Multiple-quantum NMR in solids
Yu-Sze Yen and A. Pines

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
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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 diffi cult. 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 $^1$H 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 reversal6,7 to enhance overall signal intensity so that very high quantum absorption can be observed in solids. In Fig. 1, we show a $^1$H MQ spectrum of solid adamantane C$_{10}$H$_{18}$ 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 thereby 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,8 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 domains9: preparation ($\tau$), evolution ($t_{1}$), mixing ($\tau'$), 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 $\tau$ 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. The sequence is repeated for many values of $t_{1}$ until one maps out an interferogram. Fourier transformation with respect to

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** $^1$H multiple-quantum NMR spectrum of solid adamantane at room temperature, obtained with time-reversal sequence of Fig. 2(d) and excitation time of 480 $\mu$s.
In the above equation, the invariance of the trace to \( i k \) and \( i k' \) is the case for the commonly used pulse sequences 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 \( \langle j \rangle \) and \( \langle k \rangle \) is then described by a complex vector \( \langle P_{jk} \rangle \),

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

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

The preparation density operator \( P \) and hence the phase of a transition vary with the excitation time \( \tau \).

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

\[
S(\tau, t_j) = \text{Tr} \left\{ P(\tau) \exp(-i H_{t_f} t_f) P(\tau) \exp(i H_{t_i} t_i) \right\} = \sum_{i,k} |P_{jk}|^2 \exp(-i \omega_{jk} t_i) .
\]

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

\[
V = \exp(-i \chi I_{m}) U^T \exp(i \chi I_{m}) .
\]

Then \( Q = \exp(-i \chi I_{m}) P \exp(i \chi I_{m}) \), and the signal is given by

\[
S(\tau, t_j) = \sum_{\chi} \sum_{i,k} |P_{jk}|^2 \exp(i \chi) \exp(-i \omega_{jk} t_i) .
\]

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-cycle preparation sequence creates an average density matrix \( \langle P(\tau) \rangle \) which is a pure double-quantum operator \( D \) and can excite only even-quantum orders. The excitation time is increased by adding more cycles. To account for finite rf pulse widths, \( 2\Delta + t_\phi \) is used in place of \( 2\Delta \), where \( t_\phi \) 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 \( t_\phi \), the phase of the preparation pulses is incremented by the amount

\[
\Delta \phi = \frac{2\pi}{M} t_\phi
\]

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

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typically $10^{-4}$ s for solids. The desired signal, after mixing, is in the form of populations. It has a decay time of order of $T_1$, the spin-lattice relaxation time, 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 $\mu$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 $^1$H MQ magnitude spectra of adamantane obtained with and without time reversal, using pulse sequences of Figs. 2(d) and 2(c), respectively. The $\pi$ pulses in Fig. 2(c) remove all resonance-offset terms, rendering this sequence even selective, as is the sequence of Fig. 2(d). Both spectra were obtained at 35 $^\circ$C with a preparation time of 144 $\mu$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 144 quanta. The short time behavior can be obtained from a power expansion in time dependence of MQ intensities on $n$, the number of quanta. The intensity of the double-quantum order grows in as $\tau^2$. Thus, in the short $\tau$ 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 concertedely 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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9With one exception: when $\tau = \tau'$, transitions between spin inversion states produce lines in phase, as described in detail in Ref. 8.