Spin counting experiments in the dipolar-ordered state
H. Cho, D. G. Cory, and C. Ramanathan

Citation: The Journal of Chemical Physics 118, 3686 (2003); doi: 10.1063/1.1538244
View online: http://dx.doi.org/10.1063/1.1538244
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/118/8?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
 Conversion of parahydrogen induced longitudinal two-spin order to evenly distributed single spin polarisation by optimal control pulse sequences

 On the role of collective and local molecular fluctuations in the relaxation of proton intrapair dipolar order in nematic 5CB

 Nuclear magnetic resonance scattering across interfaces via the dipolar demagnetizing field

 Residual dipolar couplings between quadrupolar nuclei in solid state nuclear magnetic resonance at arbitrary fields

 Nuclear magnetic resonance proton dipolar order relaxation in the selectively deuterated nematic para-azoxyanizole
J. Chem. Phys. 110, 8155 (1999); 10.1063/1.478718
Spin counting experiments in the dipolar-ordered state

H. Cho, D. G. Cory, and C. Ramanathan
Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 21 October 2002; accepted 25 November 2002)

The dipolar-ordered state (\(p \propto H_i \)) can be prepared from a state of Zeeman equilibrium at high field by adiabatically removing the Zeeman field. It is also possible to produce dipolar-ordered states in the rotating frame using two well-known methods—adiabatic demagnetization in the rotating frame and the Jeener–Broekaert (JB) pulse pair. Using multiple quantum nuclear magnetic resonance techniques, we illustrate the transient dynamics of the spin system following the JB pulse pair and its evolution to a dipolar-ordered state over a period of approximately 60 \(\mu\)s in a single crystal of CaF\(_2\) oriented along the [100] direction, and approximately 100 \(\mu\)s when the crystal is oriented along the [110] direction. By encoding the coherence numbers in an orthogonal basis (the \(x\) basis) to the Zeeman basis, we show that the dipolar-ordered state is a two spin correlated state. The observed ratio between double quantum and zero quantum coherences in the \(x\) basis confirms the presence of the \(I_+ I_- + I_+ I_-\) (flip–flop) terms in the experimentally prepared dipolar-ordered state.

I. INTRODUCTION

Multiple quantum (MQ) nuclear magnetic resonance (NMR) techniques in solids have generally been used to study the size and dimensionality of localized spin clusters as well as to probe the many-body dynamics of a solid state spin system.\(^1\)–\(^13\) However, these techniques cannot be used to study spin dynamics under a Hamiltonian that conserves coherence number. For example, during an FID the system evolves under the secular dipolar Hamiltonian, and the zero basis coherence number of the spins remains \(\pm 1\), but the number of correlated spins changes. However, Tomaselli et al.,\(^14\) using an extension of the earlier work by Suter and Pearson,\(^15\) recently encoded multiple quantum coherences in a \(y\) basis to characterize the evolution of multi-spin order in polarization and coherence echoes.

Another situation where standard MQ techniques are of limited utility is in the study of the dipolar-ordered state, as this state is not encoded by usual MQ techniques. Dipolar ordered states are eigenstates of the spin Hamiltonian, and hence are constants of the motion. They decay on a time scale \(T_{1D}\), as the spin system interacts with the external environment or lattice. Dipolar ordered states (in the rotating frame) can be prepared by performing an adiabatic demagnetization in the rotating frame (ADR\(^F\))\(^16,17\)), or using a pair of phase shifted RF pulses.\(^18\) While the system is in the dipolar-ordered state at the end of the ADRF process (by definition), following a Jeener–Broekaert pulse pair the spin system is in a transient state, and only evolves into a state of dipolar-order on a timescale of the order of \(T_2\).\(^18\) Emid et al. have shown that the spin system contains multiple quantum coherences immediately following the second pulse.\(^19,20\)

In this paper we use an improved version of the technique originally suggested by Suter and Pearson\(^15\) to investigate the nature of the state prepared using these two methods, as well as explore the transient response of the spin system following a Jeener–Broekaert pulse pair and its evolution to a dipolar-ordered state. We measure the coherence numbers of the dipolar-ordered state in both the \(x\) and \(z\) basis, performed by observing the response of the system to a collective rotation of the spins about the appropriate axis,\(^21\) and use this information to characterize the state.

