Composite pulse excitation in three-level systems

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It is demonstrated by theory and experiment that it is possible to excite coherence uniformly in three-level systems with a wide range of anharmonicities by using a composite pulse excitation method. The theory is based on a formal analogy between the anharmonic three-level case and the simpler system with equally spaced energy levels where composite pulse techniques are already well known to compensate for the effects of mismatch between photon energies and level separations. Computer simulations and solid-state NMR experiments on the three-level system of deuterium (spin 1) verify the uniformity of the excitation. The NMR powder spectrum of deuterated polymethylmethacrylate is faithfully reproduced even using a radio-frequency (rf) field strength weaker than the quadrupole interactions.

INTRODUCTION

The compensation of energy mismatch effects in coherent pulse experiments by using trains of pulses with carefully chosen lengths and phases ("composite pulses")[1–13] has received considerable attention recently, in both NMR[1–11] and coherent optics.[13] In NMR the replacement of conventional radiofrequency excitation procedures by methods based on composite pulses has allowed spectacular reductions in the peak power requirements in experiments like broadband heteronuclear decoupling[4–6,14] and some multiple quantum experiments.[10] In coherent optics, composite pulses have been demonstrated to increase pumping efficiencies across forbidden transitions.[13]

Various methods of designing composite pulse sequences have been used, including geometrical arguments,[1–3,6–8] computer optimization,[2,8,12] iterative recursion procedures,[9] and perturbation theory.[4,5,11,12] With few exceptions[11,12] all treatments have so far been based on Bloch-type equations of motion which are known to be valid only for the interaction of the electromagnetic field with systems with equally spaced energy levels, such as for an isolated spin in a magnetic field. This simple case is now well documented and a battery of composite pulse schemes exists for arbitrary perturbation under nonideal conditions.[9]

The purpose of this paper is to demonstrate the extension of the composite pulse method to the anharmonic three-level case. This is of theoretical interest since the anharmonic three-level system is the simplest that displays deviation from the Bloch equations and effects such as the superposition of states spanning forbidden transitions ("multiple quantum coherence"[15–19]). Practically, the introduction of composite pulses designed for manipulating three energy levels with nonequal spacing is expected to have a considerable impact on the NMR spectroscopy of spins $I = 1$ in anisotropic phase. By analogy with comparable techniques on spins $-1/2$, the power requirements will be relaxed, distortion effects due to energy mismatches will be reduced or eliminated, and the observation of spins $I = 1$ with large quadrupole moments will become easier.

THEORETICAL TREATMENT

We start the theoretical discussion by reviewing the case with equally spaced energy levels. Using NMR nomenclature, the rotating frame Hamiltonian for an isolated spin during a radiofrequency pulse of phase ϕ may be expressed

$$\mathscr{H} = \Omega I_z + \omega_1 e^{-i\phi I_z} I_x e^{i\phi I_z}. \tag{1}$$

Here ω_1 is the radiofrequency field strength and Ω the photon energy mismatch ("resonance offset") in angular frequency units. If the pulse is of duration τ_p, it may be described by a propagator $P_\phi(\tau_p)$:

$$P_\phi(\tau_p) = \exp(-i\phi I_z)\exp[i(\Omega I_z + \omega_1 I_x)\tau_p]\exp(i\phi I_z). \tag{2}$$

We use a convention as elsewhere[9,10] in which the density operator σ is transformed by the pulse as follows:

$$\sigma(t+\tau_p) = P_\phi(\tau_p)^{-1}\sigma(t)P_\phi(\tau_p). \tag{3}$$

The idea of composite pulses is to use, instead of a single pulse, a sequence of N pulses with different phases and durations ϕ_n and τ_{p_n} such that the effect of the mismatch term in Eq. (1), ΩI_z, disappears from the overall propagator. One approach to this problem is to use perturbation theory (in the guise of average Hamiltonian theory[20]), by treating the mismatch ΩI_z as a small perturbation to the large radiofrequency term $\omega_1 I_x$.[12] However, this method is practical only for $\Omega \ll \omega_1$, which is not a case of much interest. Alternative techniques, based on the juxtaposition of carefully chosen rotation operators, allowing results to be obtained even for $\Omega \sim \omega_1$, have been presented elsewhere.[1–10,14] Two particularly effective sequences of this type have been introduced recently by Shaka *et al.*[6] Using the notation for pulses $(\omega_1\tau_{p_n})_{\phi_n}$, these sequences are

