

Multiple-quantum NMR in solids

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Multiple-quantum NMR has typically been observed in small groups of spins in isolated molecules. Due to the profusion of spin transitions in a solid, individual lines are unresolved. Excitation of high quantum transitions by normal schemes is thus difficult. To ensure that overlapping lines add constructively and to enhance sensitivity, time-reversal pulse sequences are used to generate all lines in phase. Up to 22-quantum ^1H absorption in solid adamantane is observed.

I. INTRODUCTION

Multiple-quantum (MQ) NMR spectroscopy has generally been applied to systems of isolated molecules with a small number of spins.^{1,2} The small system size limits the complexity of the spectrum as well as the number of rf quanta that can be absorbed or emitted. One difficulty in studying large spin systems is that the average intensity per transition decreases rapidly with the number of spins. As a result, selective excitation schemes³ may be necessary to channel intensity into the desired n -quantum order. Thus, comparatively few applications have been performed in solids,^{4,5} where extensive dipolar coupling makes the coupled spin system essentially infinite in size.

In this article, we present the utilization of time reversal^{3,6} to enhance overall signal intensity so that very high quantum absorption can be observed in solids. In Fig. 1, we show a ^1H MQ spectrum of solid adamantane $\text{C}_{10}\text{H}_{16}$ obtained by such a time-reversal excitation-detection scheme, where up to 22-quantum absorption is observed. Adamantane is a plastic crystal; the molecule is nearly spherical and as such can tumble isotropically in the solid phase. At room temperature, this motion averages to zero all intramolecular couplings but retains the intermolecular terms. Our system is thus not an isolated molecule but rather a network of molecules. Very high quantum transitions might therefore be excited.

One of the main features of solids is the high density of spin states. Due to the continuum of transitions, individual lines within each n -quantum order are unresolved. Since both the intensity and phase of individual MQ coherences depend uniquely on the excitation time, there may occur destructive interference between overlapping lines. The integrated intensity of the MQ spectrum is decreased and the signal-to-noise ratio suffers. This problem becomes more severe as the excitation time is increased, as is observed experimentally. Very quickly, typically within 10^{-4} s, the signal-to-noise ratio is dominated by instrumental noise. It eventually becomes very difficult to observe high quantum absorption, where long excitation times are required.

What is desired then is the generation of all lines in phase at the point of detection, i. e., in some manner to reverse the dephasing that occurred in the excitation period. In solids, the dominant dephasing mechanism

is the dipole-dipole interaction, which is homogeneous in nature. If one is able to produce a homogeneous spin echo,⁶ the peak of the echo is free of the dipolar Hamiltonian. This in fact can be accomplished by applying a series of intense rf pulses to the spin system to effect what is in essence time reversal. With the method of time reversal, we were able to regain the intensity lost due to fast homogeneous dephasing of spins in solids.

II. THEORY

For the following discussions, it is convenient to introduce the time-domain MQ NMR experiment, described schematically in Fig. 2(a). The sequence can be partitioned into four time domains⁷: preparation (τ), evolution (t_1), mixing (τ'), and detection (t_2) periods. As a specific example, consider the simple three-pulse sequence in Fig. 2(b). The first two pulses separated by an excitation delay τ prepare MQ coherences, which then evolve freely for a time t_1 . Because MQ coherences do not correspond to magnetization, they are not directly observable with our detection coil. A third pulse is needed to convert them into single-quantum coherences, which are detected in time t_2 . For our experiments, only the point at $t_2 = \tau$ is sampled.⁸ The sequence is repeated for many values of t_1 until one maps out an interferogram. Fourier transformation with respect to

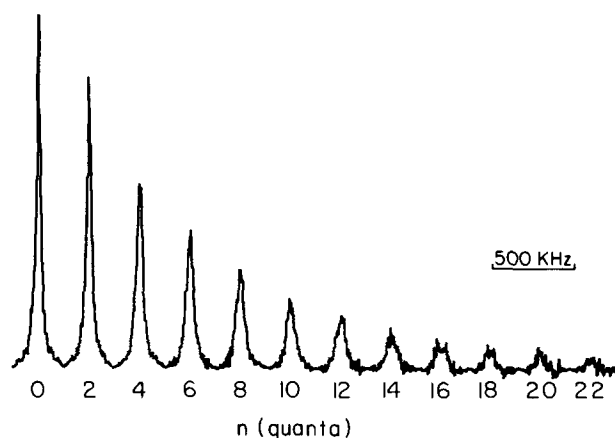


FIG. 1. ^1H multiple-quantum NMR spectrum of solid adamantane at room temperature, obtained with time-reversal sequence of Fig. 2(d) and excitation time of 480 μs .