II. THEORY

In a strong magnetic field (\(B_0 z\)), an \(N\) spin-1/2 system has \(2^N\) stationary states. These can be classified according to the magnetic quantum number, \(M_z = \sum m_{zi} = (n_{[1/2]} - n_{[-1/2]})/2\), where \(m_{zi} = \pm 1/2\) is the eigenvalue of the \(i\)th spin in the system, and the energy eigenvalue corresponding to \(M_z\) is \(E_z = -\gamma h B_o M_z\). For nondegenerate stationary states there are \(2^{2N-1}\) possible transitions between any two levels. The difference in \(M_z\) values between the coupled levels is referred to as the coherence number.

While these coherences refer to transitions between levels, it is useful to discuss multiple quantum coherences for states of a system. When the state is expressed in the eigenbasis of the system, the presence of a nonzero matrix element \(\langle z'|\rho|z\rangle\), indicates the presence of an \(n\) quantum coherence, where \(n = M_z(z_j) - M_z(z_i)\). Since \(M_z = \sum m_{zi}\) is a good quantum number, we use a collective rotation about the axis of quantization, \(\Sigma I_z\), to characterize it

\[
\langle z_i| \exp \left(-i \sum I_z \phi \right) \rho \exp \left(i \sum I_z \phi \right) | z_j \rangle = \exp (i n \phi) \langle z_i|\rho|z_j\rangle.
\]

(1)

In the dipolar-ordered state the density operator of the spin system corresponds to the dipolar Hamiltonian. In the high temperature approximation,

\[
\rho_D = \frac{\exp (-H_D^0/kT_s)}{Z} \approx \frac{1}{Z} \left( 1 - \frac{H_D^0}{kT_s} \right),
\]

(2)

\[Z = \text{Tr} \{ \exp (-H_D^0/kT_s) \}.
\]
TABLE I. Coherence numbers and selection rules of the secular dipolar Hamiltonian in the \( z \) and \( x \) bases.

<table>
<thead>
<tr>
<th>Dipolar Hamiltonian</th>
<th>( z ) basis</th>
<th>( x ) basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Sigma_{i&lt;j} d_{ij} (2I_i I_j - \frac{1}{2} (I_z^+ I_z^- + I_z^- I_z^+) )</td>
<td>( -\frac{2}{3} \frac{\gamma^2 \hbar^2}{r_{ij}^3} (1 - 3 \cos^2(\theta_{ij})) )</td>
<td>0, ( \pm 2 )</td>
</tr>
<tr>
<td>Coherence number selection rule</td>
<td>0</td>
<td>0, ( \pm 2 )</td>
</tr>
</tbody>
</table>

where

\[
H_D^0 = \sum_{i<j} d_{ij} \left\{ \frac{2}{3} I_i^+ I_j^- - \frac{1}{2} (I_z^+ I_z^- + I_z^- I_z^+) \right\},
\]

\[
d_{ij} = \frac{\gamma^2 \hbar^2}{r_{ij}^3} \left( 1 - 3 \cos^2(\theta_{ij}) \right).
\]

\( H_D^0 \) is the secular dipolar Hamiltonian, \( T_s \) is the spin temperature, \( \gamma \) is the gyromagnetic ratio, \( r \) is the distance between spins, \( \theta \) is the angle between the \( z \) axis and the internuclear vector. As the dipolar-ordered state only contains population and zero quantum terms in the \( z \) basis, its structure cannot be revealed by \( z \) basis encoding.

While these coherences have a physical meaning in the eigenbasis of the system, a generalized coherence number reports on the response of the system to any collective rotation of the spins (about the \( x \) axis, for example). This is equivalent to a requantization of the spins along the axis of rotation. The transformation between the \( z \) and \( x \) bases can be summarized as follows: \(^{22}\)

\[
I_z = -\frac{i}{2} (I_x^+ - I_x^-), \quad I_z^+ = I_x^+ + \frac{i}{2} (I_x^+ + I_x^-),
\]

\[
I_z^- = I_x^- - \frac{i}{2} (I_x^+ + I_x^-).
\]

Table I shows the secular dipolar Hamiltonian (and correspondingly the dipolar-ordered state) expressed in the two bases. The presence of both zero and double quantum terms in the \( x \) basis representation provides additional observable information about the state of the spin system.

