

Analytical Description of the Effect of Adiabatic Pulses on IS, I₂S, and I₃S Spin Systems

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Received June 25, 1997; revised October 3, 1997

An analytical description of the evolution of magnetization in I_nS spin systems ($1 \leq n \leq 3$) during the course of an adiabatic pulse applied on spin S is provided. Calculations show that multiple-quantum terms are created during the pulse and that the rate at which in-phase and antiphase I-spin magnetization components interchange during spin-echo-based pulse sequences is decreased relative to the case where a hard inversion pulse is substituted for the adiabatic pulse. This has important consequences for purging schemes making use of such frequency-swept pulses. Simulations demonstrate that the evolution of in-phase I magnetization is essentially independent of n . © 1998 Academic Press

Key Words: adiabatic pulses; purging; multiple-quantum coherences.

Recently adiabatic frequency-swept pulses have assumed an important role in high-resolution NMR spectroscopy (1–14). This is largely the result of the fact that these pulses have outstanding inversion profiles over large bandwidths despite the use of relatively low RF amplitudes. This property has also facilitated their use in wideband decoupling schemes which is of practical importance for heteronuclei with large chemical shift dispersion, such as ¹³C (2, 7–9, 11, 12). In contrast to nonadiabatic pulses which require careful calibration, the RF amplitudes of these frequency-swept pulses must only be adjusted past a certain threshold which satisfies the adiabaticity condition (15). These pulses are therefore significantly less sensitive to RF-field inhomogeneity than a conventional (π) pulse, for example. Provided that the adiabaticity condition is respected, i.e., that the magnetization vector follows the time-dependent effective field $\omega_{\text{eff}}(t)$, each individual spin is inverted by the end of a frequency-swept inversion pulse. The RF amplitude of such pulses can be apodized at the beginning and the end so that complete inversion of the magnetization is obtained. Several shapes that improve the frequency profile and power requirements have been suggested (3, 6, 7, 11, 12, 16), including sech/tanh (3), apodized CHIRPs (6, 16), and WURST pulses (11, 12). As described in detail elsewhere (14), during the time course of such pulses spins resonating with

different chemical shifts are not inverted simultaneously. For example, for a pulse swept downfield the inversion of the most upfield resonating spins will occur prior to the others. The exact time profile of magnetization will depend on the pulse specifications, including the frequency at which the sweep begins and the sweep rate, in addition to the chemical shifts of the spins in question. We have recently made use of these features, in addition to the fact that the relation between ¹³C chemical shift and the one-bond ¹H–¹³C scalar coupling, ¹J_{HC}, is to good approximation linear in biomolecules, to design pulse schemes which separate signal from protons directly coupled to ¹³C from those that are not (14). This is of particular importance in the study of molecular complexes by NMR in which intermolecular NOEs are established on the basis of selecting for through-space magnetization transfer between protons coupled to ¹³C and protons that are uncoupled (17–19). In a related study Kupče and Freeman (13) have designed experiments for improved magnetization transfer in ¹H–¹³C spin systems which make use of the linear ¹J_{HC} vs chemical shift profile often found in organic molecules.

Previous analysis of the evolution of magnetization during the course of a frequency-swept pulse has assumed either that the spins are isolated or that spin systems are of the “IS” variety [two-spin approximation] (2, 4–7, 14). In the present article we build upon the earlier work by deriving relations which allow the facile calculation of the evolution of magnetization for a spin system of the form I_nS ($1 \leq n \leq 3$) and show that during the course of the pulse transverse magnetization of spin I evolves in a manner which is essentially independent of n . Although we have published analytical expressions for the IS case previously (14), for completeness we briefly summarize this case as well in the present work. The results indicate that in the design of sequences for magnetization transfer (13) or for purging ¹H–¹³C spin pairs (14) the details of frequency-swept pulses can be appreciated by considering only the IS spin system. In this regard it is noteworthy that Bendall has recently considered how the one-bond IS scalar coupling constant is affected by

the adiabatic field (7). In this work a reduced coupling constant is derived which is related to the scalar coupling constant that is operative in the absence of the field. In the present article, we demonstrate that a complete description of the evolution of coherences is more complex than might be anticipated on the basis of a simple scaling of the coupling constant. In addition to the in-phase and antiphase transverse magnetization terms that are generated by evolution due to scalar coupling a large number of additional terms are created by the adiabatic pulse. We provide complete expressions describing the evolution of each of these density terms. The evolution predicted under the simplifying assumption that inversion of magnetization occurs instantaneously when the carrier of the adiabatic pulse is swept through the on-resonance condition is compared with what is obtained on the basis of the rigorous analysis described below.

