



Enhancing sensitivity of quadrupolar nuclei in solid-state NMR with multiple rotor assisted population transfers

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Abstract

Rotor-assisted population transfer (RAPT) was developed as a method for enhancing MAS NMR sensitivity of quadrupolar nuclei by transferring polarization associated with satellite transitions to the central $m = \frac{1}{2} \rightarrow -\frac{1}{2}$ transition. After a single RAPT transfer, there still remains polarization in the satellite transitions that can be transferred to the central transition. This polarization is available without having to wait for the spin system to return to thermal equilibrium. We describe a new RAPT scheme that uses the remaining polarization of the satellites to obtain a further enhancement of the central transition by performing RAPT-enhanced experiments multiple times before waiting for re-equilibration of the spin system. For ^{27}Al ($I = 5/2$) in albite we obtain a multiple RAPT enhancement of 3.02, a 48% increase over single RAPT. For ^{93}Nb ($I = 9/2$) in NaNbO_3 we obtain a multiple RAPT enhancement of 5.76, an 89% increase over single RAPT. We also describe a data processing procedure for obtaining the maximum possible signal-to-noise ratio.

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1. Introduction

Rotor-assisted population transfer (RAPT) was developed as a method for enhancing MAS NMR sensitivity of quadrupolar nuclei in solids [1–3]. This is

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accomplished by transferring polarization associated with satellite transitions to the central $m = \frac{1}{2} \rightarrow -\frac{1}{2}$ transition. The advantage of the RAPT method over previous schemes [4–9] for utilizing satellite transition polarization is that RAPT can be applied to a polycrystalline sample during MAS to obtain simultaneous central transition enhancement of all crystallite orientations. Additionally, RAPT has the advantage over cross polarization [10–12] that it does not require neighboring protons to enhance the sensitivity of a quadrupolar nucleus.

An interesting aspect of RAPT, not unlike cross polarization [11], is that after a single RAPT transfer, there still remains polarization in the satellite transitions that can be transferred to the central transition. This polarization is available without having to wait for the spin system to return to thermal equilibrium. In this paper, we propose a new RAPT scheme that uses the remaining polarization of the satellites to obtain a further enhancement of the central transition by performing RAPT-enhanced experiments multiple times before waiting for re-equilibration of the spin system.

2. Theoretical background

With each successive application of RAPT the polarization of the central transition, after the initial RAPT enhancement, will decrease exponentially. This is illustrated below for the spin 3/2 case. Each column vector represents the relative populations of the spin 3/2 energy levels in a multiple RAPT experiment.

$$\begin{pmatrix} \frac{3}{2} \\ \frac{1}{2} \\ -\frac{1}{2} \\ -\frac{3}{2} \end{pmatrix} \xrightarrow{\text{RAPT}} \begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \end{pmatrix} \xrightarrow{\pi/2} \begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \end{pmatrix} \xrightarrow{\text{RAPT}} \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ -\frac{1}{2} \\ -\frac{1}{2} \end{pmatrix} \xrightarrow{\pi/2} \begin{pmatrix} \frac{1}{2} \\ 0 \\ 0 \\ -\frac{1}{2} \end{pmatrix} \xrightarrow{\text{RAPT}} \begin{pmatrix} \frac{1}{4} \\ \frac{1}{4} \\ -\frac{1}{4} \\ -\frac{1}{4} \end{pmatrix} \dots$$

Assuming that the first RAPT application leads to an $I + 1/2$ enhancement of the central transition, then after the k th application of RAPT the enhancement factor, η_k , would be given by

$$\eta_k = \left(I + \frac{1}{2} \right) \frac{(I - \frac{1}{2})^{(k-1)}}{(I + \frac{1}{2})^{(k-1)}}, \quad (1)$$

where I is the nuclear spin value. If we summed all these enhancements we obtain

$$\sum_{k=1}^{\infty} \eta_k = (I + 1/2)^2. \quad (2)$$

To obtain the total experimental enhancement we have to take the noise into account. To optimize the enhancement in the signal-to-noise ratio in a multiple

Table 1
Comparison of theoretical gains in sensitivity using RAPT and multiple RAPT

