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Cross Correlated Effects of Radiation Damping and the Distant Dipolar Field with a Pulsed Field Gradient in Solution NMR

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Abstract : With a simple pulse sequence ($\pi/2$ – {gradient, duration T} – acquisition) in solution NMR, detected signal has slowly grown up to percents of the equilibrium magnetization. The source of this unusual resurrection of dephased magnetization after a crushed gradient is cross-correlated effects of radiation damping and the distant dipolar field, which has been demonstrated by a numerical simulation and theoretical analysis.
Keywords : radiation damping, distant dipolar field, cross-correlation, NMR

INTRODUCTION

Bulk magnetization effects in solution NMR, the dipolar field and radiation damping, produced significant interest in recent year since they grossly violate the conventional theory and create unusual cross-peaks in two-dimensional spectra.[1-6] In the limit where one effect dominates, the theoretical framework that describes these effects has progressed tremendously over the last several years.

Radiation damping, which is the most significant macroscopic effect with gradient-free NMR sequences has been introduced very earlier[7] and studied in many ways.[8-10] It has generally considered a nuisance to be eliminated, especially in biological NMR where the solvent peak is much larger than others. It can distort signals and generate many artifacts in 2D experiments (see Fig. 1); therefore its sup-

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pression was intensively investigated using pulsed field gradients (PFGs). In the other hand, radiation damping may also be used to suppress the water signal in some cases.[11]

The CRAZED pulse sequence (e.g. $\pi/2 - t_1 -$ {gradient, duration T} $- \pi/2 -$ {gradient, duration nT} $- t_2$) may be the most striking example of the dipolar field effects in solution NMR.[4,5,12] In conventional framework, it can be readily shown to give no signal. If, however, at least one component in the sample is highly concentrated, relatively strong signal has been observed in the indirectly detected dimension at multiple of resonance frequencies. These unexpected peaks have also been observed between different molecules (e.g. solvent and solute) and even hetero-nuclear spins.[13,14]

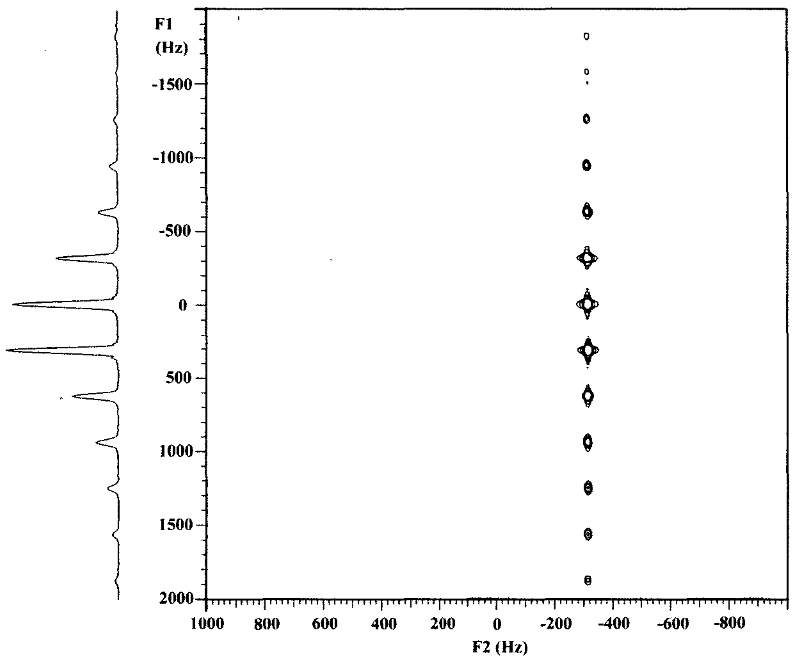

Fig. 1. Radiation damped two-dimensional spectrum of 10 % H_2O (315 Hz) with a COSY pulse sequence on Varian 600 MHz Inova NMR spectrometer at 298 K.

