# Selection and Suppression of Intra- and Inter-Molecular MQCs

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## Introduction

NMR signals from multiple-quantum coherences (MQCs) may be formed by inter-molecular dipolar and/or intra-molecular scalar couplings in a highly polarized scalar-coupled liquid system. When more than two RF pulses are applied, signals may originate from either intra- and/or inter-molecular MQCs [1]. The pulse sequence with three selective RF pulses as shown in Fig. 1 was designed for this purpose [2]. With proper phase cycling [3], the signals from a specific intra- or inter-molecular MQC order can be selected or suppressed effectively. It is shown that the theoretical predictions are in good agreement with experimental observations. The method proposed herein can be extended to heteronuclear cases as well.

## Methods

When a pulse sequence as Fig. 1 is applied to a highly polarized scalar-coupled liquid $I_p S_q$ system, the resulting signals may composed of those from intra-molecular $I$–$S$, inter-molecular $I$–$S$, and inter-molecular $S$–$S$ MQCs. When the combination of the quantum and classical treatments is employed to treat the intra-molecular scalar couplings and inter-molecular dipolar couplings, the transverse magnetizations of three kinds of signals are given by:

$$M_{intra}^{I+} \propto \cos^{p-1}(\pi J\tau)\sin(\pi J\tau), \qquad M_{inter}^{I+} \propto \cos^{p}(\pi J\tau), \qquad M_{inter}^{S+} \propto \cos^{2p}(\pi J\tau).$$

where $J$ is scalar coupling constant and $\tau$ is duration of the preparation period. With proper $\tau$, signals from intra- and inter-molecular DQCs can be detected
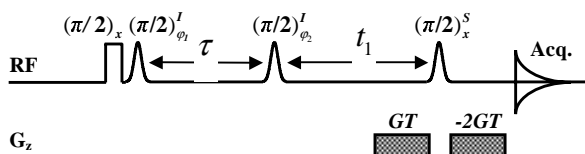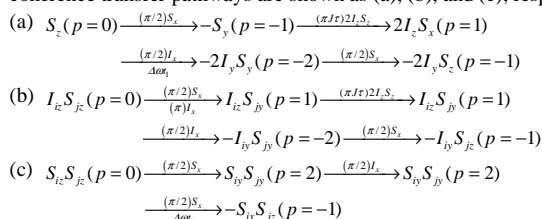


**Fig. 1.** Pulse sequence to separately detect intra- and inter-molecular MQC signals. The first RF pulse is unselective $(\pi/2)_x$, while the other three $(\pi/2)_x$ RF pulse is selective for $I$, $I$, and $S$ spins, respectively.

separately. The method is sensitive to the spin-coupling network and coupling constant. Therefore, phase cycling is employed to select a specific coherence pathway. The coherence transfer pathways are shown as (a), (b), and (c), respectively.

(a) $S_z(p=0) \xrightarrow{(\pi/2)S_x} -S_y(p=-1) \xrightarrow{(\pi J\tau)2I_zS_z} 2I_zS_x(p=1)$
$\xrightarrow[\Delta\omega_1]{(\pi/2)I_x} -2I_yS_y(p=-2) \xrightarrow{(\pi/2)S_x} -2I_yS_z(p=-1)$

(b) $I_{iz}S_{jz}(p=0) \xrightarrow{(\pi/2)S_x} I_{iz}S_{jy}(p=1) \xrightarrow{(\pi J\tau)2I_zS_z} I_{iz}S_{jy}(p=1)$
$\xrightarrow{(\pi/2)I_x} -I_{iy}S_{jy}(p=-2) \xrightarrow{(\pi/2)S_x} -I_{iy}S_{jz}(p=-1)$

(c) $S_{iz}S_{jz}(p=0) \xrightarrow{(\pi/2)S_x} S_{iy}S_{jy}(p=2) \xrightarrow{(\pi/2)I_x} S_{iy}S_{jy}(p=2)$
$\xrightarrow[\Delta\omega_1]{(\pi/2)S_x} -S_{ix}S_{jz}(p=-1)$

With different coherence transfer pathways, four kinds of phase-cycle as listed in Table 1were designed to select specific signals.