Spin I	Single RAPT enhancement	Time reduction factor	Multi-RAPT enhancement	Time reduction factor
3/2	2	4	2.31	5.34
5/2	3	9	4.02	16.16
7/2	4	16	6.05	36.60
9/2	5	25	8.33	69.39

RAPT experiment we scale the signal obtained after the k th RAPT contact by

$$\frac{(I - \frac{1}{2})^{(k-1)}}{(I + \frac{1}{2})^{(k-1)}} \quad (3)$$

before adding into the total signal. This is akin to a matched filter. Thus for the total signal we obtain

$$S_T^M = S_0 \left(I + \frac{1}{2} \right) \sum_{k=1}^{\infty} \frac{(I - \frac{1}{2})^{2(k-1)}}{(I + \frac{1}{2})^{2(k-1)}} = \frac{S_0 (2I + 1)^3}{2 \cdot 8I}, \quad (4)$$

where S_0 is the signal obtained without any RAPT enhancement. Applying the same scaling factor to the noise, we find that the total noise, σ_T , will grow according to

$$\sigma_T = \sigma_0 \left(\sum_{k=1}^{\infty} \left(\frac{(I - \frac{1}{2})^{(k-1)}}{(I + \frac{1}{2})^{(k-1)}} \right)^2 \right)^{1/2} = \frac{2I + 1}{\sqrt{8I}} \sigma_0, \quad (5)$$

where σ_0 is the standard deviation of the noise in a single acquisition, which we assume is constant in magnitude during each acquisition. Thus, the enhancement in a properly weighted multiple RAPT experiment will be given by

$$\eta_T = \frac{S_T/\sigma_T}{S_0/\sigma_0} = \frac{1}{2} \frac{(2I + 1)^2}{\sqrt{8I}}. \quad (6)$$

The theoretical gains in sensitivity enhancement by RAPT and multiple RAPT for non-integer quadrupolar nuclei are summarized in Table 1. While only a small sensitivity advantage is expected in the spin 3/2 case, a sizeable improvement in sensitivity is expected with larger nuclear spin values. Also shown in Table 1 is the corresponding reduction in signal averaging time.

3. Experimental

All NMR spectra were measured at 9.4 T (104.273 MHz ^{27}Al frequency, and 97.832 MHz ^{93}Nb frequency) with a Bruker DMX 400 spectrometer, using a Bruker 4-mm probehead. The samples used for the multiple RAPT experiments were polycrystalline albite ($\text{NaSi}_3\text{AlO}_8$) and polycrystalline sodium niobate (NaNbO_3), which have ^{27}Al quadrupolar coupling parameter of $C_q = 3.29$ MHz, and $\eta_q = 0.62$

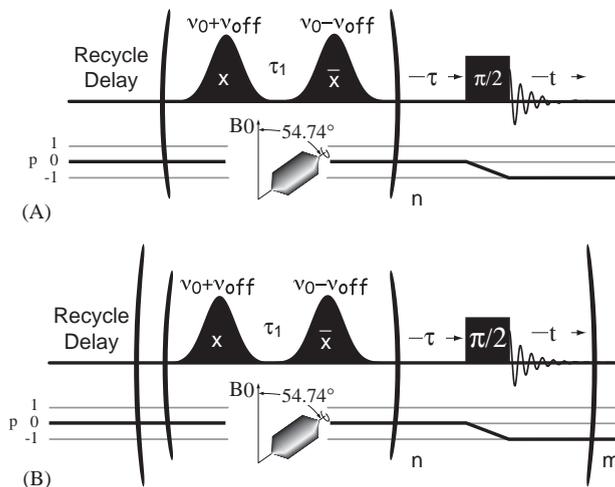


Fig. 1. (A) RAPT pulse sequence using off-resonance excitation with Gaussian pulses. The parameter n is the loop counter of RAPT pulse train. (B) Multiple RAPT pulse sequence that used the same off-resonance Gaussian pulse train of (A). The parameter m indicates the total loop counter of RAPT-Acquisition before the recycle delay. In all experiments, a $2 \mu\text{s}$ delay (τ_1) between each pulse in the RAPT pulse train was used to allow time for the transmitter phase to stabilize. The delay τ is to implement a z filter and is typically set to an integer multiple of the rotor period.