$$(\tfrac{3}{2}\pi)_0(\pi)_\pi(\tfrac{1}{2}\pi)_0$$

and

$$(\pi)_\pi(2\pi)_0(\pi)_\pi(\tfrac{3}{2}\pi)_0(\tfrac{1}{2}\pi)_\pi.$$

In the notation of Ref. 9, the sequences are both of construction $P_\pi^{-1}P_0$ and have overall propagators of the approximate form

$$P_{\phi_1}(\tau_{p_1})P_{\phi_2}(\tau_{p_2})\cdots P_{\phi_N}(\tau_{p_N}) \simeq \exp\left(-i\frac{\Omega}{\omega_1}I_z\right)\exp(i\pi I_x)\exp\left(i\frac{\Omega}{\omega_1}I_z\right). \tag{4}$$

This equation holds well for the shorter sequence for mismatches Ω in the range $-\omega_1 \lesssim \Omega \lesssim \omega_1$,[6] and even better for the longer sequence over the same range. Note that the off-resonance term ΩI_z has not in fact disappeared from the

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propagator but has been translated into a relatively innocuous phase shift which can usually be canceled by appropriate pulse sequence design.[3,10] The two sequences above were initially intended for the purpose of broadband population inversion in systems with equally spaced energy levels, in which case the phase of the propagator is irrelevant to the desirable conversion $I_z \rightarrow -I_z$.

The increase in complexity in going from a harmonic system to an anharmonic three-level system is considerable but we will show that it is possible to establish a formal analogy with the harmonic case which will allow some of the results from the simpler situation to be taken over with little modification. Tools appropriate for treating the dynamics of a system with three eigenstates $|i\rangle$, $|j\rangle$, and $|k\rangle$ are the single transition operators introduced by Wokaun and Ernst[16] and by Vega.[17] These operators $I_\nu^{(ij)}$, where $\nu = x, y, z$, have cyclic commutation properties, e.g.,

$$[I_x^{(ij)}, I_y^{(ij)}] = iI_z^{(ij)},$$
$$[I_x^{(ij)}, I_x^{(jk)}] = \tfrac{1}{2}iI_y^{(ik)}. \tag{5}$$

These cyclic commutation properties imply transformation relationships in three-dimensional operator spaces, e.g.,

$$\exp[-i\theta I_x^{(ij)}] I_y^{(ij)} \exp[i\theta I_x^{(ij)}] = I_y^{(ij)} \cos\theta + I_z^{(ij)} \sin\theta$$

and (6)

$$\exp[-i\theta I_x^{(ij)}] I_x^{(jk)} \exp[i\theta I_x^{(ij)}] = I_x^{(jk)} \cos\tfrac{1}{2}\theta + I_y^{(ik)} \sin\tfrac{1}{2}\theta.$$

Longitudinal single transition operators obey the relationship

$$I_z^{(ij)} = I_z^{(ik)} - I_z^{(jk)}. \tag{7}$$

In addition we will find it convenient to introduce "quadrupole polarization operators" $Q_z^{(ij)}$ defined by

$$Q_z^{(ij)} = \tfrac{2}{3}(I_z^{(ik)} + I_z^{(jk)}). \tag{8}$$

(Note that for three levels, specifying two indices i and j automatically defines the third.) An equivalent definition is

$$Q_z^{(ij)} = \tfrac{1}{3}\{3(2I_z^{(ij)})^2 - I(I+1)\}. \tag{9}$$

A useful property of operators $Q_z^{(ij)}$ is their commutation with all operators of the single transition $|i\rangle \leftrightarrow |j\rangle$:

$$[Q_z^{(ij)}, I_\nu^{(ij)}] = 0, \quad \nu = x, y, z. \tag{10}$$

Further properties which are of assistance in manipulating these operators include:

$$Q_z^{(ij)} = Q_z^{(ji)}, \tag{11}$$
$$Q_z^{(ij)} + Q_z^{(jk)} + Q_z^{(ki)} = 0, \tag{12}$$
$$Q_z^{(ij)} = I_z^{(ik)} - \tfrac{1}{2}Q_z^{(ik)}, \tag{13}$$
$$I_z^{(ij)} = \tfrac{1}{2}(Q_z^{(ik)} - Q_z^{(jk)}). \tag{14}$$

