionally be problematic because of limitations imposed by spectral bandwidth, relaxation or nutation effects. Sequences with fewer pulses have been proposed assuming signal modulation at the single frequency equal to the spinning frequency whereas in the common case of a second-rank tensor interaction signal modulation is generated at two frequencies [3]. A typical experimental situation does not call for a rigorous suppression of all sidebands. High-order sidebands may not exceed the noise level or are well beyond the chemical shift range, and elimination of a few pairs of closest sidebands might be sufficient.

This leaves some additional flexibility in designing pulse sequences. We propose a general description of signal evolution in a form that enables better understanding of sideband formation and more flexible design of pulse sequences in order to minimize the number of pulses, reduce the delay before data acquisition or selectively enhance anisotropic interactions. We describe a sideband suppression with three inversion pulses and compare this with some existing sequences.

2. Theory

Magic-angle sample spinning, or spinning at any other angle to the direction of the magnetic field, modulates the isotropic precession ω_I of a transverse magnetization vector. Typical nuclear magnetic resonance (NMR) interactions create in the first order a phase modulation at single and double spinning frequency, ω , expressed generally as

$$\phi(t) = \omega_I t + \sum_{n=1}^2 [A_n \sin n(\omega t + \zeta + \gamma) + B_n \cos n(\omega t + \zeta + \gamma) - \phi_n(\gamma)] \quad (1)$$

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where a convenient expression for the time-independent initial phase is

$$\phi_n(\gamma) = z_n [A_n \sin(\zeta_n + n\gamma) + B_n \cos(\zeta_n + n\gamma)] \quad (2)$$

The functions $A_n = A_n(\alpha, \beta)$ and $B_n = B_n(\alpha, \beta)$ are inversely proportional to the spinning frequency and depend on details of interaction and orientation of an atomic environment expressed in terms of the two Euler angles α and β ; the third Euler angle, γ , expressed the spread in the phase angles resulting from the distribution of crystallite orientations in the powder. The normalization coefficient

$$z_n = \sqrt{f_n^2 + g_n^2} \quad n = 1, 2 \quad (3)$$

and phase angle ζ_n are functions of experimentally controlled variables:

$$\begin{aligned} f_n &= z_n \sin \zeta_n \\ g_n &= z_n \cos \zeta_n \end{aligned} \quad (4)$$

The variables g_n and f_n as well as the phases ζ and ζ_n depend on the timing of an inversion pulse sequence.

If no pulses are used,

$$\begin{aligned} f_n &= 0 \\ z_n &= g_n = 1 \\ \zeta_n &= 0 \\ \zeta &= 0 \end{aligned} \quad (5)$$

In the case of two pulses, applied with intervals t_a and t_b , experimental variables acquire the values

$$\begin{aligned} g_n &= 1 - 2 \cos n\omega t_a + 2 \cos n\omega(t_a + t_b) \\ f_n &= -2 \sin n\omega t_a + 2 \sin n\omega(t_a + t_b) \\ \zeta &= \omega(t_a + t_b + t_q) \end{aligned} \quad (6)$$

where the delay $t_q = t_b - t_a$ ensures a refocussing of the signal. If three pulses are applied,

$$\begin{aligned} g_n &= -1 + 2 \cos n\omega t_a - 2 \cos n\omega(t_a + t_b) \\ &\quad + 2 \cos n\omega(t_a + t_b + t_c) \\ f_n &= 2 \sin n\omega t_a - 2 \sin n\omega(t_a + t_b) \\ &\quad + 2 \sin n\omega(t_a + t_b + t_c) \\ \zeta &= \omega(t_a + t_b + t_c + t_q) \end{aligned} \quad (7)$$

with the refocussing condition $t_q = t_a + t_c - t_b$.

The registered signal is proportional for a given set of orientation angles (α, β, γ) to

$$s_\gamma(t) = e^{i\omega t} \sum_{N=-\infty}^{\infty} e^{i[N(\omega t + \zeta + \gamma) + \phi_N]} I_N I(\gamma) \quad (8)$$

where the intensity can be expressed as

$$I_N = \sqrt{C_N^2 + S_N^2} \quad (9)$$

with real functions

$$\begin{aligned} C_N &= \sum_{m,k=-\infty}^{\infty} J_m(B_1) J_k(B_2) \cos(m+k)\pi/2 \\ &\quad \times \sum_{l=-\infty}^{\infty} J_{N+m+2k-2l}(A_1) J_l(A_2) \\ S_N &= \sum_{m,k=-\infty}^{\infty} J_m(B_1) J_k(B_2) \sin(m+k)\pi/2 \\ &\quad \times \sum_{l=-\infty}^{\infty} J_{N+m+2k-2l}(A_1) J_l(A_2) \end{aligned} \quad (10)$$

