

# Noise triggering of radiation damping from the inverted state

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## Abstract

Spontaneous radiation damping in nuclear magnetic resonance spectroscopy of sharp lines is commonly encountered in highly magnetized samples following magnetization inversion. The time delay for the maximum of the hyperbolic secant like signal to develop following inversion is measured and calculated. The distribution function of the measured delay times is Gaussian–Boltzmann and can be used to predict the sensitivity of both signal delay and phase to inversion errors. © 2000 Elsevier Science B.V. All rights reserved.

An inverted two-level system coupled to a cavity at resonance emits coherent radiation spontaneously above or at the maser threshold condition. This applies to nuclear magnetic resonance (NMR) as a special case [1] of radiation damping [2] for the condition  $T_2/T_R \geq 1$ . The inverse line width is given by  $T_2$ , and the radiation damping time  $T_R$ , is defined by

$$T_R = (2\pi\gamma M_0 Q \xi)^{-1} \quad (1)$$

where  $M_0$  is the equilibrium magnetization,  $\gamma$  is the gyromagnetic ratio,  $Q$  is the cavity figure of merit, and  $\xi$  is the sample filling factor. In general, a  $\theta_0$  pulse applied to the entire spin ensemble is followed by completion of a radiation damping signal, and the magnetization ends up along the polarizing field with a lesser final energy, having dissipated energy into

the circuit resistance<sup>1</sup> [3,4]. From the initial  $\theta_0$  orientation, the total angle  $\Delta\theta$  through which the magnetization component at exact resonance tilts toward the ground state is given by [5]

$$|\Delta\theta| = \frac{T_2}{T_R} \sin(\theta_0 - |\Delta\theta|). \quad (2)$$

Here  $T_2$  is determined by symmetric inhomogeneous broadening. For an exact  $\theta_0 = \pi$  inversion pulse, the transcendental Eq. (2) reduces to

$$|\Delta\theta| = \frac{T_2}{T_R} \sin|\Delta\theta|. \quad (3)$$

Eq. (3) specifies that the spin system may end up in either of two final states, as indicated in Fig. 1. For  $|\Delta\theta| \neq 0$ , emission of radiation must occur, leading toward a final lower energy polarization state; or for

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<sup>1</sup> Analogous to coherent optical superradiant emission appearing in the form of propagation.

$|\Delta\theta| = 0$ , the exactly inverted polarization remains in a metastable inverted state and does not radiate even if the condition  $T_2/T_R \geq 1$  applies. The latter condition of trapping in the inverted state must always occur first if the magnetization has been prepared in an exact inverted state because there is no radiating polarization that can couple to the tuned circuit. After a time delay [6,7] the two-level system will escape from the metastable state and radiate coherently if a weak perturbation of some kind tilts the magnetization sufficiently away from its initial exact  $\pi$  alignment. Room temperature rf noise is the ever present perturbation of importance. After the circuit noise field  $H_{1n}$  initiates a small tilt angle away from the  $-z$  direction defined by  $\theta_-$ , the radiation damping reaction field  $H_{1R}$  comes into play and reinforces the increase in  $\theta_-$ . As  $\theta_-$  increases at random, both the mean square angle  $\langle \theta_-^2 \rangle$  and the  $H_{1R}$  reaction field increase along with it. It will be seen that the combined effects of  $H_{1n}$  and  $H_{1R}$  lead to the development of amplified spin noise in the inverted state and to the establishment of steady state spin noise [8] in the equilibrium ground state. The solid lines in Fig. 2 define both the transverse in-phase  $u$  and quadrature out-of-phase  $v$  components of the signal following a  $\pi$  rf pulse. The dashed line corresponds to the envelope of the signal. The time  $t_0$  is measured from the  $\pi$  rf pulse to the maximum of this signal. The time  $t_{\text{delay}}$  corresponds to the average value for  $t_0$  following many measurements

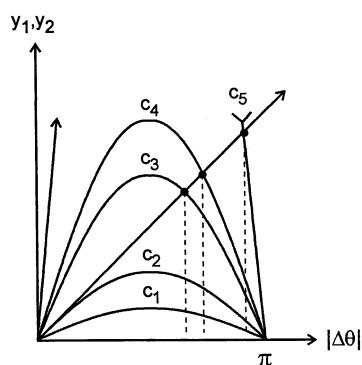


Fig. 1. Graphical solutions to the transcendental Eq. (3) as a function of  $c_n = T_2 / T_R$ . In all cases the metastable inverted state  $|\Delta\theta| = 0$  is a solution. However, when  $c_n > 1$ ,  $|\Delta\theta| \neq 0$  values exist. Under these conditions, circuit noise stimulates the transition to the ground state.

