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Triple quantum filtered spectroscopy of homonuclear three spin-1/2 systems employing isotropic mixing ☆

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ABSTRACT

We report the design and performance evaluation of novel pulse sequences for triple quantum filtered spectroscopy in homonuclear three spin-1/2 systems, employing isotropic mixing (IM) to excite triple quantum coherence (TQC). Our approach involves the generation of combination single quantum coherences (*c*SQC) from antisymmetric longitudinal or transverse magnetization components employing isotropic mixing (IM). *c*SQC's are then converted to TQC by a selective 180° pulse on one of the spins. As IM ideally causes magnetization to evolve under the influence of the spin coupling Hamiltonian alone, TQC is generated at a faster rate compared to sequences involving free precession. This is expected to be significant when the spins have large relaxation rates. Our approach is demonstrated experimentally by TQC filtered 1D spectroscopy on a ^{1}H AX_2 system (propargyl bromide in the presence of a paramagnetic additive), as well as a ^{31}P linear AMX system (ATP in agar gel). The performance of the IM-based sequences for TQC excitation are compared against the standard three pulse sequence (Ernst et al., 1987) and an AX_2 spin pattern recognition sequence (Levitt and Ernst, 1983). The latter reaches the unitary bound on TQC preparation efficiency starting from thermal equilibrium in AX_2 systems, not considering relaxation. It is shown that in systems where spins relax rapidly, the new IM-based sequences indeed perform significantly better than the above two known TQC excitation sequences, the sensitivity enhancement being especially pronounced in the case of the proton system investigated. An overview of the differences in relaxation behavior is presented for the different approaches. Applications are envisaged to Overhauser DNP experiments and to *in vivo* NMR.

1. Introduction

Triple quantum coherence (TQC) in spin systems with three or more spins-1/2 may be generated by a standard three pulse sandwich (hereafter referred to as PFP-1) [1], which incorporates two 90° pulses in phase quadrature, and includes a refocusing 180° pulse. However in the case of an AX_2 system preparation of TQC can be accomplished with higher efficiency by a spin pattern recognition sequence (PFP-2) [2] containing five pulses, including three 90° pulses of the same phase, and a refocusing 180° pulse between each 90° pulse pair. Disregarding relaxation, the PFP-2 sequence is predicted to be three times as efficient as the basic three pulse sequence; however the higher theoretical efficiency comes at the cost of doubling the preparation time. Though the PFP-2 sequence reaches the unitary bound on transfer of equilibrium magnetization to TQC for AX_2 systems [2], the longer preparation time could possibly result in large relaxation losses.

As a possible alternative strategy, we propose employing isotropic mixing to prepare multiple quantum coherences. Isotropic mixing (IM) sequences have been used extensively in NMR spectroscopy to effect coherence transfer between coupled spins in experiments such as TOCSY [3] and HOHAHA [4].

When subjected to IM, spins are known to evolve in collective spin modes under the influence of the strong coupling Hamiltonian, typically giving rise to higher coherence evolution frequencies compared to free precession experiments [3,5–7]. Although isotropic mixing conserves the coherence order, evolution under IM, supplemented by suitable additional pulse(s), may be exploited for rapid generation of multiple quantum coherences.

In the present work, we explore the application of a triple quantum preparation sequence based on isotropic mixing to general three-spin-1/2 networks, including AX_2, as well as linear and non-linear AMX systems with unequal couplings.

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In the following sections we describe the pulse sequences designed for TQC preparation in a general three spin-1/2 system employing IM; explicit expressions are given for the density matrix evolution in AX_2 and linear AMX systems with two equal couplings. An overview of the relaxation of different density matrix components that occur at different stages of the pulse sequences is also presented.

2. Theory

The pulse sequences discussed in this work are all shown in Fig. 1.

In the following, we briefly describe the evolution of the density matrix (starting from thermal equilibrium) under the various pulse sequences: PFP-1, PFP-2, IM-1 and IM-2. In the following discussion the spin 'I_1' refers to the spin 'A' in the AX_2 system and spin 'M' in the AMX system, M being coupled to both the other spins, A and X.