and a phase factor

$$\phi_N = \cos^{-1} \frac{C_N}{I_N} \quad (11)$$

The second intensity factor in Eq. 8 can be expressed as a product of Fourier expansions of the angular dependency on γ as

$$I(\gamma) = \sum_{n=1}^2 \sum_{N=-\infty}^{\infty} e^{-i[N(\zeta_n + n\gamma) + \phi_{n,N}]} I_{n,N} \quad (12)$$

where

$$e^{i\phi_{n,N}} I_{n,N} = \sum_{m=-\infty}^{\infty} J_{N+m}(z_n A_n) J_m(z_n B_n) e^{im\pi/2} \quad (13)$$

with phase $\phi_{n,N}$ and intensity $I_{n,N}$ defined analogously to Eqs. 10 and 11. The full powder signal is formed as a sum of contributions from all randomly oriented crystals but in the expressions above the dependency on γ is left explicit as this is most crucial in the formation of sidebands.

Given a sufficient number of pulses, the experimental variables f_n and g_n , and thus ζ_n , can be brought to arbitrary values. Eq. 8 is difficult to analyze due to multiple infinite summations; however, considerable simplifications can be made if certain constraints are imposed.

Case 1:

$$\zeta_2 = 2\zeta_1 = \zeta_0 \quad (14)$$

where ζ_0 has an arbitrary value. The Fourier expansions in Eq. 12 condense to

$$I(\gamma) = \sum_{N=-\infty}^{\infty} e^{-i[N(\zeta_0+\gamma)+\phi_{0,N}]} I_{0,N} \quad (15)$$

Averaging over γ yields for the signal a compact expansion indexed by a side-band order only:

$$s(t) = \sum_{N=-\infty}^{\infty} I_N I_{0,N} e^{i[\omega_I t + N(\omega t + \zeta - \zeta_0) + \phi_N - \phi_{0,N}]} \quad (16)$$

Case 2: further simplification is brought by the assumption

$$z_n = 1 \quad n = 1, 2 \quad (17)$$

Then

$$I(\gamma) = \sum_{N=-\infty}^{\infty} e^{-i[N(\zeta_0+\gamma)+\phi_N]} I_N \quad (18)$$

and averaging gives

$$s(t) = \sum_{N=-\infty}^{\infty} I_N^2 e^{i[\omega_I t + N(\omega t + \zeta - \zeta_0)]} \quad (19)$$

This is a basic expression of sidebands with an order-dependent phase shift as proposed in Ref. [1], as the sideband phase $\zeta - \zeta_0$ does not depend on atomic parameters anymore. The sideband intensities are equal to those of regular spectra as evident if the following additional constraint is imposed.

Case 3:

$$\zeta = \zeta_0 \quad (20)$$

Now the signal

$$s(t) = \sum_{N=-\infty}^{\infty} I_N^2 e^{i(\omega_I + N\omega)t} \quad (21)$$

gives a spectrum identical to the regular one, without any inversion pulses, and determined by the parameters of Eq. 5. Eq. 21 reflects the fact that all sidebands are real and positive [4].

A substitution $t = t_1 + t$ indicates a possibility of two-dimensional Fourier analyses where the additional axis stretches the spectrum according

to the isotropic shift ω_I along with related sidebands, if

$$\omega t_1 + \zeta = \zeta_0 \quad (22)$$

The related experiments have been demonstrated in Refs. [5] and [6].

Case 4:

$$f_1 = g_1 = 0 \quad (23)$$

$$I(\gamma) = \sum_{N=-\infty}^{\infty} e^{i[N(\zeta_2+2\gamma)+\phi_{2,N}]} I_{2,N} \quad (24)$$

The averaging over γ leaves every second sideband only:

$$s(t) = \sum_{N=-\infty}^{\infty} I_{2N} I_{2,N} e^{i[\omega_I t + N(2\omega t + 2\zeta - \zeta_2) + \phi_{2N} - \phi_{2,N}]} \quad (25)$$

Case 5:

$$f_n = g_n = 0 \quad (26)$$

This constraint leads to cancelling of all sidebands after averaging over γ , because

$$I(\gamma) = 1 \quad (27)$$

The signal is represented by the centerband

$$s(t) = I_0 e^{i(\omega_I t + \zeta + \phi_0)} \quad (28)$$

which is generally phase-shifted by ζ and also by ϕ_0 due to atomic parameters. The numerical simulations indicate that it is the additional averaging over the remaining two Euler angles that eliminate the ϕ_0 phase shift.