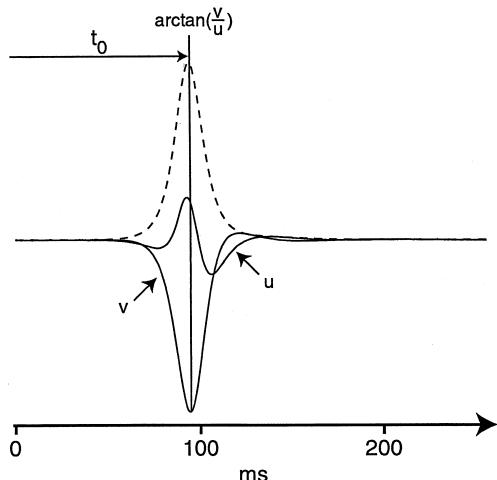


Fig. 2. An example of the signal measured following a  $\pi$  rf pulse applied to a  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (95:5%) solution at a 600 MHz  ${}^1\text{H}$  Larmor frequency for  $T_R = 7.1$  ms. The two solid lines correspond to the in-phase  $u$  and out-of-phase  $v$  magnetization, while the dashed line labels the signal envelope. The time from completion of the rf pulse to the signal maximum defines  $t_0$  as shown by the arrow in the figure. For a given  $T_R$ , circuit noise will vary the time  $t_0$  and the phase of the signal  $\arctan(v/u)$  at  $t_0$  from experiment to experiment. Therefore, the time  $t_{\text{delay}}$  calculated here is the most probable value of  $t_0$  extracted from many measurements.

of signals like those in Fig. 2. The signal phase at  $t_0$  can also be extracted from these signals as  $\arctan(v/u)$  as shown in Fig. 2.

To evaluate the time  $t_{\text{delay}}$  and to introduce some nomenclature, consider first the equation for the tilt angle  $\theta$  of the magnetization from the  $+z$  direction in the sharp line limit  $T_2 = \infty$ :

$$\frac{d\theta}{dt} = -\frac{\sin\theta}{T_R}. \quad (4)$$

The hyperbolic secant solution [2] to this equation is proportional to the transverse magnetization

$$v = M_0 \sin\theta = M_0 \operatorname{sech}\left(\frac{t - t_0}{T_R}\right) \quad (5)$$

where

$$t_0 = T_R \operatorname{arcsech}(\sin\theta_0) = T_R \ln\left(\frac{2}{\tan\theta_0}\right) \quad (6)$$

defines the duration of signal coherence extending from the application of any  $\theta_0$  pulse at  $t = 0$  to the maximum of the signal given by Eq. (5) at  $t = t_0$ . Any fluctuations in the direction of the magnetization due to an incoherent circuit noise field  $H_{1n}$  introduces an additional term  $\dot{\theta}_n = \gamma H_{1n}$  into Eq. (4). A Langevin equation of the form

$$\frac{d\theta}{dt} + \frac{\theta}{T_R} = \dot{\theta}_n \quad (7)$$

is obtained in the small tip angle limit  $\sin \theta \approx \theta$  near the ground state. We first apply Eq. (7) to evaluate the approach to thermal equilibrium when a balance in the ground state is reached between the emission of radiation damping and the circuit noise field stimulated absorption [8]. (Following this analysis, Eq. (7) will then be modified to deal with non-equilibrium time delay effects after inversion of the magnetization when the circuit noise field induces stimulated emission instead of absorption.) The time dependence of the average of the mean square deviation of the magnetization from the  $+z$  direction, given by

$$\frac{d\langle \theta^2 \rangle}{dt} + \frac{2\langle \theta^2 \rangle}{T_R} = 2\langle \theta \dot{\theta}_n \rangle \quad (8)$$

is obtained from Eq. (7) in the usual way by using the identity  $d\theta^2/dt = 2\theta d\theta/dt$  followed by application of an ensemble average as denoted by the paired brackets. To determine  $\langle \theta \dot{\theta}_n \rangle$ , consider Eq. (8) at steady state equilibrium where  $\langle \theta^2 \rangle = \langle \theta \dot{\theta}_n \rangle T_R \ll 1$ . The equipartition theorem for the energy excess in the  $\theta$  degree of freedom is given by

