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Sensitivity enhancement of the central-transition signal of half-integer spin quadrupolar nuclei in solid-state NMR: Features of multiple fast amplitude-modulated pulse transfer

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Sensitivity enhancement of solid-state NMR spectrum of half-integer spin quadrupolar nuclei under both magic-angle spinning (MAS) and static cases has been demonstrated by transferring polarisation associated with satellite transitions to the central $m = -1/2 \rightarrow 1/2$ transition with suitably modulated radio-frequency pulse schemes. It has been shown that after the application of such enhancement schemes, there still remains polarisation in the satellite transitions that can be transferred to the central transition. This polarisation is available without having to wait for the spin system to return to thermal equilibrium. We demonstrate here the additional sensitivity enhancement obtained by making use of this remaining polarisation with fast amplitude-modulated (FAM) pulse schemes under both MAS and static conditions on a spin-3/2 and a spin-5/2 system. Considerable signal enhancement is obtained with the application of the multiple FAM sequence, denoted as m-FAM. We also report here some of the salient features of these multiple FAM sequences with respect to the nutation frequency of the pulses and the spinning frequency.

1. Introduction

The potential application of solid-state NMR in the study of quadrupolar nuclei in materials of inorganic, catalytic, and biological importance is well documented [1,2]. However, due to one or many of the following factors such as, low natural abundance, small values of gyromagnetic ratios, and large values of quadrupolar interaction constants, the observable central-transition (CT) single-quantum (SQ) signal in one-dimensional (1D) experiments is often beset with sensitivity problems even under magic-angle spinning (MAS). These become more acute when spectra need to be acquired under static conditions. Hence, sensitivity enhancement of solid-state NMR spectra of half-integer spin quadrupolar nuclei is of utmost importance.

The seminal work of Vega and Naor in 1981 showed that amplitude-modulated radio-frequency (RF) pulses lead to inversion of populations across the satellite transitions giving rise to an enhanced population difference across the central transition and thereby an enhanced signal intensity in the case of single crystals under static conditions [3]. It may be noted that a similar attempt was made much earlier by Pound where a saturation of populations across the satellite transitions was shown to effect an enhanced central-transition signal again for static single crystals [4]. Many different schemes have been introduced since 1990 for the CT signal enhancement in 1D experiments, notable amongst them being "dual Q-probe" and frequency-swept adiabatic passage schemes [5–7], double-frequency sweeps (DFS) [8–11], fast amplitude-modulated (FAM) pulses [12–14], Gaussian pulse trains [15], and hyperbolic secant pulses [16–19]. All these modulated RF pulse schemes rearrange the populations across the satellite transitions, through a combination of both inversion and saturation, leading to an enhancement of the single-quantum central-transition signal. It may be noted that the FAM pulses were originally introduced in the context of signal enhancement of multiple-quantum MAS (MQMAS) experiments [20–23]. The same pulse scheme was later termed as rotor assisted population transfer (RAPT) pulses by the group of Grandinetti [12]. Although it is true that the FAM pulses are most effective under MAS, certain enhancement could be obtained in static cases as well [24]. Variants of FAM which generate a frequency sweep by modulating the pulse duration in either a linear or non-linear way, notated as SW(τ)-FAM and SW($1/\tau$)-FAM, were found to give good signal enhancement in the case of static samples [25,26].

A significant addition to these enhancement schemes was made by Kwak et al. where in they introduced multiple rotor assisted population transfers with Gaussian pulse pairs [27]. The idea was not just to repeat the Gaussian pulse pairs several times before the signal acquisition and wait for thermal equilibrium to happen, as also implemented with other schemes, but to repeat the Gauss-

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ian pulse pairs and signal acquisition multiple times before the spin system returns to thermal equilibrium. This was found to be beneficial as always there is a considerable amount of spin polarisation left in the satellite transitions that are not transferred to the central transitions. By repeating the whole sequence several times within the relaxation time it is ensured that a substantial fraction of the population in the satellite transitions is converted to central transition. This multiply repeated scheme was shown to give a signal enhancement by a factor of 2.0 or more compared to implementing it once. This was later shown in the case of DFS scheme as well [28].