Consider the experiments in Fig. 1, illustrating the \( x \) and \( z \) basis measurements. The propagator \( U_A \) corresponds to the creation of the dipolar-ordered state, while \( U_B \) represents the conversion of the dipolar-ordered state back to single-spin single-quantum terms that are observable. The final density operator in the \( z \) basis experiment is

\[
\rho_f = U_B \exp(iH_d^0 \delta) \exp(-i\phi I_x) \exp(iH_d^0 \delta^*) U_A \rho_0 U_A^\dagger
\]

\[
\times \exp(-iH_d^0 \delta) \exp(-i\phi I_z) \exp(-iH_d^0 \delta^*) U_B^\dagger
\]

while that in the \( x \) basis experiment is

\[
\rho_f = U_B \exp(iH_d^0 \delta) \exp(-i\phi I_x) \exp(iH_d^0 \delta^*) U_A \rho_0 U_A^\dagger
\]

\[
\times \exp(-iH_d^0 \delta) \exp(-i\phi I_z) \exp(-iH_d^0 \delta^*) U_B^\dagger
\]

The operator \( A \) corresponds to the application of a Jeener-Broekaert pulse pair, or an ADRF sequence. The operator \( B \) corresponds to an adiabatic remagnetization in the rotating frame (ARRF) or a 45° pulse to convert the dipolar-ordered state into observable magnetization. Fourier transforming the two-dimensional time domain data with respect to \( \phi \) yields the coherence number in the appropriate basis.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The pulse sequences used in the various experiments are shown in Figs. 2(a)–2(c). The experiments were performed at 2.35 T, using a Bruker Avance spectrometer and a home-built probe. The sample used was a single crystal of calcium fluoride, CaF\(_2\), with \( T_1 \approx 7 \) s.

In the coherence encoding experiment, the phases (\( \phi \)) were incremented from zero to 4\( \pi \) with \( \Delta \phi = \pi/8 \) to encode up to eight quantum coherences in every experiment. A fixed

\[ U_A = \exp(iAt), \quad \phi I_x \quad \text{or} \quad \phi I_z, \quad \delta \]

\[ U_B = \exp(iBt) \]

FIG. 2. Pulse sequences for \( x \) and \( z \) basis encoding of the dipolar-ordered state. (a) JB creation and 45° pulse readout for simultaneous \( z \) and \( x \) basis encoding. (b) ADRF creation and ARRF readout for \( z \) basis encoding. (c) JB creation and ADRF readout for \( x \) basis encoding. The 48 pulse sequence was used to suppress the evolution of the internal Hamiltonian between the two \( \pi/2 \) pulses (Ref. 23). We assume that relaxation effects are negligible during the sequence.
time point, corresponding to a maximum intensity signal in the echo, was sampled for each value of $\phi$ and the data Fourier transformed with respect to $\phi$ to yield the coherence numbers.

### A. Estimation of the dipolar-ordered state

In order to estimate the state of the system, the two dimensional coherence encoding experiment shown in Fig. 2(a) was performed. By incrementing the phases $\phi$ and $\eta$ independently, it is possible to simultaneously encode the system in both the $z$ and $x$ bases, and observe correlations between them.\(^{15,21}\) The pulse spacing ($\tau$) in the JB sequence was set to $13 \mu s$, and $t_1$ was set to $1 \text{ ms}$. It is assumed that all transients have decayed away by this time.

The 48 pulse sequence is used to suppress evolution of the internal Hamiltonian (the dipolar interaction) between the 90° pulses in the $x$ basis experiment.\(^{23}\) The propagator of the 48 pulse sequence is the identity operator, if relaxation effects can be neglected over the course of the pulse sequence. It is necessary to separate the two $\pi/2$ pulses in time, in order to avoid phase switching transients. The spacing between the pulses in the sequence was set to $1.5 \mu s$. The delay $\delta$ was set to $20 \mu s$.

Figure 3 shows the coherences observed for the dipolar-ordered state in a 2D experiment where the coherences in the two bases are correlated. The dipolar-ordered state was refocused.

