Polarization Echoes in NMR

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It is demonstrated that it is possible to reverse the time evolution of polarization in a dipole-coupled nuclear spin system (by refocusing the "spin diffusion" process), leading to the appearance of a new type of echoes, called polarization echoes. The polarization echoes for abundant I spins can be measured conveniently by a two-step polarization-transfer process from and to rare S spins that allows a local perturbation and local detection of the I-spin polarization. Polarization echoes have been recorded for a single crystal sample of ferrocene.

We consider in this Letter a dipole-coupled nuclear spin system in a solid. Whenever the spin polarization is locally perturbed, the system will evolve in time towards an equidistribution of polarization among all spins, often in a time short compared to the spin lattice relaxation time T_1. This process is caused by pairwise energy-conserving flip-flop processes among neighboring spins. In spite of its deterministic quantum mechanical nature, it is often described as a dissipative spin diffusion process, a term coined by Bloembergen when studying relaxation phenomena in the presence of paramagnetic centers [1]. A description in terms of an irreversible diffusion process is adequate for one-pulse experiments performed on complex spin systems with an intricate coupling network. However, when more elaborate pulse experiments are performed, effects that reflect the deterministic nature of the system often become apparent. Such an effect, the polarization echo, will be described in this Letter.

Echo effects have been observed for more than forty years in the context of the refocusing of free induction decays (FID's). Well-known examples are the Hahn echo experiment in liquids [2] and the "magic echo" sequence applied to solids [3,4]. In liquids, the effect of the spatial field inhomogeneity is refocused. In solids, the free induction decay leads, under the influence of the dipolar interaction, to unobservable multiple-spin single-quantum coherence that can be refocused by a suitable pulse sequence. In an analogous way, multiple-spin multiple-quantum coherence, created under multiple-pulse irradiation, has also been refocused by an inverted pulse sequence [5,6].

To our knowledge, so far no echo effects have been described that refer to the time evolution of the polarization (i.e., refocusing the "spin diffusion" process). In principle, it is conceivable to refocus, in full analogy to an FID, also the evolution of an initial nonequilibrium polarization state. It is sufficient to change the sign of the effective Hamiltonian to initiate a reverse time evolution that leads back to the initial polarization state.

It should be noticed that the total polarization in such an evolution process remains constant, and a frequency-selective or spatially selective measurement technique is required to observe polarization-echo effects. Several

possible experiments can be conceived. It is, for example, possible to prepare a nonequilibrium state among chemically shifted resonances by selective irradiation under high resolution conditions in the presence of dipolar decoupling, followed by evolution in the presence of dipolar coupling, and finally using frequency-selective detection again under high resolution conditions.

We prefer in this Letter to exploit the heteronuclear dipolar interaction to a rare spin species S in order to locally perturb the abundant I-spin system and to measure indirectly via S-spin resonance the state of the I spins to monitor the refocusing process. This requires a two-way cross-polarization experiment [7] that is conveniently based on Hartmann-Hahn cross polarization in the rotating frame [8,9].

The sign change of the dipolar coupling Hamiltonian required to induce refocusing can be effected by a change of the quantization axis of the dipolar Hamiltonian that is in the laboratory frame given by [10]

$$\mathcal{H}_d = \sum_{k<l} d_{kl}(3I_{kz}I_{lz} - \mathbf{I}_k \cdot \mathbf{I}_l) \tag{1}$$

with

$$d_{kl} = -(\mu_0/4\pi)\gamma_k\gamma_l\hbar r_{kl}^{-3}\tfrac{1}{2}(3\cos^2\Theta_{kl} - 1). \tag{2}$$

Following first-order perturbation theory, $\mathcal{H}_d$ has been truncated with respect to the dominant Zeeman interaction in the static magnetic field, retaining only terms which commute with $\sum_i I_{zi}$, where the sum extends over all spins. Applying a strong transverse spin-locking radio-frequency field along the y axis, which greatly exceeds in its strength the dipolar interactions, leads to a further truncation of the dipolar interaction, this time with respect to the interaction with the radio-frequency field [11]. Discarding terms which do not commute with $\sum_i I_{yi}$ leads to

$$\mathcal{H}_d' = -\tfrac{1}{2}\sum_{k<l} d_{kl}(3I_{ky}I_{ly} - \mathbf{I}_k \cdot \mathbf{I}_l). \tag{3}$$