We consider the case in which irradiation is applied with the mean frequency of the two allowed transitions $|1\rangle \rightarrow |2\rangle$ and $|2\rangle \rightarrow |3\rangle$ of the three-level system $\Omega = 0$. We do not use perturbation theory, but calculate the motion of the density operator under the full Hamiltonian. Again using NMR nomenclature, the rotating frame Hamiltonian during a pulse of phase ϕ may be expressed in terms of single transition operators[16,17]

$$\mathscr{H} = \mathscr{H}_Q + \sqrt{2}\omega_1 \exp(-2i\phi I_z^{(13)})(I_x^{(12)} + I_x^{(23)}) \times \exp(2i\phi I_z^{(13)}), \tag{15}$$

where the quadrupole interaction $\mathscr{H}_Q$ responsible for the anharmonicity is

$$\mathscr{H}_Q = \omega_Q Q_z^{(13)}. \tag{16}$$

The frequency difference between the two allowed transitions $|1\rangle \rightarrow |2\rangle$ and $|2\rangle \rightarrow |3\rangle$ is $2\omega_Q$.

It has been shown[16,17] that the motion under the Hamiltonian of Eq. (15) may be solved analytically by applying a unitary transformation defined by

$$U_y^{(13)} = \exp\left(i\frac{\pi}{2} I_y^{(13)}\right).$$

Using this transformation and Eqs. (5)–(14), the propagator for a pulse of duration τ_p may be expressed as

$$P_\phi(\tau_p) = \exp(-2i\phi I_z^{(13)})(U_y^{(13)})^{-1} \exp[i(\omega_Q I_z^{(12)} + 2\omega_1 I_x^{(12)})\tau_p] \times \exp(i\omega_Q \tfrac{1}{2}\tau_p Q_z^{(23)}) U_y^{(13)} \exp(2i\phi I_z^{(13)}) \exp(i\omega_Q \tfrac{1}{2}\tau_p Q_z^{(13)}). \tag{17}$$

If we consider the action of such a propagator on an equilibrium density operator

$$\sigma(0) = I_z = 2I_z^{(13)},$$

it is easily shown that the fourth operator in this equation has no effect on the observable magnetization, which is associated only with operators of the form $I_\nu^{(23)}$ at this stage of transformation and so commutes with $Q_z^{(23)}$. Hence the only operators which are responsible for undesirable ω_Q-dependent distortion effects are the third and the final operator

$$\exp(i\omega_Q \tfrac{1}{2}\tau_p Q_z^{(13)}).$$

This latter operator is only responsible for an apparent time shift in the free induction decay, which appears to start at a time $\tfrac{1}{2}\tau_p$, midway through the pulse.[21] Countermeasures are well known.[21–23] It is the third operator

$$\exp[i(\omega_Q I_z^{(12)} + 2\omega_1 I_x^{(12)})\tau_p]$$

which is the origin of the most troublesome features when the irradiation strength ω_1 becomes comparable to the quadrupole interaction ω_Q and which claims our attention.

First we notice an obvious formal analogy between this operator and the corresponding operator for off-resonance irradiation in the harmonic case

$$\exp[i(\Omega I_z + \omega_1 I_x)\tau_p],$$

[Eq. (2)]. In the harmonic case the distortion effects will be related to the ratio of the resonance mismatch Ω to the irradiation field ω_1, while in the anharmonic three-level case, in which two allowed transitions are perturbed simultaneously, the quadrupolar frequency ω_Q must be compared with $2\omega_1$. This doubling of the effective irradiation field causes the three-level case to be somewhat less sensitive to mismatch than might be anticipated. Our second observation is that in the absence of mismatch $\Omega = \omega_Q = 0$ and for the usual pulse durations $\omega_1\tau_p = \pi/2$, the crucial third operator for an anharmonic three-level system takes the form of a selective *inversion* operator $\exp(i\pi I_x^{(12)})$, in contrast to the form $\exp(i\frac{1}{2}\pi I_x)$ encountered in a harmonic system [Eq. (2)]. If this inversion fails, due to the interference of the noncommuting mismatch term $\omega_Q I_z^{(12)}$, signal intensity is lost from the resultant free induction decay, appearing instead as undesired double-quantum coherence. Bloom *et al.*[21] have given the signal intensity $\langle I_y \rangle$ after a pulse of duration τ_p and phase $\phi = 0$ as