IS SPIN SYSTEMS

For two coupled spins I and S where the S spin is irradiated by a frequency-swept pulse, the system can be described by the following Hamiltonian:

$$H^{\text{SF}} = 2\pi^1 J_{\text{IS}} I_z S_z + \Delta\omega(t) S_z + \omega_1(t) S_x. \quad [1]$$

The Hamiltonian, H^{SF} , is expressed in a doubly rotating frame [referred to as the “sweep frame,” (SF)] rotating at the resonance frequency of spin I and for spin S at a frequency given by the instantaneous frequency of the S-spin carrier, $\omega_0(t)$. In Eq. [1] $^1J_{\text{IS}}$ is the scalar J coupling between I and S, I_α is the α component ($\alpha = x, y, z$) of the I-spin magnetization, S_α is the α component of the S-spin magnetization, $\Delta\omega(t) = (\Omega_S - \omega_0(t))$ is the time-dependent frequency difference between the chemical shift of spin S, Ω_S , and the carrier frequency, and $\omega_1(t)$ is the RF amplitude. The exact form of $\omega_1(t)$ can vary slightly; in our laboratory we have employed a profile given by

$$\begin{aligned} \omega_1(n) &= \omega_1^{\text{max}} \sin\left(\frac{n\pi}{2f}\right), \quad 1 \leq n < f \\ &= \omega_1^{\text{max}}, \quad f \leq n \leq np - f \\ &= \omega_1^{\text{max}} \sin\left(\frac{\pi}{2} + \frac{\pi}{2} \frac{n - (np - f)}{f}\right), \\ &\quad np - f < n \leq np, \end{aligned} \quad [2]$$

where f/np corresponds to the fraction of the pulse during which the B_1 field is ramped up or down, typically 20%, and np is the number of points in the profile. It is clear from Eqs. [1] and [2] that the Hamiltonian of Eq. [1] is time-dependent. In order to compute the evolution of the density matrix, the pulse must therefore be divided into sufficiently small time intervals, Δt , during which the Hamiltonian can

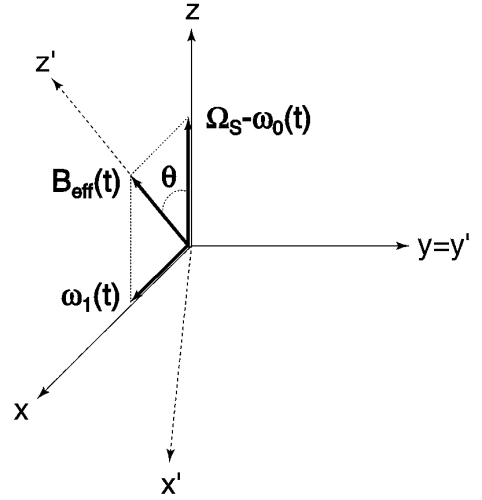


FIG. 1. Representation of the two reference frames used in this work. The x , y , and z (accelerating or sweep frame, SF) reference frame follows the S-spin carrier during the time course of the time-dependent frequency-swept RF pulse. The x' , y' , and z' frame is tilted so that the z' axis is aligned along the effective field $B_{\text{eff}}(t)$ which points in the direction defined by the vector sum of x and z components with magnitudes given by the RF amplitude, $\omega_1(t)$ (x axis), and the frequency difference between the S spin resonance frequency and the carrier, $\Omega_S - \omega_0(t)$ (z axis).

be considered time-independent. In this case numerical diagonalization of the Hamiltonian at each step, Δt , must be performed, a very inefficient and time-consuming approach. In contrast, calculation of the time dependence of the density operator with the relations presented here is far less time-consuming than the diagonalization approach and, in addition, provides insight into the magnetization behavior during the time course of the frequency-swept pulse. Taking the approach described above in which the Hamiltonian is parsed into small steps, an analytical calculation can be performed for any arbitrary interval, Δt . The result is a finite number of product operator terms describing the evolution of various coherence orders.

At time $t_{j+1} = t_j + \Delta t$ from the start of the frequency-swept pulse, the Hamiltonian can be diagonalized by rotating into a tilted frame whose z axis coincides with the axis of the effective field. This is achieved by the operator

$$U = \exp\{i\theta_{j+1} S_y\}, \quad [3]$$

where θ_{j+1} is the angle between the effective field and the static magnetic field \mathbf{B}_0 at time t_{j+1} . The angle θ is depicted in the graphical representation of the tilted frame (Fig. 1) and is given by

$$\begin{aligned} \cos \theta_{j+1} &= \frac{\Delta\omega(t_{j+1})}{\tilde{\omega}(t_{j+1})} = c_\theta, \\ \sin \theta_{j+1} &= \frac{\omega_1(t_{j+1})}{\tilde{\omega}(t_{j+1})} = s_\theta, \\ \tilde{\omega}(t_{j+1}) &= \sqrt{\Delta\omega^2(t_{j+1}) + \omega_1^2(t_{j+1})}. \end{aligned} \quad [4]$$

Using Eqs. [1], [3], and [4], the Hamiltonian in the tilted frame, H' , is expressed as

$$\begin{aligned} H'_{j+1} &= U H_{j+1}^{\text{SF}} U^{-1} \\ &= 2\pi^1 J_{\text{IS}} I_z S'_z c_\theta - 2\pi^1 J_{\text{IS}} I_z S'_x s_\theta \\ &\quad + S'_z (\Delta\omega(t_{j+1}) c_\theta + \omega_1(t_{j+1}) s_\theta) \\ &\quad + S'_x (\omega_1(t_{j+1}) c_\theta - \Delta\omega(t_{j+1}) s_\theta) \\ &= 2\pi^1 J_{\text{IS}} I_z S'_z c_\theta + \tilde{\omega}_{j+1} S'_z, \end{aligned} \quad [5]$$

where S'_α is the α component of the S spin in the tilted frame. The nonsecular part of the Hamiltonian in the tilted frame—the term $2\pi^1 J_{\text{IS}} I_z S'_x s_\theta$ —can be neglected. This has been established by performing full density matrix simulations with and without this term in the Hamiltonian.

