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Application of shaped adiabatic pulses to MQMAS NMR spectroscopy of spin 3/2 nuclei

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ABSTRACT

Competition between nutation (r.f. driven) and adiabatic (rotor-driven) multi-quantum coherence transfer mechanisms in spin 3/2 systems results in diminished performance of rotation induced adiabatic coherence transfer (RIACT) in isotropic multiple-quantum magic-angle spinning (MQMAS) experiments for small e^2qQ/h (<2 MHz) and high radio-frequency powers. We present a simple shaped RIACT pulse consisting of a truncated sine wave (spanning 0–0.8π) that corrects the sensitivity losses, phase twist and relative intensity errors that can arise in MQMAS spectra utilizing constant-amplitude RIACT pulses. The shaped RIACT pulse may enhance the study of metals in biomolecules where quadrupole couplings of $S = 3/2$ nuclei such as ^{23}Na tend to be small.

1. Introduction

A great deal of activity has been devoted to improving the efficiency of multi- quantum (MQ) coherence transfers of half-integer quadrupolar nuclei in order to improve the sensivity and information content of the isotropic multiple-quantum magic-angle spinning (MQMAS) experiment [1–4]. The MQMAS experiment has been of broad value in the study of condensed phases, giving researchers the option to exploit diverse nuclei as exquisitely sensitive reporters on local structure [3,4]. Briefly, the principal experimental concerns in MQMAS are the excitation of a symmetric multi-quantum coherence (e.g. connecting $\pm m_S$ states, where $m_S = 3/2, 5/2, \ldots$) of half-integer quadrupolar nuclei and the subsequent conversion of the MQ coherence to central transition (CT) coherence. A great deal of progress has been made in developing methods to improve the efficiency of these two basic steps of MQMAS (review articles [3,4]). A closely related experimental approach is the satellite transition magic-angle-spinning (STMAS) experiment [5,6] which also provides isotropic spectra for half-integer quadrupolar nuclei. While offering a number of desirable performance characteristics such as enhanced sensitivity and quantitative accuracy, STMAS yields less intrinsic resolution in the isotropic dimension than MQMAS for $S = 3/2$ nuclei and is sensitive to small mis-settings of the magic-angle. In this work, we are interested in observing ^{23}Na, which is 100% abundant, exhibits small quadrupole couplings, and has a gyromagnetic ratio similar to carbon-13. Further, poor chemical shift dispersion is observed among sodium cations so that the enhanced resolution in the isotropic dimension of MQMAS due to the contribution of the second order quadrupole coupling can be valuable in discerning distinct sites such as DNA bound sodium cations [7–10]. It appears at this time that the MQMAS approach is advantageous for detecting abundant nuclei with high gyromagnetic ratios such as ^{23}Na in biomolecules, while STMAS is advantageous for nuclei with small magnetogyric ratios and low natural abundances [11,12].

The use of rotation induced adiabatic coherence transfer [13] (RIACT) in MQMAS significantly enhanced the sensitivity of nuclei with e^2qQ/h greater than about 2.0 MHz and provided isotropic lines whose relative intensities corresponded to site populations of crystallographically distinct species, with integer precision (i.e. correct values are obtained when relative signal intensities are rounded to nearest integer values) [14]. The initial report of adiabatic coherence transfers to enhance the MQMAS experiment focused on the value of achieving coherence transfer that is largely insensitive to the magnitude of the quadrupole coupling [14]. For sodium sites exhibiting large quadrupole couplings (e.g. e^2qQ/h >2.0 MHz), the sensitivity of their MQMAS spectra were enhanced often several fold by the RIACT mechanism compared to MQMAS spectra obtained with short high power pulses (a.k.a. nutation) to drive multi-quantum coherence transfers. The performance of RIACT in the case of quadrupole couplings (e.g. e^2qQ/h <2.0 MHz) was not considered in detail, which is the focus of this work.

In this study we demonstrate for spin 3/2 nuclei that the RIACT mechanism is undermined by competing nutation mechanisms as e^2qQ/h decreases and as the r.f. power increases. Adverse effects

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resulting from this competition among the nutation and RIACT transfer mechanisms are phase twist, diminished sensitivity, and loss of quantitative accuracy in RIACT MQMAS spectra. We show it is possible to significantly suppress unwanted nutation pathways by the use of simple amplitude modulated pulses, and thereby select for pure adiabatic coherence pathways. By exerting this control over coherence transfer pathways, the shaped RIACT pulse restores quantitative accuracy, moderately enhances sensitivity, and eliminates phase twist in MQMAS spectra of sites with e^2qQ/h <2 MHz for ^{23}Na (S = 3/2).