$$\begin{aligned} \langle \vec{M} \cdot \vec{H} \rangle - M_0 H_0 &= M_0 H_0 (\langle \cos \theta \rangle - 1) \\ &\approx \frac{M_0 H_0}{2} \langle \theta^2 \rangle = kT_c/V_s \end{aligned} \quad (9)$$

where  $k$  is Boltzmann's constant,  $H_0$  is the magnetic field,  $V_s$  is the sample volume, and  $T_c$  is the temperature of the circuit resistance. Eq. (9) is then applied to Eq. (8) to evaluate the quantity  $\langle \theta \dot{\theta}_n \rangle$ , and the solution for  $\langle \theta^2 \rangle$  becomes

$$\langle \theta^2 \rangle = \frac{2kT_c}{M_0 H_0 V_s} [1 - \exp(-2t/T_R)]. \quad (10)$$

At  $t = \infty$  this equation indicates that on average the single magnetization vector initially aligned along the  $+z$  direction will spread to a final mean square angular width  $\langle \theta^2 \rangle_\infty$  due to the balance between absorption caused by  $H_{1n}$  and emission caused by  $H_{1R}$ . This mean square angle established at equilibrium for  $I = 1/2$  is given by

$$\langle \theta^2 \rangle_\infty = \frac{2kT_c}{M_0 H_0 V_s} = \frac{\langle M_x^2 \rangle + \langle M_y^2 \rangle}{M_0^2} = \frac{N\gamma^2 \hbar^2}{2M_0^2}, \quad (11)$$

identical to that anticipated for spin noise fluctuations [8] when the temperature  $T_c$  is equal to the lattice temperature  $T_{lat}$ . In the more general case when  $T_c \neq T_{lat}$ , the right-hand side of Eq. (11) must be multiplied by  $T_c/T_{lat}$ .

More explicitly, it follows that  $\langle \theta^2 \rangle_\infty = \gamma^2 \langle H_{1R}^2 \rangle T_R^2 = \gamma^2 \langle H_{1n}^2 \rangle T_R Q/\omega$  defines the thermal equilibrium angle where  $\langle H_{1R}^2 \rangle = \langle H_{1n}^2 \rangle Q/T_R \omega$  and  $\langle H_{1n}^2 \rangle = 4\pi kT_c/V_s$  is obtained from the Nyquist theorem. Thus the average intensity of the radiation damping field emission is balanced by the fraction  $Q/T_R \omega$  of the circuit noise field intensity of absorption within the bandwidth  $1/T_R$  of the spins, neglecting relaxation. Data obtained at 600 MHz gives  $\langle \theta^2 \rangle_\infty = 7 \times 10^{-14} \text{ rad}^2$  and  $T_R = 10 \text{ ms}$ , yielding  $\langle H_{1R}^2 \rangle^{1/2} \approx 1 \text{ nG}$ .

Before proceeding with the calculation of  $t_{delay}$ , one must be completely aware of the experimental conditions. To achieve essentially exact initial alignment in practice, care must be taken to avoid a small initial tilt angle of the inverted magnetization due to slight inaccuracies in pulse width, the inhomogeneity of the applied rf field over the sample, and excitation caused by insufficiently shielded rf leakage. This leakage is avoided by using both high isolation rf switches and incorporating additional crossed diodes between the rf-transmitter and NMR probehead. Unwanted macroscopic coherence due to pulse width errors and rf inhomogeneity are removed by the application of a sufficiently strong DC field gradient pulse just after the  $\pi$  rf pulse. Care must be exercised in the choice of field gradient pulse shapes. The eddy currents due to square pulses tend to produce transients that reintroduce small tipping of the inverted magnetization. These effects were mini-