There was no direct correlation between the dipolar field and radiation damping because one of these effects usually dominates the spin dynamics depending on the experiment (or pulse sequence). For example, experiments and numerical studies have shown that radiation damping induced by average magnetization only reduces the signal intensity in the CRAZED type pulse sequences. Recently, however, it has been demonstrated that the joint action of these nonlinear macroscopic dynamics could induce a chaotic spin dynamics resulting in resurrection of crashed magnetization in a simple pulse sequence (an *rf* pulse and a gradient pulse).[15] In this paper, we investigate the coupling mechanism between radiation damping and the distant dipolar field to produce unexpected signals by numerical simulations and theoretically.

EXPERIMENTS and THEORY

Fig. 2 shows unusual profiles of free-induction decay (FID) of water sample with a simple pulse sequence ($\pi/2$ – {gradient, duration T} – acquisition). Immediately after the gradient pulse there is only a small average magnetization due to the imperfection of the gradient (non-linearity, imperfect turn, and etc.). In general, when the *rf*-flip angle is much larger than $\pi/2$, radiation damping induced by transverse magnetization can rotate the unmodulated *z*-magnetization, which is aligned $-z$ direction, into transverse plane. Radiation damping, however, makes signal even weaker if the flip angle is not bigger than $\pi/2$. Therefore the residual magnetization should simply decay with time due to the relaxation and/or radiation damping processes. But, detected signal slowly grows up to percents of the equilibrium magnetization. When the magic angle gradient is applied instead of a *z*-gradient with the same total strength (see Fig. 2 bottom), there is no significant increasing magnetization despite a relative large initial average magnetization due to the non-linearity of the gradient. This implies strongly that the dipolar field is deeply incorporated in the signal growing. In principle, however, the dipolar field has been ignored in that time period since there is no modulated *z*-magnetization. What is the source of this growing magnetization and unusual behaviors? Here we will briefly propose a new dynamics which comes from the cross-correlation between the dipolar field and radiation damping.

The time evolution of uncoupled spins including relaxation processes is described by the Bloch equation:

$$\frac{d\mathbf{M}}{dt} = \gamma\mathbf{M}\times\mathbf{B} - \frac{(M_z\hat{\mathbf{x}} - M_0\hat{\mathbf{y}})}{T_2} - \frac{(M_z - M_0)\hat{\mathbf{z}}}{T_1}. \quad (1)$$

Interactions with other nuclei in the sample through dipole-dipole interaction (dipolar field) and interaction between the magnetization and receiver coil (radiation damping) create additional fields to the applied field. The dipolar demagnetization field or distant dipolar field (DDF), $\mathbf{B}_d(\mathbf{r})$ in the most general case is a complicated function of position that depends on the spin distribution within the whole sample, hence is time dependent as well. If, however, the magnetization is fully modulated and varies only one direction (s), then the DDF can be written in the simple form[16]

$$\mathbf{B}_\mathrm{d}(s) = \mu_0\Delta_s\left[M_z(s)\hat{\mathbf{z}} - \tfrac{1}{3}\mathbf{M}(s)\right] \qquad \Delta_s = \left[3(\hat{\mathbf{s}}\cdot\hat{\mathbf{z}})^2 - 1\right]/2, \quad (2)$$

which depends only in the local value of the magnetization. Warren et al. further noted the importance of omitting the average magnetization,[17] yielding a modified equation as

$$\begin{aligned}\mathbf{B}_\mathrm{d}(s) &= \mu_0\Delta_s\left[(M_z(s) - \langle M_z\rangle)\hat{\mathbf{z}} - \tfrac{1}{3}(\mathbf{M}(s) - \langle\mathbf{M}\rangle)\right] \\ &= \mu_0\Delta_s\begin{bmatrix} -\tfrac{1}{3}(M_z(s) - \langle M_z\rangle)\hat{\mathbf{x}} - \tfrac{1}{3}(M_z(s) - \langle M_z\rangle)\hat{\mathbf{y}} \\ +\tfrac{2}{3}(M_z(s) - \langle M_z\rangle)\hat{\mathbf{z}}\end{bmatrix}.\end{aligned} \quad (3)$$

