Boosting Sensitivity and Suppressing Artifacts via Multi-Acquisition in Direct Polarization NMR Experiments with Small Flip-Angle Pulses

Fu, R. (NHMFL); Yuxuan, X., Yang, Y. (Xiamen U., Chemistry) and Hernández-Maldonado, A.J. (U. of Puerto Rico-Mayagüez, Chemical Engineering)

Introduction

Nowadays, direct polarization (DP) is still commonly used in many materials applications such as catalysts/zeolites, batteries, silicates, etc., where either no abundant spin is available in the lattice of the materials for a source for uniform polarization enhancement or it is crucial to quantify various compositions. It has been known that the maximum signals in DP scheme are achieved by a 90º pulse, which directly brings the magnetization along the longitudinal direction into the transverse plane for detection. In such 90º pulse excitation experiments, the recycle delay between scans is required to be about five times that of the spin-lattice relaxation time (T_1) so that the magnetization could go back to its equilibrium state and thus this polarization scheme can be repeated for signal accumulation in order to improve the signal-to-noise ratio (SNR) and to obtain the quantitative information. However, when T_1 is long, although this 90º pulse excitation gives rise to a maximum signal per scan, it cannot produce a maximum SNR per time unit due to the long recycle delay. For a better quantification, a small flip-angle pulse excitation should always be used. However, it gives a low SNR per scan and generates background signals either from the probe components outside the sample coil or from the deadtime ringdown effects, which arise from acoustic ringing of the RF pulse right before the receiver opening. Here, we proposed a multi-acquisition scheme to boost the SNR per scan while retaining the advantages of the small flip-angle pulse excitation, and at the same time suppressing artifacts from the background signals and the deadtime ringdown effects [1].

Experimental

All NMR experiments were carried out on a Bruker Avance 600 MHz NMR spectrometer using a Bruker 1.3 mm HX MAS NMR probe, where the ^{1}H channel was tuned to ^{19}F. A mixture of Flufenamic acid (FFA) and 3,5-difluorobenzoic acid (FBA) spinning at 40 kHz was used to illustrate the advantages of this multi-acquisition scheme.

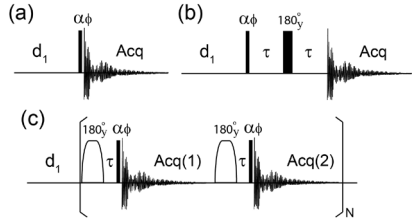

Figure 1: (a) A small flip-angle pulse excitation. (b) Small flip-angle pulse excitation using spin-echo refocusing. (c) Multi-acquisition scheme. N is the number of loops. The solid rectangles represent hard pulses, while the open shaped pulses stand for adiabatic 180° inversion. The excitation pulse has a flip-angle α with a phase ϕ.

Results and Discussion

Figure 1 shows the pulse sequence schemes using small flip-angle pulse excitation. Figure 2a is the ^{19}F spectrum obtained using Figure 1a, clearly showing a distorted baseline due to the background signals, which can be removed by a spin-echo scheme (Fig. 2b). However, the signal intensities were reduced because the recycle delay d_1 was long enough. While the multi-acquisition scheme (c.f. Fig. 2c) not only enhances the signals in exactly the same experimental time, it also suppresses the baseline distortion. The signals could be improved further with more loops N. The sensitivity enhancement factor ε after the Nth loop in the multi-acquisition scheme over the single small flip-angle pulse excitation is:

$$\varepsilon = \frac{S_{obs}^{N}}{M_2^2(0)\sin(\alpha)\sqrt{2N}} = [1+\cos(\alpha)]\sum_{i=1}^{N}\cos^{2i-2}(\alpha)/\sqrt{2N}$$

It is anticipated that this new multi-acquisition method offers an opportunity to obtain quantitative proportions of various structurally distinct sites with improved sensitivity in materials applications at high field NMR and at low temperature such as under DNP conditions.

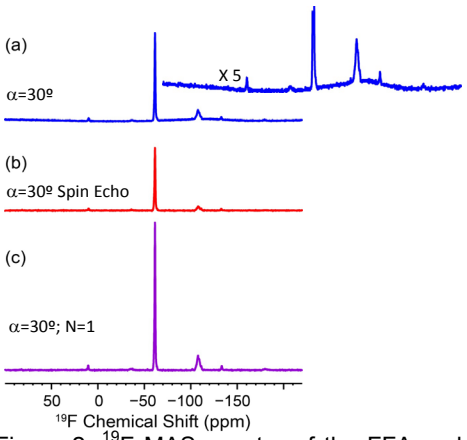

Figure 2: ^{19}F MAS spectra of the FFA and FBA mixture using the pulse schemes shown in Fig. 1.

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References

[1] Fu, R., *et al.*, J. Magn. Reson., **293**, 34-40 (2018).