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TOP-PASS: A processing algorithm to reduce 2D PASS acquisition time

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ABSTRACT

A slow speed MAS spectrum contains a pattern of spinning sideband resonances separated by integer multiples of the rotor frequency and centered about an isotropic frequency. The 2D signal acquired in a two-dimensional Phase Adjusted Spinning Sideband (PASS) experiment correlates this slow speed MAS spectrum, obtained in the direct dimension, to an indirect dimension spectrum containing the same pattern of spinning sideband resonances centered about a frequency of zero. An affine transformation is used to convert the acquired 2D PASS signal into a 2D signal that correlates a spectrum of pure isotropic frequencies to a spectrum of spinning sideband resonances with no isotropic frequency contributions. The conventional affine transform applied to 2D PASS consists of an active shear of the signal parallel to the indirect time domain coordinate followed by a passive scaling of the indirect time domain coordinate. Here we show that an alternative affine transform, previously employed in the Two-dimensional One Pulse (TOP) experiment, can be employed to create the same 2D signal correlation with an enhanced spectral width in the anisotropic (spinning sideband) dimension. This enhancement can provide a significant reduction in the minimum experiment time required for a 2D PASS experiment, particularly for spectra where the individual spinning sideband patterns are dispersed over a wider spectral range than the isotropic resonance frequencies. The TOP processing consists of an active shear of the signal parallel to the direct time domain, followed by an active shear of the signal parallel to the new indirect time domain coordinate followed by a passive scaling of the new direct time domain coordinate. A theoretical description of the affine transformation in the context of 2D PASS is given along with illustrative examples of ^{29}Si in Clinoenstatite and ^{13}C in L-Histidine.

1. Introduction

Frequency anisotropy in magnetic resonance spectroscopy is a rich source of detail concerning structure and dynamics at the macroscopic level down to the molecular level. At the macroscopic level these anisotropies can occur as a result of inhomogeneities in the external magnetic field, variations in magnetic susceptibilities, or through the intentional use of magnetic field gradients as in magnetic resonance imaging. At the molecular level frequency anisotropy arises through magnetic dipolar couplings among nuclei and through interactions of the nuclear multipole moments with surrounding electrons. While the manifestation of these molecular level anisotropies in solution state NMR is primarily through relaxation, its effects are seen directly in solid-state NMR spectra as the powder pattern lineshape.

Early in the history of NMR it was realized that inhomogeneous anisotropic broadenings can be removed through sample rotation [1–3]. In solution state NMR, sample rotation is a standard approach to average away broadenings from magnetic field inhomogeneities [1], while magic-angle sample spinning (MAS) [2,3] has become a popular and routine method in solid-state NMR for eliminating second-rank anisotropic broadenings, particularly when combined with the sensitivity enhancement of cross-polarization (CP/MAS) [4,5]. With sample rotation, the inhomogeneous lineshape breaks up into a set of spinning sidebands centered about a centerband lineshape and spaced at integer multiples of the spinning frequency. As the spinning frequency is increased the intensities of the spinning sidebands are reduced and transferred into the centerband. In the limit of infinite spinning speed only the centerband frequency remains.

A few years after the introduction of CP/MAS, Herzfeld and Berger [6] developed an approach for analyzing the sideband intensities in a slow speed MAS spectrum to obtain the same details about the anisotropic spin interactions as found in the static powder pattern lineshape. With the introduction of two-dimensional NMR spectroscopy [7], a number of approaches have been designed to correlate a high or infinite speed MAS spectrum with either the static [8–13], slow speed MAS spectrum [14–18] or only spinning sideband intensities [19,14–18]. One of the more popular approaches is the elegant Phase Alternating Spinning Sidebands (PASS) experiment of Dixon [19]. While 2D PASS [16] robustly

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correlates isotropic frequencies to spinning sideband patterns, it has a drawback that experiment times can become lengthy when spectra contain sites having a large number of spinning sidebands. In such situations, the sampling rate in the indirect dimension is increased or the spinning speed is increased. The latter approach, however, could result in a loss of sideband information from other sites with smaller anisotropies. Here, we describe an alternative approach for processing 2D PASS signals, based on the TOP experiment [20–22], which increases the spectral width in the anisotropic (spinning sideband) dimension without increasing the sampling rate in the indirect (rotor pitch) dimension (or even changing the spinning speed). We refer to this combination of TOP processing applied to the 2D PASS signal as the TOP-PASS experiment. This new approach can provide a significant reduction in the minimum experiment time required for a 2D PASS experiment, particularly for samples with large anisotropies as well as those simply having long relaxation times.

2. Experimental

NMR experiments on Clinoenstatite, $MgSiO_3$, were performed on a Bruker Avance operating at a field strength of 9.4 Tesla corresponding to an operating frequency of 79.576 MHz for ^{29}Si with a 4 mm Bruker MAS probe spinning at 1000 ± 2 Hz using ^{29}Si rf field strength of 94 kHz. NMR experiments on L-Histidine were performed on a hybrid Tecmag Apollo-Chemagnetics CMX II NMR spectrometer operating at a field strength of 9.4 Tesla, corresponding to an ^{13}C NMR frequency of 100.605 MHz and a ^{1}H NMR frequency of 400.068 MHz, and using a 4 mm Chemagnetics double resonance MAS probe spinning at 1500 ± 2 Hz with a ^{1}H rf field strength of 83 kHz for initial excitation and TPPM decoupling, a ^{1}H–^{13}C cross-polarization contact rf field strength of 104.17 kHz and contact time of 1.1 ms. An exponential apodization of 50 Hz in the direct dimension and 100 Hz in the indirect dimension was applied to all 2D datasets. L-Histidine monochloride monohydrate was obtained from Sigma Aldrich and used without further purification. The acquisition time for a single 2D PASS cross-section in the indirect dimension for Clinoenstatite and L-Histidine was 9 h and 1.5 h, respectively.