Given the axial symmetry of the secular dipolar Hamiltonian, a generic two spin zero quantum state is

$$\rho = \sum_{i<j} \{a_i^+ b_i^- + b_i^+ a_i^- \}.$$  

Transforming this state to the $x$ basis yields

$$\rho = \sum_{i<j} \left\{ \frac{1}{4} (-a + 2b)(I_x^i I_x^j + I_x^i I_x^j) + 2b I_x^i I_x^j \right\}.$$  

We expect the $\pm 2$ and $\mp 2$ coherences to have the same intensity, and the ratio of the double quantum coherence to the zero quantum coherence to be

$$R = -\frac{a + 2b}{6b + 2a}.$$  

We performed one dimensional $x$ basis encoding experiments in order to measure the ratio between the zero and double quantum terms, following the ADRF and JB sequences. The pulse sequences for this experiment are shown in Figs. 2(b) and 2(c). Adiabatic remagnetization in the rotating frame (ARRF) was used to refocus the state in both cases these experiments, in order to ensure that the full dipolar state was refocused.

The pulse spacing ($\tau$) in the JB sequence was set to $13 \mu s$, and $t_1$ varied from $1 \text{ ms}$ to $5 \text{ s}$. A 3 ms long hyperbolic secant pulse, corresponding to an adiabatic half passage of the amplitude, was used for both the ADRF (decreasing amplitude) and the ARRF (increasing amplitude). A delay of $20 \mu s$ was inserted before the ARRF to minimize transient effects.

Figure 4 shows the experimentally obtained ratio using both the JB and ADRF sequences as a function of $t_1$. As the dipolar-ordered state decays, the intensity of the double and zero quantum orders decays. However, the ratio is maintained at $\sim 1.5$. The errors were estimated from the variance of the noise in a signal free region of the spectrum. The increase in the error with longer evolution time is due to the deteriorating signal-to-noise ratio as the signal decays.
the ratio between the two coherences remains constant at 1.5 in both cases. When this is set equal to \( R \), we get \( a = -4b \), indicating that the state measured is
\[
\rho = \sum_{i<j} a \left\{ I_i^z I_j^z - \frac{1}{4} (I_i^+ I_j^- + I_i^- I_j^+) \right\}
\]
(10)
which is exactly the state shown in Table I.

B. Zeeman contamination in \( T_{1D} \) measurements

\( T_{1D} \) measurements are done exclusively on resonance in order to avoid possible contamination of the data by encoded Zeeman magnetization. However, it can be difficult to find the exact resonance condition in strongly coupled dipolar solids such as single crystal CaF\(_2\), and impossible to be simultaneously on resonance everywhere in a powder. Emid et al. designed an offset-independent method to measure dipolar relaxation times, by summing the results of two experiments using a \( \pi/4 \) and a \(-3 \pi/4\) pulse to convert dipolar order back to Zeeman order. The difference in pulse lengths can be a problem in strongly coupled dipolar systems, as the evolution under a long pulse becomes non-negligible. In the \( x \) basis measurements presented here, the Zeeman term (\( \Sigma / I^z \)) is encoded into single quantum coherence while the dipolar-ordered state is encoded into zero and double quantum coherence. Figure 5 shows the \( x \) basis coherences measured following a JB pulse pair [Fig. 2(c)] when the experiment is performed on and off resonance by 21 kHz.

This clean separation of the two terms allows very accurate \( T_{1D} \) measurement, without any \( T_1 \) contamination. Figure 6 shows the relaxation data for dipolar-ordered states created by the JB and ADRF methods. The measured \( T_{1D} \) was essentially identical for the zero and double quantum \( x \) basis coherences in both sets of experiments (255 \( \pm \) 3.1 ms and 254 \( \pm \) 3.1 ms for the zero and double quantum terms, respectively, in the ADRF experiment, and 254 \( \pm \) 2.9 ms for both the zero and double quantum terms in the JB experiment). The pulse sequences in Figs. 2(b) and 2(c) were used. The 90° pulse was 1.5 \( \mu \)s and a 4 ms hyperbolic secant pulse was used for the ADRF and ARRF (decaying and growing respectively). The error bars shown were obtained from the variance of the noise in a signal free region of the spectrum. The errors in \( T_{1D} \) measurement were observed from a standard propagation of errors, following a linear fit.

tively, in the ADRF experiment, and 254 \( \pm \) 2.9 ms for both the zero and double quantum terms in the JB experiment) as expected, as dipolar relaxation rates should not depend on the method used to prepare the state.