The transition from Eq. (1) to Eq. (3) may be considered as a special case of truncation with respect to a strong effective field applied at a tilt angle β from the magnetic field direction. Because of the transformation properties of the dipolar interaction as an irreducible tensor of rank

two, truncation leads to a scaling factor $\frac{1}{2}(3\cos^2\beta-1)$ [11]. At $\beta_m=54.7°$ (the well-known magic angle), the dipolar Hamiltonian changes sign. This opens the possibility of echo refocusing by the sequential application of two effective Hamiltonians with tilt angles above and below the magic angle.

For the special case of Eqs. (1) and (3), where $\beta=0$ and $\pi/2$, the scaling factors are 1 and $-\frac{1}{2}$ and echo formation is obtained by defocusing in the rotating frame followed by refocusing in the laboratory frame where the refocusing time is half the defocusing time. Obviously, the reverse arrangement of the rotating frame and laboratory frame periods is equally feasible.

The pulse sequence is shown in Fig. 1. After cross polarization from I to S spins during the time t_c, the S magnetization is kept spin locked for a sufficiently long time t_S during which the I-spin coherence decays to zero. During the short time t_d, cross polarization from S to I spins polarizes just the nearest-neighbor I spins and establishes the desired initial nonequilibrium state. Dipolar evolution of the spin-locked I-spin polarization is then allowed for a time τ_1. A following $(\pi/2)_x$ pulse causes a transformation into the laboratory frame where evolution in the reverse sense occurs during the time period τ_2. A $(\pi/2)_{-x}$ pulse followed by a cross-polarization period causes again a spatially selective polarization transfer from I to S spins, leading finally to an S-spin FID that is observed during the acquisition period. Variation of τ_2 (or τ_1) allows one to monitor the formation and decay of the polarization echo. It should be noted that the heteronuclear dipolar interaction is effective exclusively during the three cross-polarization periods. In all other periods, the heteronuclear spins remain decoupled.

The relevant part of the experiment is described by the following density operator evolution:

$$\sigma(\tau_1,\tau_2)=e^{i(\pi/2)F_x}e^{i\mathcal{H}_d\tau_2}e^{-i(\pi/2)F_x}e^{-i\mathcal{H}'_d\tau_1}\sigma(\tau_1=0)$$

$$\times e^{i\mathcal{H}'_d\tau_1}e^{i(\pi/2)F_x}e^{i\mathcal{H}_d\tau_2}e^{-i(\pi/2)F_x}$$

$$=e^{-i\mathcal{H}'_d(\tau_2-\tau_1/2)}\sigma(\tau_1=0)e^{i\mathcal{H}'_d(\tau_2-\tau_1/2)}, \qquad (4)$$

with an echo expected for $\tau_2=\tau_1/2$.

Polarization-echo experiments have been applied to a ferrocene single crystal with natural abundance ^{13}C. The interaction of the ^{13}C (S) spin with its directly bonded ^{1}H (I) spin is stronger by approximately a factor of 4 than the interaction between the I spins of the same C_5H_5 ring. It is also much stronger than all other heteronuclear interactions, except for the special case where the fivefold molecular symmetry axis is oriented close to the magic angle with respect to the static magnetic field. There are two crystallographically inequivalent sites in the crystal. The experimental data were recorded for one of the two sites where the fivefold molecular symmetry axis is oriented approximately perpendicularly to the external magnetic field B_0. For this orientation, the heteronuclear dipole interaction ($\mathcal{H}_{IS}=2d_{IS}I_zS_z$) has a coupling constant $d_{IS}/2\pi=5.8$ kHz. The experiments were performed on a modified Bruker CXP300 NMR spectrometer.

The experimental results are shown in Fig. 2. The crosses indicate the time evolution of the polarization of ^{13}C-bonded I spins as a function of τ_1 in an experiment where τ_2 was set equal to zero. The decay towards an asymptotic value of 0.2 (with the initial polarization normalized to 1) is nearly exponential. The process can be interpreted as unhindered spin diffusion among five protons that may be identified with the five ring protons. The system seems to reach a quasiequilibrium state among all protons in the same ring. Spin diffusion to protons of the other rings appears to be slower and does not become evident within the first 600 μs.