$$\langle I_y \rangle = -\left[1 + \left(\frac{\omega_Q}{2\omega_1}\right)^2\right]^{-1/2} \sin\left\{\omega_1 \tau_p \left[1 + \left(\frac{\omega_Q}{2\omega_1}\right)^2\right]^{1/2}\right\}, \tag{18}$$

the result of which follows straightforwardly from Eq. (17). This equation disregards the time shift in the signal.

The important conclusion that a proper *inversion* is necessary for efficient excitation of transverse magnetization in a three-level system is rather surprising but allows us to transfer, with some care, the well-tried sequences developed for broadband inversion in harmonic systems into the three-level context. Compared to the harmonic case, all durations of pulses should be *halved*, again because of the factor 2 in the rotation operator

$$\exp\left[i(\omega_Q I_z^{(12)} + 2\omega_1 I_x^{(12)})\tau_p\right].$$

Also, it may be shown that only sequences involving phase shifts of multiples of π behave similarly for the two situations, for then the phase shift operators $\exp(i2\phi I_z^{(13)})$ in Eq. (17) commute with the transformations $U_y^{(13)}$. The two sequences given above fulfill this condition, so from these we can derive two new composite pulses for exciting transverse coherence in anharmonic three-level systems:

$$\left(\frac{3\pi}{4}\right)_0 \left(\frac{\pi}{2}\right)_\pi \left(\frac{\pi}{4}\right)_0 \qquad \text{(sequence I)}$$

$$\left(\frac{\pi}{2}\right)_\pi (\pi)_0 \left(\frac{\pi}{2}\right)_\pi \left(\frac{3\pi}{4}\right)_0 \left(\frac{\pi}{4}\right)_\pi \qquad \text{(sequence II)}.$$

Using Eqs. (4)–(17), these may be demonstrated to have overall propagators given approximately by

$$P_{\phi_1}(\tau_{p_1}) \cdots P_{\phi_N}(\tau_{p_N}) \simeq (U_y^{(13)})^{-1} \exp(i\pi I_x^{(12)}) \times \exp\left[i\frac{1}{2}\left(\omega_Q T - \frac{\omega_Q}{\omega_1}\right) Q_z^{(23)}\right] U_y^{(13)} \times \exp\left[i\frac{1}{2}\left(\omega_Q T + \frac{\omega_Q}{\omega_1}\right) Q_z^{(13)}\right], \tag{19}$$

where the total duration of the composite pulse is $T = \Sigma_n \tau_{p_n}$. The approximation is good for sequences I and II in the range $|\omega_Q| \lesssim 2|\omega_1|$. By analogy with the arguments following Eq. (17), we note that the free induction decay appears to start at a time $\frac{1}{2}T + (1/2\omega_1)$ before the end of the pulse, analogous to the shift $\frac{1}{2}\tau_p$ in the single pulse case. The serious effect caused by the noncommutation of the operators $\omega_Q I_z^{(12)}$ and $2\omega_1 I_x^{(12)}$ has disappeared to a good approximation.

Instead of recording the free induction decay after a single pulse, it is usual in NMR spectroscopy of spins $I = 1$ to induce a "quadrupole echo" by applying a second pulse, shifted in phase by $\pi/2$, at a time t_1 after the first pulse.[22,23] The echo appears at a time $t_2 = t_1 + \frac{1}{2}\tau_p$ after the second pulse.[21] Acquisition of the echo rather than the direct free-induction decay avoids problems due to the finite recovery time of the receiver electronics. However, distortion effects due to the effect of the quadrupole interaction during the finite pulse are aggravated by this two-pulse method.[21] The usual approach to reducing these distortions is to make the pulses as short as possible, either by increasing the magnitude of the peak radiofrequency field or by using deliberately small rotation angles. The first method leads to serious technical problems in the transmitter and probe electronics since ω_1 must greatly exceed ω_Q if distortion effects are to be suppressed. The second method leads to an undesirable loss in signal intensity. We propose instead using composite pulse echo sequences of the form

