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Selective excitation in dipole coupled systems

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Abstract

In this Letter the possibility of selective excitation in coupled multispin systems is studied theoretically. A general method of transforming any selective pulse developed for uncoupled systems into a form that is selective in coupled systems is presented. This is accomplished by adding a small perturbation to a decoupling radiofrequency (RF) field. When viewed in an interaction frame given by the decoupling RF field, this method generates, in an averaged sense, a propagator similar to the propagator of uncoupled spins under a shaped RF pulse. Preliminary experimental results are presented for the case of selective excitation in proton nuclear magnetic resonance in liquid crystals.

1. Introduction

Selective excitation is a very important and versatile tool in nuclear magnetic resonance (NMR) studies of spin-diffusion [1,2], imaging [3,4], structural studies [5], quantum computing [6,7], and various other applications. The need to tailor radiofrequency (RF) pulses to create a desired excitation profile has motivated much research into designing pulse sequences, and an entire literature on calculating selective pulses in the absence of strong couplings exists [8]. The problem of selective excitation typically reduces to the problem of finding an RF pulse acting on either a two-level system or on pairs of uncoupled two-level systems that generates a desired excitation profile. For a two-state system, this problem can be solved exactly by inverting the Bloch equations [9,10]. In addition, a variety of other selective pulses based on either linear-response theory (e.g., the sinc pulse and Gaussian pulses [11]) or numerical optimization (e.g., BURP pulses [12]) have been developed.

The above methods of selective excitation fail in the presence of strong dipolar couplings since the system can no longer be thought of as sets of uncoupled, two-state systems, making selective excitation difficult to accomplish. In the past, selective excitation in dipole-coupled systems has been performed by taking a homonuclear decoupling sequence like MREV-8 [13,14] and intermeshing it

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with a DANTE [15,16] sequence. DANTE consists of a series of small-tip pulses separated by time τ_{tip} that characterizes the excitation profile. Such an approach has been used in the past for selective excitation in solids based on isotropic shift [17] and gradient fields [18]. The MREV-8 homonuclear decoupling sequence results, in an averaged sense, in the system appearing to be sets of uncoupled two-state systems, leaving the DANTE excitation sequence to excite the spins as if the homonuclear couplings did not exist. Such techniques require that the cycle time of the MREV-8 sequence, τ_c, be chosen to satisfy the criterion $N\tau_c = \tau_{\text{tip}}$ (where N is an integer) in order to implement the DANTE selective excitation. This approach is limited for two reasons. Firstly, the delays and pulse lengths of the MREV-8 sequence that optimize the decoupling performance may not satisfy the condition $N\tau_c = \tau_{\text{tip}}$. Secondly, a different excitation profile than that of the DANTE sequence may be required experimentally. To our knowledge there have been no successful attempts to intermesh *an arbitrary selective pulse into an arbitrary homonuclear decoupling sequence*.

The purpose of this Letter is to propose a new experimental method that will allow general selective pulses to be implemented in the presence of strong couplings. This is accomplished by modifying a decoupling sequence in a systematic way that takes into account the selective pulse. This treatment requires that the selective pulse acts as a small perturbation to the decoupling field. The appropriate modification to the decoupling sequence is obtained by transforming into an interaction frame defined by the exact decoupling sequence. In this frame, the required RF pulses needed in order to make the effective propagator resemble the propagator for the selective excitation in an uncoupled system are obtained. Experiments have been performed that confirm this methodology.