Table 1 Phase cycles for suppression and selection of three signals

| | (I) Suppression of signal from inter-molecular S–S DQC | | (II) Selection of signal from intra-molecular I–S DQC | | | | (III) Selection of signal from inter-molecular I–S DQC | | | | (IV) Selection of signal from inter-molecular S–S DQC | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\varphi_1$ | $+x$ | $+x$ | $+x$ | $+x$ | $-x$ | $-x$ | $+x$ | $+x$ | $-x$ | $-x$ | $+x$ | $+x$ |
| $\varphi_2$ | $+x$ | $-x$ | $+x$ | $-x$ | $+x$ | $-x$ | $+x$ | $-x$ | $+x$ | $-x$ | $+x$ | $-x$ |
| Receiver phase | $+x$ | $-x$ | $+x$ | $-x$ | $+x$ | $-x$ | $+x$ | $-x$ | $-x$ | $+x$ | $+x$ | $+x$ |

Experiments were verified on a Varian Unity+ 500 spectrometer, equipped with self-shielded z-gradient coil and 5 mm HCN triple-resonance RF coil of a 1.5 cm effective length. A sample of 1,1,2-Trichloroethane [CHCl$_2$CH$_2$Cl] solution (60% solution in acetone-$d_6$ solvent) was used as an $IS_2$ system.
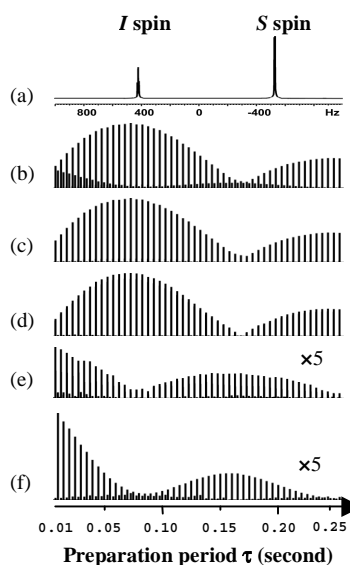
## Results and discussion



**Fig. 2.** (a) 1D spectrum of 1,1,2-Trichloroethane. Amplitude variations of two peaks with an array of preparation periods from 0.01 s to 0.255 s in increments of 0.005 s, with no phase cycle (b); phase cycle I (c), phase cycle II (d), phase cycle III (e), and phase cycle IV (f) were used. Amplitudes were magnified 5 times in (e) and (f).

Figure 2 shows that when the pulse sequence as shown in Fig. 1 with no phase cycle was applied to an $IS_2$ system, the resulting NMR signals were originated from intra-molecular DQC of $I$ spin, inter-molecular $I$–$S$ DQC, and inter-molecular $S$–$S$ DQC. In a 1D spectrum, the first two kinds of signals were both in the offset of $I$ spin, while the third one was in the offset of $S$ spin. When phase cycle I was applied, signal from inter-molecular $S$–$S$ DQC was suppressed effectively. When phase cycle II was applied, signal from intra-molecular DQC was selected while the other two signals were suppressed effectively. When phase cycle III was applied, signal from inter-molecular $I$–$S$ DQC was selected. When phase cycle VI was applied, signal from inter-molecular $S$–$S$ DQCs was selected. There are small residual signal of $I$ spin in Figs. 2 (e) and (f), which may be due to the precision of the selective RF pulses. Experimental results showed that the method proposed herein can be used to select signal of a specific coherence pathway, and effectively suppress other interfering signals. The method can be extended to heteronuclear cases. Methods for selection and suppression of signals from intra- and/or inter-molecular MQCs will help us to understand the underlying physical mechanisms in coupled spin systems.

## Acknowledgments

## References

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