We here report on similar enhancement obtained with the FAM pulse scheme and its variants performed multiply, notated as multiple FAM (*m*-FAM), under both MAS and static conditions. We further examine the robustness of these schemes with respect to the MAS frequency ν_r and the nutation frequency of both the "CT selective 90° pulse $\nu_{nut}^{90°}$ used to create the transverse magnetisation and the FAM and the *m*-FAM pulses ν_{nut}^{FAM}. *m*-FAM performs much better under both spinning and static conditions. We report also on the signal enhancement obtained by repeating the SW(1/τ)-FAM scheme for the static case which in turn surpasses the performance of *m*-FAM.

Higher signal enhancement and much smaller dependence to the MAS frequency under spinning and nutation frequency of the FAM pulses for both spinning and static conditions are some of the desirable features of *m*-FAM and *m*-SW(1/τ)-FAM.

2. Experimental

All experiments were carried out on a Bruker Avance-500 spectrometer operating at a field strength of 11.7 T with a Bruker 4 mm triple-resonance probe. Experiments were performed observing the spin-3/2 ^{23}Na resonance of Na_2SO_4 at a Larmor frequency of 132.25 MHz and the spin-5/2 ^{27}Al resonance of the gibbsite sample at a Larmor frequency of 130.28 MHz. The quadrupolar coupling constant χ of ^{23}Na in Na_2SO_4 is 2.6 MHz and asymmetry parameter η is 0.6 [29]. Gibbsite has Al in two different environments with χ = 2.0 MHz and η = 0.8 and χ = 4.3 MHz and η = 0.4 [30].

We denote the FAM pulse train consisting of a pulse pair and windows of delays of equal duration separating them by a concise notation of the form $F_n^I(\tau)$, where *n* corresponds to the total number of pulse pairs in the FAM scheme and τ is the duration of one FAM block in μs [31]. The Roman numeral in the superscript suggests that FAM-I is used here. For ^{23}Na (spin *I* = 3/2) the FAM train was of the form $F_{18}^I(2.8)$ and for ^{27}Al (*I* = 5/2) we used FAM train of the form $F_{10}^I(6)F_{12}^I(7)$ to obtain maximum enhancement. Two FAM blocks were used for spin-5/2 nuclei with the first one affecting the outer satellite transition and the second one affecting the inner satellite transition. Fig. 1a shows the pulse scheme employing FAM for signal enhancement in spin-3/2 systems.

The *m*-FAM scheme has FAM as the basic building block where the optimised FAM cycle along with the central-transition selective 90° pulse and the acquisition were repeated multiple times until maximum enhancement of the signal was obtained. The pulse scheme is given in Fig. 1b again for spin-3/2 systems. We denote the *m*-FAM scheme as $F_{n:m}^I(\tau)$ where *m* in the subscript indicates the number of times FAM and acquisition are repeated. For ^{23}Na (*I* = 3/2) we used *m*-FAM of the type $F_{18:10}^I$ (2.8) and for ^{27}Al (*I* = 5/2) we used *m*-FAM of the form $F_{10:12}^I(6)F_{20:12}^I(7)$. For rotor synchronised *m*-FAM experiments on ^{27}Al we made use of *m*-FAM of the form $F_{10:12}^I(6)F_{20:12}^I(6)$.

For the spin-3/2 system the nutation frequency of the FAM pulses was 53 kHz and that for the central-transition selective 90° pulse was 25 kHz. For the spin-5/2 system the nutation frequency of the FAM pulses was 62 kHz and that for the 90° pulse was 25 kHz. For both the nuclei recycle delay was 2 s.

