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Two dimensional One Pulse MAS of Half-Integer Quadrupolar Nuclei

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Abstract

We show that the Two-dimensional One Pulse (TOP) representation of magic-angle spinning nuclear magnetic resonance data of half-integer quadrupolar nuclei has significant advantages over the conventional one-dimensional spectrum. The TOP spectrum, which correlates NMR frequency to spinning sideband order, provides a rapid determination of the number of sites as well as size of the their quadrupolar coupling. Additionally, synchronous acquisition spectra of the central and satellites transition resonances can be separated by different projections of the TOP spectrum, with higher resolution spectra often found in the satellite transitions projection. A previously perceived problem of centerband aliasing in TOP can be eliminated with an algorithm that uses larger subspectral widths and the sideband order dimension to distinguish centerbands from sidebands.

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1 Introduction

Magic Angle Spinning (MAS) improves resolution in solid-state NMR by averaging away frequency anisotropy. Under MAS, a broad anisotropic resonance is broken up into a centerband flanked by sidebands at multiples of the rotor frequency. At high MAS speeds only the centerband survives. At lower speeds, the sideband intensities can be analyzed to retrieve information about the anisotropy of the interactions [1] (e.g., chemical shift anisotropy, quadrupolar coupling) which provide further sample structure characterization. Several years ago, Blümich and coworkers [2, 3] proposed the Two-dimensional One Pulse (TOP) MAS method where a 1D MAS spectrum is mapped into a 2D spectrum correlating frequency and spinning sideband order. The experimental simplicity of TOP makes it a compelling method, and it is surprising that TOP has not been more widely utilized [4]. A limitation of TOP, however, is the spectral width in the frequency dimension is limited to integer divisors of the rotor frequency, and this cannot be easily corrected by increasing the rotor frequency since it also reduces the information content in the sideband intensities. Here, we show that TOP applied to half-integer quadrupolar nuclei, with minor modification, does not suffer as greatly from this limitation, and has other advantages that significantly increase the power of this overlooked approach. Additionally, since the TOP experiment only requires a single pulse, it is ideal for satellite transitions of quadrupolar nuclei, where rf fields strengths are often too weak to generate the kind of broadband π pulse excitation needed for the more sophisticated sideband manipulation experiments like PASS [5].

2 Theoretical Background

A multipole expansion of the NMR frequency as a function of time during magic-angle spinning can be separated into non-rotor and rotor modulated components:

\[ \Omega(t, \phi_0) = \sum_{l=0}^\infty \omega_{l,0} + \sum_{l>0, m \neq 0} \omega_{l,m} e^{im(\Omega_R t + \phi_0)}, \]

where \( \phi_0 \) is the initial rotor phase, \( \Omega_R \) is the rotor speed, the index \( m \) runs from \(-l\) to \( l \), and \( l \) typically runs from zero to two for spin 1/2 nuclei and zero to four for half-integer quadrupolar nuclei experiencing second-order quadrupolar broadenings. In a one pulse NMR experiment the signal phase as function of \( t \) is

\[ \Phi(t) = \int_0^t \Omega(s)ds = W_0 t - \sum_{l,m \neq 0} i W_{l,m} \left[ e^{im(\Omega_R t + \phi_0)} - e^{i m \phi_0} \right] \]

where we have defined

\[ W_0 = \sum_{l=0}^\infty \omega_{l,0} \text{ and } W_{l,m} = \frac{\omega_{l,m}}{m \Omega_R}. \]

Here, \( W_0 \) is the non-rotor modulated frequency, which will be orientation dependent for quadrupolar nuclei broadened to second-order or higher.

Following a derivation found in various NMR texts [6], the signal of a polycrystalline sample undergoing magic-angle spinning can be shown to have the form:

\[ S(t) = \sum_{N_0=-\infty}^{\infty} I_{N_0} e^{i W_0 t} e^{i N_0 \Omega_R t} e^{-t/T_2}. \]  \hspace{1cm} (1)

2.1 Time Domain Approach

The 1D time domain signal can be mapped into an intermediate 2D coordinate system with variables \( k \) and \( \Xi \), as shown in Fig. 1, by defining

\[ t = (\Xi/2\pi + k)t_R, \]

where \( t_R = 2\pi/\Omega_R \) and \( k \) is an integer. In TOP, a more restricted mapping, with

\[ \Xi = \Omega_R t \pmod{2\pi} \text{ and } k = \left\lfloor \frac{t}{t_R} \right\rfloor, \]
where \( \lfloor x \rfloor \) represents the integer part or floor function of \( x \), is used to extract the 2D data-subset, indicated by the dots inside the dashed lines in Fig. 1B. The 2D signal in the \( k-\Xi \) coordinate system is

\[
S(k, \Xi) = \sum_{N_0=-\infty}^{\infty} I_{N_0} e^{iW_0 t_1} e^{iN_0 \Theta} e^{-t_1/T_2},
\]

(3)

and as shown in Fig. 1C. The 2D Fourier transform of Eq. (3) gives the 2D spectrum correlating frequency with spinning sideband order,

\[
S(\omega_1, N) = I_N L(\omega_1 - W_0),
\]

(4)

where \( L(\omega) \) represents the lineshape of a single resonance.