mized in all measurements by using a 10 ms Gaussian gradient pulse shape having a 29 G/cm peak amplitude and 4 ms full width at half height. While radiation damping dominates the evolution with a line width of 10 Hz, during the 10 ms gradient pulse period the linewidth jumps from  $\approx 10$  Hz to  $\approx 250$  kHz and radiation damping is suppressed. This can be justified from Eq. (3) by comparing  $|\Delta\theta|$  for both the 10 Hz and 250 kHz wide lines where  $T_2 = 100$  and 4 ms, respectively. Taking  $T_R = 5$  ms gives  $|\Delta\theta| = 0^\circ$  and  $171.4^\circ$  for the narrow line, indicating that both the metastable and ground state are accessible to the magnetization as shown in Fig. 1 for  $c_3$ ,  $c_4$ , and  $c_5$ . On the other hand, for the same  $T_R$  value, the wide line gives only  $|\Delta\theta| = 0$ , suggesting that radiation damping does not effect a rotation of the magnetization towards the ground  $+z$  direction as shown in Fig. 1 for  $c_1$  and  $c_2$ . Since application of the gradient has the dual effect of removing any unwanted tilt and suspending the effects of radiation damping, the development of  $\langle\theta_-^2\rangle$  from zero due to nearly exact alignment along the  $-z$  direction immediately after the field gradient pulse can be evaluated.

The solution for the time delay

$$t_0 = T_R \ln\left(\frac{2}{\theta_-}\right) \quad (12)$$

may be expressed in terms of the small tip angle  $\theta_-$  from the  $-z$  direction using Eq. (6), where  $\theta_0 = \pi - \theta_-$  and  $\tan\theta_- \approx \theta_-$ . In the inverted state,  $M_0$  changes sign and the sign of  $T_R$  changes in Eq. (10) to give

$$\begin{aligned} \langle\theta_-^2\rangle &= \langle\theta^2\rangle_\infty [\exp(2t/T_R) - 1] \\ &= \theta_-^2 = 4 \exp[2(t - t_0)/T_R] \end{aligned} \quad (13)$$

after equating Eq. (10) to Eq. (5) in the small angle limit. Eq. (13) exhibits gain in the exponential regime of Eq. (6) but can only be applied for restricted times  $0 < t < t_{\text{delay}}$ . Therefore  $\langle\theta_-^2\rangle$  may be equated with the solution for  $\theta_-^2$  from Eq. (5) in the exponential regime near  $t = 0$ , but where  $t = t'$  is large enough so that in Eq. (13)

$$\langle\theta_-^2\rangle \approx \langle\theta^2\rangle_\infty \exp[2t'/T_R] \gg \langle\theta^2\rangle_\infty. \quad (14)$$

Therefore a connection is made between the incoherent and coherent properties of the tipping magnetization for  $\theta_- \ll 1$ . The time  $t'$  is chosen long enough so that the coherence of angle  $\gamma H_{IR} T_R$  associated with  $H_{IR}$  dominates over the smaller induced incoherent angle caused by  $H_{In}$  field fluctuations from the circuit. Under these conditions, the solution for  $t_0$  in Eq. (14) leads directly to the average time

$$t_{\text{delay}} = \frac{T_R}{2} \ln\left(\frac{4}{\langle\theta^2\rangle_\infty}\right). \quad (15)$$

The paradox that  $t_0 = \infty$  obtained from Eq. (12) when  $\theta_- = 0$  is thus avoided when  $M_0$  is perfectly inverted after an ideal  $\pi$  pulse. Instead, after sufficient time  $t'$  the diffusion Eq. (13) develops an intermediate mean square angle  $\langle\theta_-^2(t')\rangle$  which defines

$$t' = \frac{T_R}{2} \ln\left(\frac{\langle\theta_-^2(t')\rangle}{\langle\theta^2\rangle_\infty}\right). \quad (16)$$

This means that  $\langle\theta_-^2(t')\rangle = \gamma^2 H_{IR}^2 T_R^2 \gg \langle\theta^2\rangle_\infty$  specifies a coherent tipping angle much larger than any tipping caused by  $\langle H_{In}^2 \rangle$  due to circuit noise. The coherent relation Eq. (12) then gives an additional delay time

$$t'_0 = \frac{T_R}{2} \ln\left(\frac{4}{\langle\theta_-^2(t')\rangle}\right) \quad (17)$$

to be added to  $t'$ . The sum  $t'_0 + t' = t_{\text{delay}}$  is again given by Eq. (15). The essential assumption here is that while incoherence is dominant, the relation Eq. (15) which is obtained for a coherent model cannot be applied. It is only valid when initial angles  $\theta_-$  in the distribution are large enough above the influence of circuit noise so that they appear equivalent to coherent initial tip angles  $\theta_0$  in Eqs. (2) and (6). The sum of the logarithms given by  $t'_0 + t'$  reduces to a  $t_{\text{delay}}$  independent of  $t$  itself because  $\langle\theta_-^2(t')\rangle$  cancels out leaving only the dependence on the equilibrium mean square angle  $\langle\theta^2\rangle_\infty$ .