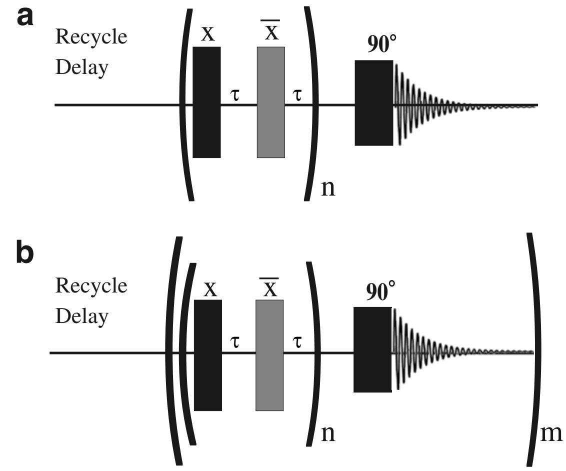

Fig. 1. (a) FAM pulse sequence for spin-3/2 nuclei where *n* is the loop counter of the FAM pulse train. (b) *m*-FAM pulse sequence for spin-3/2 nuclei where *m* is the total loop counter of FAM-90°-acquisition before the recycle delay. τ is the interpulse delay of the FAM train.

3. Results and discussion

We report on the results obtained from the spin-3/2 and spin-5/2 samples using FAM and *m*-FAM pulses under both MAS and static conditions. The signal-enhancement factor η reported with the use of FAM schemes is with respect to the signal obtained with only a single 90° pulse.

3.1. ^{23}Na (I = 3/2) in Na_2SO_4

Table 1 shows the results obtained with the application of FAM and *m*-FAM pulses observing the ^{23}Na resonance of Na_2SO_4. *m*-FAM outperforms FAM as seen from Table 1. To investigate the robustness of the FAM sequences with respect to the nutation frequency of the pulses and the MAS frequency, the signal-enhancement factors were noted for FAM and *m*-FAM as a function of these variables. Fig. 2a shows the signal enhancement factor for FAM and *m*-FAM plotted as a function of the nutation frequency of the FAM pulses, ν_{nut}^{FAM}. The FAM blocks were optimised for a nutation frequency of 53 kHz. Fig. 2b shows the signal-enhancement factor for FAM and *m*-FAM plotted as a function of the nutation frequency of the central-transition selective 90° pulses, $\nu_{nut}^{90°}$. In both Fig. 2a and b the respective nutation frequencies were varied from 25 to 95 kHz. Fig. 2c shows the signal-enhancement factor for FAM and *m*-FAM plotted as a function of the MAS frequency ν_r where ν_r was varied from 6 to 12 kHz in steps of 1 kHz. The maximum drop in the efficiency of the schemes for the three experimental variables considered is given in Table 2. It is clearly seen that *m*-FAM is much superior to and robust than normal FAM for signal enhancement under MAS conditions.

m-FAM applied on Na_2SO_4 under static conditions gave a signal enhancement of a factor of 2.0 compared with a single 90° pulse, whilst regular FAM did not yield any appreciable signal enhancement (data not shown). This aspect will be discussed in detail in the next Section with reference to the spin-5/2 system.

Table 1
Signal enhancement obtained with FAM and *m*-FAM for ^{23}Na and ^{27}Al spin systems (quoted with an error of ±0.1)

Nucleus	Spin	FAM enhancement	*m*-FAM enhancement
^{23}Na	3/2	1.7	3.3
^{27}Al	5/2	2.1	6.9

