Detection of multiple-quantum coherences with projective nuclear magnetic resonance measurement

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It is shown that in nuclear magnetic resonance, multiple-quantum (MQ) coherences can be detected "instantly" by exploiting the principle of quantum-mechanical projective measurement. Therefore, the mixing period, which involves collective multispin dynamics and converts MQ coherences into observable single-quantum coherence (magnetization), is not necessary. The experimental examples are given for two finite clusters: benzene in liquid crystal and liquid crystal 4′-*n*-pentyl-4-cyanobiphenyl, and for solid adamantane with an infinite network of dipolar couplings. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2357949]

I. INTRODUCTION

Multiple-quantum (MQ) spectroscopy[1] is an established area of nuclear magnetic resonance (NMR). A conventional MQ experiment can be divided into the following steps. (1) The preparation period, wherein the initial Zeeman order of a spin system is converted, by collective multispin dynamics, into MQ coherences. (2) The evolution period, wherein the MQ coherences evolve under the system's Hamiltonian, or some effective Hamiltonian. This step is necessary for acquiring MQ spectra. (3) The mixing period, during which the MQ coherences are converted back to magnetization. Conveniently, this can be accomplished by time reversing the preparation period, using the effective Hamiltonian of the opposite sign.[2–5] And finally, (4) the detection period, wherein the total magnetization of the sample is measured.

MQ coherences can be defined as the corresponding parts of the density matrix. The system's density matrix ρ can be expanded as a sum of terms of different symmetries with respect to rotations around the quantization axis z,

$$\rho = \sum_n \rho_n, \quad \exp(i\varphi S_Z)\rho_n \exp(-i\varphi S_Z) = \exp(in\varphi)\rho_n, \quad (1)$$

where S_Z is the projection of the total spin on the z axis. The term ρ_n is called the n-quantum (nQ) coherence and n is the order of the coherence. nQ coherence requires correlations between at least n spins $\frac{1}{2}$. The intensity of the nQ coherence can be calculated as $I_n = \mathrm{Tr}(\rho_n \rho_{-n})$. Coherences of different orders n have different n-fold symmetries with respect to z rotations. This property is used to separate them experimentally by creating relative phase shifts between the preparation and mixing periods.

Since NMR spectrometers allow measuring only the total magnetization of the spin system, it is commonly assumed that MQ coherences are not directly observable. In other words, average magnetization (polarization) does not contain information about correlations between spins. At the same time, probabilities of possible outcomes of projective quantum measurement[6] contain more information about the state of the system and strongly depend on correlations between spins. We will show below how the idea of projective quantum measurement can be used in NMR for detecting MQ coherences.

II. PROJECTIVE MEASUREMENT

Let us choose the x and y axes of the rotating frame so that the observable transverse magnetization is proportional to $\langle S_X \rangle$, the quantum-mechanical average of the x component of the total spin. Suppose that it is possible to obtain different outcomes m (magnetic quantum numbers) of measuring S_X and probabilities p_m of such outcomes. Then, it is possible to calculate not only $\langle S_X \rangle$ but also the average values of all powers of S_X,

$$\langle S_X^k \rangle = \sum_m p_m m^k. \quad (2)$$

Alternatively, if all values $\langle S_X^k \rangle$ are known, it is possible to reconstruct all probabilities p_m of the outcomes of projective measurement. Therefore, the ensemble average values $\langle S_X^k \rangle = \mathrm{Tr}(\rho S_X^k)$ for all k's provide information about all probabilities of the S_X measurement outcomes for an individual quantum system.

Similar to the density matrix in Eq. (1), one can expand the operator S_X^k as a sum of terms of different symmetries with respect to rotations about the z axis,

$$S_X^k = \sum_{n=-k}^{k} S_{X,n}^k, \quad \exp(i\varphi S_Z)S_{X,n}^k \exp(-i\varphi S_Z)$$
$$= \exp(in\varphi)S_{X,n}^k, \quad (3)$$

where the possible orders n are now limited by k. The ensemble average of S_X^k can be written as

$$\langle S_X^k \rangle = \mathrm{Tr}(\rho S_X^k) = \sum_{n=-k}^{k} \mathrm{Tr}(\rho_n S_{X,-n}^k), \quad (4)$$

where we used the fact that $\mathrm{Tr}(\rho_n S_{X,l}^k)$ is not zero only for $l = -n$.