3. Results and discussion

3.1. Bloch decay MAS

The first-order contribution of the nuclear shielding to the NMR frequency for a single crystallite as a function of rotor angle and phase can be expanded in a Fourier series [23] as

$$\Omega_\sigma^{(1)}(\theta_R,\phi_R) = \varpi_0(\theta_R,\alpha,\beta) + \sum_{m\neq 0} \varpi_m(\theta_R,\alpha,\beta) e^{im(\phi_R+\gamma)}, \tag{1}$$

where θ_R is the rotor angle, ϕ_R is the rotor phase, α, β, and γ are the Euler angles between the rotor coordinate frame and the crystallite coordinate frame. In the simple Bloch decay MAS experiment the signal phase as function of time, t, where $\phi_R(t) = \omega_R t + \chi_R$, is

$$\begin{aligned}\Phi(t) &= \int_0^t \Omega_\sigma^{(1)}(\theta_R,\phi_R(t'))dt' \\ &= W_0 t + \sum_{m\neq 0} W_m e^{im(\chi_R+\gamma)}\left[e^{im\omega_R t} - 1\right],\end{aligned} \tag{2}$$

where χ_R is the initial rotor phase, and we define

$$W_0 = \varpi_0(\theta_M,\alpha,\beta), \tag{3}$$

and

$$W_m = \frac{\varpi_m(\theta_M,\alpha,\beta)}{im\omega_R}. \tag{4}$$

Here $\theta_M = \cos^{-1}(1/\sqrt{3})$. One can show [23] that the Bloch decay MAS signal is given by

$$\mathfrak{s}_B(\alpha,\beta,t,\chi_R) = \mathfrak{s}^e(t)e^{iW_0 t} \times \sum_{N_1,N_2} A_{N_1} A^*_{N_2} e^{-iN_1\omega_R t} e^{i(N_2-N_1)(\chi_R+\gamma)}, \tag{5}$$

where

$$A_N = \frac{1}{2\pi}\int_0^{2\pi} \exp\left\{ i\sum_{m\neq 0} W_m e^{im\Theta}\right\} e^{iN\Theta} d\Theta, \tag{6}$$

and $\mathfrak{s}^e(t)$ represents the envelope function due to the relaxation. A partial averaging of the Bloch decay signal over the angle γ eliminates the dependence on the initial rotor phase, χ_R, yielding

$$\langle \mathfrak{s}_B(\alpha,\beta,t)\rangle_\gamma = \mathfrak{s}^e(t)e^{iW_0 t} \sum_N |A_N|^2 e^{-iN\omega_R t}. \tag{7}$$

The Bloch decay MAS signal from all crystallites, $\mathcal{S}_B(t)$, is then given by

$$\begin{aligned}\mathcal{S}_B(t) &= \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \langle \mathfrak{s}_B(\alpha,\beta,t)\rangle_\gamma \\ &= \mathfrak{s}^e(t)e^{iW_0 t}\sum_N I_N e^{-iN\omega_R t},\end{aligned} \tag{8}$$

where

$$I_N = \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta |A_N|^2. \tag{9}$$

Notice that W_0 during MAS is only dependent on isotropic frequency contributions, whereas the spinning sideband intensities, I_N, are only dependent on anisotropic frequency contributions.

3.1.1. TOP

One can rewrite Eq. 8 in the form

$$\mathcal{S}(t_1,t_2) = \mathfrak{s}^e(t_2)e^{iW_0 t_2}\sum_N I_N e^{-iN\omega_R t_1}, \tag{10}$$

and visualize the 1D Bloch decay MAS signal from a rotating sample as a signal filling a 2D t_1–t_2 coordinate system, as illustrated in Fig. 1. Note that

$$\mathcal{S}_B(t_1 + nt_R, t_2) = \mathcal{S}_B(t_1,t_2), \tag{11}$$

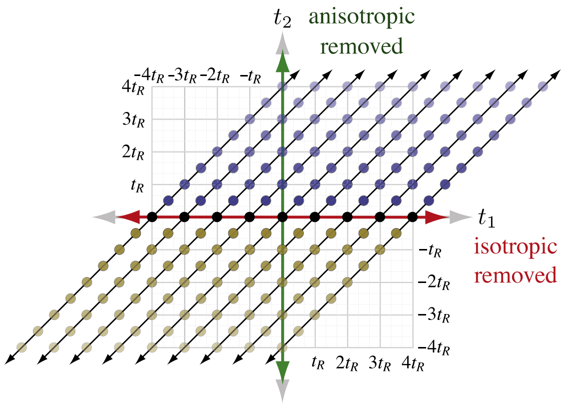

Fig. 1. Solid circles and arrows represent the sampling trajectory of the 1D Bloch decay MAS signal (blue circles) and its complex conjugate signal (brown circles) in the t_1–t_2 coordinate system. The slope of the sampling trajectory in the t_1–t_2 coordinate system is 1. Identical signal run parallel, separated by t_R in t_1 and t_2, respectively. Only anisotropic frequency contributions are present along the t_1 dimension, and only isotropic frequency contributions are present along the t_2 dimension (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).