The existing and demonstrated inversion pulse sideband manipulations are confined to cases 2, 4 and 5. Averaging over acquisitions with different pulse timing and lifting some of the constraints may add valuable flexibility in the design of pulse sequences. The pulse sequences can be developed to (a) minimize the total duration, (b) minimize the number of pulses, (c) maximize the signal of a centerband and (d) maximize the sensitivity to variation of modulation coefficients for a selective study of anisotropy properties. These expressions also indicate possibilities for designing complementary pulse timing sequences, where imperfections are orthogonal and cancel mutually. This is an extension to the original approach by Dixon [1] and was demonstrated recently on a

double-rotation experiment [7]. As an example of combining complementary acquisitions that leads to a reduction of pulses we propose a three-pulse sequence that leaves to a good approximation sidebands with index modulo 4.

The complementary sequences (186.97, 316.16, 263.03) and (173.03, 43.84, 96.97) generate experimental variables

$$\begin{aligned} g_1 &= f_1 = 0 \\ g_2 &= -0.3 \\ f_2 &= \pm 4.4 \end{aligned} \quad (29)$$

Neglecting g_2 , the signal can be expanded as

$$\begin{aligned} s(t) &= \sum_{N=-\infty}^{\infty} I_{2N} I_{2,N} e^{i[\omega_1 t + N(2\omega t + 2\xi \pm \pi/2) + \phi_{2N} - \phi_{2,N}]} \end{aligned} \quad (30)$$

Averaging over two experiments leads to cancellation of all sidebands with uneven N , giving a

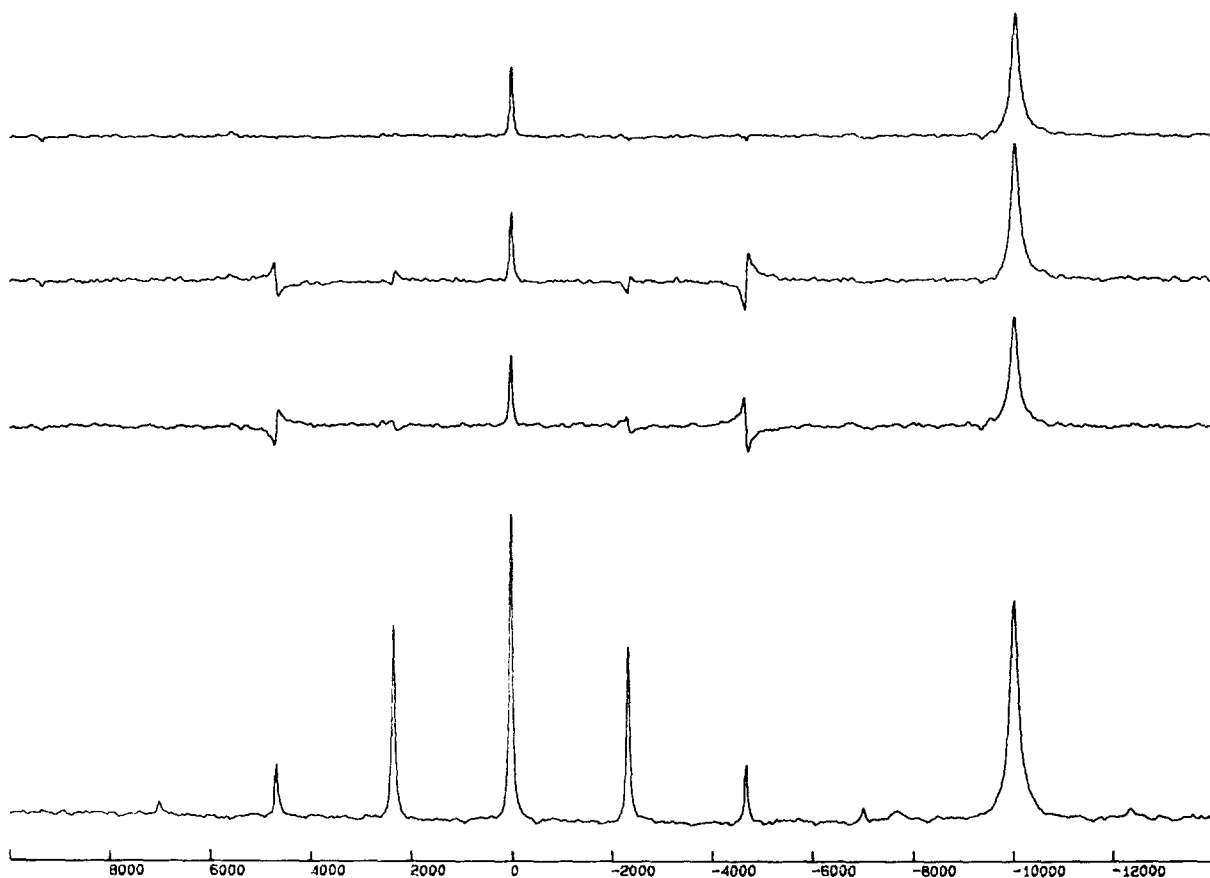


Fig. 1. 75-MHz ^{13}C spectra of glycine. From bottom to top: regular MAS, three-pulse I, three-pulse II and a weighted sum. All spectra have equal numbers of acquisitions.