2. Theory

We examine mechanisms for generating triple quantum coherence for a half-integer quadrupolar nucleus.

2.1. Nutation in the triple quantum subspace

We review first the nutation of Zeeman polarization of a spin 3/2 quadrupolar nucleus. In this case, an r.f. pulse is applied to an initial condition of the equilibrium polarization of central and triple quantum transitions; this case has been well characterized [15–17] and was widely exploited during the initial development of MQMAS methodology [1,18,19]. We review the approach of Vega in using fictitious spin-1/2 operators to describe the nutation of triple quantum coherence for an S = 3/2 nucleus in the regime of $\omega_Q > \omega_1$, where ω_Q (defined below) is proportional to the magnitude of the quadrupole coupling and $\omega_1 = \gamma B_1$ represents the strength of the applied r.f. field [15]. We treat the other limiting case $\omega_1 > \omega_Q$ in the Appendix, but discuss the result in this section. Sample rotation is not considered, which may be viewed as the static case, or as a short-time treatment since nutation is observed over just a few microseconds (e.g. compared to a 100 µs rotor period at 10 kHz MAS).

The rotating frame Hamiltonian for a S = 3/2 nucleus under r.f. irradiation and in the fictitious spin-1/2 basis is [13,15,16]

$$H^Q_{LAB} = -\Delta\omega(3\mathbf{I}^{14}_{Z} + \mathbf{I}^{23}_{Z}) + \omega_Q(\mathbf{I}^{12}_{Z} - \mathbf{I}^{34}_{Z}) - \omega_1(\sqrt{3}\mathbf{I}^{12}_{X} + 2\mathbf{I}^{23}_{X} + \sqrt{3}\mathbf{I}^{34}_{X}), \quad (1)$$

where ω_1 is the magnitude of the r.f. field, ω_Q is the quadrupole coupling frequency,

$$\omega_Q = \frac{e^2qQ/h}{6}\left(\frac{1}{2}(3\cos^2\theta - 1) + \eta\sin^2\theta\cos 2\phi\right), \quad (2)$$

and θ and ϕ are Euler angles relating the principal axes system (PAS) of the quadrupolar tensor to the laboratory (LAB) frame. Spin angular momentum operators are given in boldface for fictitious spin-1/2 transitions where the 2–3 superscript denotes the central transition and the 1–2 and 3–4 superscripts denote the satellite transitions. The offset term $\Delta\omega$ will be neglected. In this first case, we will monitor 3Q coherence if the initial condition is equilibrium polarization (ignoring constants for convenience):

$$\rho_{LAB}(0) \propto \mathbf{I_Z} = \mathbf{I}^{23}_{Z} + 3\mathbf{I}^{14}_{Z}. \quad (3)$$

In Eq. (1) the 1–2 subspace is tilted away from $\mathbf{I}^{12}_{Z}$ by $\theta_{12} = \tan^{-1}[\frac{\sqrt{3}\omega_1}{\omega_Q}]$ and the 3–4 subspace is tilted by $\theta_{34} = -\tan^{-1}[\frac{\sqrt{3}\omega_1}{\omega_Q}]$ away from $-\mathbf{I}^{34}_{Z}$. Setting $\theta = \theta_{12} = -\theta_{34}$, the doubly tilted frame Hamiltonian is

$$H^Q_{TILT} = \omega_{eff}\left(\mathbf{I}^{12}_{Z} - \mathbf{I}^{34}_{Z}\right) - \omega_1\left[2\cos^2\left(\frac{\theta}{2}\right)\mathbf{I}^{23}_{X} + 2\sin^2\left(\frac{\theta}{2}\right)\mathbf{I}^{14}_{X} + \sin(\theta)\mathbf{I}^{13}_{X} + \sin(\theta)\mathbf{I}^{24}_{X}\right], \quad (4)$$

where $\omega_{eff} = (\omega_Q^2 + 3\omega_1^2)^{1/2}$. Next assume that

$$\rho_{TILT}(0) \cong \rho_{LAB}(0) = \mathbf{I}^{23}_{Z} + 3\mathbf{I}^{14}_{Z}. \quad (5)$$

The limiting condition $\omega_Q > \omega_1$ gives[15]

$$H^Q_{TILT}(\omega_Q >> \omega_1) \cong \omega_{eff}\left(\mathbf{I}^{12}_{Z} - \mathbf{I}^{34}_{Z}\right) - \omega_1 2\mathbf{I}^{23}_{X} + \frac{3\omega_1^3}{2\omega_Q^2}\mathbf{I}^{14}_{X} + \frac{\sqrt{3}\omega_1^2}{\omega_Q}\left(\mathbf{I}^{13}_{X} + \mathbf{I}^{24}_{X}\right). \quad (6)$$

