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The Nonlinear Stimulated Echo

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Almost five decades after the discovery of spin echoes (*1*), a hitherto unknown coherence-refocusing phenomenon was found with uncoupled spins in inhomogeneous magnetic fields. A comprehensive review of the standard echo formation mechanisms can be found in Ref. (*2*). In the present Communication, we report on experiments demonstrating the *no*nlinear *s*timulated *e*cho (NOSE).

The pulse sequence

$$(\alpha_1)_X - \tau_1 - (\alpha_2)_Y - \tau_2 - (\alpha_3)_Y,$$

which is known to generate a stimulated echo in liquids at time τ_1 after the third pulse, also produces ''multiple stimulated echoes'' at times $2\tau_1, 3\tau_1, \ldots,$ with decreasing amplitude. The condition is merely that the magnetic field is inhomogeneous and high enough. In the following, we will restrict ourselves to the first (and largest) of these echoes.

The origin of these echoes is due to the ''dipolar demagnetizing field'' (*3–5*) which is also the basis of the ''multiple spin echoes'' (MSE) occurring in two-pulse experiments (*3, 6–8*). The dipolar demagnetizing field is a consequence of long-range dipolar interactions which are not averaged out by translational diffusion and rapid molecular motion. This field is generated by the bulk spin magnetization and is given by (*3–5*)

$$\mathbf{B}_d(\mathbf{r}) = \frac{\mu_0}{4\pi}\int \frac{d^3r'}{|\mathbf{r}-\mathbf{r}'|^3} \times \left[\mathbf{M}(\mathbf{r}') - 3\left(\frac{\mathbf{M}(\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^2}\right)(\mathbf{r}-\mathbf{r}')\right], \quad [1]$$

where $\mathbf{M}(\mathbf{r})$ is the local magnetization at position $\mathbf{r}$ and μ_0 is the vacuum permeability.

Even for uniform samples, this expression of $\mathbf{B}_d(\mathbf{r})$ is too difficult to evaluate because of its nonlocal character and because of its dependence on the shape of the sample. Nevertheless, it can be significantly simplified, as shown by Deville *et al.* (*3*), if a constant field gradient G of sufficient strength is applied.

The evolution of the magnetization $\mathbf{M}(\mathbf{r})$ after the application of a nonselective RF pulse in the presence of a main magnetic field $\mathbf{B}_0$ and a constant magnetic field gradient G along the direction defined by the unit vector $\hat{\mathbf{s}}$ is described by a set of modified Bloch equations

$$\frac{d\mathbf{M}(\mathbf{r})}{dt} = \gamma\mathbf{M}(\mathbf{r}) \times [\mathbf{B}(\mathbf{r}) + \mathbf{B}_d(\mathbf{r})] - \left(\frac{M_z(\mathbf{r}) - M_0}{T_1}\right)\hat{\mathbf{z}} - \left(\frac{M_x(\mathbf{r})\hat{\mathbf{x}} + M_y(\mathbf{r})\hat{\mathbf{y}}}{T_2}\right) + D\nabla^2\mathbf{M}(\mathbf{r}), \quad [2]$$

where $\mathbf{B}(\mathbf{r}) = (\mathbf{B}_0 + \mathbf{Gs})\hat{\mathbf{z}}$ is the external magnetic field, γ is the magnetogyric ratio, T_1 and T_2 are the relaxation times, D is the self-diffusion coefficient, and $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ are Cartesian unit vectors.

Immediately after the first RF pulse, the magnetization is uniform in the sample. It then develops into a spatial helix along the $\hat{\mathbf{s}}$ direction with a pitch $p = 2\pi/(\gamma G t)$. Here we have assumed that the dipolar demagnetizing field is small enough so that the helix formation by the field gradient is not disturbed. With the proportionality $B_d \sim \mu_0 M_0$ applies, this means that the demagnetizing field is negligible compared with the magnetic field variation in the sample of length l, i.e.,

$$\mu_0 M_0 \frac{1}{Gl} \ll 1. \quad [3]$$

If this condition is fulfilled for times $t > 2\pi/\gamma Gl$, the helical magnetization over the sample produces a simple helical dipolar demagnetizing field (*3*)

$$\mathbf{B}_d(\mathbf{s}) = \mu_0\Delta[M_z(s)\hat{\mathbf{z}} - \tfrac{1}{3}\mathbf{M}(s)], \quad [4]$$

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where

$$\Delta = \tfrac{1}{2}[3(\hat{\mathbf{s}}\cdot\hat{\mathbf{z}})^2 - 1]. \quad [5]$$

As a consequence of the form of Eq. [4], it produces only a small modulation of the precession frequency because the component of $\mathbf{B}_d(\mathbf{r})$ parallel to $\mathbf{M}(\mathbf{r})$ does not affect the evolution of the magnetization.

