

A Simple Method to Increase the Spectral Window for Ultra Wide NMR Spectroscopy

Zhehong Gan

*Center of Interdisciplinary Magnetic Resonance (CIMAR), National High Magnetic Field Laboratory (NHMFL),
1800 East Paul Dirac Drive, Tallahassee, Florida 32310*

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In Fourier-transform NMR spectroscopy, the width of the spectral window is determined by the sampling rate of time-domain signal (I). According to Nyquist theory, resonance lines with frequencies higher than the sampling rate are folded back into the spectral window. To avoid spectral folding, NMR spectrometers are usually equipped with digitizers fast enough to cover wide-line spectra such as ^1H and ^2H NMR of solids. However, cases which require a spectral window wider than the speed of digitizers still exist. Here, a simple method is described to increase the spectral window without the requirement of faster digitizers.

The problem of an insufficient sampling rate arises in our recent work on detecting satellite transitions of quadrupolar nuclei. For $S = \frac{5}{2}$ spins, the second-order quadrupolar effect under MAS is much smaller for $\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$ satellite transitions than the commonly observed central transition; therefore, satellite transition MAS spectra offer higher spectral resolution (2–5). By coherence transfer from satellite to central transition, the 2D satellite transition magic-angle spinning (STMAS) experiment completely averages the anisotropic second-order quadrupolar effect leading to isotropic NMR spectra of quadrupolar nuclei (6). Because satellite transitions are shifted by the first-order quadrupolar effect, their NMR frequencies in powder samples often span several MHz. Figure 1 shows ^{27}Al MAS spectra of a polycrystalline $9\text{Al}_2\text{O}_3 + 2\text{B}_2\text{O}_3$ sample. The modulation of first-order quadrupolar interaction by MAS yields large numbers of spinning sidebands for the satellite transitions. Clearly a 1 MHz spectral window, the maximum available on the Bruker DRX console, is not enough to cover all spinning sidebands and the peaks outside the spectral window are folded back.

Spectra with folded peaks are highly sensitive to the timing of data sampling. The phase of folded peaks depends on the time of the first data point to $t = 0$, the

moment when the magnetization of all peaks is in-phase (7, 8). Because of dead-time by RF pulse, data acquisition cannot start at $t = 0$ and spectral folding often causes dispersively shaped peaks and even intensity cancellation between folded and unfolded peaks. Figure 1 shows the change of both phase and intensity to spinning sidebands near two edges of the 1 MHz window by only a $0.5 \mu\text{s}$ shift to the data sampling.

The problems associated with insufficient sampling rate can be solved without the requirement of faster digitizers. Two spectra are acquired under identical conditions using the maximum digitizing rate except a shift of data sampling by a half dwell-time. New time-domain data can be constructed by filling the data points alternatively from the two acquired signals. The effective sampling rate of the generated data is twice of the digitizing rate and therefore doubles the spectral window. Figure 1c shows the resulting spectrum which has a 2 MHz spectral window using the maximum 1 MHz digitizing rate of the spectrometer. The increase in spectral window unfolds the satellite transition spinning sidebands which fold into the original spectral window in Fig. 1a. The unfolded spectrum of Fig. 1c directly shows the spinning sideband powder patterns of the first-order quadrupolar interaction excited by an $1 \mu\text{s}$ pulse with $\gamma B_1/2\pi = 80 \text{ kHz}$. A further increase in the spectral window when necessary can be implemented by acquiring multiple spectra with data sampling sequentially shifted by a fraction of the dwell-time.

The described method offers a simple solution for ultra wide NMR spectroscopy when available digitizers are not fast enough to cover the required spectral window. The increase in the spectral window avoids the problems from insufficient sampling rate such as spectral overlap, dispersive lineshape, and peak cancellation for observing ultra wide NMR spectra such as satellite transitions of quadrupolar nuclei.

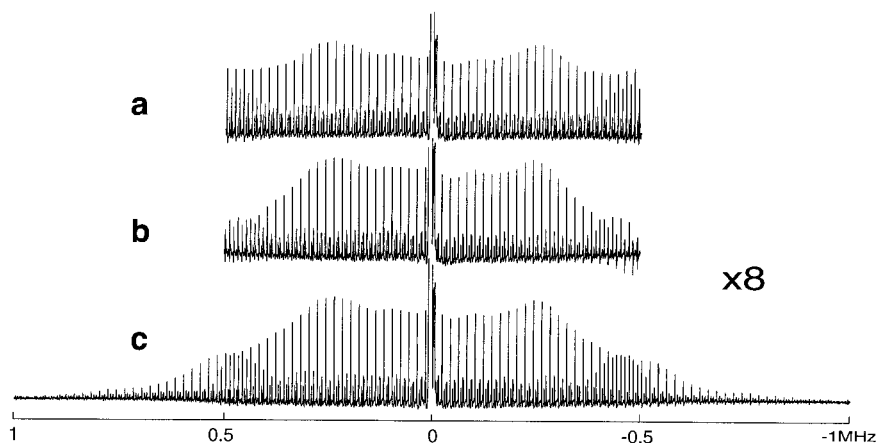


FIG. 1. (a) ^{27}Al satellite transition MAS spectrum of $9\text{Al}_2\text{O}_3 + 2\text{B}_2\text{O}_3$. (b) Same as (a) but the data sampling was delayed by $0.5 \mu\text{s}$. (c) Unfolded spectrum obtained using the method described in the text. Experiments were performed on a 833 MHz (^1H resonance frequency) Bruker DRX spectrometer using a 2.75 mm MAS probe. The 20 kHz sample spinning was carefully adjusted to the magic-angle for observing satellite transitions by a $1 \mu\text{s}$ excitation pulse ($\gamma B_1 / 2\pi = 80 \text{ kHz}$). All spectra were acquired using the maximum 1 MHz digitizing rate of the spectrometer. The baseline roll caused by the dead-time of RF pulse was reduced by filling the first nine distorted points with the signal intensity of the tenth point.

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