Commutation relations [15,16] show that the $(\mathbf{I}^{13}_{X} + \mathbf{I}^{24}_{X})$ term will not produce 3Q coherence from an initial density operator of $(\mathbf{I}^{23}_{Z} + 3\mathbf{I}^{14}_{Z})$. The term in Eq. (6) governing triple quantum coherence excitation is $H^Q_{TILT}(\omega_Q >> \omega_1) \cong \frac{3\omega_1^3}{2\omega_Q^2}\mathbf{I}^{14}_{X}$, which will nutate the triple quantum term of Eq. (5) only; it is a sensitive function of ω_1, and is attenuated quadratically by ω_Q. The dependence of nutation on ω_1 and ω_Q is well supported by computational and empirical optimizations of coherence transfers for MQMAS [1,18,19].

A very similar approach is employed in the Appendix to obtain the following expression incorporating the opposite limiting condition $\omega_1 > \omega_Q$,

$$H^Q_T = -2\omega_1\mathbf{I}^{23}_{X} - \frac{\omega_Q^2}{6\omega_1}\mathbf{I}^{14}_{X} + \omega_{eff}\left(\mathbf{I}^{12}_{X} + \mathbf{I}^{34}_{X}\right) - \frac{\omega_Q}{\sqrt{3}}\left(\mathbf{I}^{13}_{X} + \mathbf{I}^{24}_{X}\right). \quad (7)$$

In Eq. (7) it can be seen that nutation in the triple quantum subspace now depends *directly* on the square of the quadrupole frequency, and this behavior was qualitatively investigated previously [7]. Achieving this limit in practice is challenging since even quadrupole couplings that would be considered small in the sense that they yield MAS line shapes that are too narrow to show typical shoulders and horns characteristic of the quadrupolar interaction tensor (e.g. $e^2qQ/h \sim$0.5 MHz) nonetheless have quadrupole frequencies on the order of 10^3 kHz.

2.2. Nutation of the central transition

We consider applying an r.f. pulse to central transition coherence and monitoring the creation of triple quantum coherence. This situation arises in a two pulse experiment in which the first pulse employs low power to selectively excite central transition coherence, while the second is a 90-degree phase-shifted high power pulse. Although this scheme will lead to adiabatic rotor-driven coherence transfer during the second pulse, [13,14,20] we are interested in the question: if the initial density operator is $\rho(0) \propto \mathbf{I}^{23}_{X}$, can there be r.f. driven triple quantum excitation?

In the limiting condition $\omega_Q > \omega_1$, the term $\frac{\sqrt{3}\omega_1^2}{\omega_Q}(\mathbf{I}^{13}_{X} + \mathbf{I}^{24}_{X})$ in Eq. (6) leads to triple quantum coherence when acting upon $\mathbf{I}^{23}_{X}$, which can be seen using $e^{iA}Be^{-iA} = B + i[A,B] - \frac{1}{2}[A,[A,B]] + \ldots$ and taking $A = \mathbf{I}^{13}_{X} + \mathbf{I}^{24}_{X}$ and $B = \mathbf{I}^{23}_{X}$ (e.g. see Ref. [21]). However with $\omega_Q > \omega_1$, the factor $\frac{\sqrt{3}\omega_1^2}{\omega_Q}$ can become much smaller than w_1. We expect then that nutation of the central transition into 3Q coherence will be a minor mechanism when $\omega_Q > \omega_1$, and will show that simulations verify this as well.

In the limiting condition $\omega_1 > \omega_Q$, the term $\omega_{eff}(\mathbf{I}^{12}_{X} + \mathbf{I}^{34}_{X}) - \frac{\omega_Q}{\sqrt{3}}(\mathbf{I}^{13}_{X} + \mathbf{I}^{24}_{X})$ leads to triple quantum coherence. To obtain a rough approximation, the last part can be neglected, giving the nutation of 3Q coherence proportional to $\omega_{eff} = (\omega_Q^2 + 3\omega_1^2)^{1/2}$ which approaches $\sqrt{3}\omega_1$. In either limiting condition, we note again that these predictions are useful only for predicting initial nutation rates since we consider static conditions.

In this work we are especially interested in S = 3/2 nuclei in the regime $e^2qQ/h = 0.5 - 2.0$ MHz subjected to r.f. powers on the order of 100–150 kHz, so that ω_Q and ω_1 are of the same order of magnitude and neither of the above conditions is fully satisfactory.