Assuming that the Hamiltonian H'_{j+1} is time-independent (Eq. [5]), the evolution of the density matrix between the intervals t_j and $t_{j+1} = t_j + \Delta t$ is given by

$$\begin{aligned} \sigma^{\text{SF}}(t_{j+1}) &= U^{-1} \exp\{-i H'_{j+1} \Delta t\} \\ &\quad \times U \sigma^{\text{SF}}(t_j) U^{-1} \exp\{i H'_{j+1} \Delta t\} U. \end{aligned} \quad [6]$$

The density matrix $\sigma^{\text{SF}}(t_j)$ is therefore rotated into the titled frame by the transformation matrix U , allowed to evolve for a time Δt under H'_{j+1} , and subsequently rotated back into the sweep frame. It can be shown that if the density matrix immediately prior to the pulse is given by

$$\sigma^{\text{SF}}(0) = A_0 I_x + B_0 2I_y S_z, \quad [7]$$

then at a time $t_j = j\Delta t$ after the start of the pulse the density matrix can be expressed as

$$\sigma^{\text{SF}}(j\Delta t) = A_j I_x + B_j 2I_y S_z + C_j 2I_y S_x + D_j 2I_y S_y. \quad [8]$$

It is of interest to note that the magnetization evolves within a closed subspace spanned by in-phase and antiphase components (I_x and $2I_y S_z$) and a combination of zero- and double-quantum coherences ($2I_y S_x$ and $2I_y S_y$). Carrying out the transformation described by Eq. [6] yields an expression for the density matrix at time $(j+1)\Delta t$,

$$\begin{aligned} \sigma^{\text{SF}}((j+1)\Delta t) &= A_{j+1} I_x + B_{j+1} 2I_y S_z \\ &\quad + C_{j+1} 2I_y S_x + D_{j+1} 2I_y S_y, \end{aligned} \quad [9]$$

with the coefficients

$$\begin{aligned} A_{j+1} &= A_j c_J - (B_j c_\theta + C_j s_\theta) s_J, \\ B_{j+1} &= [(B_j c_\theta + C_j s_\theta) c_J + A_j s_J] c_\theta \\ &\quad - [(-B_j s_\theta + C_j c_\theta) c_\omega - D_j s_\omega] s_\theta, \end{aligned}$$

$$\begin{aligned} C_{j+1} &= [(-B_j s_\theta + C_j c_\theta) c_\omega - D_j s_\omega] c_\theta \\ &\quad + [(B_j c_\theta + C_j s_\theta) c_J + A_j s_J] s_\theta, \\ D_{j+1} &= (-B_j s_\theta + C_j c_\theta) s_\omega + D_j c_\omega, \end{aligned} \quad [10]$$

where

$$\begin{aligned} c_\omega &= \cos(\tilde{\omega}_{j+1} \Delta t), \\ s_\omega &= \sin(\tilde{\omega}_{j+1} \Delta t), \\ c_J &= \cos(\pi^1 J_{\text{IS}} \Delta t c_\theta), \\ s_J &= \sin(\pi^1 J_{\text{IS}} \Delta t c_\theta). \end{aligned} \quad [11]$$

I₂S SPIN SYSTEMS

For I₂S spin systems where the two I spins have identical scalar coupling to the S spin ($^1J_{\text{IS}} = ^1J_{\text{IS}} = ^1J_{\text{IS}}$) and where only the S spin is irradiated by a frequency-swept pulse, the Hamiltonian during the pulse is given by

$$\begin{aligned} H^{\text{SF}} &= 2\pi^1 J_{\text{IS}} I_{z,1} S_z + 2\pi^1 J_{\text{IS}} I_{z,2} S_z \\ &\quad + \Delta\omega(t) S_z + \omega_1(t) S_x. \end{aligned} \quad [12]$$

As before, transformation to the tilted frame yields

$$\begin{aligned} H'_{j+1} &= U H_{j+1}^{\text{SF}} U^{-1} = 2\pi^1 J_{\text{IS}} I_{z,1} S'_z c_\theta \\ &\quad + 2\pi^1 J_{\text{IS}} I_{z,2} S'_z c_\theta + \tilde{\omega}_{j+1} S'_z. \end{aligned} \quad [13]$$

Inserting the Hamiltonian of Eq. [13] into Eq. [6], and assuming that the initial density matrix is given by Eq. [7], establishes that the evolution of the density operator can be described by a basis set involving the following product operator elements: ($I_{x,1} + I_{x,2}$), ($2I_{y,1} S_z + 2I_{y,2} S_z$), ($2I_{y,1} S_x + 2I_{y,2} S_x$), ($2I_{y,1} S_y + 2I_{y,2} S_y$), ($4I_{y,1} I_{z,2} S_y + 4I_{z,1} I_{y,2} S_y$), ($4I_{y,1} I_{z,2} S_x + 4I_{z,1} I_{y,2} S_x$), ($4I_{y,1} I_{z,2} S_z + 4I_{z,1} I_{y,2} S_z$), and ($2I_{x,1} I_{z,2} + 2I_{z,1} I_{x,2}$).