$$\left(\frac{3\pi}{4}\right)_0 \left(\frac{\pi}{2}\right)_\pi \left(\frac{\pi}{4}\right)_0 - t_1 - \left(\frac{3\pi}{4}\right)_{\pi/2} \left(\frac{\pi}{2}\right)_{3\pi/2} \left(\frac{\pi}{4}\right)_{\pi/2} - t_2$$

and likewise for sequence II. By this means distortion effects can be minimized without using unacceptably high radiofrequency fields or sacrificing sensitivity. A treatment given in the Appendix shows that in the range $|\omega_Q| \lesssim 2|\omega_1|$ the quadrupole echo is formed with high intensity at a time

$$t_2 = t_1 + \tfrac{1}{2}T - (1/2\omega_1).$$

In fact it is even feasible to leave no gap between the two pulses $t_1 = 0$.

The proposed pulse sequences are of course not unique and many other sequences may be generated by principles given elsewhere.[6,9,14] Any pulse sequence involving phase shifts only in multiples of π radians and which generates a broadband population inversion in harmonic systems will provide a broadband excitation in the anharmonic three-level system if the pulse durations are halved.

COMPUTER SIMULATIONS

The theoretical conclusions are verified by the computer simulations shown in Fig. 1. These were produced by an

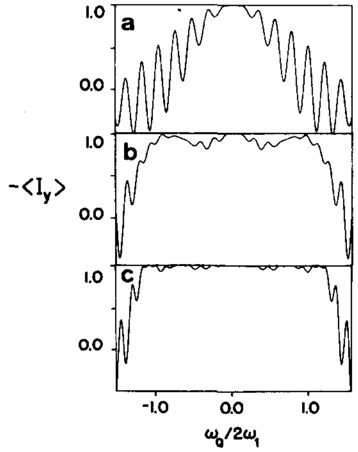

FIG. 1. Computer simulations of the y magnetization $-\langle I_y \rangle$ at the maximum of the quadrupole echo produced by three pulse sequences: (a) conventional two-pulse echo $(\frac{1}{2}\pi)_0 - t_1 - (\frac{1}{2}\pi)_{\pi/2} - t_2$; (b) composite pulse echo $(\frac{3}{4}\pi)_0\, (\frac{1}{2}\pi)_\pi (\frac{1}{4}\pi)_0 - t_1 - (\frac{3}{4}\pi)_{\pi/2} (\frac{1}{2}\pi)_{3\pi/2} (\frac{1}{4}\pi)_{\pi/2} - t_2$; and (c) composite pulse echo $(\frac{1}{2}\pi)_\pi (\pi)_0 \quad (\frac{1}{2}\pi)_\pi (\frac{3}{4}\pi)_0 \quad (\frac{1}{4}\pi)_\pi - t_1 - (\frac{1}{2}\pi)_{3\pi/2} (\pi)_{\pi/2} (\frac{1}{2}\pi)_{3\pi/2} (\frac{3}{4}\pi)_{\pi/2}$ $(\frac{1}{4}\pi)_{3\pi/2} - t_2$. The y magnetization at the echo maxima is plotted against $(\omega_Q/2\omega_1)$. The tolerance of the excitation to the size of the quadrupole interaction is much improved for the composite pulse sequences.

exact dynamical calculation of the evolution involving a numerical diagonalization of the Hamiltonian during the pulses. The calculated expectation value of y magnetization

$$-\langle I_y \rangle = -\mathrm{Tr}\{\sigma I_y\}/\mathrm{Tr}\{I_y^2\}$$

at the echo maximum is shown for three pulse sequences as a function of the parameter $\omega_Q/2\omega_1$. The parameters used in the simulations correspond to $\omega_1/2\pi = 100$ kHz with $\omega_Q/2\pi$ running from -300 to 300 kHz, and $t_1 = 10\,\mu$s.