2. Theory

The internal Hamiltonian of a dipole-coupled spin system can be written in the rotating frame as $H_{\text{INT}} = H_{\text{DIP}} + H_J + H_{\text{CS}}$. Here $H_{\text{DIP}} = \sum_{i<j} D_{ij} T^{ij}_{2,0}$ is the secular dipolar Hamiltonian, $H_J = \sum_{i<j} J_{ij} T^{ij}_{0,0}$ is the scalar coupling Hamiltonian, and $H_{\text{CS}} = \sum_i \omega_i I^i_Z$ contains the chemical shifts of all nuclei. The dipolar and scalar coupling Hamiltonians are written in terms of spherical spin tensor operators [19] (e.g., $T^{ij}_{2,0} = 3I^i_Z I^j_Z - \vec{I}^i \cdot \vec{I}^j$). In the following, scalar couplings are neglected since their effects are negligible on the time scale of the selective excitation for the systems studied here. The problem now arises as to how to construct a series of RF pulses that selectively excite in the presence of dipolar couplings. In order to solve this problem, consider an RF field consisting of two parts, $H_{\text{RF}} = H_{\text{DEC}} + H_{\text{SEL}}$, where H_{DEC} is some known decoupling sequence that averages away the dipolar interactions (or any other particular interaction that is desired to be removed), and H_{SEL} is the part of the RF which will be used to perform the selective pulse. There are many H_{DEC} schemes that are available to the experimenter; in the following, the purely phase-modulated scheme, phase-modulated Lee–Goldburg (PMLG-n) [20,21], will be used to illustrate how to combine arbitrary selective pulses with a decoupling scheme. PMLG was chosen since in most commercial spectrometers, phases can be specified to an accuracy on the order of a tenth of a degree independent of RF amplitude, whereas amplitude modulation is much less accurate at larger RF amplitudes. Therefore in the following, the selective pulses calculated will be purely phase modulated pulses; a generalization of the theory to both amplitude and phase modulated pulses will be presented elsewhere.

Consider a dipole coupled spin system being irradiated by a fixed amplitude, phase-modulated RF pulse. The Hamiltonian is given by

$$H(t) = H_{\text{INT}} + \omega_{\text{RF}} \times \{I_X \cos[\phi(t)] + I_Y \sin[\phi(t)]\}, \tag{1}$$

where $I_{X(Y)} = \sum_i I^i_{X(Y)}$. This Hamiltonian $H(t)$ can be rewritten as $V^\dagger(t)(\widehat{H} + \omega_{\text{RF}} I_X)V(t)$, where

$$\begin{aligned} \widehat{H} &= H_{\text{DIP}} + H_{\text{CS}}, \\ V(t) &= \exp[\mathrm{i}\phi(t) I_Z] \\ &= \exp\left\{\mathrm{i}\left[\int_0^t \mathrm{d}t' \left[\frac{\mathrm{d}\phi(t')}{\mathrm{d}t'}\right] + \phi(0)\right] I_Z\right\}. \end{aligned} \tag{2}$$

The propagator for this Hamiltonian is given by

$$\begin{aligned} U(t) &= T\exp\left[-\mathrm{i}\int_0^t \mathrm{d}t' H(t')\right] \\ &= T\exp\left[-\mathrm{i}\int_0^t \mathrm{d}t' V^\dagger(t')\left(\widehat{H}+\omega_{\mathrm{RF}} I_X\right)V(t')\right] \\ &= V^\dagger(t) T\exp\left\{-\mathrm{i}\int_0^t \mathrm{d}t'\left[\widehat{H}+\omega_{\mathrm{RF}} I_X - \frac{\mathrm{d}\phi(t')}{\mathrm{d}t'} I_Z\right]\right\}. \end{aligned} \tag{3}$$

Under the standard PMLG homonuclear decoupling sequence, the phase modulation, $\phi_{\mathrm{PMLG}}(t)$, is given by

$$\phi_{\mathrm{PMLG}}(t) = \begin{cases} \frac{\omega_{\mathrm{RF}}}{\sqrt{2}} t & \text{for } 0 < t < t_{\mathrm{c}}, \\ -\frac{\omega_{\mathrm{RF}}}{\sqrt{2}}(t - t_{\mathrm{c}}) + 27.8^\circ & \text{for } t_{\mathrm{c}} < t < 2t_{\mathrm{c}}, \end{cases} \tag{4}$$

where $t_{\mathrm{c}} = 1/\omega_{\mathrm{EFF}}$ and $\omega_{\mathrm{EFF}} = \sqrt{\frac{3}{2}}\omega_{\mathrm{RF}}$. Consider first the time interval, $0 < t < t_{\mathrm{c}}$. The spin system evolves under an effective field, $H_{\mathrm{LG}} = \omega_{\mathrm{EFF}}\frac{1}{\sqrt{3}}[\sqrt{2}I_X - I_Z] = \omega_{\mathrm{EFF}}\widehat{I}_Z$ in the interaction frame defined in Eq. (3). The effective field lies along the magic-angle, which is responsible for averaging away the homonuclear dipolar interaction to lowest order [22].