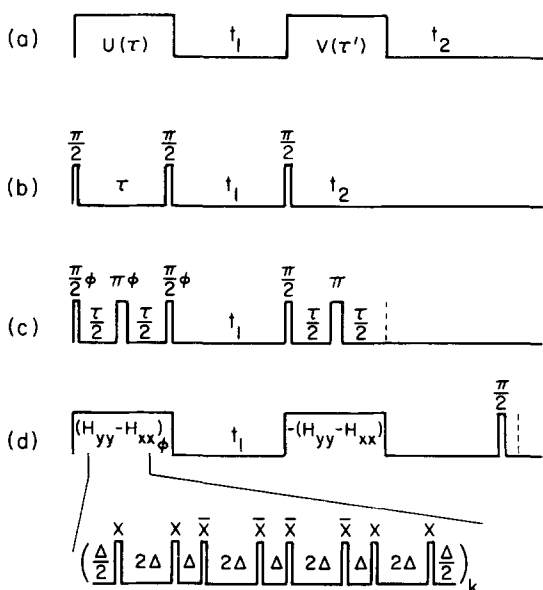


FIG. 2. Multiple-quantum pulse sequences: (a) Schematic pulse sequence showing relevant periods. (b) Nonselective three-pulse experiment. (c) Even-selective sequence with preparation pulses phase shifted by an amount $\phi = \Delta\omega t_1$ (TPPI) to separate n -quantum orders. (d) Time-reversed preparation and mixing periods with the preparation $\pi/2$ pulses phase shifted by an amount ϕ (TPPI). The preparation and mixing periods are composed of cycles of the eight-pulse $(H_{xx}-H_{yy})$ sequence shown below. A delay of 1.6 ms separates the mixing period from the final detecting pulse to allow transients to decay away. 30 μ s is allowed for receiver deadtime before sampling is taken at the dotted line.

t_1 of this interferogram yields the MQ spectrum.

The equation of motion of a coupled spin system is conveniently described in the density matrix formalism. In this formalism, neglecting relaxation, the signal in the time domain is given by the trace of the product of the observable and the reduced density matrix:

$$\begin{aligned} S(\tau, t_1, \tau') &= \text{Tr}\{I_x \rho(\tau, t_1, \tau')\} \\ &= \text{Tr}\{VI_x V^\dagger \exp(-iH_1 t_1) U^\dagger I_x U \exp(iH_1 t_1)\} \\ &= \text{Tr}\{Q(\tau') \exp(-iH_1 t_1) P(\tau) \exp(iH_1 t_1)\} \\ &= \sum_{j,k} P_{jk}(\tau) Q_{kj}(\tau') \exp(-i\omega_{jk} t_1). \end{aligned} \quad (1)$$

Here $U = \exp(iH\tau)$ is the preparation propagator, $V = \exp(iH'\tau')$ is the mixing propagator, $P = U^\dagger I_x U$ is the preparation density operator, $Q = VI_x V^\dagger$ is the mixing density operator, $|j\rangle$'s are eigenstates of the Hamiltonian H_1 , and $\omega_{jk} = \omega_j - \omega_k$ is the transition frequency. In the above equation, the invariance of the trace to cyclic permutation is used. The spin system is assumed to be initially at equilibrium. For notational convenience, a virtual $\pi/2$ pulse is applied at end of τ' so that I_x rather than $I_x + iI_y$ is our observable.