[13], and ^{93}Nb quadrupolar coupling parameter of $C_q = 19.6 \text{ MHz}$, and $\eta_q = 0.82$ [14], respectively. The effective T_1 of the ^{27}Al central transition of albite and ^{93}Nb central transition of NaNbO_3 were measured to be 38.6 s and 125 ms, respectively. The spinning rate for all experiments was 12 kHz.

The Gaussian RAPT sequence, shown in Fig. 1A, consists of a train of Gaussian pulses with alternating off resonant frequencies of $\pm v_{off}$. For optimum enhancement $|v_{off}|$ is set near $|\frac{3}{2}C_q/(2I(2I-1))|$. For ^{27}Al in albite and ^{93}Nb in NaNbO_3 we used $v_{off} = 350$ and 550 kHz , respectively.

Fig. 1B shows the multiple RAPT sequence, which consists of multiple loops of Gaussian RAPT and acquisition. To simplify the data processing of the multiple RAPT experiment we acquired data in a two-dimensional experiment with m as the second dimension. A two-dimensional Fourier transform with respect to t and m yields a two-dimensional spectrum, and the cross-section taken parallel to the ω_t axis at $\omega_m = 0$ yields the multiple RAPT spectrum. A matched filter applied to the m dimension before Fourier transform will yield the spectrum with the highest possible sensitivity enhancement.

4. Results and discussion

Fig. 2 shows the comparison between theoretical and experimental multiple RAPT sensitivity enhancement factor for $I = \frac{5}{2}$ (^{27}Al) and $I = \frac{9}{2}$ (^{93}Nb) nuclei as a function

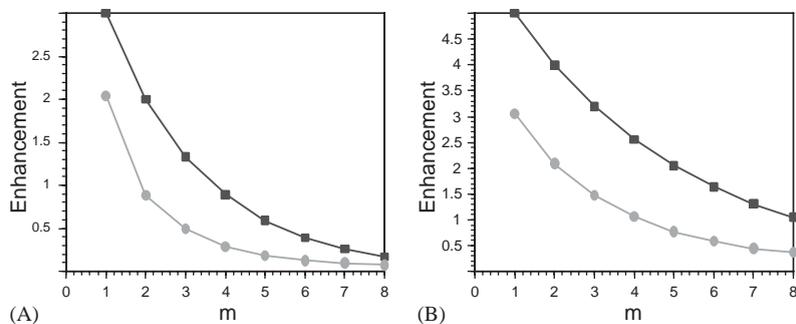


Fig. 2. (A) The comparison between theoretical (square) and experimental (circle) multiple RAPT ($m = 8$) central transition sensitivity enhancement factor for each RAPT-acquisition unit of ^{27}Al ($I = 5/2$) in albite. (B) The comparison between theoretical (square) and experimental (circle) multiple RAPT ($m = 8$) central transition sensitivity enhancement factor for each RAPT-acquisition unit of ^{93}Nb ($I = 9/2$) in NaNbO_3 .

of m , the number of RAPT applications. In both cases the trend with increasing m matches our theoretical prediction of an exponential decay.

The differences between the experimental and predicted curves arise because the Gaussian RAPT sequence is not able to produce the maximum $I + 1/2$ efficiency when $I > 3/2$. Generally, the RAPT excitation scheme needs to selectively saturate the two transitions that connect the central levels to the outer most levels, that is, a selective *multiple* quantum excitation is required when $I > 3/2$ to excite the $\Delta m = I \leftrightarrow \frac{1}{2}$ and $-I \leftrightarrow -\frac{1}{2}$ transitions. In contrast, an enhancement factor of two is easily obtained with selective single quantum excitation of the $\Delta m = \frac{3}{2} \leftrightarrow \frac{1}{2}$ and $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transitions. For spin $I > 3/2$, we obtain experimental enhancements greater than two but less than $I + 1/2$ using the Gaussian RAPT scheme currently employed in this work. In spite of these difficulties, one can still obtain significant sensitivity enhancements with multiple RAPT beyond the already substantial sensitivity enhancements of single RAPT. If improved single RAPT sequences can be designed, then one might expect even greater enhancements with the multiple RAPT approach.