The result of the polarization-echo experiment is represented in Fig. 2 by circles. The time τ_1 is fixed to $\tau_1=160$ μs while τ_2 is varied from 0 to 440 μs. The initial signal amplitude with a value of 0.37 at $\tau_2=0$ is refocused and assumes a maximum of 0.85 at $\tau_2=110$ μs.
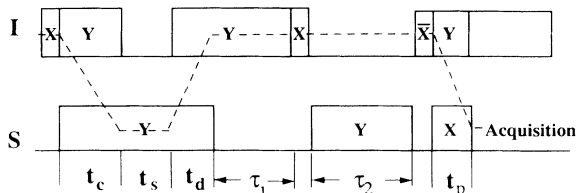

FIG. 1. Pulse sequence for refocusing the evolution of I-spin polarization. The initial nonequilibrium I-spin polarization at $\tau_1=0$ is created by a two-way IS cross-polarization process. A third cross-polarization period (t_p) is necessary for the indirect measurement of the I-spin polarization at the end of the τ_2 period. The capital letters X and Y indicate the rf phases. The pathway of the polarization is shown by the broken line.
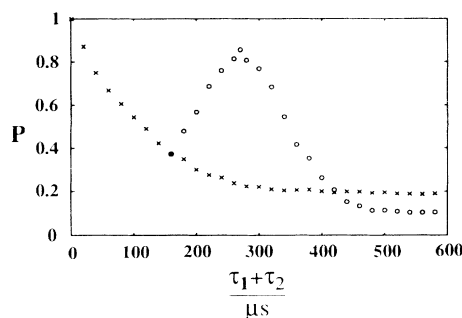

FIG. 2. Time evolution of the polarization P of the proton spins strongly coupled to natural abundance ^{13}C spins in a single crystal of ferrocene obtained by the pulse sequence of Fig. 1 with the experimental conditions $t_c=2$ ms, $t_s=1$ ms, $t_d=t_p=85$ μs, and $\omega_{11}/2\pi=40.3$ kHz. The results of two experiments are superimposed. The crosses result from an experiment with $\tau_2=0$ and variable τ_1. The circles measure the I-spin polarization in an experiment with $\tau_1=160$ μs and variable τ_2.

The signal finally reaches a plateau value of 0.1 in contrast to 0.2 found in the first experiment. This reduction is partially due to the imperfection of the refocusing pulses.

The polarization echo does not occur at the expected time $\tau_2 = \tau_1/2$ but is slightly delayed. This can be explained by the fact that already during the cross-polarization time t_d some evolution of proton polarization occurs, leading to a longer effective evolution time $\tau_1' > \tau_1$, reflected in a delayed echo. The echo is, in fact, a superposition of echo contributions with different values τ_1'. For an IS spin pair, the buildup of I-spin polarization during cross polarization is given by $P_I(t_d) \propto [1 - \cos 2\pi d_{IS} t_d]$ [12]. Assuming that the evolution of the I-spin polarization is the same during t_d in the presence of the heteronuclear coupling as during τ_1 in the absence of heteronuclear interactions, one obtains for the echo amplitude

$$P_{\text{echo}}(\tau_1, \tau_2) = \int_0^{t_d} \frac{dP_I(t)}{dt_d'} f(\tau_1 + t_d - t, \tau_2) dt , \quad (5)$$

where $f(\tau_1, \tau_2)$ is the normalized echo amplitude with $f(\tau_1 = 0, \tau_2 = 0) = 1$. Assuming a Gaussian echo shape,

$$f(\tau_1, \tau_2) = \exp[-(M_2/2)(\tau_2 - \tau_1/2)^2] \quad (6)$$

with a second moment $M_2 = 180 \times 10^6 \text{ s}^{-2}$, one finds by numerical integration of Eq. (5) an echo delay of 25 μs in agreement with the experimental result.

The experimental results of this Letter provide further verification of the fact that the dipolar evolution of nuclear spins in solid state, often referred to as spin

diffusion, is deterministic in nature and can be reversed when the sign of the effective Hamiltonian is changed by external means. It is conceivable that polarization echoes can be utilized for the study of molecular dynamics in solids that cause a characteristic attenuation of the echo amplitude.

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