C. Initial transient dynamics for JB sequence

Emid et al.\(^{19,20}\) have previously shown that multiple quantum coherences are contained in the transverse magnetization following the JB sequence. By performing the JB experiment off-resonance they were able to detect the presence of single, double, and triple quantum coherences during the initial transient regime following the \( \pi/4 \) pulse. Using a combination of JB experiments with different phases, they were also able to selectively observe the even and odd coherences in this initial transient regime as well in a sample of l-alanine powder, in which the NH\(_3\) group had been deuterated\(^{25}\). Their experimental data showed the evolution of the transients out to about 60 \( \mu \)s.

We used the pulse sequence shown in Fig. 2(a) to study the transient response of the spin system following a JB pulse pair, and the evolution of the system to a state of dipolar order. Figure 7 shows the transient response of the spin system following a JB sequence, for a single crystal of calcium fluoride oriented along the [110] direction with respect to the external field (the crystal was actually between the [110] and [111] directions). Immediately after the \( \pi/4 \) pulse, the largest intensity is present in the \( z = 0 \) \( x = \pm 2 \) term, but zero, single and double quantum \( z \) basis terms correlated to

FIG. 5. Pulse sequence in Fig. 2(c) was used to encode the \( x \) basis coherences (a) on resonance, and (b) 21 kHz off resonance. \( t_1 \) was set to 5 ms in both experiments.

FIG. 6. Decay of \( x \) basis double and zero quantum signals in the (a) ADRF and (b) JB experiments. The measured decay constant was 255 \( \pm \) 3.1 ms and 254 \( \pm \) 3.1 ms for the zero and double quantum terms, respectively, in the ADRF experiment, and 254 \( \pm \) 2.9 ms for both the zero and double quantum terms in the JB experiment. The errors in both experiments were obtained from the variance of the noise in a signal free region of the spectrum.
zero, single, double, and even a little triple quantum $x$ basis contributions are observed. As the spin system evolves under the secular dipolar Hamiltonian, the coherence distribution appears to expand in the $x$ basis and contract in the $z$ basis. This is expected as the Hamiltonian is zero quantum selective in the $z$ basis, and contains both zero and double quantum selective terms in the $x$ basis. The intensity of the triple quantum grows indicating the presence of three spin terms. The presence of four spin terms have also been observed albeit at low intensity. These coherences then decay and at around 100 $\mu$s, the system appears to have reached a dipolar-ordered state.

Figures 8(a) and 8(b) show the FIDs measured for a single crystal of calcium fluoride at two orientations (a) the $[100]$ direction and (b) the $[110]$ direction. Figures 8(c) and 8(d) show the projection of the measured 2D data onto the $z$ axis for the two orientations, and Figs. 8(e) and 8(f) show the corresponding projection on the $x$ axis. When the crystal is aligned along the $[110]$ direction, the dipolar couplings between the nearest-neighbor fluorine spins becomes small. In the $z$ basis, the double quantum term is seen to decay while the single quantum term initially grows, reaches a maximum around 30 $\mu$s and then decays. The intensity of the zero quantum term remains constant, as expected. In the $x$ basis the single quantum term is seen to peak around 20 $\mu$s and the triple quantum term to peak around 45 $\mu$s, while the zero and double quantum terms are seen to oscillate before settling down to constant values. The dipolar-ordered state appears to be created after approximately 100 $\mu$s. When the crystal is oriented along the $[100]$ direction the transient signal decay much faster as expected, as the dipolar coupling between the nearest neighbor spins is the strongest. The dipolar-ordered state appears to be established within approximately 60 $\mu$s. As the data plotted are absolute values, the curves do not go down to zero, and the limiting values are determined by the noise floor.

**IV. CONCLUSION**

We have been able to illustrate the nature of the dipolar-ordered state by simultaneously encoding the state in the $x$ and $z$ bases. We have also been able to show the dynamical evolution of the spin system to the state of quasi-equilibrium represented by the dipolar-ordered state, following the application of a Jeener–Broekaert pulse pair. Such techniques open up the possibility of experimentally investigating the details of spin dynamics in a strongly dipolar coupled spin system.

**ACKNOWLEDGMENTS**

The authors thank P. Capperallo and G. S. Boutis for helpful discussions and the NSF and DARPA DSO for financial support.

References