To see how phase terms can arise in a MQ NMR experiment, let us consider the situation $V = U$, which is the case for the commonly used pulse sequences in Figs. 2(b) and 2(c). The transition between states $|j\rangle$ and $|k\rangle$ is then described by a complex vector $(P_{jk})^2$,

where the intensity is given by $|P_{jk}|^2$ and the phase is a complicated function of the preparation period

$$\theta_{jk}(\tau) = \tan^{-1} \left\{ \frac{\text{Im}[P_{jk}^2(\tau)]}{\text{Re}[P_{jk}^2(\tau)]} \right\}. \quad (2)$$

The preparation density operator P and hence the phase of a transition vary with the excitation time τ .⁹

If we now look at the case $V = U^\dagger$, then $Q = P = P^\dagger$, and the signal can be written as an autocorrelation function of the preparation density operator $P(\tau)$

$$\begin{aligned} S(\tau, t_1) &= \text{Tr}\{P^\dagger(\tau) \exp(-iH_1 t_1) P(\tau) \exp(iH_1 t_1)\} \\ &= \sum_{j,k} |P_{jk}(\tau)|^2 \exp(-i\omega_{jk} t_1). \end{aligned} \quad (3)$$

Note that here the signal contains no phase factor for all lines. Suppose further that V differs from U^\dagger only in phase by an amount χ , i. e.,

$$V = \exp(-i\chi I_x) U^\dagger \exp(i\chi I_x). \quad (4)$$

Then $Q = \exp(-i\chi I_x) P \exp(i\chi I_x)$, and the signal is given by

$$S(\tau, t_1) = \sum_n \sum_{j,k} |P_{jk}|^2 \exp(i n \chi) \exp(-i\omega_{jk} t_1). \quad (5)$$

This states that all lines within order $n = m_j - m_k$, where the m_j 's are Zeeman magnetic quantum numbers, have the same phase, and lines between neighboring orders differ in phase by $\pm\chi$. Thus, if orders are well separated, the condition in Eq. (4) is sufficient to ensure no phase cancellation. In practice, Hermitian conjugation of U or V is achieved by negating the Hamiltonian, which has the same effect as reversing time, hence the term time reversal.

III. EXPERIMENTAL

The actual pulse sequence used to generate the time-reversed spectra is shown in Fig. 2(d). The eight-pulse cycle preparation sequence creates an average Hamiltonian¹⁰ $(H_{xx} - H_{yy})$, which is a pure double-quantum operator³ and can excite only even-quantum transitions. The excitation time is increased by adding more cycles. To account for finite rf pulse widths, $2\Delta + t_p$ is used in place of 2Δ , where t_p is the pulse duration. The experiment was performed on resonance, causing all MQ orders to overlap. To create the large artificial offset required for separation of orders, the method of time proportional phase incrementation (TPPI)¹¹ is used. For each incrementation in t_1 , the phase of the preparation pulses is incremented by the amount

$$\Delta\phi = \frac{2\pi}{2M}, \quad (6)$$

where M is the maximum MQ order to be observed.

In principle, detection can be made immediately after the mixing pulses with a final detecting pulse. In practice, however, due to pulse imperfections and relaxation, a delay of 1.6 ms is introduced after the mixing pulses, allowing transients to decay before applying a detecting pulse. These transients should decay on the order of T_2 , the spin-spin relaxation time,¹² which is

typically 10^{-4} s for solids. The desired signal, after mixing, is in the form of populations. It has a decay time on the order of T_1 , the spin-lattice relaxation time,¹² which is on the order of seconds, and should essentially be preserved during the 1.6 ms delay. The final $\pi/2$ pulse rotates it into the transverse plane for detection. The detecting pulse can be of arbitrary phase, as long as it remains fixed from point to point in t_1 . A delay of $30 \mu\text{s}$ is inserted before sampling to allow for receiver deadtime.

IV. RESULTS AND DISCUSSION

To demonstrate the severity of intensity loss due to phase cancellation in the normal nontime-reversal approach to MQ NMR, in Fig. 3 we compare ^1H MQ magnitude spectra of adamantane obtained with and without time reversal, using pulse sequences of Figs. 2(d) and 2(c), respectively. The π pulses in Fig. 2(c) remove all resonance-offset terms, rendering this sequence even selective,¹³ as is the sequence of Fig. 2(d). Both spectra were obtained at 35°C with a preparation time of $144 \mu\text{s}$. Without time reversal, phase cancellation results in a significant reduction of absolute integrated intensity. This difference in intensity becomes more pronounced as the excitation time increases. We emphasize here that without time reversal, we were not able to increase the excitation time long enough to observe high quantum absorption. Comparison of line shapes, in particular second moments, with and without incorporation of time reversal will be discussed elsewhere.¹⁴