The density matrix at time $(j+1)\Delta t$ after the start of the pulse is given by

$$\begin{aligned} \sigma^{\text{SF}}((j+1)\Delta t) &= A_{j+1} (I_{x,1} + I_{x,2}) \\ &\quad + B_{j+1} (2I_{y,1} S_z + 2I_{y,2} S_z) + C_{j+1} (2I_{y,1} S_x + 2I_{y,2} S_x) \\ &\quad + D_{j+1} (2I_{y,1} S_y + 2I_{y,2} S_y) + E_{j+1} (4I_{y,1} I_{z,2} S_y \\ &\quad + 4I_{z,1} I_{y,2} S_y) + F_{j+1} (4I_{y,1} I_{z,2} S_x + 4I_{z,1} I_{y,2} S_x) \\ &\quad + G_{j+1} (4I_{y,1} I_{z,2} S_z + 4I_{z,1} I_{y,2} S_z) \\ &\quad + H_{j+1} (2I_{x,1} I_{z,2} + 2I_{z,1} I_{x,2}), \end{aligned} \quad [14]$$

with coefficients

$$\begin{aligned}
A_{j+1} &= A_j c_J - (B_j c_\theta + C_j s_\theta) s_J, \\
B_{j+1} &= [(B_j c_\theta + C_j s_\theta) c_J + A_j s_J] c_\theta \\
&\quad - \{ [(-B_j s_\theta + C_j c_\theta) c_\omega - D_j s_\omega] c_J \\
&\quad - [(F_j c_\theta - G_j s_\theta) s_\omega + E_j c_\omega] s_J \} s_\theta, \\
C_{j+1} &= [(B_j c_\theta + C_j s_\theta) c_J + A_j s_J] s_\theta \\
&\quad + \{ [(-B_j s_\theta + C_j c_\theta) c_\omega - D_j s_\omega] c_J \\
&\quad - [(F_j c_\theta - G_j s_\theta) s_\omega + E_j c_\omega] s_J \} c_\theta, \\
D_{j+1} &= [(-B_j s_\theta + C_j c_\theta) s_\omega + D_j c_\omega] c_J \\
&\quad + [(F_j c_\theta - G_j s_\theta) c_\omega - E_j s_\omega] s_J, \\
E_{j+1} &= [(-B_j s_\theta + C_j c_\theta) c_\omega - D_j s_\omega] s_J \\
&\quad + [(F_j c_\theta - G_j s_\theta) s_\omega + E_j c_\omega] c_J, \\
F_{j+1} &= \{ -[(-B_j s_\theta + C_j c_\theta) s_\omega + D_j c_\omega] s_J \\
&\quad + [(F_j c_\theta - G_j s_\theta) c_\omega - E_j s_\omega] c_J \} c_\theta \\
&\quad + [(F_j s_\theta + G_j c_\theta) c_J + H_j s_J] s_\theta, \\
G_{j+1} &= \{ [(-B_j s_\theta + C_j c_\theta) s_\omega + D_j c_\omega] s_J \\
&\quad - [(F_j c_\theta - G_j s_\theta) c_\omega - E_j s_\omega] c_J \} s_\theta \\
&\quad + [(F_j s_\theta + G_j c_\theta) c_J + H_j s_J] c_\theta, \\
H_{j+1} &= -(F_j s_\theta + G_j c_\theta) s_J + H_j c_J, \tag{15}
\end{aligned}$$

where $A_j, B_j, C_j, \dots, H_j$ are the coefficients of the density matrix at time $(j)\Delta t$. Note that the rotation of the density matrix into the tilted frame modifies the coefficients of half of the terms, mixing B_j with C_j and F_j with G_j . The subsequent evolution in the tilted frame affects all terms. It is important to realize that the coefficient A_{j+1} is the same for both IS (Eq. [10]) and I₂S (Eq. [15]) spin systems, indicating that the evolution of I_x will be very similar in both cases. In fact, simulations demonstrate that the time evolution of the four terms $\{I_x, 2I_y S_z, 2I_y S_x, \text{ and } 2I_y S_y\}$ is essentially the same for IS and I₂S spin systems. The terms described by coefficients $E_{j+1}, F_{j+1}, G_{j+1}$, and H_{j+1} have a negligibly small intensity relative to the two-spin double- and zero-quantum terms (coefficients C_{j+1} and D_{j+1}) and the in-phase and antiphase I-spins coherences, with coefficients A_{j+1} and B_{j+1} , respectively. These results are illustrated in Fig. 2.

I₃S SPIN SYSTEMS

For I₃S spin systems ($^1J_{I_1 S} = ^1J_{I_2 S} = ^1J_{I_3 S} = ^1J_{IS}$) where the adiabatic frequency-swept pulse affects only the S spin, the Hamiltonian in the sweep frame is