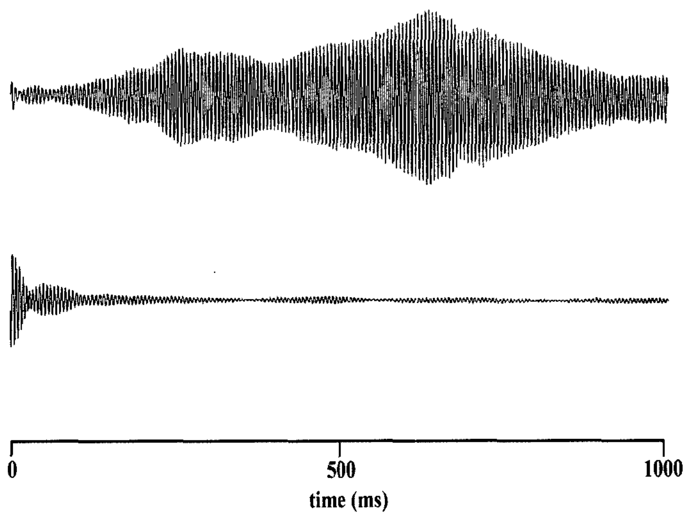

Fig. 2. Experimental [1]H FIDs of 90% H_2O after at 298 K after a 90° pulse and a gradient pulse (top: z-direction, bottom: magic-angle): G = 5 G/cm, T = 1 msec.

Note that $<M_x>$ and $<M_y>$ represent the real and imaginary parts of the signal that we measure. The correlation terms from the average magnetization play a role whenever the signal intensity is important. We will assume that the gradient pulses are applied along the z-axis parallel to the main field (Δ_s =1) which will also imply that the x- and y-spatial derivatives of the magnetization can be ignored in the diffusion terms.

The induced current in the coil by the magnetization creates an additional field $\mathbf{B}_r$, which is known as radiation damping.[7] In the presence of inhomogeneous field such as gradient pulses, the original equation for $\mathbf{B}_r$ should be modified to include current induced in the coil by the average magnetization. The induced field in the rotating frame can be written as

$$\mathbf{B_r} = -\frac{\langle M_y \rangle}{\gamma M_0 \tau_r}\hat{\mathbf{x}} + \frac{\langle M_x \rangle}{\gamma M_0 \tau_r}\hat{\mathbf{y}}, \qquad \tau_r = \frac{1}{2\pi\eta M_0 Q\gamma}, \tag{4}$$

where η is the filling factor and Q is the probe Q-factor. This result agrees with the expressions obtained by Vlassenbroek *et al.* In contrast to the dipolar demagnetizing field, $\mathbf{B}_r$ is independent of position and depends only on the average magnetization. Therefore a pulsed field gradient right after a 90^0 pulse can be used to suppress radiation damping by diminishing the transverse magnetization.

The modified Bloch equations in the rotating frame (modified to include the DDF, radiation damping, diffusion and relaxation processes) can be written as

$$
\begin{aligned}
\frac{\delta M_x}{\delta t} &= \Delta\omega M_y + \frac{M_y M_z}{M_0\tau_d} - \frac{2M_y\langle M_z\rangle}{3M_0\tau_d} - \frac{\langle M_y\rangle M_z}{3M_0\tau_d} - \frac{\langle M_x\rangle M_z}{M_0\tau_r} \\
&\quad + D\frac{d^2 M_x}{dz^2} - \frac{M_x}{T_2} \\
\frac{\delta M_y}{\delta t} &= \Delta\omega M_y - \frac{M_x M_z}{M_0\tau_d} + \frac{2M_x\langle M_z\rangle}{3M_0\tau_d} + \frac{\langle M_x\rangle M_z}{3M_0\tau_d} - \frac{\langle M_y\rangle M_z}{M_0\tau_r} \\
&\quad + D\frac{d^2 M_y}{dz^2} - \frac{M_y}{T_2} \\
\frac{\delta M_z}{\delta t} &= \frac{M_x\langle M_y\rangle - \langle M_x\rangle M_y}{3M_0\tau_d} + \frac{M_x\langle M_x\rangle + \langle M_y\rangle M_y}{M_0\tau_r} \\
&\quad + D\frac{d^2 M_z}{dz^2} - \frac{M_z - M_0}{T_1}
\end{aligned}
\qquad (5)
$$