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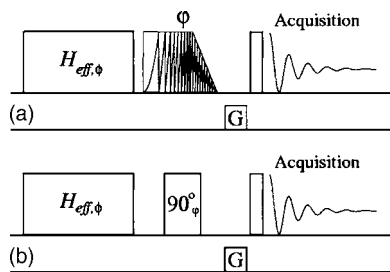
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FIG. 1. Pulse sequences for detecting MQ coherences by using (a) adiabatic frequency-sweeping lock pulse and (b) 90° hard pulse. MQ coherences can be excited by some effective Hamiltonian H_{eff}, created with an appropriate pulse sequence, and a specific coherence order can be filtered by phase cycling ϕ. Relative z rotation of the multiple-quantum coherence by an angle φ is implemented by shifting the phases of the lock or 90° pulses.

Suppose that the density matrix contains only the nQ coherence,

$$\rho = 1/\text{Tr}(1) + \rho_n + \rho_{-n}. \tag{5}$$

Then, the average value (4) becomes

$$\langle S_X^k \rangle = \text{Tr}(S_X^k)/\text{Tr}(1) + \text{Tr}(\rho_n S_{X,-n}^k) + \text{Tr}(\rho_{-n} S_{X,n}^k). \tag{6}$$

When the measurement axis is not the x axis of the rotating frame, but some arbitrary direction in the xy plane obtained by rotating the x axis by the angle φ around the z axis, the operator S_X transforms into

$$S_X(\varphi) = \exp(i\varphi S_Z)S_X \exp(-i\varphi S_Z) = S_X \cos\varphi - S_Y \sin\varphi. \tag{7}$$

In the same way, S_X^k becomes $S_X^k(\varphi)=\{S_X(\varphi)\}^k = \exp(i\varphi S_Z)S_X^k \exp(-i\varphi S_Z)$. By using Eqs. (6) and (3), one can now calculate the average values of powers of the transverse magnetization measured along the new axis,

$$\langle S_X^k(\varphi) \rangle = \text{Tr}(S_X^k)/\text{Tr}(1) + \{\text{Tr}(\rho_n S_{X,-n}^k)\exp(-in\varphi)$$
$$+ \text{Tr}(\rho_{-n}S_{X,n}^k)\exp(in\varphi)\} = \text{Tr}(S_X^k)/\text{Tr}(1)$$
$$+ 2\,\text{Tr}(\rho_n S_{X,-n}^k)\cos(n\varphi). \tag{8}$$

For $k < n$, the dependence on φ in Eq. (8) disappears since the trace in front of $\cos(n\varphi)$ is zero [see Eq. (4)]. At the same time, when $k=n$, $\langle S_X^n(\varphi) \rangle$ completely determines both the amplitude and the phase of the nQ coherence. According to Eq. (2), oscillation of $\langle S_X^n(\varphi) \rangle$, as a function of φ, means that the probabilities p_m of obtaining the magnetic quantum number m for the $S_X(\varphi)$ measurement are also periodic functions of φ with the period $2\pi/n$.

Projective NMR measurement of S_X can be done by one of the two methods.[7] The first one [Fig. 1(a)] involves applicaiton of a strong field along the x axis of the rotating frame and then adiabatically changing its direction until it coincides with the z axis. This adiabatic lock pulse preserves the magnetic quantum numbers m and, therefore, the probabilities p_m will be transferred to the operator S_Z, which has a common set of eigenfunctions with the system's Hamiltonian. Each of the probabilities p_m is a sum of all populations of the states with corresponding magnetic number m. The populations of individual states can be extracted from the NMR linear-response spectrum.[7] The second method

[Fig. 1(b)] involves using a "hard" $\pi/2$ pulse which converts S_X into S_Z and S_X^k into S_Z^k. Although the resulting populations of individual states in these two methods and, therefore, NMR spectra are different,[7] they give the same values of $\langle S_Z^k \rangle$ and p_m.

When the measurement axis is rotated by the angle φ, according to Eq. (8), $\langle S_Z^n \rangle$ oscillates with the period $2\pi/n$. This means that p_m and the populations of individual states also oscillate with φ. Since the sum of all populations is constant (1), the oscillation of individual populations also suggests that the differences of populations and, therefore, intensities of peaks in the linear-response spectrum oscillate with the period $2\pi/n$. It is interesting that $\langle S_Z^k \rangle$ for $k < n$ does not depend on φ despite the oscillatory behavior of the populations of individual states.