The exact calculation for the conventional two-pulse sequence

$$\left(\frac{\pi}{2}\right)_0 - t_1 - \left(\frac{\pi}{2}\right)_{\pi/2} - t_2,$$

with

$$t_2 = t_1 + \tfrac{1}{2}\tau_p = 11.25\ \mu\mathrm{s}\,,$$

shows the expected strong dependence of signal on $\omega_Q/2\omega_1$. Taking the maximum acceptable signal loss as 20%, the bandwidth of this conventional excitation procedure is given by $|\omega_Q/2\omega_1| \lesssim 0.37$, while if only a 10% loss is acceptable, the bandwidth is further reduced to $|\omega_Q/2\omega_1| \lesssim 0.20$.

The two composite pulse sequences display a much reduced dependence of echo magnetization $-\langle I_y \rangle$ on mismatch parameter $\omega_Q/2\omega_1$. For the sequence involving composite pulses I, less than a 20% loss in intensity is achieved for all quadrupoles $|\omega_Q/2\omega_1| \lesssim 1.10$ [Fig. 1(b)]. For the longer sequence II, the magnetization from all quadrupoles in the range $|\omega_Q/2\omega_1| \lesssim 1.18$ is refocused with a less than 10% intensity loss [Fig. 1(c)]. The delay t_2 took the theoretical values 12.95 and 16.70 μs for Figs. 1(b) and (c), respectively. To reproduce such bandwidths using single pulses would require an increase in peak power of an order of magnitude.

EXPERIMENTAL VERIFICATIONS

Some experimental results are presented in Fig. 2. These are quadrupole echo ^{2}D-NMR spectra of polycrystalline deuterated polymethylmethacrylate (plexiglass, PMMA) taken at 46.0 MHz on a modified BRUKER CXP-300 spectrometer. The spectrum is a superposition of two main powder patterns, one originating from the freely rotating methyl deuterium spins and one from the more rigid methine deuteriums. The former gives a strong pattern in the center of the spectrum corresponding to an axially symmetric quadrupole tensor with principal values $(\omega_Q/2\pi)_\perp = 18.5$ kHz and $(\omega_Q/2\pi)_\parallel = 37.0$ kHz. The latter gives a broader pattern with $(\omega_Q/2\pi)_\perp \approx 59$ kHz. The spectra were taken with a radiofrequency field strength of $(\omega_1/2\pi) = 31.6$ kHz corresponding to $\pi/2$ pulses of duration 7.9 μs. This field strength was calibrated by finding the pulse duration τ_p for which no signal appears in the center of the powder pattern $\omega_1\tau_p = \pi$.

Spectrum 2(a) was taken with the conventional quadrupole echo sequence employing two $\pi/2$ pulses separated by 20 μs. The badly sloping wings of the methyl powder pattern are obvious and indicate distortion effects due to the quadrupole interaction acting during the radiofrequency pulses. This effect is corrected by replacing each $\pi/2$ pulse by a composite pulse of type I [Fig. 2(b)]. The wings of the central pattern are now nearer to expectation and signals from the broader component become clearly visible. With the use of composite pulses of the form II, the appearance of this broad component is further improved [Fig. 2(c)].

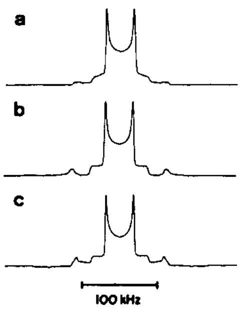

FIG. 2. Experimental ^{2}D NMR spectra of deuterated plexiglass, taken with a radiofrequency field strength corresponding to a $\pi/2$ pulse of duration 7.9 μs: (a) conventional echo, $t_1 = 20\,\mu$s, $t_2 = 21\,\mu$s; (b) composite pulse echo based on $(\frac{3}{4}\pi)_0\,(\frac{1}{2}\pi)_\pi(\frac{1}{4}\pi)_0$ sequence: $t_1 = 20\,\mu$s, $t_2 = 33\,\mu$s; and (c) composite pulse echo based on $(\frac{1}{2}\pi)_\pi(\pi)_0\,(\frac{1}{2}\pi)_\pi(\frac{3}{4}\pi)_0(\frac{1}{4}\pi)_\pi$ sequence: $t_1 = 20\,\mu$s, $t_2 = 36\,\mu$s. The bandwidth of the excitation as observed through the experimental spectral line shapes improves as expected in passing from (a) to (c). All spectra were taken with 300 scans repeated only every minute, to allow the rigid methine deuterons to relax.