where $\tau_d = (\gamma\, \mu_0\, M_0)^{-1}$ is the characteristic dipolar demagnetizing time and D is the diffusion constant of the spin. Equation (5) clearly shows the non-linearity of the evolution under the DDF and radiation damping field. For pure water samples in a 600 MHz NMR spectrometer, the two characteristic time constants are $\tau_d \sim 67$ ms and $\tau_r \sim 12$ ms. Since both characteristic time constants are inversely proportional to the gyromagnetic ratio and spin concentration, these effects become important when we have concentrated proton spins in the sample.

Now we briefly sketch the way in which the dipolar field and radiation damping in a simple one-pulse sequence (π/2 – {gradient, duration T} – acquisition), affect the magnetization using the modified Bloch equation. After the gradient pulse the magnetization (on resonance case for easy description)

$$M^{+} = M_x + iM_y = M_0 \exp(i\gamma GTz). \quad (6)$$

If radiation damping slightly rotates the magnetization during a short time period δ,

$$\begin{aligned} M^{+} &= M_x + iM_y \\ &= M_0 \cos\theta_x \cos(\gamma GTz) + M_0 \cos\theta_y \sin(\gamma GTz) \end{aligned} \quad (7)$$

$$\begin{aligned} M_z &= M_0 \sin\theta_x \cos(\gamma GTz) + M_0 \sin\theta_y \sin(\gamma GTz); \\ &\sin\theta_x = \langle M_x \rangle_0 \delta / M_0 \tau_r, \quad \sin\theta_y = \langle M_y \rangle_0 \delta / M_0 \tau_r \end{aligned} \quad (8)$$

where $<M_x>_0$ and $<M_y>_0$ are the initial average magnetization of the real and imaginary part, and θ is the angle between the magnetization vector and the static magnetic field. These modulated z-magnetization can generate the dipolar filed. The transverse magnetization evolves under the dipolar field during δ (when we ignore the other dynamics),

$$\begin{aligned} M^{+} &= \left[M_0 \cos\theta_x \cos(\gamma GTz) + M_0 \cos\theta_y \sin(\gamma GTz)\right] \\ &\times \exp\left\{ i\frac{\delta}{\tau_d}\left[\sin\theta_x \cos(\gamma GTz) + \sin\theta_y \cos(\gamma GTz)\right]\right\} \end{aligned} . \quad (9)$$

Using the Bessel function properties,

$$\exp(iz\cos\varphi) = \sum_m i^m J_m(z)\exp(im\varphi), \quad \exp(iz\sin\varphi) = \sum_n J_n(z)\exp(in\varphi),$$

the magnetization

$$M^{+} = \left[M_0 \cos\theta_x \cos(\gamma GTz) + M_0 \cos\theta_y \sin(\gamma GTz)\right] \times \sum_m i^m J_m\left(\frac{\sin\theta_x}{\tau_d}\delta\right)\exp(im\gamma GTz) \times \sum_n J_n\left(\frac{\sin\theta_y}{\tau_d}\delta\right)\exp(in\gamma GTz) \quad (10)$$

To survive after spatial averaging $m+n = \pm 1$. The strong signal can come with $m = \pm 1$ and $n = 0$, or $n = \pm 1$ and $m = 0$,

$$M^{+} = iM_0 \cos\theta_x J_1\left(\frac{\sin\theta_x}{\tau_d}\delta\right)J_0\left(\frac{\sin\theta_y}{\tau_d}\delta\right) - M_0 \cos\theta_y J_1\left(\frac{\sin\theta_y}{\tau_d}\delta\right)J_0\left(\frac{\sin\theta_x}{\tau_d}\delta\right), \quad (11)$$

where the first and second terms come from the x- and y-magnetization, respectively. Simple expansion of the Bessel function gives

$$M^{+} = i\frac{M_0 \sin 2\theta_x}{4\tau_d}\delta - \frac{M_0 \sin 2\theta_y}{4\tau_d}\delta, \quad (12)$$