The dipolar demagnetizing field is expected to have a relevant contribution at times for which the magnetic field variation over the helix pitch $(2\pi/\gamma Gt)G$ is smaller than $B_d \sim \mu_0 M_0$, i.e., at times fulfilling

$$\gamma\mu_0 M_0 t > 1 \quad [6]$$

and $t \lessapprox T_2$. Furthermore, the pitch of the spatial helix must be large enough so that self-diffusion does not become effective (*2*). That is,

$$D(\gamma G)^2 t^3 \ll 1. \quad [7]$$

We note that the conditions [3] and [6] are independent from each other. The dipolar demagnetizing field has a significant effect if condition [6] is fulfilled, even if condition [3] is not. However, in this case, the mathematical treatment of the problem is less easy to handle. On the other hand, conditions [3] and [7] are interdependent, but can be met simultaneously. Also, the condition [6] is not critical for obtaining an observable effect of the dipolar demagnetizing field. It is rather sufficient that $\gamma\mu_0 M_0 t$ should not be much smaller than one.

In our experiment, we used a three pulse sequence $(\alpha_1)_X$—τ_1—$(\alpha_2)_Y$—τ_2—$(\alpha_3)_Y$ where the main magnetic field $\mathbf{B}_0$ as well the field gradient G are oriented along the z direction. In the interval between two pulses, the magnetization evolves according to the modified Bloch equations [2]. The dipolar demagnetizing field is given by Eq. [4] (with $\Delta = 1$) if condition [3] is fulfilled.

The dipolar demagnetizing field gives rise to a nonlinear term in the Bloch equations producing harmonics which, in turn, lead to multiple echoes (*2, 7, 8*). The nonlinear term makes the Bloch equations difficult to solve analytically. Einzel *et al.* (*8*) have shown a solution in the simple case when T_1 and T_2 are much longer than the evolution time. They expanded the expressions for the transverse and longitudinal components of magnetization into a Fourier series. The problem is then reduced to finding the coefficients in the Fourier expansion.

In the present treatment, we used the same procedure but took into account relaxation effects. The coefficients of the Fourier expansion therefore depend on relaxation. In order to achieve an analytical solution, it was necessary to assume $\gamma\mu_0 M_0 \tau$ to be smaller than one. This assumption predicts a smaller effect of the dipolar demagnetizing field compared to the case in which condition [6] is fulfilled. Moreover, if $\tau_1 \ll T_1$ and $\tau_2 > T_2$, the problem simplifies because the transverse component of the magnetization relaxes totally during the τ_2 interval.

As a result of the calculations, one obtains the following expression for the amplitude of the NOSE

$$\begin{aligned} A(2\tau_1) = {} & \frac{\sqrt{\pi}}{8}\sin^2\alpha_1 \sin^2\alpha_2 \sin(2\alpha_3)(\gamma\mu_0 M_0^2 \tau_1) \\ & \times \exp\left(-\frac{4\tau_1}{T_2}\right)\exp\left(-\frac{2\tau_2}{T_1}\right) \\ & \times \exp\left[-D^*\left(2\frac{\tau_2}{\tau_1} + \frac{7}{3}\right)\right]\frac{\operatorname{erf}(\sqrt{D^*})}{\sqrt{D^*}}, \end{aligned} \quad [8]$$

where $D^* = D(\gamma G)^2 \tau_1^3$ and $\operatorname{erf}(x)$ is the error function. Because of relaxation and the condition imposed in order to have an analytical solution $(\gamma\mu_0 M_0 \tau_1 < 1)$, the amplitudes of the other nonlinear echoes which are expected at times $3\tau_1, 4\tau_1, \ldots$ tend to be much smaller than the first one.

Experiments were carried out on a Bruker MSL 300 spectrometer using a cylindrical glass tube of 10 mm diameter containing bidistilled water with a filling height of 14 mm. The measurements were performed with a conventional broadband probehead at room temperature (293 K). The equilibrium magnetization M_0 in the field of $B_0 = 7.05$ T was computed to be 0.023 A/m, and a linear gradient of $G = 0.7$ mT/m was applied along the z direction. The second