III. EXPERIMENTAL EXAMPLES

The experiments have been performed at 25 °C using Varian Unity/Inova 500 MHz NMR spectrometer. The physical systems were (1) the cluster of six dipolar-coupled proton spins of benzene in the liquid crystal ZLI-1167, (2) 19 dipolar-coupled proton spins of the liquid crystal $4'$-n-pentyl-4-cyanobiphenyl (5CB), and (3) the proton spins of powdered solid adamantane. Figure 1 shows the NMR pulse sequences, which consist of the preparation periods, when MQ coherences are excited with an effective Hamiltonian H_{eff} and filtered by a phase cycling,[8] a frequency-sweeping lock pulse [Fig. 1(a)] or a 90° hard pulse [Fig. 1(b)] followed by a gradient pulse, and signal detection after a small-angle reading pulse. The gradient pulse is needed in the experiment in Fig. 1(b) to dephase the off-diagonal part of the density matrix. In the experiment in Fig. 1(a) the dephasing occurs naturally during the long adiabatic evolution, and the gradient pulse plays only a cosmetic role to reduce some experimental imperfections. In heteronuclear systems, it is possible to replace the gradients by temporarily turning off the heteronuclear decoupling. In the preparation period, MQ coherences have been excited by an eight-pulse sequence,[5] which creates a double-quantum effective Hamiltonian. Only even-order MQ coherences are excited when the initial state is the thermal equilibrium.

For the benzene molecule, the preparation periods for exciting 2Q, 4Q, and 6Q coherences were, respectively, 552, 2976, and 2472 μs long. For 5CB, the excitation times were 138 μs for 2Q and 297.6 μs for 4Q coherences. For adamantane, the excitation duration was 96 μs for both 2Q and 4Q coherences.

A. Benzene

Figure 2 shows the experimental results for the 2Q [Figs. 2(a) and 2(a′)], 4Q [Figs. 2(b) and 2(b′)], and 6Q [Figs. 2(c) and 2(c′)] coherences. As the relative phase shift φ between the multipulse sequence of the preparation period and the lock or 90° pulse is incremented, all the spectra demonstrate the expected oscillation with the period $2\pi/n$ $(n=2,4,6)$. One can notice that the spectra obtained with the lock and 90° pulses are different. Besides that, there is an additional $\pi/2$ shift between the two sets, because the adiabatic pulse
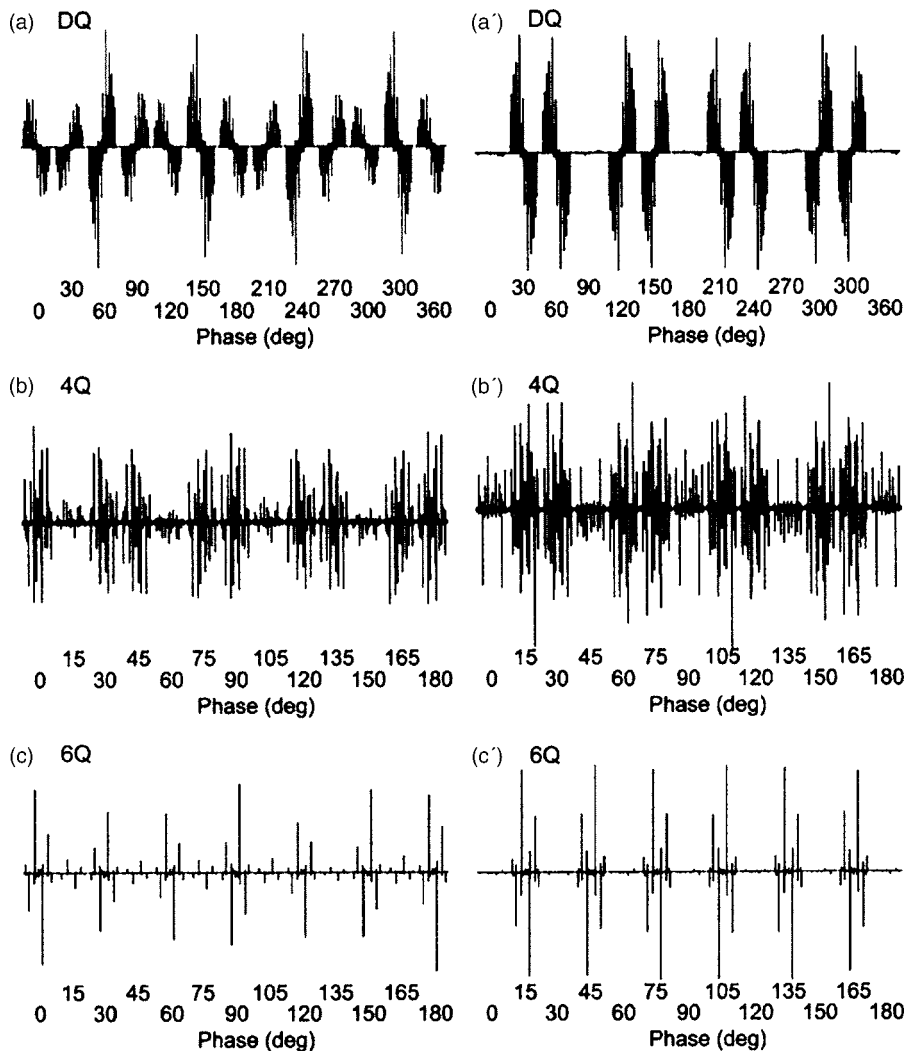
FIG. 2. Experimental results for the proton spin cluster of a benzene molecule in liquid crystal ZLI-1167. With an adiabatic frequency-sweeping pulse, the filtering of (a) the 2Q, (b) 4Q, and (c) 6Q coherences produces the spectra with the expected periods of oscillation when the relative phase between the multipulse sequence of the preparation period and the lock pulse is incremented. The corresponding results when the lock pulse is replaced by 90° hard pulse are shown in (a′), (b′), and (c′).