2.1. PFP-1 sequence

Disregarding relaxation and employing an inter-pulse delay of $1/(4J)$, the density matrix at the end of the preparation sequence PFP-1 is given by Eq. (1):

$$\begin{aligned} I_{1z}+I_{2z}+I_{3z} &\overset{90^\circ_x}{\rightarrow} -I_{1y}-I_{2y}-I_{3y} \overset{\frac{1}{4J}}{\rightarrow} \overset{180^\circ_x}{\rightarrow} \overset{\frac{1}{4J}}{\rightarrow} \overset{90^\circ_y}{\rightarrow} -4I_{1y}I_{2x}I_{3x}+2I_{1x}I_{2z} \\ &+2I_{1x}I_{3z} \equiv \frac{1}{2}iI_{1+}I_{2+}I_{3+}-\frac{1}{2}iI_{1-}I_{2-}I_{3-}+\frac{1}{2}iI_{1+}I_{2-}I_{3-}-\frac{1}{2}iI_{1-}I_{2+}I_{3-} \\ &-\frac{1}{2}iI_{1-}I_{2-}I_{3+}+\frac{1}{2}iI_{1+}I_{2+}I_{3-}+\frac{1}{2}iI_{1+}I_{2-}I_{3+}-\frac{1}{2}iI_{1-}I_{2+}I_{3+}+I_{1-}I_{2z} \\ &+I_{1-}I_{3z}+I_{1+}I_{2z}+I_{1+}I_{3z} \end{aligned} \tag{1}$$

Besides the desired triple quantum terms (*viz.*, the first two), this includes single quantum terms (*viz.*, the last four), as well as combination single quantum terms (*i.e.*, three-spin single quantum coherences). Relaxation losses during preparation may be taken into account at the simplest level by optimizing the oscillatory coherence transfer function that leads from in-phase SQC to anti-phase SQC, by including an exponential relaxation factor:

$$e^{(-t/T_2)}\sin^2(\pi Jt) \tag{2}$$

This leads to an estimated optimal preparation time given by Eq. (3):

$$t_{opt}=\frac{1}{\pi J}\tan^{-1}(2\pi JT_2) \tag{3}$$

2.2. PFP-2 sequence

Disregarding relaxation and with an inter-pulse delay of $1/(4J)$, the density matrix evolution leads to Eq. (4):

$$\begin{aligned} I_{1z}+I_{2z}+I_{3z} &\overset{90^\circ_x}{\rightarrow} -I_{1y}-I_{2y}-I_{3y} \overset{\frac{1}{4J}}{\rightarrow} \overset{180^\circ_x}{\rightarrow} \overset{\frac{1}{4J}}{\rightarrow} \overset{90^\circ_x}{\rightarrow} 2I_{1y}I_{2x}+2I_{1y}I_{3x} \\ &-4I_{1z}I_{2y}I_{3y} \equiv MQC \overset{\frac{1}{4J}}{\rightarrow} \overset{180^\circ_x}{\rightarrow} \overset{\frac{1}{4J}}{\rightarrow} \overset{90^\circ_x}{\rightarrow} -4I_{1y}I_{2x}I_{3x}-4I_{1x}I_{2y}I_{3x} \\ &-4I_{1x}I_{2x}I_{3y} \equiv \frac{3}{2}iI_{1+}I_{2+}I_{3+}-\frac{3}{2}iI_{1-}I_{2-}I_{3-}-\frac{1}{2}iI_{1+}I_{2-}I_{3-}-\frac{1}{2}iI_{1-}I_{2+}I_{3-} \\ &-\frac{1}{2}iI_{1-}I_{2-}I_{3+}+\frac{1}{2}iI_{1+}I_{2+}I_{3-}+\frac{1}{2}iI_{1+}I_{2-}I_{3+}+\frac{1}{2}iI_{1-}I_{2+}I_{3+} \end{aligned} \tag{4}$$