From knowledge of the mean square thermal equilibrium angle  $\langle\theta^2\rangle_\infty$  a Boltzmann probability distribution in  $\theta_-$  may be defined as

$$P(\theta_-) = \frac{1}{\sqrt{2\pi\langle\theta^2\rangle_\infty}} \exp[-\theta_-^2/(2\langle\theta^2\rangle_\infty)] \quad (18)$$

that can be applied immediately following application of the field gradient pulse. The probability that  $M_0$  is oriented at any initial angle  $\theta_-$  is determined by the distribution  $P(\theta_-)$ . The average value of the time delay is then given by the normalized average

$$t_{\text{delay}} = \langle t_0 \rangle = T_R \sqrt{\frac{2\pi}{\langle \theta^2 \rangle_\infty}} \times \int_0^\pi \ln\left(\frac{2}{\theta_-}\right) P(\theta_-) \sin \theta_- d\theta_- . \quad (19)$$

This expression incorporates the solid angle weighting factor ( $\sin \theta_-/2$ ) of  $M_0$  on the unit sphere about the  $-z$  direction. Note that the application of  $\sin \theta_-$  in Eq. (19) implies that for  $\theta_- = 0$  the single vector magnetization is never exactly aligned along the  $z$  axis. It is in fact tipped slightly off axis in a direction representing an eigenstate of the magnetization because the spin system is coupled to the single mode of the cavity [8] as well as to the field  $H_0$ . It turns out that  $t_{\text{delay}}$  expressed by Eq. (15) depends upon the most probable (peak) value  $\theta_-^2 = \langle \theta^2 \rangle_\infty$  of the weighted distribution  $\sin \theta_- P(\theta_-) \approx \theta_- P(\theta_-)$  in Eq. (19), at which  $t_0$  displays its average value.

The validity of the expressions for  $t_{\text{delay}}$  in Eqs. (15) and (19) for the probability were tested experimentally using the  $^1\text{H}$  signal in  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixtures at 600 MHz as shown in Fig. 3. For a specific  $T_R$  value the histograms summarize 250 separate measurements of  $t_0$ . A summary of experimental  $T_R$ ,  $\langle \theta^2 \rangle_\infty$ , and  $t_{\text{delay}}$  values measured from the width and center of the hyperbolic secant bursts summarized in Fig. 3 is provided in Table 1 along with a comparison to theoretical estimates of these parameters from Eqs. (1), (11) and (15) with  $Q\xi = 9.3$ . Superimposed on each histogram for each choice of  $T_R$  in Fig. 3 is a solid line representing the distribution of  $t_0$  determined from the  $T_R$  value calculated from Eq. (1) and the  $\langle \theta^2 \rangle_\infty$  value calculated from Eq. (15) and  $t_{\text{delay}}$ . Here the abscissa is determined from Eq. (15) by scaling  $\langle \theta^2 \rangle_\infty^{1/2}$  from its peak value by an amount  $\pm \delta\theta_-$ , while the ordinate is calculated from Eq. (18) using  $\theta_- = \langle \theta^2 \rangle_\infty^{1/2} \pm \delta\theta_-$ . Returning to Table 1, both the experimental and theoretical  $T_R$  and  $t_{\text{delay}}$  values are consistent for the three highest concentrations. The shape of the curve