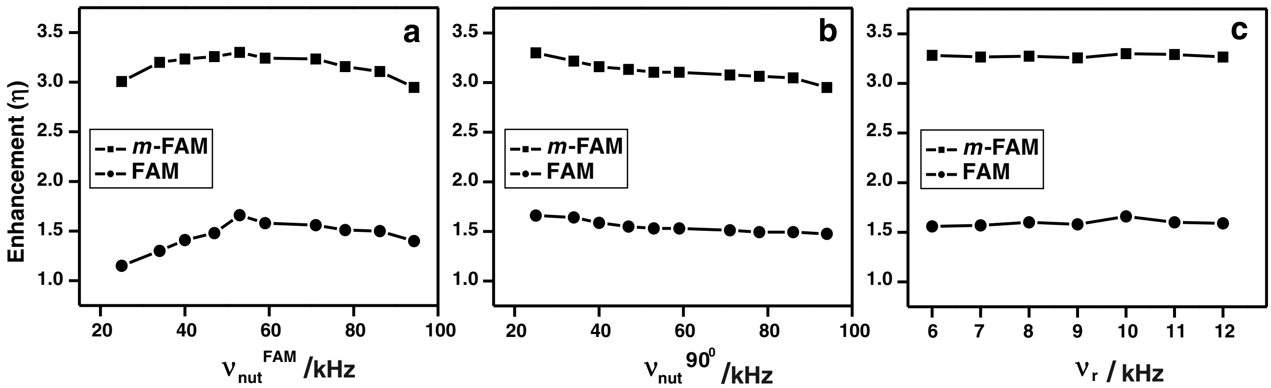

Fig. 2. Signal-enhancement factor for spinning ^{23}Na sample as a function of (a) the nutation frequency of the FAM pulses ν_{nut}^{FAM}, (b) the nutation frequency of the 90° pulse $\nu_{nut}^{90^\circ}$, and (c) the spinning speed ν_r. Squares represent the result with *m*-FAM and circles represent the result with FAM.

Table 2
Maximum drop in the optimised signal (expressed in terms of %) with FAM and *m*-FAM as a function of ν_{nut}^{FAM}, $\nu_{nut}^{90^\circ}$, and ν_r for ^{23}Na ($I = 3/2$)

Variables	FAM	*m*-FAM
ν_{nut}^{FAM}	30.8	10.7
$\nu_{nut}^{90^\circ}$	11.2	10.6
ν_r	4.9	1.1

3.2. ^{27}Al ($I = 5/2$) in gibbsite

For the spin-5/2 case the performance efficiency of FAM, *m*-FAM, and rotor-synchronised *m*-FAM schemes were investigated observing the ^{27}Al resonance of a sample of gibbsite.

Fig. 3 shows the one-dimensional (1D) MAS ^{27}Al spectra of gibbsite acquired at $\nu_r = 10$ kHz with a single 90° pulse, multiple 90° pulse (90° pulses were implemented as in the case of *m*-FAM scheme), FAM, *m*-FAM, and rotor-synchronised *m*-FAM schemes. Clearly *m*-FAM performs better than regular FAM with enhancement factors reported in Table 1. It may be noted that the rotor-synchronised *m*-FAM scheme performs as well as *m*-FAM (factor of 6.7 against 6.9 with respect to a single 90° pulse scheme). Interestingly, the *m*-90° scheme outperforms regular FAM, whilst *m*-FAM is still better by a factor of nearly 2.5 in comparison with *m*-90°. There are no appreciable line shape distortions here which were also evident in the case of spin-3/2 system (data not shown).

To investigate the robustness of the FAM sequences with respect to the nutation frequency of the pulses and the MAS rate, the signal enhancement factors were noted for FAM, *m*-FAM, and rotor-synchronised *m*-FAM schemes as a function of these variables. Fig. 4a shows the signal-enhancement factor for all the schemes plotted as a function of the nutation RF of the FAM pulses, ν_{nut}^{FAM}. The FAM blocks were optimised for a nutation frequency of 53 kHz. Fig. 4b shows signal-enhancement factor for all the schemes plotted as a function of the nutation frequency of the central-transition selective 90° pulses, $\nu_{nut}^{90^\circ}$. In both Fig. 4a and b the respective nutation frequencies were varied from 30 to 95 kHz. Fig. 4c shows the signal-enhancement factor for all the schemes plotted as a function of the MAS frequency ν_r where ν_r was varied from 6 to 12 kHz in steps of 1 kHz. The maximum drop in the efficiency of the schemes for the three experimental variables considered is given in Table 3. It is clearly seen that *m*-FAM is much superior to normal FAM and rotor-synchronised *m*-FAM in terms of robustness with respect to experimental parameters and could be easily implemented experimentally.