By taking the weighted sum of all the spectra as a function of m we obtain the multiple RAPT enhanced spectrum. Fig. 3 shows the experimental comparison among spectra with no RAPT, single-RAPT, and multiple-RAPT for albite and NaNbO_3 . Generally, the multiple RAPT enhancement improves with increasing spin as expected. For ^{27}Al ($I = 5/2$) in albite we obtain a multiple RAPT enhancement of 3.02. This is a 48% increase over single RAPT. Overall this represents over a factor of 9 in reducing the signal averaging time compared to acquisition without any enhancements. For ^{93}Nb ($I = 9/2$) in NaNbO_3 we obtain a multiple RAPT enhancement of 5.76. This is an 89% increase over single RAPT, and provides an overall reduction of nearly a factor of 33 in the signal averaging time compared to central transition detection with no enhancement.

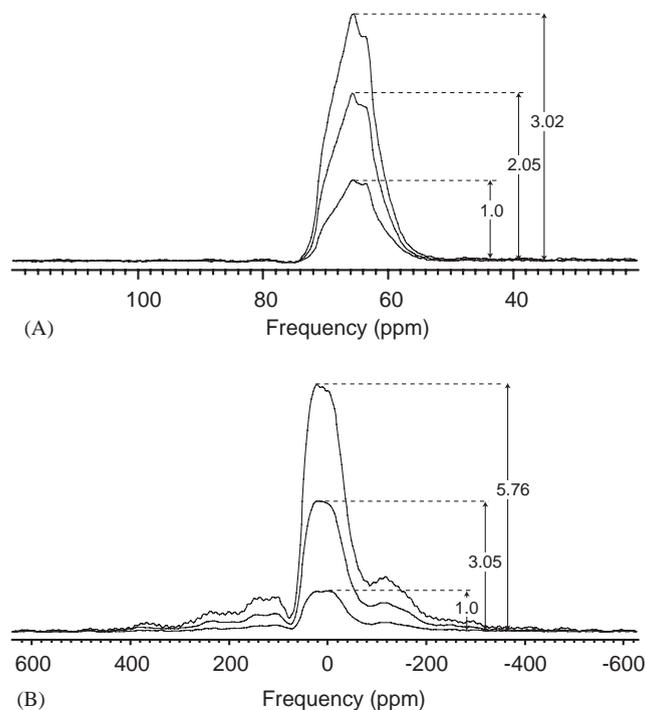


Fig. 3. (A) ^{27}Al spectra from polycrystalline albite with increasing intensity obtained with no RAPT, single RAPT, and multiple RAPT enhancements, respectively. The experiments were performed with a RAPT Gaussian pulse duration of $18\ \mu\text{s}$ with $2.0\ \mu\text{s}$ interpulse delay, $n = 21$, $m = 8$, $\omega_{\text{off}}/2\pi = 350\ \text{kHz}$, and $\omega_1/2\pi = 30\ \text{kHz}$. The recycle delay was $200\ \text{s}$, and number of scans was 64. (B) ^{93}Nb spectra from polycrystalline NaNbO_3 with increasing intensity obtained with no RAPT, single RAPT, and multiple RAPT enhancements, respectively. The experiments were performed with a RAPT Gaussian pulse duration of $17.0\ \mu\text{s}$ with $2.0\ \mu\text{s}$ interpulse delay, $n = 21$, $m = 8$, $\omega_{\text{off}}/2\pi = 550\ \text{kHz}$, and $\omega_1/2\pi = 40\ \text{kHz}$. The recycle delay was $2\ \text{s}$, and number of scans was 256.

5. Conclusion

After a single rotor-assisted population transfer, there still remains polarization in the satellite transitions that can be transferred to the central transition. We have proposed a new RAPT scheme that uses the remaining polarization of the satellites to obtain a further enhancement of central transition by performing RAPT-enhanced experiments multiple times before waiting for re-equilibration of the spin system. We have demonstrated this approach in the case of ^{27}Al in polycrystalline albite and ^{93}Nb in polycrystalline NaNbO_3 . In both cases we experimentally obtained significant sensitivity enhancements beyond the already substantial sensitivity enhancements of single RAPT. We have also described the procedure for processing the data from this experiment in order to obtain the maximum possible signal-to-noise ratio. The approach described here can be readily adapted

for increasing the sensitivity of any solid-state NMR experiment on quadrupolar nuclei that draws its polarization from the central transition.

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