It should be noted that the TOP data processing in the time domain outlined by Blümlich and coworkers did not include the shearing transformation of Eq. (2). As a result, TOP spectra processed using their time domain approach will contain a mixed frequency and sideband order dimension, as found in the MAT experiment [7–9], instead of a pure sideband order dimension, as found in the 2D PASS experiment [10]. On the other hand, the TOP data processing in the frequency domain outlined by Blümlich and coworkers, and described below, does provide a pure sideband order dimension.

We also note that the spectral width limitation in the isotropic dimension of TOP is overcome by employing well known strategies for shifting the rotor pitch and isotropic time origins away from each other [5]. In such strategies the signal trajectories with different isotropic evolution time and rotor pitch origins are interleaved onto the sampling grid in Fig. 1 to obtain a two-dimensional spectrum with arbitrary isotropic dimension spectral width. For example, in the 2D-PASS experiment of Levitt and coworkers [10], a 5π pulse sequence is used to vary the rotor pitch while keeping isotropic evolution time constant. Conversely, in the FIREMAT experiment of Grant and coworkers [11], a 5π pulse sequence is used to vary the isotropic evolution time while keeping the rotor pitch constant.
Then, a shearing transformation

\[
\begin{pmatrix}
\omega_1 \\
N
\end{pmatrix}
= \begin{pmatrix}
1 & \Omega_R \\
0 & 1
\end{pmatrix}
\begin{pmatrix}
\omega'_1 \\
N'
\end{pmatrix},
\]

is applied to move the signal into a coordinate system where

\[
S(\omega_1, N) = \sum_{N_0=-\infty}^{\infty} I_{N_0} \mathcal{L}(\omega_1 - W_0 - (N_0 - N)\Omega_R),
\]

as shown in Fig. 2C. Finally, since

\[
\mathcal{L}(\omega_1 - W_0 - (N_0 - N)\Omega_R) = \mathcal{L}(\omega_1 - W_0)\delta(N_0 - N)
\]

we obtain

\[
S(\omega_1, N) = I_N \mathcal{L}(\omega_1 - W_0).
\]

We found the TOP spectrum more easily constructed using the frequency domain approach with the conventional 1D spectrum, after it has been phase corrected and any baseline roll removed. Subspectra can be extracted with arbitrary spectral width (vide infra), although \(\Omega_R\) is typically used.

The spinning rate can often be measured more accurately from the sideband spacing in the 1D spectrum. Errors in the \(\Omega_R\) used in the TOP processing are easily detected and corrected since they will result in skewed sideband patterns in the TOP spectrum. Interpolation inside the 1D spectrum when extracting subspectra is used to eliminate acquisition timing constraints. The TOP processing is freely available in the NMR data processing software package “dminfit” [12]. Because satellite transitions are detected in TOP, the magic-angle must be set with same level of accuracy needed for STMAS [13]. In practice, we found the TOP spectrum, itself, provides a straightforward approach for using the satellite transition lineshapes to set the magic-angle.

2.2 Frequency Domain Approach

The 1D spectrum obtained from the Fourier transform of Eq. (1) is

\[
S(\omega) = \sum_{N_0=-\infty}^{\infty} I_{N_0} \mathcal{L}(\omega - W_0 - N_0\Omega_R), \tag{5}
\]

This 1D spectrum be mapped into the TOP spectrum by first defining

\[
\omega = \omega'_1 \quad \text{for all } N',
\]

where \(N'\) is an integer, as shown in Fig. 2B, to become

\[
S(\omega'_1, N') = \sum_{N_0=-\infty}^{\infty} I_{N_0} \mathcal{L}(\omega'_1 - W_0 - N_0\Omega_R).
\]
3 Discussion

Figure 3 shows the $^{27}$Al TOP spectrum of YAG: Y$_3$Al$_5$O$_{12}$ constructed by stacking subspectra of spectral width $\Omega_R$ from its MAS spectrum. YAG has two aluminum sites, AlO$_4$ and AlO$_6$, with axially symmetric quadrupolar couplings of 6.07 MHz and 0.6 MHz, respectively [14]. These sites are easily distinguished in the TOP spectrum, with the AlO$_4$ resonance spanning a wider sideband order range than the AlO$_6$ resonance, as expected. The sideband intensity pattern for each site can be separated with a partial projection onto the sideband order dimension and analyzed for the anisotropy tensor parameters. The large quadrupolar coupling of AlO$_4$ results in its central and satellite transitions being separated and shifted by the second order quadrupolar interaction.