The signal-enhancement feature of *m*-FAM can be attributed to the multiple transfer of population from satellite transitions to central transition before the spin system attains thermal equilib-

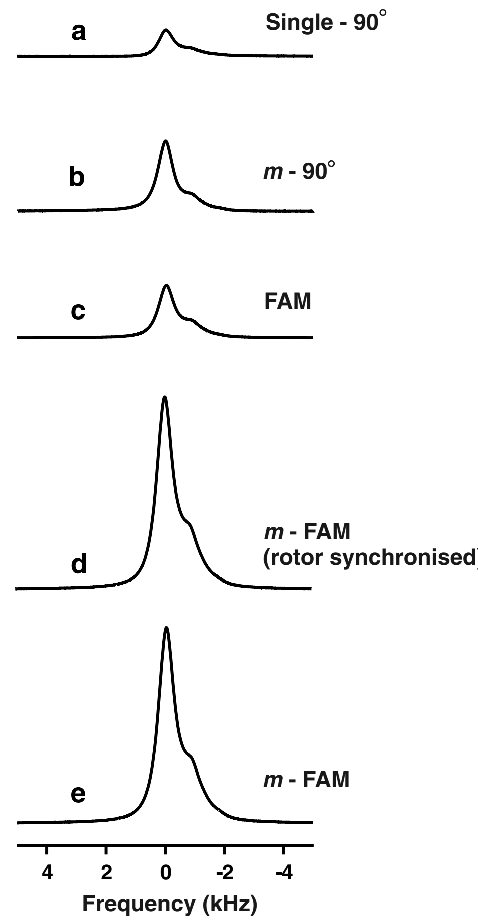

Fig. 3. ^{27}Al NMR spectra of gibbsite with different pulse schemes under MAS. (a) Single 90° pulse, (b) repetitive 90° pulse *m*-90°, (c) FAM, (d) rotor-synchronised *m*-FAM, and (e) *m*-FAM.

rium. For every such transfer made possible, the central-transition selective 90° pulse acts nearly on a similar range of crystallites accounting for the almost similar dependence on $\nu_{nut}^{90^\circ}$ of all the schemes. Additional robustness of the *m*-FAM with respect to both ν_{nut}^{FAM} and ν_r may be attributed to different parts of the powder being influenced by the FAM pulses as either of these change where then a multiple transfer of population takes place. In other words, any change in the experimental variable, either ν_{nut}^{FAM} or ν_r, simply changes the domain of action of the FAM pulses in a powder, but wherever they act an optimum multiple transfer of population