$$\langle M_x \rangle_\delta = \langle M_x \rangle_0 - \frac{M_0 \sin 2\theta_y}{4\tau_d} \approx \langle M_x \rangle_0 - \frac{\langle M_y \rangle_0 \delta^2}{2\tau_d \tau_r} \quad (13)$$

$$\langle M_y \rangle_\delta = \langle M_y \rangle_0 + \frac{M_0 \sin 2\theta_y}{4\tau_d} \approx \langle M_y \rangle_0 + \frac{\langle M_x \rangle_0 \delta^2}{2\tau_d \tau_r} \quad (14)$$

$$\langle M^{+} \rangle_\delta = \langle M^{+} \rangle_0 \left\{1 + i\frac{\delta^2}{2\tau_d \tau_r}\right\}. \quad (15)$$

After time evolution this interaction becomes more complex. But, this created magnetization makes the radiation damping field stronger, which can generate the stronger dipolar field again. Therefore, radiation damping (from the residual magnetization) trigger this chain interaction by generating the modulated z-magnetization that can induce the dipolar filed. This interaction can give a strong signal after time evolution. Note the x-magnetization of the initial magnetization creates the y-component of the average magnetization and *vice versa.* This cross-correlation produces an additional nonlinear evolution which can be added into the offset frequency evolution and produce unusual modulation in FID profiles.

If we introduce also transverse DDF effect shown in Eq. (3) (usually this effect is smaller than radiation damping), the angle between the magnetization vector and the static field (see Eqs. (5) and (8)) can be written as;

$$\begin{aligned} \sin\theta_x &= \langle M_x \rangle_0 \delta / M_0\tau_r + \langle M_y \rangle_0 \delta / 3M_0\tau_d \, , \\ \sin\theta_y &= \langle M_y \rangle_0 \delta / M_0\tau_r - \langle M_x \rangle_0 \delta / 3M_0\tau_d \end{aligned} \qquad (16)$$

which can yield the following magnetization;

$$\left\langle \dot{M}^+ \right\rangle_\delta = \left\langle M^+ \right\rangle_0 \left\{ 1 + \frac{\delta^2}{6\tau_d^2} + i\frac{\delta^2}{2\tau_d\tau_r} \right\}. \qquad (17)$$

From the Eq. (17) one can easily expect that, differing from the effect of radiation damping, the additional term creates the intensity variation of FIDs but no frequency modulation (no crossing between x- and y-magnetization) since this field is perpendicular to the radiation damping field. The effect of this term could be significant only when $\tau_d < \tau_r$ (for example a sample in a very thin capillary tube).

SIMULATIONAL RESULTS and DISCUSSION

Numerical simulation clearly shows the signal is produced by the signal is produced by the chain interaction between radiation damping and the dipolar field as expected by the modified Bloch equation (See Fig. 3). The signal can increase only when both the dipolar filed and radiation damping field are effective. This could be a reason why multiple gradient pulses and/or magic angle gradients have been used instead of single pulse or single direction in many successful solvent suppression techniques. Particularly, Fig. 4 shows that radiation damping can create the modulated z-magnetization (as the source of the dipolar field, see Eq. (8)) and that amplitude of the modulation increases with time. This behavior is quite different than that of the conventional radiation damping field, which rotates the magnetization vector to the equilibrium position (e.g. +z-direction). The physical explanation for this result is that the spatially modulated magnetization will cause the radiation damping effect to be different, depending on the position of each magnetization, although the radiation damping field itself (proportional to the average magnetization) is uniform across the sample (see Eq. (4)).