An interesting result of these experiments is the initial time dependence of MQ intensities on n , the number of quanta. The short time behavior can be obtained from a power expansion in τ of the preparation density operator¹:

$$\begin{aligned} P(\tau) &= \exp(-iH\tau)P(0)\exp(iH\tau) \\ &= P(0) - i\tau[H, P(0)] - \frac{\tau^2}{2}[H, [H, P(0)]] + \dots \quad (7) \end{aligned}$$

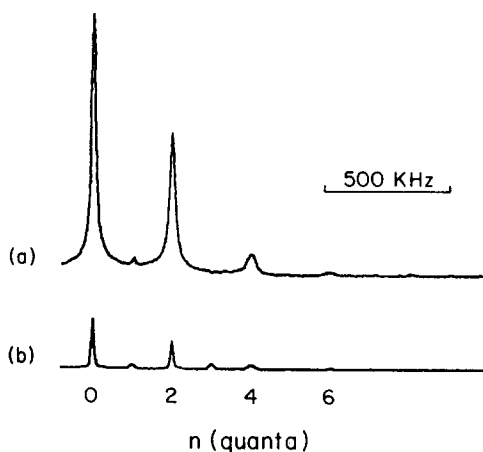


FIG. 3. Comparison of adamantane ^1H multiple-quantum NMR spectra obtained with $144 \mu\text{s}$ excitation time and using (a) time-reversal pulse sequence of Fig. 2(d) with $\Delta = 0.8 \mu\text{s}$ and $t_p = 3.2 \mu\text{s}$, and (b) nontime-reversal pulse sequence of Fig. 2(c).

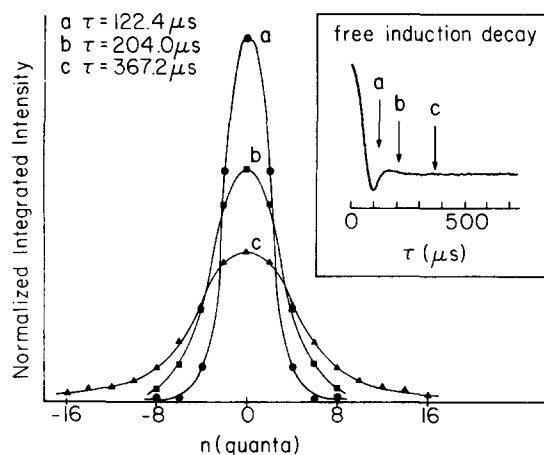


FIG. 4. Normalized integrated intensity of n -quantum order for various excitation times extracted from adamantane time-reversal spectra, showing how the spin correlations diffuse out to higher n . These intensities are normalized so that the total integrated intensity for each excitation time is unity. The corresponding excitation times on the single-quantum free induction decay are indicated in the insert.

For the $(H_{xx} - H_{yy})$ pulse sequence in Fig. 2(d), assuming perfect δ -function pulses, evaluation of the commutators for $P(0) = I_x$ reveals that the integrated intensity of a given order ($n = 0, 4, 6, 8, \dots$) grows in as

$$\sum_{j,k} |P_{jk}|^2 \propto \tau^{n/4}, \quad (8)$$

where the summation runs through all j, k such that $m_j - m_k = n$. The intensity of the double-quantum order grows in as τ^2 . Thus, in the short τ limit, the higher quantum operators appear at a later excitation time than the lower quantum operators. This behavior is illustrated in experimental results for adamantane in Fig. 4. We observe that indeed the coherences "diffuse" outward toward higher n as the excitation time is increased. A physical interpretation for this behavior can be obtained by realizing that MQ coherence is a many-spin correlation phenomenon—at least n spins are interacting concertedly to absorb n photons. The higher the number of quanta, the more spins involved, and hence the longer it takes for correlations to occur. A random walk picture connecting spin diffusion with evolution of multiple spin correlations and MQ coherences is appealing.

In summary, the incorporation of time reversal enables all transition lines to be phased with respect to each other, thereby enhancing the signal-to-noise ratio. Using time-reversal pulse sequences, we were able to obtain very high quantum absorption spectra of solid adamantane. From a time-dependence study, we observed an increase in spin correlations as the excitation time increased.

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