In order to implement the selective excitation scheme, an additional phase modulation is added so that $\phi(t) = \phi_{\mathrm{PMLG}}(t) + \psi(t)$, where $\psi(t)$ will be responsible for the selective excitation. The only additional requirement is that $|H_{\mathrm{LG}}| \gg \mathrm{d}\psi(t)/\mathrm{d}t$ in order that the additional phase modulation, $\psi(t)$, does not interfere too much with the decoupling. Defining the decoupling propagator as $W(t) = \exp(-\mathrm{i}\omega_{\mathrm{EFF}} t\widehat{I}_Z)$, the propagator can be written in the decoupling frame as

$$U(t) = V^\dagger(t) W(t) T\exp\left\{-\mathrm{i}\int_0^t \mathrm{d}t' \widehat{H}_{\mathrm{INT}}(t')\right\}, \tag{5}$$

$$\begin{aligned} \widehat{H}_{\mathrm{INT}}(t) &= W^\dagger(t)\left[\widehat{H} + \frac{\mathrm{d}\psi(t)}{\mathrm{d}t}\right] W(t) \\ &= \sum_{i<j}\sum_{m=-2}^{2} d^{(2)}_{m,0}(\theta_{\mathrm{LG}}) D_{ij}\widehat{T}^{ij}_{2,m}\exp(\mathrm{i}m\omega_{\mathrm{EFF}}t) \\ &\quad + \sum_i \omega_i\{-\widehat{I}^i_Z\cos(\theta_{\mathrm{LG}}) + \sin(\theta_{\mathrm{LG}}) \\ &\quad \times [\widehat{I}^i_X\cos(\omega_{\mathrm{EFF}}t) - \widehat{I}^i_Y\sin(\omega_{\mathrm{EFF}}t)]\} \\ &\quad + \frac{\mathrm{d}\psi(t)}{\mathrm{d}t}\{\widehat{I}_Z\cos(\theta_{\mathrm{LG}}) - \sin(\theta_{\mathrm{LG}}) \\ &\quad [\widehat{I}_X\cos(\omega_{\mathrm{EFF}}t) - \widehat{I}_Y\sin(\omega_{\mathrm{EFF}}t)]\}, \end{aligned} \tag{6}$$

where $d^{(2)}_{m,0}(\theta_{\mathrm{LG}})$ are the reduced Wigner matrix elements relating the laboratory frame to the decoupling frame, with $\theta_{\mathrm{LG}} = \tan^{-1}(\sqrt{2})$, the magic angle, and $\widehat{\ }$ indicates that the operators are written in the decoupling frame. Over one decoupling cycle $t_{\mathrm{c}} = 1/\omega_{\mathrm{EFF}}$, the RF propagator $W(t_{\mathrm{c}}) = 1$, and average Hamiltonian theory [23] can be used to evaluate the propagator as

$$\begin{aligned} U(t_{\mathrm{c}}) &= V^\dagger(t_{\mathrm{c}}) T\exp\left[-\mathrm{i}\int_0^{t_{\mathrm{c}}} \mathrm{d}t' \widehat{H}_{\mathrm{INT}}(t')\right] \\ &= V^\dagger(t_{\mathrm{c}})\exp[-\mathrm{i}t_{\mathrm{c}}(\widehat{H}^{(0)}_{\mathrm{INT}} + \widehat{H}^{(1)}_{\mathrm{INT}} + \cdots)], \end{aligned} \tag{7}$$

where the first two terms of the average Hamiltonian are given by

$$\begin{aligned} \widehat{H}^{(0)}_{\mathrm{INT}} &= \frac{1}{t_{\mathrm{c}}}\int_0^{t_{\mathrm{c}}} \mathrm{d}t' \widehat{H}_{\mathrm{INT}}(t'), \\ \widehat{H}^{(1)}_{\mathrm{INT}} &= \frac{-\mathrm{i}}{2t_{\mathrm{c}}}\int_0^{t_{\mathrm{c}}} \mathrm{d}t' \int_0^{t'} \mathrm{d}t''[\widehat{H}_{\mathrm{INT}}(t'), \widehat{H}_{\mathrm{INT}}(t'')]. \end{aligned} \tag{8}$$