2.3. Sequences IM-1 and IM-2

The IM-based pulse sequences used for TQC excitation are shown in Fig. 1. In both the pulse sequences antisymmetric longitudinal magnetization components are first generated by inverting a spin which has two couplings (labeled spin 1). In sequence IM-1 this is then converted to transverse magnetization using a non-selective 90° pulse, and is followed by IM. In sequence IM-2, on the other hand, IM precedes the non-selective 90° pulse. It should be noted that the order in which IM and the non-selective pulse are applied is theoretically immaterial, since the propagators corresponding to them commute with each other. The resultant density matrix contains some combination single quantum coherence (*c*SQC, defined *vide infra*) terms which are then converted to TQC using a selective 180° pulse that has the same frequency offset as the first selective 180° pulse.

The isotropic mixing Hamiltonian in the case of an AX_2 system or a linear AMX system with two equal couplings is given by Eq. (5):

$$\mathcal{H}=2\pi J(\mathbf{I_1}\cdot\mathbf{I_2}+\mathbf{I_1}\cdot\mathbf{I_3}) \tag{5}$$

For the IM-1 pulse sequence the density matrix transformations are given in Eq. (6):

$$\begin{aligned} I_{1z}+I_{2z}+I_{3z} &\xrightarrow{180^\circ_x(1)} -I_{1z}+I_{2z}+I_{3z} \xrightarrow{90^\circ_{-y}} I_{1x}-I_{2x}-I_{3x} \\ &\xrightarrow{IM} \frac{1}{9}(1+8\cos(3\pi Jt))I_{1x}-\frac{1}{9}(5+4\cos(3\pi Jt))(I_{2x}+I_{3x}) \\ &+\frac{4}{3}\sin(3\pi Jt)(I_{1y}I_{2z}+I_{1y}I_{3z}-I_{1z}I_{2y}-I_{1z}I_{3y}) \\ &+\frac{4}{9}(1-\cos(3\pi Jt))(-4I_{1x}I_{2z}I_{3z}+2I_{1z}I_{2x}I_{3z}+2I_{1z}I_{2z}I_{3x}) \\ &+\frac{4}{9}(1-\cos(3\pi Jt))(-4I_{1x}I_{2y}I_{3y}+2I_{1y}I_{2x}I_{3y}+2I_{1y}I_{2y}I_{3x}) \end{aligned} \tag{6}$$

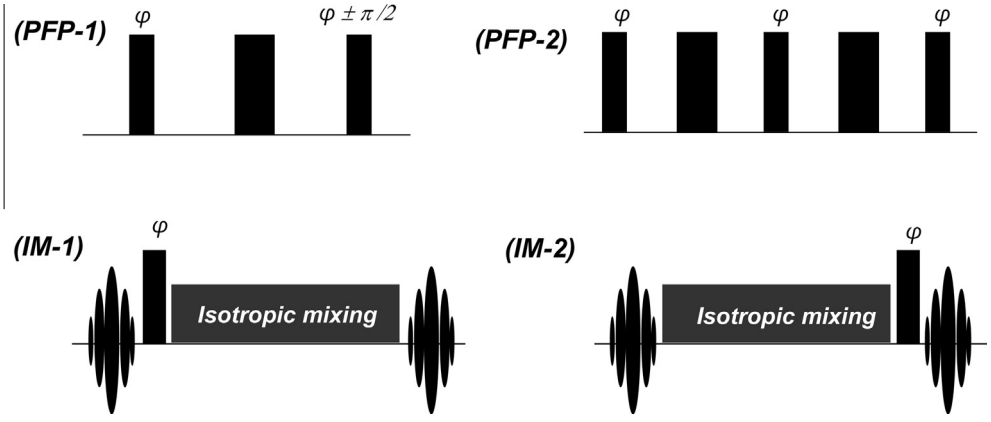

Fig. 1. TQC excitation pulse sequences. Thin and thick solid bars represent non-selective 90° and 180° pulses respectively. Shaped pulses represent selective 180° pulses. PFP-1 is the standard TQC excitation sandwich with the two 90° pulses in phase quadrature. PFP-2 is the AX_2 spin pattern recognition sequence with all 90° pulses of the same phase.