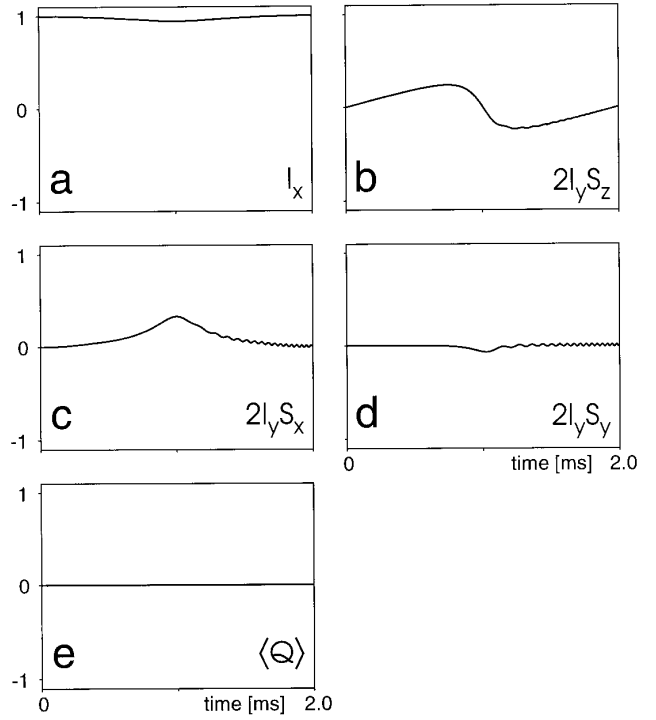


FIG. 2. Time evolution of product operator terms obtained from the analytical expressions described in Eq. [10] (IS), Eq. [15] (I₂S), and Eq. [19] (I₃S) with the initial condition $A_0 = 1$ and all other coefficients 0. (a)–(d) Evolution of the four terms of Eq. [8] for I_nS spin systems calculated according to Eqs. [9] and [10] for $n = 1$, Eqs. [14] and [15] for $n = 2$, and Eqs. [18] and [19] for $n = 3$. Results for $1 \leq n \leq 3$ are superimposable. (e) Time evolution of product operator terms $\langle Q \rangle$ with $\langle Q \rangle = \emptyset$ for an IS spin system, $\langle Q \rangle = 4I_{y,1}I_{z,2}S_y, 4I_{z,1}I_{y,2}S_y, 4I_{y,1}I_{z,2}S_x, 4I_{z,1}I_{y,2}S_x, 4I_{y,1}I_{z,2}S_z, 4I_{z,1}I_{y,2}S_z, 2I_{x,1}I_{z,2}, \text{ and } 2I_{z,1}I_{x,2}$ for an I₂S spin system, and $\langle Q \rangle = 4I_{y,1}I_{z,2}S_y, 4I_{y,1}I_{z,3}S_y, 4I_{z,1}I_{y,2}S_y, 4I_{z,1}I_{y,3}S_y, 4I_{z,2}I_{y,3}S_y, 4I_{y,1}I_{z,2}S_x, 4I_{y,1}I_{z,3}S_x, 4I_{z,1}I_{y,2}S_x, 4I_{y,2}I_{z,3}S_x, 4I_{z,1}I_{y,3}S_x, 4I_{z,2}I_{y,3}S_x, 4I_{y,1}I_{z,2}S_z, 4I_{y,1}I_{z,3}S_z, 4I_{z,1}I_{y,2}S_z, 4I_{y,2}I_{z,3}S_z, 4I_{z,1}I_{y,3}S_z, 4I_{z,2}I_{y,3}S_z, 2I_{x,1}I_{z,2}, 2I_{z,1}I_{x,2}, 2I_{x,2}I_{z,3}, 2I_{z,1}I_{x,3}, 2I_{z,2}I_{x,3}, 8I_{y,1}I_{z,2}I_{z,3}S_y, 8I_{z,1}I_{y,2}I_{z,3}S_y, 8I_{z,1}I_{z,2}I_{y,3}S_y, 8I_{y,1}I_{z,2}I_{z,3}S_x, 8I_{z,1}I_{y,2}I_{z,3}S_x, 8I_{z,1}I_{z,2}I_{y,3}S_x, 8I_{y,1}I_{z,2}I_{z,3}S_z, 8I_{z,1}I_{y,2}I_{z,3}S_z, 4I_{x,1}I_{z,2}I_{z,3}, 4I_{z,1}I_{x,2}I_{z,3}, \text{ and } 4I_{z,1}I_{z,2}I_{x,3}$ for an I₃S spin system. The following parameters were used: sweep of 60 kHz, sweep rate $\dot{\nu} = \dot{\omega}/2\pi = 3 \cdot 10^7 \text{ s}^{-2}$, center of sweep at 20 ppm, shape of the frequency-swept pulse given by Eq. [2] with apodization of the first and last 20% using a sine function, pulse duration 2.0 ms, maximum RF amplitude $\omega_1(\text{max})/2\pi = 5 \text{ kHz}$, $^1J_{IS} = 125 \text{ Hz}$, and $\Omega_S = 20 \text{ ppm}$.

$$\begin{aligned}
H^{\text{SF}} &= 2\pi ^1J_{IS}I_{z,1}S_z + 2\pi ^1J_{IS}I_{z,2}S_z \\
&\quad + 2\pi ^1J_{IS}I_{z,3}S_z + \Delta\omega(t)S_z + \omega_1(t)S_x, \tag{16}
\end{aligned}$$

and in the tilted frame,

$$\begin{aligned}
H'_{j+1} &= UH^{\text{SF}}_{j+1}U^{-1} \\
&= 2\pi ^1J_{IS}(I_{z,1} + I_{z,2} + I_{z,3})S'_z c_\theta + \tilde{\omega}_{j+1}S'_z. \tag{17}
\end{aligned}$$