In the case of PMLG homonuclear decoupling, $\widehat{H}^{(0)}_{\mathrm{INT}}$ is given by

$$\begin{aligned} \widehat{H}^{(0)}_{\mathrm{INT}} &= \sum_i -\omega_i\widehat{I}^i_Z\cos(\theta_{\mathrm{LG}}) + \frac{1}{t_{\mathrm{c}}}\int_0^{t_{\mathrm{c}}} \mathrm{d}t' \frac{\mathrm{d}\psi(t')}{\mathrm{d}t'} \\ &\quad \times \{\cos(\theta_{\mathrm{LG}})\widehat{I}_Z - \sin(\theta_{\mathrm{LG}}) \\ &\quad \times [\widehat{I}_X\cos(\omega_{\mathrm{EFF}}t) - \widehat{I}_Y\sin(\omega_{\mathrm{EFF}}t)]\}. \end{aligned} \tag{9}$$

The homonuclear dipolar couplings have been averaged away over the time t_{c} since $d^{(2)}_{0,0}(\theta_{\mathrm{LG}}) = 0$, and the remaining terms involve the scaled chemical shifts, $\widehat{\omega_i} = \omega_i\cos(\theta_{\mathrm{LG}})$, and an additional field depending on $\mathrm{d}\psi/\mathrm{d}t$, which is needed in order to perform the selective pulse. The task of finding a particular $\psi(t)$ that can perform the selective excitation can be solved by examining the propagator of a single spin under a pulse of time varying amplitude, $\delta(t)$. For simplicity, assume the pulse is applied along the $-Y$ direction. As is typically done in liquid-state spectrometers, the shaped pulse can be approximated by a series of square pulses of varying amplitude (Fig. 1). The kth pulse amplitude should not change too dramatically or be too oscillatory over the time interval t_k, otherwise a shorter time step is needed in order to accurately reproduce the pulse. Let the amplitude of the kth segment of the shaped pulse be labelled by δ_k. The Hamiltonian for the kth segment is then given by

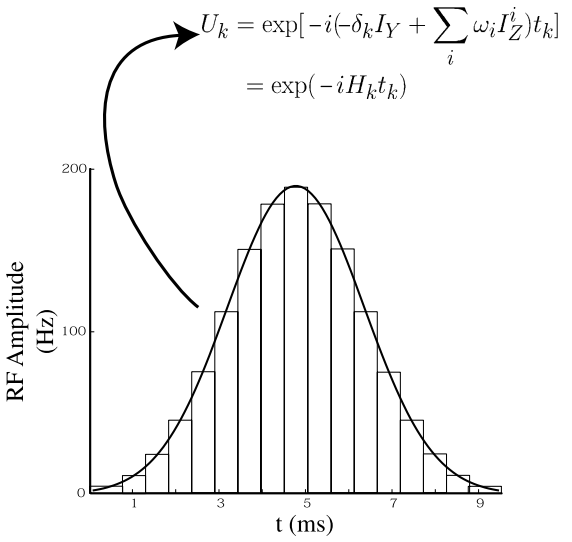

Fig. 1. Implementation of a shaped pulse. Typically, a shaped pulse is constructed using piecewise constant square pulses of different amplitudes, lengths, and/or phases. For the pulses considered in this paper, selective pulses in the decoupling frame involving only amplitude modulation are considered. The propagator of the kth segment, U_k, is shown in the figure, where the amplitude of the kth pulse is given by δ_k.