The inner satellite $\langle \pm 3/2, \pm 1/2 \rangle$ transition pair occurs to the left of the central transition $\langle \pm 1/2 \rangle$, while the outer satellite $\langle \pm 5/2, \pm 3/2 \rangle$ transition pair is shifted furthest left and lower in intensity. In contrast, since the AlO$_6$ resonance has negligible second-order effects there are no shifts in the center of gravity for each of its transitions. This results in all its spinning sidebands being lined up with the $N = 0$ (i.e., central transition) component. Also in Fig. 3 are the partial and full projections onto the frequency dimension. In the $N = 0$ cross section the central transitions for the AlO$_4$ and AlO$_6$ sites dominate. Contributions from the satellite transitions in the $N = 0$ cross section are generally weaker, although they are higher for the AlO$_6$ site, due to its small quadrupolar coupling, and thus care should be taken if a quantitative analysis of the spectrum is performed [14]. The full projection, equivalent to the synchronous acquisition spectrum [15] shows all the transitions, and the projection over cross-sections with $N \neq 0$ contains only the satellite transitions (minus the intensity of the $N = 0$ band). Note that the full projection has a substantially lower signal-to-noise ratio than the $N = 0$ cross-section.

Also note in Fig. 3 that the linewidth of the inner satellite transition is narrower than the outer satellite and central transition. This well-known narrowing [16–18], summarized in Table 1, can be readily exploited with TOP. For spin $I = 5/2$ it is the inner satellite pair which are the narrowest, whereas for spins $I = 7/2$ and $9/2$ it is the 2nd inner satellite pair, $\langle \pm 5/2, \pm 3/2 \rangle$. In Fig. 4 is the TOP spectrum at 17.6 Tesla of A9B2 (9Al$_2$O$_3$ 2B$_2$O$_3$), a crystalline compound with four different Al sites [18]. Although the four sites are not resolved in the $N = 0$ cross section (central transitions), the projection over the inner satellite transition ($N \neq 0$) has much better resolution and compares well with the central transition spectrum obtained at ultra high field (40 T) [19]. Such an approach could also be useful for detecting third order quadrupolar [20] or quadrupolar CSA cross terms [21] which only affect the satellite transitions.

In Fig. 5 is another example of an $^{27}$Al MAS spectrum of a Calcium Alumino-Silicate glass of hyper aluminous composition (50% SiO$_2$, 40% Al$_2$O$_3$, 10% CaO) which exhibits overlapping contributions of AlO$_4$, AlO$_5$, and AlO$_6$ environments. In previous MQMAS and MAS experiments[29] the different sites

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Fig. 3. $^{27}$Al TOP spectrum with projections of YAG (Y$_3$Al$_5$O$_{12}$) acquired at 17.6 T while spinning at 31,250 Hz (1 MHz spectral width, 1 µs pulse $\approx \pi/6$, 5 s recycle time, 128 scans).
could be resolved and quantified. In the satellite transition projection of the TOP spectrum they are also clearly resolved. Moreover, because the second order anisotropy is significantly reduced on the inner satellite \(\langle \pm 3/2, \pm 1/2 \rangle_{ST_1}\) transitions, most of their linewidth is due to the distribution of chemical shift that can be measured by fitting the spectrum.

\[
\begin{array}{c|cccc}
\text{Transition} & I = 3/2 & I = 5/2 & I = 7/2 & I = 9/2 \\
1/2 & \text{cg} & 3 & 8 & 15 & 24 \\
 & \text{br} & 18 & 48 & 90 & 144 \\
3/2 & \text{cg} & -6 & -1 & 6 & 15 \\
 & \text{br} & -16 & 14 & 56 & 110 \\
5/2 & \text{cg} & -28 & -21 & -12 \\
 & \text{br} & -88 & -46 & 8 \\
7/2 & \text{cg} & -66 & -57 \\
 & \text{br} & -216 & -162 \\
9/2 & \text{cg} & -120 \\
 & \text{br} & -400 \\
\end{array}
\]

Table 1

Scaling factors for second order isotropic shifts: \(\text{cg} = I(I+1) - 9m(m-1) - 3\), and second order anisotropy: \(\text{br} = 6I(I+1) - 34m(m-1) - 13\).
nant, provided $\Omega_R$ is sufficiently fast that the centerband is most intense. For example, in Fig. 6 is the $^{17}$O TOP spectrum of a Titanium Oxocluster [22] Ti$_{16}O_{16}(OEt)_{32}$ constructed with a subspectral width of 1.76$\Omega_R$. Six oxygen ($1\mu_2$, $3\mu_3$, and $2\mu_4$) are resolved in the frequency dimension of the TOP spectrum and their centerbands identified as the resonances with maximum intensities in the $N=0$ cross-section. The remaining resonances (shown in gray) are sidebands.

4 Conclusions

We have demonstrated here that the TOP experiment, originally proposed by Blümich and coworkers [2, 3], has a number of added advantages when applied to half-integer quadrupolar nuclei. The main strength of this new approach for presenting MAS data of half-integer quadrupolar nuclei lies in its rapid interpretation. The simplicity in performing the TOP rearrangement makes it quite compelling, generally applicable, and potentially, of interest to a wide range of scientists in materials chemistry using solid-state NMR. Additionally, the ability of the TOP approach to reconstruct the higher resolution satellite transition spectrum in a simple one pulse experiment is a unique feature by itself.

We have also presented a general theoretical framework in which the data processing for TOP, as well, as MAT and PASS can be viewed. The 1D to 2D mapping of TOP can also be extended to any direct or indirect dimension having spinning sidebands. Further work investigating such possibilities for half-integer quadrupolar nuclei is warranted.

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