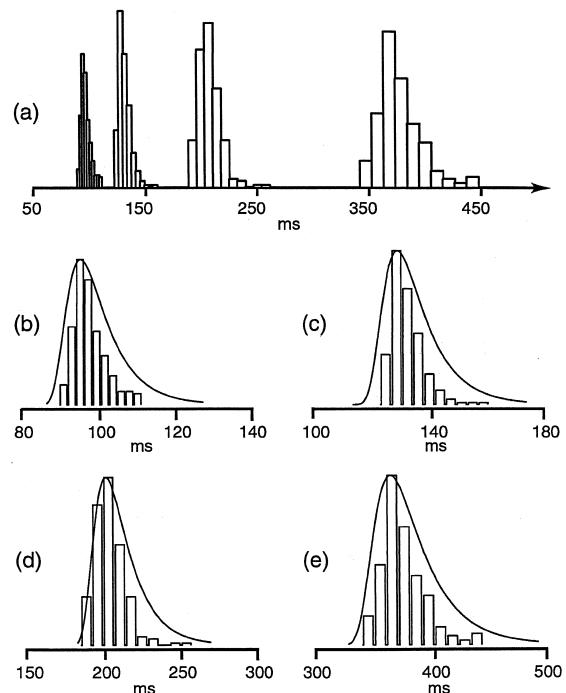


Fig. 3. Summary of  $t_0$  measurements for  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (95:5%),  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (75:25%),  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (50:50%), and  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (25:75%) solutions in (b), (c), (d), and (e), respectively. Each histogram represents 250 separate determinations of  $t_0$  at each concentration or equivalently each specific  $T_R$ . The time  $t_{\text{delay}}$  at each  $T_R$  corresponds to the average value of the distribution in Eq. (18) as seen in the compilation in (a). These values for  $t_{\text{delay}}$  along with theoretical estimates are provided in Table 1. The solid line in each graph corresponds to the distribution anticipated from Eq. (18).

predicted by Eq. (19) is similar to that predicted by Glauber [9]. The NMR measurements in Fig. 3 more literally conform to the theoretical predictions of Eq. (19) than do previous optical measurements by Vehren [10] in an inhomogeneously broadened optical two-level system with damping [11].

One source of error between experimental and theoretical  $\langle \theta^2 \rangle_\infty$  values could lie in the assumption that the gradient pulse completely removes any initial tip angle, and therefore the Gaussian distribution  $P(\theta_-, \phi_-)$  in the angle  $\theta_-$  becomes skewed. For perfect inversion, the distribution in signal phase  $\phi_-$  is expected to be random since  $P(\theta_-)$  is independent of  $\phi_-$ . Fig. 4 summarizes the distribution of phases at  $t_0$  extracted from the same 250 measurements used to determine  $t_{\text{delay}}$  in Fig. 3. Fig. 4a represent-

Table 1

Summary of theoretical and experimental values

$H_2O$ (%)	$t_R$		$\langle \theta^2 \rangle_\infty$		$T_{\text{delay}}$	
	Experiment (ms)	Theory (ms)	Experiment	Theory	Experiment (ms)	Theory (ms)
95	7.1	7.0	$1.2 \times 10^{-11}$	$7.0 \times 10^{-14}$	96.6	110.8
75	9.8	9.0	$1.1 \times 10^{-11}$	$9.8 \times 10^{-14}$	131.4	141.0
50	15.0	13.3	$7.9 \times 10^{-12}$	$1.5 \times 10^{-13}$	207.3	205.6
25	27.6	26.6	$1.0 \times 10^{-11}$	$3.0 \times 10^{-13}$	377.7	401.9

ing the highest  $H_2O$  concentration is clearly a random phase distribution while the data for both the 75% and 25%  $H_2O$  concentrations in Fig. 4b,d deviate from the completely random result. Most pronounced is the very tight distribution about  $89^\circ$  for the data in Fig. 4c. The data in Fig. 3a, Fig. 4a, and Table 1 indicate that the discrepancy between experimental and theoretical  $\langle \theta^2 \rangle_\infty$  values persists even when inversion performance is nearly ideal. A likely cause of this error is linebroadening due to magnetic

field inhomogeneity, an effect not included in the current treatment. To account for the phase deviations for the three other  $^1H$  concentrations studied here, the distribution in Eq. (18) must be adjusted to account for a small tip angle  $\eta$  remaining after application of the field gradient pulse. Here, the distribution is still independent of phase  $\chi$  about the axis tipped away from the  $-z$  direction by the angle  $\eta$ , but dependent on both polar angles  $\theta_-$  and  $\phi_-$  concentrated on the  $-z$  axis. Recasting the distribution in terms of the  $\theta_-$  and  $\phi_-$  polar angles as in shown in Fig. 5 gives

$$P(\theta_-, \phi_-) = \frac{1}{\sqrt{2\pi\langle\theta^2\rangle_\infty}} \exp[-(\eta^2 + \theta_-^2 - 2\eta\theta_- \cos\phi_-)/(2\langle\theta^2\rangle_\infty)] \quad (20)$$