$$H_k = \sum_i \widehat{\omega_i} I_Z^i - \delta_k I_Y. \tag{10}$$

Equating the exact Hamiltonian for the kth element of the shaped pulse (Eq. (10)) to the zeroth-order average Hamiltonian in the decoupling frame (Eq. (9)) gives

$$\cos(\theta_{\mathrm{LG}}) \int_0^{t_c} \mathrm{d}t' \frac{\mathrm{d}\psi(t')}{\mathrm{d}t'} = 0, \tag{11}$$

$$\sin(\theta_{\mathrm{LG}}) \int_0^{t_c} \mathrm{d}t' \frac{\mathrm{d}\psi}{\mathrm{d}t'} \cos(\omega_{\mathrm{EFF}} t') = 0, \tag{12}$$

$$\frac{\sin(\theta_{\mathrm{LG}})}{t_c} \int_0^{t_c} \mathrm{d}t' \frac{\mathrm{d}\psi}{\mathrm{d}t'} \sin(\omega_{\mathrm{EFF}} t') = -\delta_k. \tag{13}$$

One way to satisfy the above equations is to make $\mathrm{d}\psi(t)/\mathrm{d}t$ an odd function over the time interval t_c, i.e.,

$$\frac{\mathrm{d}\psi(t)}{\mathrm{d}t} = -\frac{\mathrm{d}\psi(t_c - t)}{\mathrm{d}t}. \tag{14}$$

In order to eliminate the next order term (and all odd order terms for that matter), the interaction Hamiltonian can be symmetrized in time, i.e., $\widehat{H}_{\mathrm{INT}}(t) = \widehat{H}_{\mathrm{INT}}(\tau_c - t)$, where τ_c is the given cycle time. This symmetrization of the decoupling sequence in PMLG (Eq. (4)) requires that $\mathrm{d}\psi(t)/\mathrm{d}t$ satisfy

$$\frac{\mathrm{d}\psi}{\mathrm{d}t}(t) = \frac{\mathrm{d}\psi}{\mathrm{d}t}(2t_c - t) \tag{15}$$

then $\widehat{H}_{\mathrm{INT}}(t) = \widehat{H}_{\mathrm{INT}}(2t_c - t)$ and so the first-order average Hamiltonian vanishes.

One of the simplest modulations that satisfies Eqs. (14) and (15) under PMLG decoupling (Eq. (4)) is given as follows: $\psi(t)$ during the kth interval of the selective pulse is given by

$$\psi(t) = \begin{cases} -\frac{\delta_k \pi \sqrt{3} t}{2\sqrt{2}} & \text{for } 0 < t < \frac{t_c}{2}, \\ \frac{\delta_k \pi \sqrt{3}(t-(t_c/2))}{2\sqrt{2}} - \frac{\delta_k \pi \sqrt{3} t_c}{4\sqrt{2}} & \text{for } \frac{t_c}{2} < t < t_c, \\ \frac{\delta_k \pi \sqrt{3}(t-t_c)}{2\sqrt{2}} & \text{for } t_c < t < \frac{3t_c}{2}, \\ -\frac{\delta_k \pi \sqrt{3}(t-(3t_c/2))}{2\sqrt{2}} + \frac{\delta_k \pi \sqrt{3} t_c}{4\sqrt{2}} & \text{for } \frac{3t_c}{2} < t < 2t_c. \end{cases} \tag{16}$$

This phase modulation leads to an average Hamiltonian over the interval $2t_c$ up to second order

$$H_k = \sum_i -\frac{\omega_i}{\sqrt{3}} \widehat{I}_Z^i - \delta_k \widehat{I}_Y \tag{17}$$

and a propagator during the kth interval is given by

$$U_k(2t_c) = \exp[-\mathrm{i}2t_c H_k]. \tag{18}$$

The overall propagator for the selective pulse, which was divided in N steps, is then given by

$$\begin{aligned} U(2Nt_c) &= U_N(2t_c) U_{N-1}(2t_c) \cdots U_2(2t_c) U_1(2t_c) \\ &= \prod_{k=1}^{N} U_k(2t_c). \end{aligned} \tag{19}$$

In summary, the procedure for creating selective pulses is accomplished as follows:

1. Take a given selective pulse and divide it up into time intervals which are some multiple of the decoupling cycle time ($2t_c$) and assign an amplitude, δ_k as shown in Fig. 1.
2. For the kth segment, using δ_k given from step 1 and using Eqs. (11)–(13), construct a $\psi(t)$ to be added to the decoupling scheme for the kth step. A simple way of accomplishing this is given in Eq. (16).