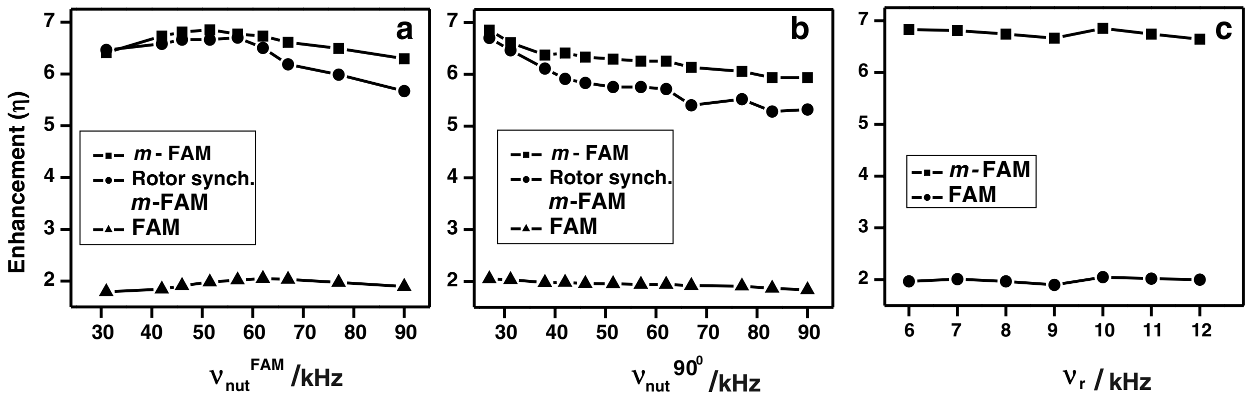

Fig. 4. Signal-enhancement factor for spinning ^{27}Al sample as a function of (a) the nutation frequency of the FAM pulses ν_{nut}^{FAM}, (b) the nutation frequency of the 90° pulse $\nu_{nut}^{90^\circ}$, and (c) the spinning speed ν_r. In (a) and (b) squares, circles, and triangles correspond to *m*-FAM, rotor-synchronised *m*-FAM, and FAM, respectively. In (c) squares and circles correspond to *m*-FAM and FAM, respectively.

Table 3
Maximum drop in the optimised signal (expressed in terms of %) with FAM, *m*-FAM, and rotor-synchronised *m*-FAM as a function of ν_{nut}^{FAM}, $\nu_{nut}^{90^\circ}$, and ν_r for ^{27}Al ($I = 5/2$)

Variables	FAM	*m*-FAM	Rotor-synchronised *m*-FAM
ν_{nut}^{FAM}	12.5	8.1	15.4
$\nu_{nut}^{90^\circ}$	10.5	13.4	20.6
ν_r	7.5	3	—

from satellite transition to central transition is obtained thereby keeping the signal-enhancement factor nearly the same. If this were true, a rotor-synchronised *m*-FAM scheme would not be as effective as the *m*-FAM scheme as by virtue of rotor synchronisation the FAM pulses can only affect the same range of crystallites in a powder for all values of ν_{nut}^{FAM} or $\nu_{nut}^{90^\circ}$. This would then lead to a dependence of the rotor-synchronised *m*-FAM scheme on these variables, and this is clearly borne out from the experiments as shown in Table 3. All the above arguments are also valid in the earlier discussed case of spin-3/2 system.

It has been shown earlier that SW(1/τ)-FAM performs best in static cases with respect to the simple FAM [26]. Experiments were performed observing ^{27}Al resonance of gibbsite under static conditions with SW(1/τ)-FAM, *m*-FAM, and multiple SW(1/τ)-FAM. The SW(1/τ)-FAM scheme was composed of 12 pulse pairs with the pulse length and the window duration being the same. The initial pulse duration was 0.4 μs and the final pulse duration was 7.2 μs. The sweep width was 590.3 kHz. The nutation frequency of the FAM pulses was 62 kHz. Both *m*-FAM and *m*-SW(1/τ)-FAM schemes were repeated 10 times before the spin system attained thermal equilibrium. Regular FAM pulses were nearly ineffective in the static case. Compared to a single 90° pulse, SW(1/τ)-FAM gave a signal enhancement of 2.1. The *m*-FAM scheme gave a signal enhancement of 5.46 whilst the *m*-SW(1/τ)-FAM gave a factor of 6.64. Such enhancements could be very useful in the NMR of quadrupolar nuclei under static cases.

Fig. 5a and b shows the signal-enhancement factor obtained with *m*-FAM, SW(1/τ)-FAM, and *m*-SW(1/τ)-FAM as a function of ν_{nut}^{FAM} and $\nu_{nut}^{90^\circ}$, respectively, with the former being varied from 30 to 85 kHz and the latter being varied from 25 to 85 kHz. As evident from Fig. 5a and b *m*-FAM and *m*-SW(1/τ)-FAM show lesser dependence on ν_{nut}^{FAM} whilst all the three schemes show a similar dependence on $\nu_{nut}^{90^\circ}$. This observation again proves the superior performance of multiple FAM schemes. The maximum drop in the efficiency of the schemes for the two experimental variables considered is given in Table 4.