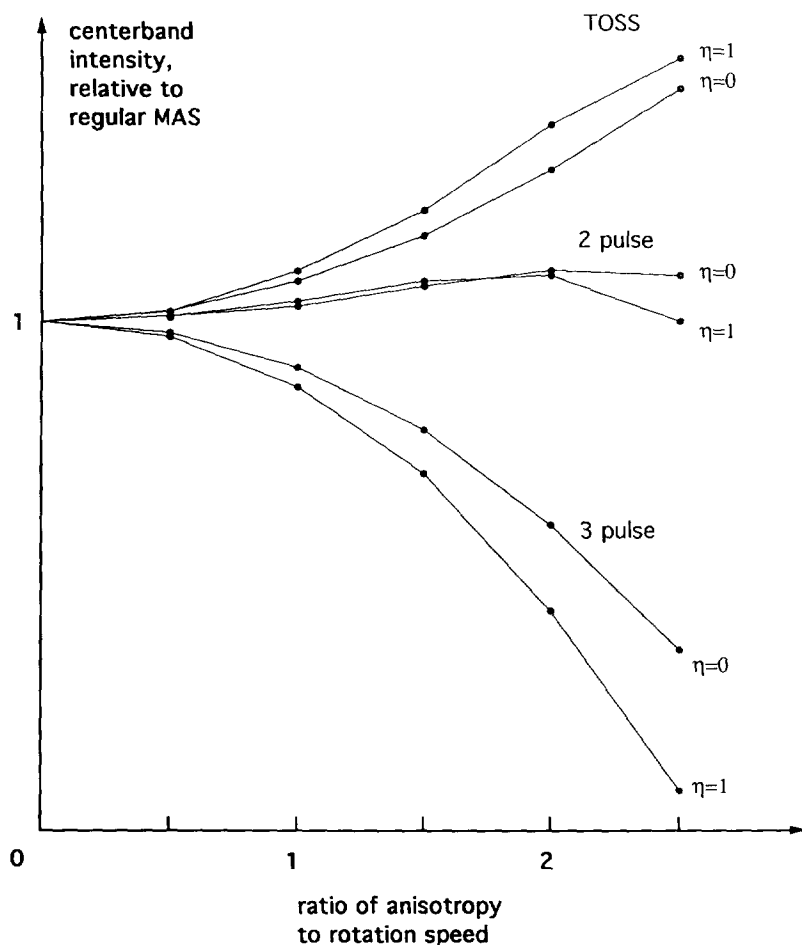


Fig. 2. Theoretical simulation of the centerband intensity relative to a regular MAS centerband; η denotes asymmetry of the chemical shielding tensor.

Table 1
Parameters of selected sideband suppression timings

Suppression	ωt_A	ωt_B	ωt_C	ωt_D	ωt_Q	ζ	f_1	f_2	g_1	g_2
–	–	–	–	–	–	0	0	0	1	1
Two-pulse	75.53	28.95	–	–	–46.58	57.9	0	–1.936	0	1
Three-pulse I	186.97	316.16	263.03	–	132.84	180	0	4.4	0	0.3
Three-pulse II	173.03	43.84	96.97	–	226.16	180	0	–4.4	0	0.3
TOSS	67.86	14.83	209.45	345.17	82.69	0	0	0	0	0

Delays before inversion pulses and data acquisition are given in degrees of a rotor motion after (excitation or inversion) pulse.

signal where the time modulation is a multiple of 4ω

$$s(t) = \sum_{N=-\infty}^{\infty} I_{4N} I_{2,2N} e^{i[\omega_1 t + 2N(2\omega t + 2\xi) + \phi_{4N} - \phi_{2,2N}]} \quad (31)$$

This is demonstrated experimentally on a spectrum of glycine (Fig. 1). Only a very small remainder of low-order sidebands is visible due to a finite value of g_2 . A relatively strong reduction in centerband intensity is observed, but the performance is comparable to other sequences at moderate initial line broadening, as evidenced in Fig. 2. The timing and experimental variables are shown in Table 1. The negative value of the t_q delay in the case of a two-pulse sequence indicates that refocussing is not possible, but the spectrum can still be phased properly with respective first-order phase correction.

Acknowledgements

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