It can be shown that for the initial condition at the start of

the pulse described by Eq. [7] the density matrix at time $(j + 1)\Delta t$ later is given by

$$\begin{aligned} \sigma^{\text{SF}}((j+1)\Delta t) = & A_{j+1}(I_{x,1} + I_{x,2} + I_{x,3}) \\ & + B_{j+1}(2I_{y,1}S_z + 2I_{y,2}S_z + 2I_{y,3}S_z) \\ & + C_{j+1}(2I_{y,1}S_x + 2I_{y,2}S_x + 2I_{y,3}S_x) \\ & + D_{j+1}(2I_{y,1}S_y + 2I_{y,2}S_y + 2I_{y,3}S_y) \\ & + E_{j+1}(4I_{y,1}I_{z,2}S_y + 4I_{y,1}I_{z,3}S_y + 4I_{z,1}I_{y,2}S_y \\ & + 4I_{y,2}I_{z,3}S_y + 4I_{z,1}I_{y,3}S_y + 4I_{z,2}I_{y,3}S_y) \\ & + F_{j+1}(4I_{y,1}I_{z,2}S_x + 4I_{y,1}I_{z,3}S_x + 4I_{z,1}I_{y,2}S_x \\ & + 4I_{y,2}I_{z,3}S_x + 4I_{z,1}I_{y,3}S_x + 4I_{z,2}I_{y,3}S_x) \\ & + G_{j+1}(4I_{y,1}I_{z,2}S_z + 4I_{y,1}I_{z,3}S_z + 4I_{z,1}I_{y,2}S_z \\ & + 4I_{y,2}I_{z,3}S_z + 4I_{z,1}I_{y,3}S_z + 4I_{z,2}I_{y,3}S_z) \\ & + H_{j+1}(2I_{x,1}I_{z,2} + 2I_{x,1}I_{z,3} + 2I_{z,1}I_{x,2} \\ & + 2I_{x,2}I_{z,3} + 2I_{z,1}I_{x,3} + 2I_{z,2}I_{x,3}) \\ & + I_{j+1}(8I_{y,1}I_{z,2}I_{z,3}S_y + 8I_{z,1}I_{y,2}I_{z,3}S_y + 8I_{z,1}I_{z,2}I_{y,3}S_y) \\ & + J_{j+1}(8I_{y,1}I_{z,2}I_{z,3}S_x + 8I_{z,1}I_{y,2}I_{z,3}S_x + 8I_{z,1}I_{z,2}I_{y,3}S_x) \\ & + K_{j+1}(8I_{y,1}I_{z,2}I_{z,3}S_z + 8I_{z,1}I_{y,2}I_{z,3}S_z + 8I_{z,1}I_{z,2}I_{y,3}S_z) \\ & + L_{j+1}(4I_{x,1}I_{z,2}I_{z,3} + 4I_{z,1}I_{x,2}I_{z,3} + 4I_{z,1}I_{z,2}I_{x,3}). \quad [18] \end{aligned}$$

The coefficients A_{j+1}, \dots, L_{j+1} are related to the corresponding values A_j, \dots, L_j evaluated at time $j\Delta t$ according to

$$\begin{aligned} A_{j+1} &= A_j c_J - (B_j c_\theta + C_j s_\theta) s_J, \\ B_{j+1} &= [(B_j c_\theta + C_j s_\theta) c_J + A_j s_J] c_\theta \\ &\quad - \{ [(-B_j s_\theta + C_j c_\theta) c_\omega - D_j s_\omega] c_J c_J \\ &\quad - [(F_j c_\theta - G_j s_\theta) s_\omega + E_j c_\omega] s_{2J} \\ &\quad + [-(J_j c_\theta - K_j s_\theta) c_\omega + I_j s_\omega] s_J s_J \} s_\theta, \\ C_{j+1} &= [(B_j c_\theta + C_j s_\theta) c_J + A_j s_J] s_\theta \\ &\quad + \{ [(-B_j s_\theta + C_j c_\theta) c_\omega - D_j s_\omega] c_J c_J \\ &\quad - [(F_j c_\theta - G_j s_\theta) s_\omega + E_j c_\omega] s_{2J} \\ &\quad + [-(J_j c_\theta - K_j s_\theta) c_\omega + I_j s_\omega] s_J s_J \} c_\theta, \\ D_{j+1} &= [(-B_j s_\theta + C_j c_\theta) s_\omega + D_j c_\omega] c_J c_J \\ &\quad + [(F_j c_\theta - G_j s_\theta) c_\omega - E_j s_\omega] s_{2J} \\ &\quad - [(J_j c_\theta - K_j s_\theta) s_\omega + I_j c_\omega] s_J s_J, \\ E_{j+1} &= [(-B_j s_\theta + C_j c_\theta) c_\omega - D_j s_\omega] c_J s_J \\ &\quad + [(F_j c_\theta - G_j s_\theta) s_\omega + E_j c_\omega] c_{2J} \\ &\quad + [(J_j c_\theta - K_j s_\theta) c_\omega - I_j s_\omega] c_J s_J, \end{aligned}$$