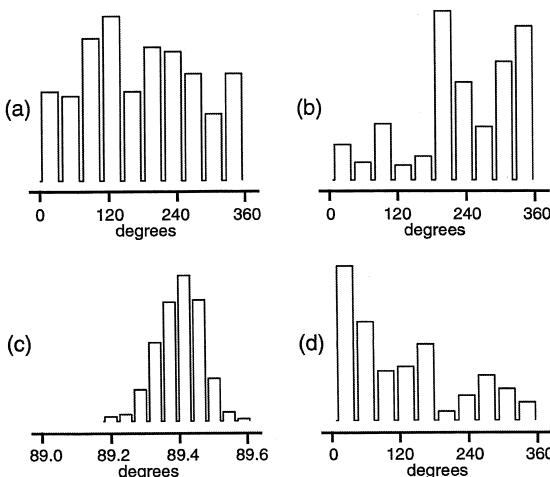


Fig. 4. Summary of signal phase measurements at  $t = t_0$  for  $H_2O/D_2O$  (95:5%),  $H_2O/D_2O$  (75:25%),  $H_2O/D_2O$  (50:50%), and  $H_2O/D_2O$  (25:75%) solutions in (a), (b), (c), and (d), respectively. Each histogram represents 250 separate determinations of the phase at each  $T_R$  value. The phase in (a) is random as expected from the distribution in Eq. (18) but the spread of the data in (b), (c), and (d) display a phase buildup at  $220^\circ$ ,  $89^\circ$ , and  $0^\circ$ , respectively. The departure from random phase and its anisotropy caused by small tip angle  $\eta$  in (c) is explained with the distribution function in Eq. (20) and does not generate appreciable error in the time  $t_{\text{delay}}$ .

which can be used to determine just the distribution in  $\phi_-$  by weighting  $P(\theta_-, \phi_-)$  by  $\theta_-$ , normalizing, and integrating over the variable  $\theta_-$ :

$$P(\phi_-) = \sqrt{\frac{2\pi}{\langle\theta^2\rangle_\infty}} \int_{-\infty}^{+\infty} P(\theta_-, \phi_-) \theta_- d\theta_- = \exp[-(\eta^2 \sin^2 \phi_-)/(2\langle\theta^2\rangle_\infty)] \times \left(1 + \eta \cos \phi_- \sqrt{\frac{2\pi}{\langle\theta^2\rangle_\infty}}\right). \quad (21)$$

For  $\eta = 0$  the distribution centered around the  $-z$  direction is uniform from  $0 \leq \phi_- \leq 2\pi$ . As  $\eta$  is

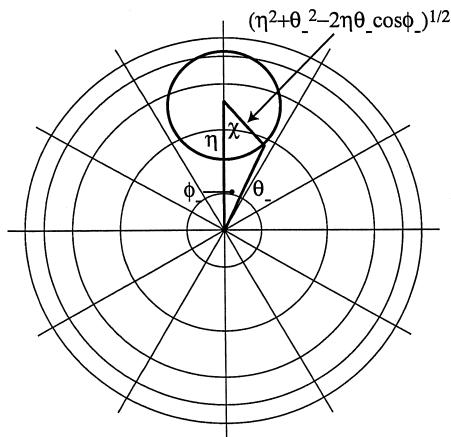


Fig. 5. Graphical determination of the Gaussian probability distribution appropriate for tip angle error. The Gaussian is symmetric in the angle  $\chi$  about the axis inclined by angle  $\eta$  away from the  $-z$  direction. The displacement in terms of  $\eta$ ,  $\theta_-$ , and  $\phi_-$  for small  $\theta_-$  can be determined by the law of cosines.

increased, the distribution of phase begins to concentrate around the direction of  $\eta$ . As the term proportional to  $\eta \cos \phi_-$  in Eq. (21) becomes negative for  $\pi/2 \leq \phi_- \leq 3\pi/2$  values and less than  $-1$ ,  $P(\phi_-)$  becomes a negative probability and the values of  $\phi_-$  that satisfy this condition cannot occur. Very large values of  $\eta$  cause the phase distribution in the regions from  $0 \leq \phi_- \leq \pi/2$  and  $3\pi/2 \leq \phi_- \leq 2\pi$  to concentrate in a narrow region along the direction of  $\eta$  as the width of the distribution in Eq. (20)  $2\langle\theta^2\rangle_\infty/\eta^2$  becomes smaller.