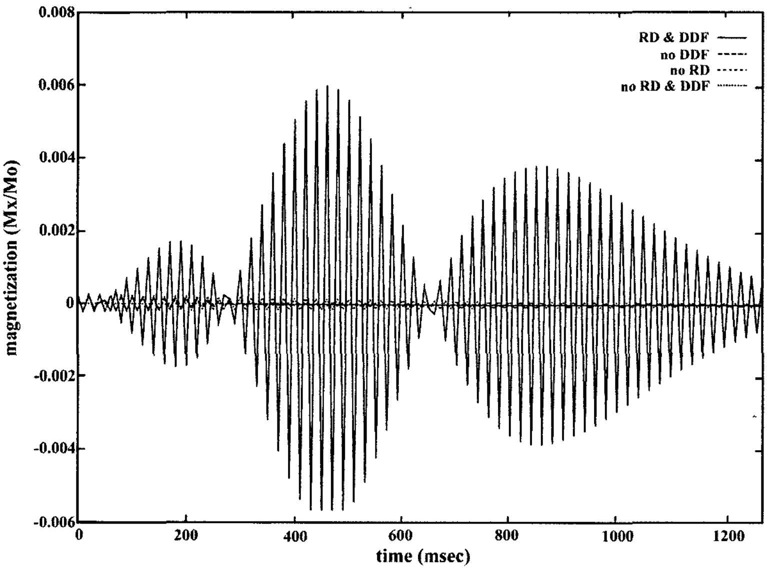

Fig. 3. Simulated [1]H FIDs of 90% H_2O after at 298 K after a 90° pulse and a gradient pulse (z-direction): G = 5 G/cm, T = 1 msec, T_1 = 2 sec, T_2 = 1 sec, τ_r =12 msec.

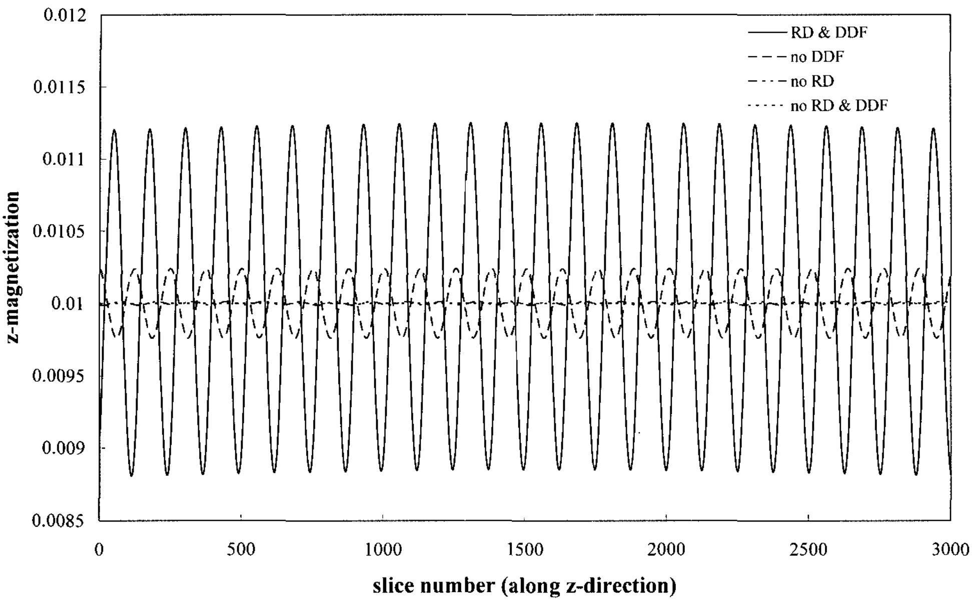

Fig. 4. Space modulation patterns of z-magnetization across slices after 500 msec: $G = 5$ G/cm, $T = 1$ msec, $T_1 = 2$ sec, $T_2 = 1$ sec, $\tau_r = 12$ msec.

The quantum picture can be useful to understand these phenomena since it retains predictive power differing from the nonlinear classical picture.[12,14] The density matrix after the pulsed filed gradient can be written as (without the high temperature approximation)

$$\begin{aligned} &\rho = 2^{-N}\prod_i\left[1 - \Im I_{xi}\cos(\gamma GTz_i) - \Im I_{yi}\sin(\gamma GTz_i)\right]; \\ &\Im = 2\tanh\left(\frac{\hbar\omega}{2kT}\right) \end{aligned}, \qquad (18)$$

where ω is the Larmor frequency of spin. The weak radiation damping field can rotate each operator slightly (like a small pulse), which creates the modulated *z*-components