3. Repeat steps (1) and (2) for each time division of the selective pulse.

Fig. 2 shows a selective pulse implementing a simple Gaussian pulse during a PMLG decoupling sequence. By subtracting the phases for pure PMLG decoupling from the phases of the selective pulse (Fig. 2a), the difference gives $\psi(t)$ in the laboratory frame (Fig. 2b). As can be seen in Fig. 2b, the difference in phase modulation between ordinary PMLG and PMLG combined with selective excitation can be very small, requiring very accurate phase specifications. Simulations and discussions of the tolerance of these selective pulses versus phase imperfections will be discussed elsewhere.

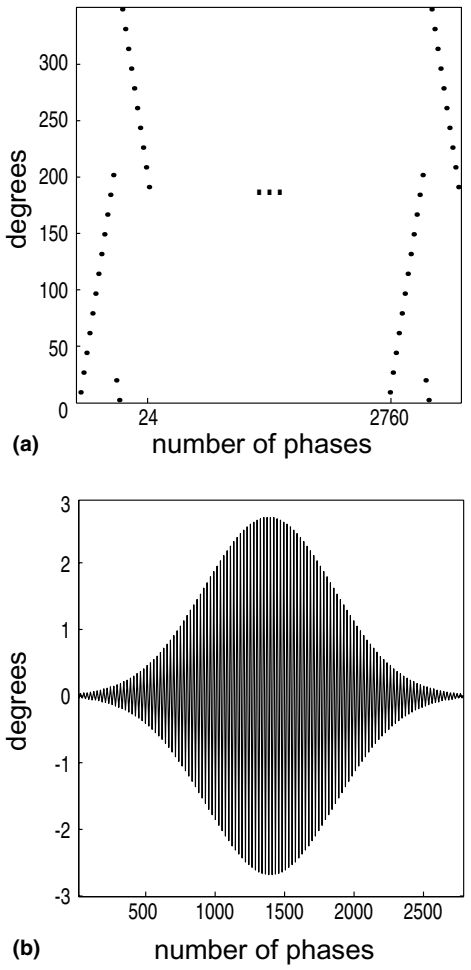

Fig. 2. (a) The phases for the first 24 and last 24 pulses of a purely phase-modulated pulse created by combining a Gaussian pulse with a PMLG-12 decoupling sequence, as calculated using Eq. (16). This pulse is comprised of 2784 phases. (b) The difference, $\psi(t)$, between the phases in the PMLG-12 decoupling pulse and the selective pulse. The profile of $\psi(t)$ is Gaussian, with a maximum phase deviation between $\pm 3°$.

3. Experimental

The different solutes, chloroform and 1,2-dichloro-4-fluoro-5-nitrobenzene, were purchased from Aldrich Chemical Company, and the liquid crystalline solvent, ZLI 1132, from EM Industries and used without further purification. Experimental verification of the selective excitation profiles was carried out at ambient temperature on chloroform dissolved in ZLI 1132 contained in 4 mm Wilmad NMR tube using 499.74 MHz Chemagnetics spectrometer equipped with 4 mm triple channel MAS probe using the sequence shown in Fig. 3a. The two-dimensional spectra were recorded using 399.83 MHz Chemagnetics spectrometer equipped with 5 mm HD Bruker liquid-state probe. Each selective pulse consisted of 2784 phase changes in total time of 9471.6 μs. Phases could be specified experimentally to an accuracy of $\pm 0.1°$. A constant RF amplitude of 20 kHz was used in all experiments for both selective pulses and phase modulated Lee–Goldburg decoupling. The duration of a 90° pulse was 12.5 μs, and a relaxation delay of 10 s was used between scans to prevent sample overheating.