locks the magnetization in the direction of the applied rf field, while the 90° pulse rotates the magnetization in a plane perpendicular to the rf field. All the spectra in Fig. 2 have zero integral intensity, which is a consequence of zero total magnetization.

We compared the sensitivity of the projective schemes with the conventional "time-reversal" method.[2] When the same small-angle reading pulse (5° in our experiments) was used in both methods, the projective schemes gave higher intensities of the spectral peaks. However, the maximum sensitivity of the projective schemes would be somewhat lower, because it is possible to use the 90° reading pulse in the time-reversal method while the 90° reading pulse produces no NMR signal if used in the projective experiment.

B. 5CB and adamantane

The molecule of liquid crystal 5CB contains 19 proton spins coupled by residual dipole-dipole interaction. It is a large cluster and, in contrast to benzene in liquid crystal, individual peaks are not resolved in the proton NMR spectrum of about 35 kHz width. However, oscillatory behavior of the populations of individual states, as a function of φ, produces clear oscillations of the spectra. Both of the sequences in Fig. 1 work well for 5CB and adamantane. Here

we present only the results obtained with the 90° hard pulse [experiment in Fig. 1(b)]. The results for 5CB are shown in Figs. 3(a) and 3(b).

Solid adamantane has an infinite network of dipole-dipole couplings. Each finite region of its spectrum is contributed to by an infinite number of transitions between individual quantum states. Nevertheless, the spectra in Figs. 3(c) and 3(d) demonstrate clear oscillations with the expected period $2\pi/n$ ($n=2,4$). For practical detection of the MQ coherences, one can use oscillation of the intensity of a single peak if the spectrum is resolved or oscillation of the intensity at some fixed frequency for continuous spectrum.