From the experiments considered here, *m*-FAM schemes gave much higher signal enhancement than FAM both in the spinning and the static case, which was also true between SW(1/τ)-FAM and *m*-SW(1/τ)-FAM in the static case where the latter gave much higher enhancement than the former. This happens as performing FAM and SW(1/τ)-FAM in a multiple way without allowing the spin system to reach thermal equilibrium transfers a larger part of polarisation from the satellite to the central transition. It is also observed that *m*-FAM is quite robust with respect to change in the nutation RF of the modulation pulses, ν_{nut}^{FAM}, and the MAS rate, ν_r, but when the nutation RF of the 90° pulses, $\nu_{nut}^{90^\circ}$, was changed

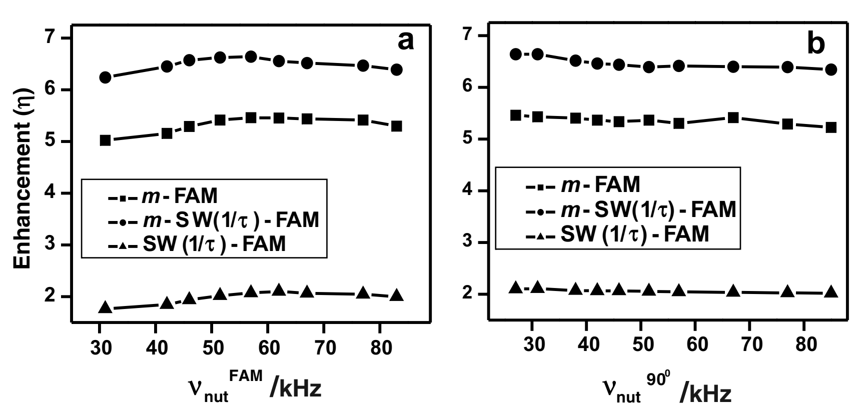

Fig. 5. Signal-enhancement factor as a function of (a) the nutation frequency of the FAM pulses ν_{nut}^{FAM} and (b) the nutation frequency of the 90° pulse $\nu_{nut}^{90^\circ}$ for static ^{27}Al sample. Squares, circles, and triangles represent *m*-FAM, *m*-SW(1/τ)-FAM, and SW(1/τ)-FAM, respectively.

Table 4
Maximum drop in the optimised signal (expressed in terms of %) with SW(1/τ)-FAM, *m*-FAM, and *m*-SW(1/τ)-FAM as a function of ν_{nut}^{FAM} and $\nu_{nut}^{90^\circ}$ for ^{27}Al ($I = 5/2$) in static condition

Variables	SW(1/τ)-FAM	*m*-FAM	*m*-SW(1/τ)-FAM
ν_{nut}^{FAM}	16.1	8.1	6.2
$\nu_{nut}^{90^\circ}$	3.9	4.3	4.5

m-FAM scheme behaves almost comparably in different nuclei (^{23}Na and ^{27}Al) and also under different conditions (spinning and static). One can argue that since the 90° pulse is not a part of the modulation changing the nutation RF of the 90° pulse manifests relatively similarly with FAM and *m*-FAM under different conditions and with different nuclei.

4. Conclusions

The present study suggests that *m*-FAM gives better signal enhancement than FAM and is much more robust to the nutation RF of the FAM pulses and the MAS frequency than FAM. *m*-FAM also performs better than SW(1/τ)-FAM in static condition, however, *m*-SW(1/τ)-FAM outperforms *m*-FAM. Both *m*-SW(1/τ)-FAM and *m*-FAM show very little dependence on the change of the nutation frequency of the FAM pulses from the optimised value where as SW(1/τ)-FAM showed an appreciable amount of dependence. We expect that the Gaussian pulse pairs, DFS scheme, and hyperbolic secant pulses also will show the same robustness features as was shown for FAM when applied in a multiple fashion. It is expected that the robustness features of these schemes will make the application of these towards sensitivity enhancement of the spectra of half-integer spin quadrupolar nuclei more routine.

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