$$\rho = 2^{-N}\prod_i \begin{bmatrix} 1 - \Im I_{xi}\cos\theta_{xi}\cos(\gamma GTz_i) - \Im I_{zi}\sin\theta_{xi}\cos(\gamma GTz_i) \\ - \Im I_{yi}\cos\theta_{yi}\sin(\gamma GTz_i) - \Im I_{zi}\sin\theta_{yi}\sin(\gamma GTz_i) \end{bmatrix}, \tag{19}$$

where θ is the angle between the spin vector and the static field. There are two requirements for observation these coherences; the multi-spin components should be transferred onto a 1-spin single-quantum terms in the acquisition period, and the spatial average of the terms must be nonzero. For example, parts of 2-spin single-quantum terms can be free from the spatial averaging,

$$\begin{aligned} &I_{xi}I_{zj}\cos\theta_{xi}\sin\theta_{xj}\cos(\gamma GTz_i)\cos(\gamma GTz_j) \\ &\quad\Rightarrow I_{xi}I_{zj}\cos\theta_{xi}\sin\theta_{xj}\cos[\gamma GT(z_i - z_j)] \end{aligned} \tag{20}$$

$$\begin{aligned} &I_{yi}I_{zj}\cos\theta_{yi}\sin\theta_{yj}\cos(\gamma GTz_i)\cos(\gamma GTz_j) \\ &\quad\Rightarrow I_{yi}I_{zj}\cos\theta_{yi}\sin\theta_{yj}\cos[\gamma GT(z_i - z_j)]. \end{aligned} \tag{21}$$

As it was shown elsewhere, these coherences are rendered observable by a number of small distant dipolar couplings (of the form $D_{ij}I_{zi}I_{zj}$). Just as the J coupling, this dipolar coupling operator removes the I_z term leaving 1-spin single-quantum $I^{\pm}$ for detection.[12,14]

In summary, we have shown theoretically and experimentally an unusual cross-correlated effect between radiation damping and the distant dipolar field. This cross-correlation induces a chain interaction, which originated from triggering effects of small residual magnetization, and results in the resurrection of gradient-dephased magnetization.

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REFERENCES

1. M. McCoy and W. S. Warren, *J. Chem. Phys.* **93**, 858 (1990).
2. R. Bowtell, R. M. Bowley, P. Glover, *J. Magn. Reson.* **88**, 643 (1990).
3. G. E. Ball, G. J. Bowden, T. H. Hesltine, M. J. Prandolini, and W. Bermel, *Chem. Phys. Lett.* **261**, 421 (1996).
4. W. S. Warren, W. Richter, A. H. Andreotti, and B. T. Farmer II, *Science* **262**, 2005 (1993)
5. W. Richter, S. Lee, W. S. Warren, and Q. He, *Science* **267**, 654 (1995).
6. R. Bowtell and P. Robyr, NMR, *Phys. Rev. Lett.* **76**, 4971 (1996).
7. N. Bloembergen, E. M. purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).
8. Q. He, W. Richter, S. Vathyam, and W. S. Warren, *J. Chem. Phys.* **98**, 6779 (1993).
9. A. Vlassenbroek, J. Jeener, and P. Broekaert, *J. Chem. Phys.* **103**, 5886 (1995).
10. V. Sklenar, *J. Magn. Reson. A* **114**, 132 (1994).
11. G. Otting, and E. Liepinsh, *J. Boimol. NMR* **8**, 420 (1995).
12. S. Lee, W. Richter, S. Vathyam, and W. S. Warren, *J. Chem. Phys.* **105**, 874 (1996).
13. S. Ahn, W. S. Warren, and S. Lee, *J. Magn. Reson.* **128**, 114 (1997).
14. S. Ahn, S. Lee, and W. S. Warren, *Mol. Phys.* **95**, 769 (1998).
15. Y.-Y. Lin, N. Lisitza, S. Ahn, and W. S. Warren, *Science* **290**, 207 (2000).
16. G. Deville, M. Bernier, and J. M. Derieux, *Phys. Rev. B* **19**, 5666 (1979).
17. W. S. Warren, S. Lee, W. Richter, and S. Vathyam, *Chem. Phys. Lett.* **247**, 207 (1995).