4. Results and discussion

In order to test the above methodology, both a Gaussian pulse and a cosine-modulated Gaussian pulse were implemented into a PMLG-12 decoupling using the formalism presented in the theory section. Fig. 4 shows the theoretical and experimental profiles of a Gaussian pulse (a) and a cosine-modulated Gaussian pulse (b) added to a PMLG-12 decoupling sequence. The experimental profiles show good agreement with the theoretical profiles. Differences in the excitation profiles could be a result of either phase imperfections and/or

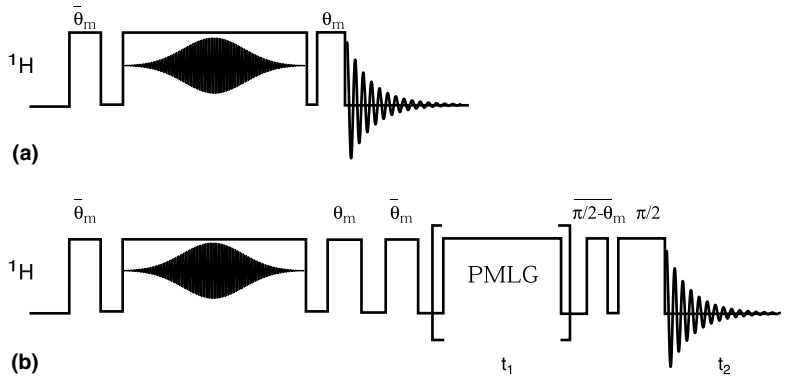

Fig. 3. (a) Pulse sequence used to measure the excitation profiles for the selective pulses. The selective pulse is sandwiched between magic-angle tilt pulses in order to transform $\widehat{I}_Z$ in the decoupling frame to I_Z in the laboratory frame. (b) Pulse sequence used to measure the selective excitation in a dipole-coupled spin system. After the selective pulse, a PMLG decoupling sequence is used in the indirect dimension, t_1, in order to observe the proton-decoupled local field [24] of the fluorine nucleus.