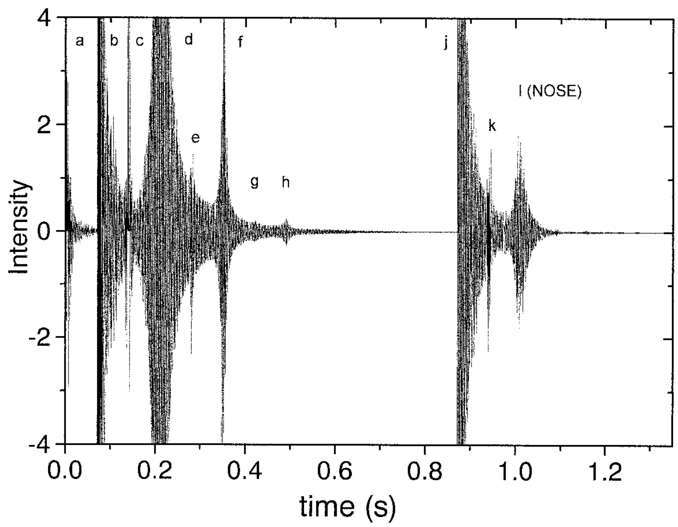

FIG. 1. Echo trains during the pulse sequence $(\pi/2)_X$—τ_1—$(\pi/2)_Y$—τ_2—$(\pi/4)_Y$. The pulse intervals were $\tau_1 = 70$ ms and $\tau_2 = 800$ ms. The length for the $\pi/2$ pulses was set to 17 μs and for $\pi/4$ pulses to 8.5 μs. A total of 1400 transients with a repetition time of 15 s were accumulated. The letters a, b, . . . , 1 indicate free-induction signals and echoes as explained in the text. As a sample, bidistilled water at $T = 293$ K was used.

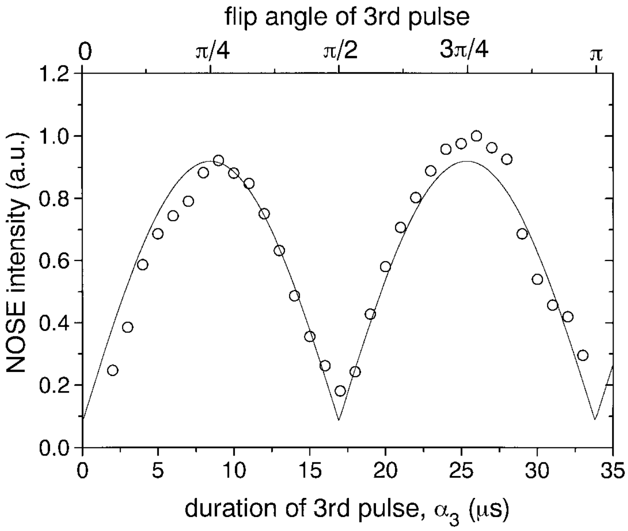

FIG. 2. NOSE intensity, in arbitrary units, as a function of the length (flip angle) of the third RF pulse for $\alpha_1 = \alpha_2 = \pi/2$, $\tau_1 = 65$ ms, and $\tau_2 = 800$ ms. A total number of 200 scans with a repetition time of 12 s were accumulated. As a sample, bidistilled water at $T = 293$ K was used.

interval τ_2 was chosen at values between 0.5 and 0.8 s, and the duration of the first time interval τ_1 was varied between 50 and 110 ms.

Figure 1 shows the induction signals in the course of the whole pulse sequence. The acquisition started just before the first RF pulse. The $\pi/2$ pulse length was 17 μs. The free-induction signals following the first, second, and third RF pulses are labeled by the letters a, b, and j, respectively. Ordinary two-pulse ''multiple echoes'' appear at $3\tau_1$, $5\tau_1$, $7\tau_1$ [see Ref. (*7*)] (letters d, f, and h, respectively).

The nonlinear stimulated echo NOSE marked by the letter l arises at times $\tau_2 + 3\tau_1 = 1.01$ s. As a consequence of the phase cycle used, the primary (c) and stimulated (k) echoes as well as the multiple spin echoes at times $4\tau_1$ (e) and $6\tau_1$ (g) and the nonlinear echo at $\tau_2 + 4\tau_1$ are cancelled. Residual signals at these positions are due to imperfections in the pulse length at different positions in the sample. The complementary experiment with the echoes visible in Fig. 1 suppressed and those suppressed in Fig. 1 visible with full intensity may be carried out using another phase cycle.

The intensities of the nonlinear echoes relative to the stimulated echo following the $\pi/2$—$\pi/2$—$\pi/4$ pulse sequence were found by integration of the echo areas to be 0.07 and 0.009, respectively. In Fig. 2, the NOSE intensity is shown as a function of the length of the third RF pulse, α_3. The parameters chosen were $\tau_1 = 65$ ms, $\tau_2 = 800$ ms; 200 scans were accumulated with a recycle delay of 12 s. The dependence on the pulse length can be described by a sine function with a maximum value of 8.3 ± 0.3 μs, in accordance with our theoretical predictions. Note that intensity is minimal for a pulse length of 17 μs which is equivalent to $\pi/2$.

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