CONCLUSIONS

The composite pulse techniques demonstrated above are useful in the manipulation of any three-level system in magnetic resonance and optical spectroscopy, but the NMR of spins $I = 1$ in anisotropic phase will benefit especially. Deuterium NMR is widely used as a sensitive probe of motional processes[24,25] and a composite pulse technique for reducing the distortion of quadrupolar lineshapes without increasing peak radiofrequency power and without attenuating the signal will be welcome. A more thorough discussion of the properties of composite pulses in the NMR spectroscopy of spins $I = 1$, including applications for population inversion and excitation of double quantum coherence, will be given elsewhere.

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APPENDIX

We calculate here the time t_2 at which the quadrupole echo forms after the second of two composite pulses separated by a time t_1 and shifted in phase by $\pi/2$ relative to one another.

The evolution following the first composite pulse appears to have an origin in time at a point $\frac{1}{2}T + (1/2\omega_1)$ before the end of the pulse. The propagator V for the delay $\frac{1}{2}T + (1/2\omega_1) + t_1$, the refocusing pulse, and the evolution time

t_2 is given from Eq. (19) by

$$V \simeq \exp(i\omega_Q t_1' Q_z^{(13)}) \exp(-i\pi I_z^{(13)})(U_y^{(13)})^{-1} \times \exp(i\pi I_x^{(12)}) \exp\left[i \frac{1}{2}\left(\omega_Q T - \frac{\omega_Q}{\omega_1}\right) Q_z^{(23)}\right] U_y^{(13)} \times \exp(i\pi I_z^{(13)}) \exp(i\omega_Q t_2' Q_z^{(13)}), \tag{20}$$

where

$$t_1' = \frac{1}{2}T + \frac{1}{2\omega_1} + t_1$$

and

$$t_2' = \frac{1}{2}T + \frac{1}{2\omega_1} + t_2 . \tag{21}$$

The echo condition is that the observable signal produced by this propagator be independent of ω_Q. It is convenient to evaluate the transformed propagator $\widetilde{V}$ which excludes nonessential terms not depending on ω_Q:

$$\widetilde{V} \simeq U_y^{(13)} \exp(i\pi I_z^{(13)}) V \exp(-i\pi I_z^{(13)})(U_y^{(13)})^{-1} = \exp(i\omega_Q t_1' Q_z^{(13)}) \exp(i\pi I_x^{(12)}) \times \exp\left[i \frac{1}{2}\left(\omega_Q T - \frac{\omega_Q}{\omega_1}\right) Q_z^{(23)}\right] \exp(i\omega_Q t_2' Q_z^{(13)}) .$$

Using Eq. (10)–(14) this may be cast in the form

$$\widetilde{V} \simeq \exp(i\omega_Q t_1' I_z^{(12)}) \exp(i\pi I_x^{(12)}) \times \exp\left[i\omega_Q \left(t_2' - \frac{1}{2}T + \frac{1}{2\omega_1}\right) I_z^{(12)}\right] \times \exp\left[-i\omega_Q \tfrac{1}{2}\left(t_1' + t_2' + \frac{1}{2}T - \frac{1}{2\omega_1}\right) Q_z^{(12)}\right] . \tag{22}$$

A more explicit calculation shows that the density operator consists only of terms of the form $I_\nu^{(12)}$ at this stage of transformation and so commutes with the last term on the right-hand side. The condition

$$t_1' = t_2' - \frac{1}{2}T + \frac{1}{2\omega_1} \tag{23}$$

ensures that the product of the first three terms on the right-hand side of Eq. (22) is independent of ω_Q and so gives the echo time

$$t_2 = t_1 + \frac{1}{2}T - \frac{1}{2\omega_1} . \tag{24}$$

It is interesting to note that in the composite pulse echo the time evolution is not symmetric about the center of the refocusing pulse.

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