$$\begin{aligned} F_{j+1} &= - \{ [(-B_j s_\theta + C_j c_\theta) s_\omega + D_j c_\omega] c_J s_J \\ &\quad + [-(F_j c_\theta - G_j s_\theta) c_\omega + E_j s_\omega] c_{2J} \\ &\quad + [(J_j c_\theta - K_j s_\theta) s_\omega + I_j c_\omega] c_J s_J \} c_\theta \\ &\quad + [(F_j s_\theta + G_j c_\theta) c_J + H_j s_J] s_\theta, \\ G_{j+1} &= \{ [(-B_j s_\theta + C_j c_\theta) s_\omega + D_j c_\omega] c_J s_J \\ &\quad + [-(F_j c_\theta - G_j s_\theta) c_\omega + E_j s_\omega] c_{2J} \\ &\quad + [(J_j c_\theta - K_j s_\theta) s_\omega + I_j c_\omega] c_J s_J \} s_\theta \\ &\quad + [(F_j s_\theta + G_j c_\theta) c_J + H_j s_J] c_\theta, \\ H_{j+1} &= -(F_j s_\theta + G_j c_\theta) s_J + H_j c_J, \\ I_{j+1} &= -[(-B_j s_\theta + C_j c_\theta) s_\omega + D_j c_\omega] s_J s_J \\ &\quad + [(F_j c_\theta - G_j s_\theta) c_\omega - E_j s_\omega] s_{2J} \\ &\quad + [(J_j c_\theta - K_j s_\theta) s_\omega + I_j c_\omega] c_J c_J, \\ J_{j+1} &= \{ [(-B_j s_\theta + C_j c_\theta) c_\omega + D_j s_\omega] s_J s_J \\ &\quad - [(F_j c_\theta - G_j s_\theta) s_\omega + E_j c_\omega] s_{2J} \\ &\quad + [(J_j c_\theta - K_j s_\theta) c_\omega - I_j s_\omega] c_J c_J \} c_\theta \\ &\quad + [(J_j s_\theta + K_j c_\theta) c_J + L_j s_J] s_\theta, \\ K_{j+1} &= \{ [(-B_j s_\theta + C_j c_\theta) c_\omega - D_j s_\omega] s_J s_J \\ &\quad + [(F_j c_\theta - G_j s_\theta) s_\omega + E_j c_\omega] s_{2J} \\ &\quad - [(J_j c_\theta - K_j s_\theta) c_\omega - I_j s_\omega] c_J c_J \} s_\theta \\ &\quad + [(J_j s_\theta + K_j c_\theta) c_J + L_j s_J] c_\theta, \\ L_{j+1} &= -(J_j s_\theta + K_j c_\theta) s_J + L_j c_J, \quad [19] \end{aligned}$$

where

$$\begin{aligned} c_{2J} &= \cos(2\pi^1 J_{\text{IS}} \Delta t c_\theta), \\ s_{2J} &= \sin(2\pi^1 J_{\text{IS}} \Delta t c_\theta). \quad [20] \end{aligned}$$

Rotation into the tilted frame again modifies the coefficients of half of the terms, mixing B_j with C_j , F_j with G_j , and J_j with K_j . The subsequent evolution under H'_{j+1} affects all terms.

The time dependence of the 12 coefficients of Eq. [19] can be summarized as follows: the four terms I_x , $2I_y S_z$, $2I_y S_x$ and $2I_y S_y$ have essentially the same time evolution for IS, I₂S, and I₃S spin systems (Fig. 2). (Note that the expression for the term A_{j+1} is identical in all cases considered.) The coefficients of the three- and four-spin terms (E_{j+1} , F_{j+1} , G_{j+1} , I_{j+1} , J_{j+1} , K_{j+1} , and L_{j+1}) have a negligibly small intensity, as does H_{j+1} , in relation to the two-spin double- and zero-quantum terms (coefficients C_{j+1} , D_{j+1}) and the in-phase and antiphase I-spin coherences (coefficients A_{j+1} and B_{j+1}).

APPLICATION OF ADIABATIC PULSES TO FILTERING EXPERIMENTS

Isotope filtering experiments are extremely important in the study of molecular complexes in which only one component is labeled, since these schemes allow for the separation of magnetization associated with labeled and unlabeled components. It is crucial that the separation be as artifact free as possible. One of the most common (and most difficult) applications is in the selection of ^{12}C -bound protons from an ensemble of ^{12}C -bound and ^{13}C -bound protons in a macromolecular complex consisting of ^{13}C -labeled and unlabeled (i.e., ^{12}C) components (14, 17–21). We have recently developed such a filtering pulse scheme (elimination of magnetization originating from I spins coupled to S spins), the basic element of which is illustrated in Fig. 3a (14).