IV. CONCLUSION

The adiabatic frequency-sweeping lock pulse of the experiment in Fig. 1(a) should be long compared to a characteristic time of spin-spin interactions. Although the magnetic quantum numbers are locked by this pulse "instantly," a considerable time is required to transport these magnetic quantum numbers to the operator S_Z. In contrast to this, the detection scheme in Fig. 1(b) is implemented by a "hard" pulse, which produces single-spin rotations. The time needed for this type of projection can be arbitrarily short and is limited only by the available rf power and gradient strength.
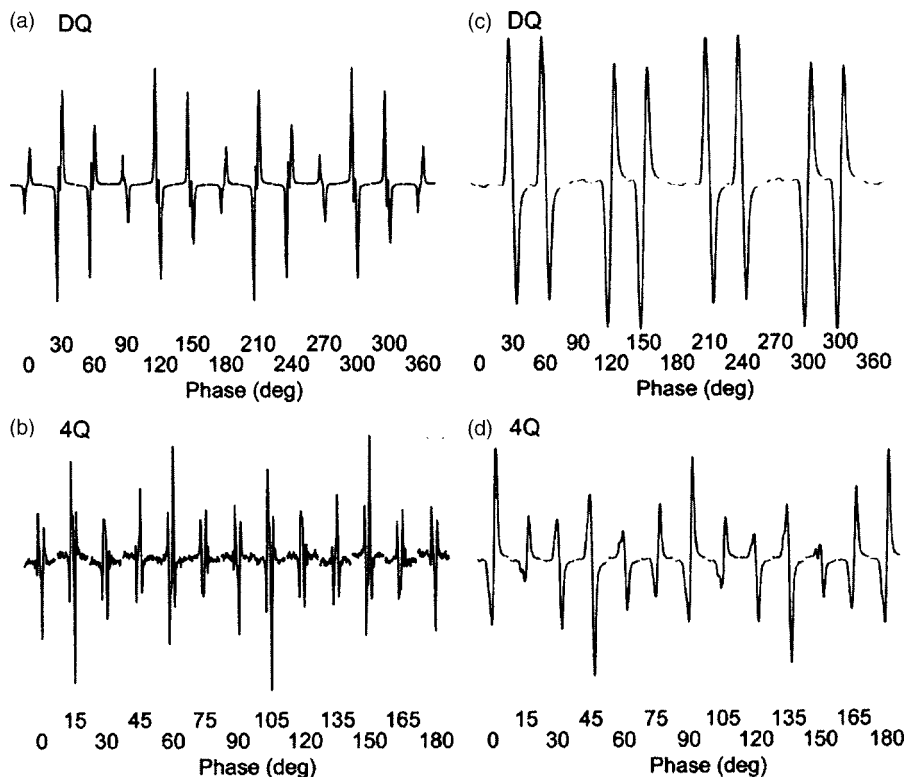
FIG. 3. The results for liquid crystal 5CB [(a) and (b)] and solid adamantane [(c) and (d)] obtained with the experimental scheme in Fig. 1(b).

"Instant" projection does not mean, however, that the detection of MQ coherences can be performed arbitrarily fast. After the projection is done, some time Δt is necessary to discriminate eigenstates with the difference of energies ΔE according to the uncertainty principle: $\Delta E \ \Delta t > \hbar/2$. This would be true for any type of projective measurement. In our NMR experiment, it means that the acquisition time, used to record the resulting spectrum, should be long enough to distinguish spectral regions, which oscillate with different phases.

Similar to conventional schemes of detecting MQ coherences, our direct detection also requires spin-spin interactions. In the absence of such interactions, the energy levels are highly degenerate. As a result, positive and negative differences of populations are added together at the same transition frequency, and the projective detection scheme would produce no NMR signal.

In conclusion, a NMR scheme for the direct and instant detection of MQ coherences has been described. It is based on the idea of projective quantum measurement and makes it possible to eliminate the mixing period, which involves collective multispin dynamics and converts MQ coherences into an observable single-quantum coherence.

ACKNOWLEDGMENTS

[1] R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Clarendon, Oxford, 1987).
[2] W. S. Warren, S. Sinton, D. P. Weitekamp, and A. Pines, Phys. Rev. Lett. **43**, 1791 (1979).
[3] W. S. Warren and A. Pines, J. Chem. Phys. **74**, 2808 (1981).
[4] Y. Yen and A. Pines, J. Chem. Phys. **78**, 3579 (1983).
[5] J. Baum, M. Munowitz, A. N. Garroway, and A. Pines, J. Chem. Phys. **83**, 2015 (1985).
[6] J. J. Sakurai, *Modern Quantum Mechanics* (Addison-Wesley, New York, 1994).
[7] J.-S. Lee and A. K. Khitrin, Appl. Phys. Lett. **89**, 074105 (2006).
[8] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1996).