In the limit that  $\eta$  is small, the full width at half height of the distribution in Eq. (21) is  $2\sqrt{\langle\theta^2\rangle_\infty} 2\ln 2/\eta^2$  and can be used to determine the sensitivity of the signal phase on  $\eta$ . For example, the full width at half height in Fig. 4c of  $0.2^\circ$  translates into a tip angle error of only  $\eta = 0.08^\circ$ . The remarkable feature of the data in Figs. 3 and 4 is the insensitivity of  $t_{\text{delay}}$  to tip angle error. The comparison of  $t_{\text{delay}}$  with theory for  $\eta = 0$  in Table 1 suggests that the actual  $\eta = 0.08^\circ$  error in the data sets in Fig. 4c does not appreciably affect  $t_{\text{delay}}$ . To appreciate this dependence on  $\eta$  consider the most probable value  $t_{\text{delay}}$  from the integral of  $T_R \ln(2/\theta_-)$  over the  $\theta_-$  weighted distribution function in Eq. (20). Since the distribution function in Eq. (20) depends on both  $\eta$  and  $\phi_-$ , the resulting

integral which extracts the most probable value of  $\theta_-$  will also depend on  $\eta$  and  $\phi_-$  as

$$t_{\text{delay}} = \frac{T_R}{2} \ln \left( \frac{4}{\theta_-^2} \right) \\ \approx \frac{T_R}{2} \ln \left( \frac{4}{\langle\theta^2\rangle_\infty + \eta \cos \phi_- \sqrt{\langle\theta^2\rangle_\infty}} \right) \quad (22)$$

where quadratic and higher-order terms in  $\eta$  are neglected. Notice that for  $\eta^2 \ll \langle\theta^2\rangle_\infty$ , Eq. (22) reduces to Eq. (15). This relation implies that unless  $\eta^2 \gg \langle\theta^2\rangle_\infty$ ,  $t_{\text{delay}}$  will not appreciably change from the  $\eta = 0$  value. Also, since the  $\eta$  dependence following integration over  $\theta_-$  still remains in the natural logarithm the overall effect of  $\eta$  on  $t_{\text{delay}}$  will be less pronounced.

In summary, we have shown that a Gaussian–Boltzmann distribution in the tipping angle degree of freedom of a single vector magnetization  $M_0$ , governed by the circuit resistance temperature, accounts for the evolution in time of radiation damping emission of Zeeman energy from the inverted state, and also for the evolution toward equilibrium with the circuit near the ground state. Further refinement of the theory will take into account magnetic field inhomogeneity. The strong phase dependence of the hyperbolic secant radiation damping signal on tip angle error  $\eta$  may become a very sensitive detector of magnetic field. Any slight tip of the perfectly inverted magnetization from the  $-z$  direction by either increased rf noise, low-level coherent rf, the bulk demagnetizing field of dilute solutes, or the radiation damping signal for a dilute solute, will induce the phase transition from random to coherent as in Fig. 3. It is this transition that could form the basis for an extremely sensitive measurement of NMR in dilute solution, much like the performance of an injection seeded laser in optical spectroscopy.

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## References

- [1] P. Bosiger, E. Brun, D. Meier, Phys. Rev. Lett. 38 (1977) 602.
- [2] N. Bloembergen, R.V. Pound, Phys. Rev. 95 (1954) 8.
- [3] R.H. Dicke, Phys. Rev. 93 (1954) 99.
- [4] M.S. Feld, J.C. MacGillvary, in: M.S. Feld, V.S. Letokhov (Eds.), Coherent Nonlinear Optics, Springer, Berlin, 1980.
- [5] M.P. Augustine, E.L. Hahn, J. Phys. Chem. 102 (1998) 8229.
- [6] A. Sodickson, W.E. Maas, D.G. Cory, J. Mag. Res. B 110 (1991) 298.
- [7] J.H. Chen, X.A. Mao, J. Phys. D 32 (1999) 764.
- [8] T. Sleator, E.L. Hahn, C. Hilbert, J. Clarke, Phys. Rev. B 36 (1987) 1969.
- [9] R. Glauber, F. Haake, Phys. Lett. 68A (1978) 29.
- [10] Q.H.F. Vrehen, in: H. Walther, D.W. Rothe (Eds.), Laser Spectroscopy IV, Springer, Berlin, 1979.
- [11] F. Haake, J.W. Haus, H. King, G. Schroder, R. Glauber, Phys. Rev. A 23 (1981) 1322.