The initial ^1H (I) 90° pulse excites proton transverse magnetization which subsequently evolves due to the one-bond ^1H – ^{13}C scalar coupling until the final 90° (I) pulse immediately prior to gradient g2. During this spin-echo period of total duration $2\tau_a$, proton chemical shift evolution is refocused by the ^1H (I) 180° pulse and can therefore be neglected in what follows. As discussed in detail previously (14), to first approximation evolution due to $^1J_{\text{HC}}$ proceeds for a given ^{13}C – ^1H pair for a duration of $2\tau_a - 2t$, where t is the time between application of the proton π pulse and the point at which the carrier of the frequency-swept pulse passes through the carbon resonance. This approximation assumes that inversion of the carbon magnetization occurs instantaneously and neglects the fact that the adiabatic pulse “slows down” the rate of J evolution (see Fig. 3b and Eq. [10]). Figure 3b illustrates the time dependence of the four important terms $\{I_x, 2I_yS_z, 2I_yS_x, 2I_yS_y\}$ during the course of the pulse scheme indicated in Fig. 3a. Results for IS, I_2S , and I_3S spin systems are superimposable and the coefficients for the higher spin-order terms are essentially zero throughout the scheme. Note that the center of the frequency-swept pulse is at 20 ppm. Thus, a classical description of the trajectory of I magnetization in an I_nS spin system (dashed lines in Fig. 3b) (which assumes instantaneous inversion of the S spin when the carrier of the frequency-swept pulse is on resonance for spin S) predicts that for an S spin resonating at 20 ppm and for $2\tau_a = 1/(2^1J_{\text{HC}})$, $I_x(2\tau_a) = 0$ and $2I_yS_z(2\tau_a) = 1$. The antiphase term is subsequently removed by the action of the gradient g2 and in this way ^{13}C -coupled proton magnetization is eliminated. The utility of the adiabatic S pulse lies in the fact that it is possible to tune the sweep rate so as to minimize the amount of in-phase proton magnetization at the end of the spin-echo period in a manner which is insensitive to the value of $^1J_{\text{HC}}$ (14). A complete description of the evolution of I magnetization is, however, more complex as illustrated in Fig. 3b (solid lines). There is a decrease in the rate at which in-phase and antiphase I components interchange, partly the result of the creation

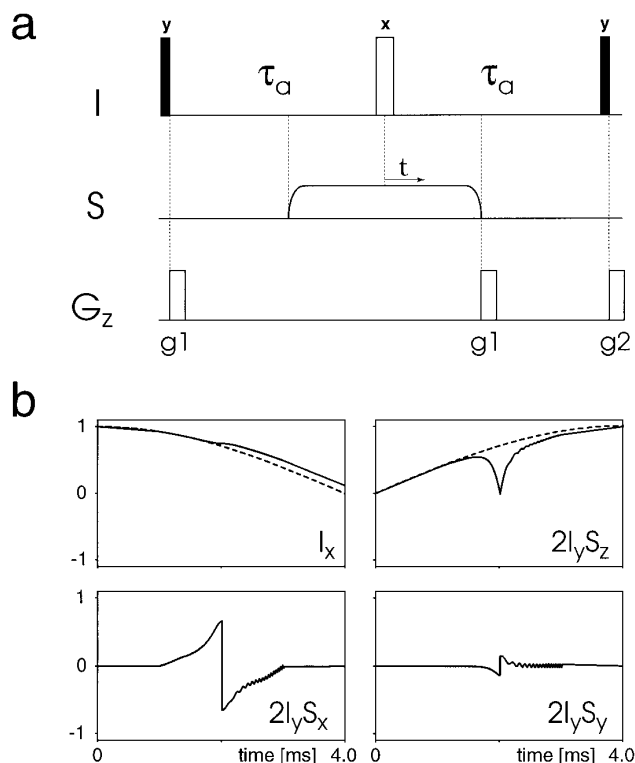


FIG. 3. (a) Purging scheme using a carbon frequency-swept pulse to minimize residual magnetization from I spins (^1H) attached to an S spin (^{13}C). Magnetization from different S spins is inverted at different times during the pulse in a manner dependent on the S-spin chemical shift, the sweep rate of the pulse, and the start of the sweep (see text). The shape of the frequency-swept pulse is given by Eq. [2], with apodization of the first and last 20% using a sine function. Gradients g1 eliminate I-spin 180° pulse artifacts, while gradient g2 dephases magnetization originating from I spins scalar coupled to S spins (^1H – ^{13}C), leaving only proton magnetization originating from I spins which are not directly coupled to ^{13}C . (b) Time evolution of product operator terms during the filtering sequence of (a). An initial condition of $A_0 = 1$ after the first 90° (I) pulse is used, the evolution time in the spin-echo sequence of (a) is $\tau_a = 2$ ms, and the 180° (I) pulse is considered to be ideal and infinitely short. All other conditions are as in Fig. 2. The solid lines correspond to results obtained from a quantum mechanical calculation, while the dashed lines describe results derived on the basis of a classical treatment.

of double- and zero-quantum terms, with the exact details depending on the sweep rate employed, the resonance frequency of the S spin, and the magnitude of $^1J_{\text{IS}}$. This establishes the importance of considering a full quantum treatment in the design of sequences involving frequency-swept inversion pulses, especially where the goal is to purge ^1H magnetization coupled to ^{13}C . In addition, the derivations and simulations presented in the present article establish that the magnetization behavior for I_nS ($1 \leq n \leq 3$) spin systems during an S-spin frequency-swept pulse is described adequately by a two-spin (IS) approximation.

ACKNOWLEDGMENTS

C.Z. was a post-doctoral fellow of the Swiss Science National Fund and the recipient of a Human Frontiers Science Program fellowship. S.J.F.V.

acknowledges a post-doctoral fellowship from the Swiss Science National Fund and a long-term fellowship from the Human Frontiers Science Program. This research was supported by grants from the Natural Sciences and Engineering Research Council of Canada and the Medical Research Council of Canada (L.E.K.). L.E.K. is an Alfred P. Sloan Fellow.

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