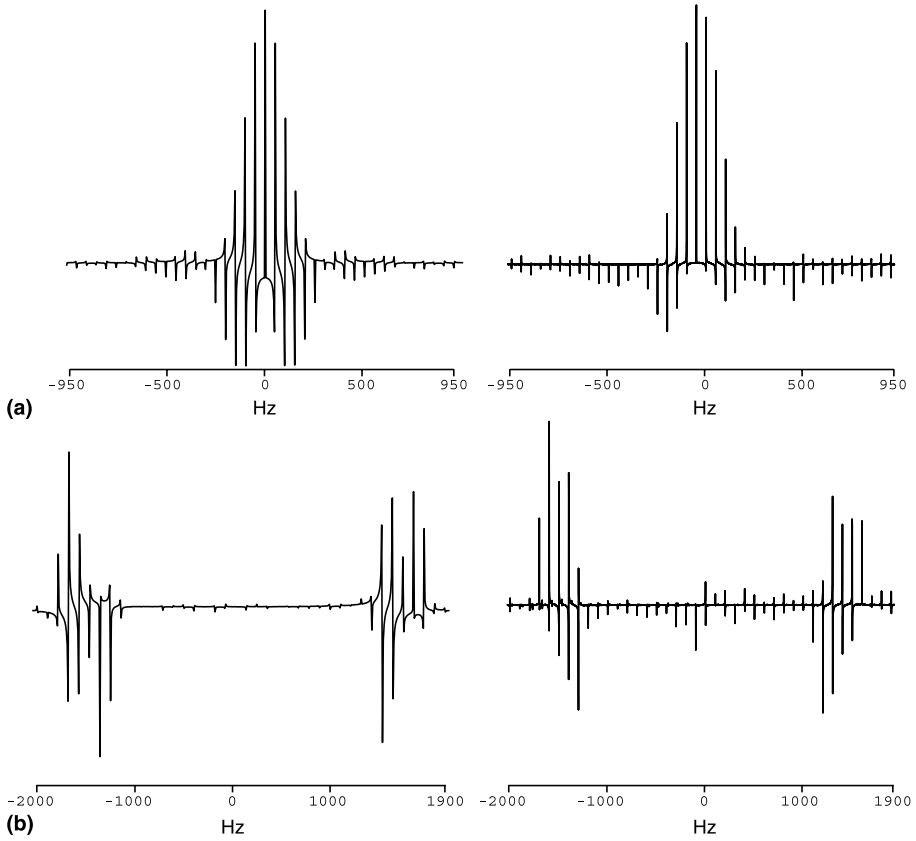

Fig. 4. Theoretical (left) and experimental (right) excitation profiles for (a) a Gaussian pulse and (b) a cosine-modulated Gaussian combined with PMLG-12 decoupling and calculated using Eq. (16). The experimental profiles were generated using the pulse sequence in Fig. 3a. Good aggreement is obtained between the experimental and theoretical profiles.

improper tilt pulses used in the pulse sequence (Fig. 3a), which could explain the small residual magnetization seen for offsets far away from resonance.

These selective pulses were then used for selective excitation in the simple molecule, 1,2-dichloro-4-fluoro-5-nitrobenzene dissolved in nematic solvent ZLI 1132 using the pulse sequence shown in Fig. 3b. Here the selective excitation was based on the heteronuclear dipole coupling between the protons and a fluorine nucleus. Since the dipolar coupling between the protons (≈200 Hz) is smaller than the heteronuclear coupling with the fluorine (≈1 kHz), the spectra appears first-order (Fig. 5a). The Gaussian selective pulse was used to excite the inner transitions, whereas the cosine-modulated Gaussian selective pulse was used to excite the outer transitions. The one-dimensional projections are shown in Figs. 5b and c, and show reasonably good selectivity. Although this is not a strongly dipolar coupled system, the above spectra demonstrate the validity of the methodology presented in this paper. Work in more strongly coupled systems in liquid crystals and solids is currently under way and will be presented elsewhere.

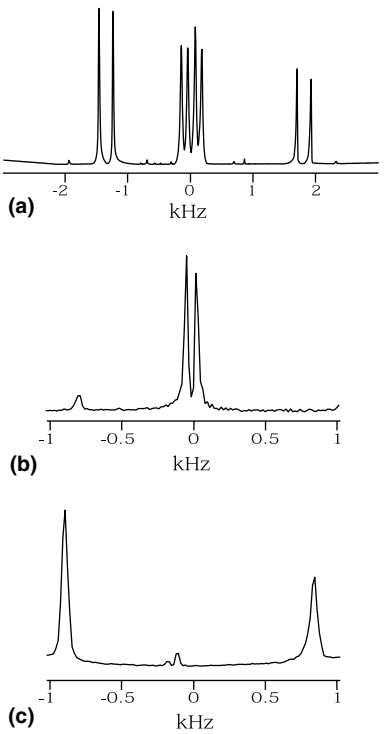

Fig. 5. (a) One-dimensional spectrum of 1,2-dichloro-4-fluoro-5-nitrobenzene dissolved in ZLI 1132. (b) Projection in the indirect dimension obtained using pulse sequence in Fig. 3b for a Gaussian pulse combined with PMLG-12 decoupling. (c) Projection in the indirect dimension obtained using the pulse sequence in Fig. 3b for a cosine-modulated Gaussian pulse combined with PMLG-12 decoupling. The scaling factor of 0.58 characteristic of PMLG decoupling is observed.

The above methodology allows for the implementation of general selective excitation in the presence of homonuclear decoupling. This was demonstrated by implementing a Gaussian pulse and a cosine-modulated Gaussian pulse with a PMLG decoupling sequence, and preliminary experimental verification of the technique was presented. Generalizations of this technique to other RF interaction frames might allow different excitations based on relaxation times (T_1 in quadrupoles, or $T_{1\rho}$ for imaging experiments). Additionally, pulses developed for adiabatic inversions and/or excitations, calculated in the absence of dipolar couplings, might be able to be implemented in the presence of couplings by performing similar transformations as described in this letter. Finally, the above methodology might aid in the development of better pulse sequences for decoupling, where the small perturbation to the decoupling sequence could be used to second-average higher-order corrections to the decoupling sequence.

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