Multiple-Pulse Spin Locking in Dipolar Solids*

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We report our preliminary results on a multiple-pulse spin-locking effect in dipolar solids. This effect has significant experimental advantages over prior techniques because of its high duty cycle for data collection. We show that the spin temperature assumption can be applied to explain the rather long-term behavior of the spin system. We also demonstrate how this method can be applied to obtain magnetization curves almost instantly for $T_{1\rho}$ decay and adiabatic demagnetization.

In this Letter we report the spin-locking effect we observed when the cw rf irradiation in the Hartman-Hahn sequence[1] was replaced by a string of short rf pulses. This sequence is analogous to the Ostroff-Waugh sequence[2,3] except that the pulse angles are not limited to 90°. We show the conditions under which such discrete rf excitation will have the same effect as continuous-wave rf excitation in dipolar solids. By a proper coordinate transformation, we show that the spin temperature hypothesis can be safely applied[4] and we demonstrate that even the observation of adiabatic demagnetization and inverse remagnetization within a single rf burst is possible using discrete rf pulses.

In order to simplify the discussion, let us consider a nuclear spin system consisting of only one nuclear species, and let the amplitude of the rf field be modulated by a series of square pulses. Only the first two Fourier components of this modulation, a dc level plus a sinusoidal modulation of frequency Ω, will be considered in discussing the Hamiltonian for the system. The discussion can easily be generalized by including higher harmonics. However, the inclusion these harmonics does not add any physically interesting phenomena to the present experiments. In the strong static field $H_0 = \omega_0/\gamma$, the Hamiltonian is given by

$$\mathcal{H} = -\omega_0 I_z - 2\bar{\omega}_1 I_x[1-\eta\cos(\Omega t)]\cos(\omega_0 t) + \mathcal{H}_D^{(z)}, \quad (1)$$

where $\mathcal{H}_D^{(z)}$ is the secular part of the dipolar Hamiltonian and η is the modulation constant. At exact resonance the Hamiltonian can be transformed to the rotating frame, with the result that

$$\mathcal{H}_{RT} = -\bar{\omega}_1[1-\eta\cos(\Omega t)]I_x + \mathcal{H}_D^{(z)}. \quad (2)$$

The explicitly time-dependent Zeeman field can be replaced by a time-independent Zeeman field and an explicitly time-dependent dipolar term by the transformation

$$U(t) = \exp[(i\eta\bar{\omega}_1 I_x/\Omega)\sin(\Omega t)]. \quad (3)$$

In this new frame, the Hamiltonian is given by

$$\mathcal{H}_{RTU} = -\bar{\omega}_1 I_x + \mathcal{H}_D^{(z)} + \mathcal{H}_\epsilon(t), \quad (4)$$

where

$$\mathcal{H}_\epsilon(t) = \mathcal{H}_D^{(2)}\epsilon_2(t) + \mathcal{H}_D^{(-2)}\epsilon_{-2}(t), \quad (5)$$

with

$$\epsilon_{\pm 2}(t) = [J_0(2\eta\bar{\omega}_1/\Omega) - 1] + \sum_{k=-\infty}^{\infty}{}' J_k(2\eta\bar{\omega}_1/\Omega)\exp(\pm k\Omega t), \quad (6)$$

where $\sum'$ designates omission of the term for $k = 0$ from the summation. $\mathcal{H}_D^{(\pm 2)}$ are the nonsecular parts in $\mathcal{H}_D^{(z)}$, and therefore they do not commute with the Zeeman terms.[5]

We note in Eq. (4) that $-\bar{\omega}_1 I_x + \mathcal{H}_D^{(z)}$ is the same Hamiltonian as in the continuous rf irradiation case, which can be obtained from Eq. (2) if $\eta = 0$. Considering the fact that $2\eta\bar{\omega}_1/\Omega = \eta\theta/\pi$, where θ corresponds to the rotation angle of the magnetization during a single pulse of the sequence, and also considering the behavior of Bessel functions $J_n(x)$ near $x \approx 0$, we can make $\mathcal{H}_\epsilon(t)$ arbitrarily small if we let $\theta \to 0$ while Ω satisfies the condition

$$\Omega \gg \bar{\omega}_1, \gamma H_{1oc}, \quad (7)$$

but not necessarily $\bar{\omega}_1 \gg \gamma H_{1oc}$. In this case one can expect the discrete excitation to have an effect closely approaching the cw excitation case. Since the Zeeman term in Eq. (4) does not commute with the dipolar term $\mathcal{H}_D^{(z)}$, these two systems (or reservoirs) will attain a common spin temperature, and this new spin temperature will be preserved forever unless it is affected by the

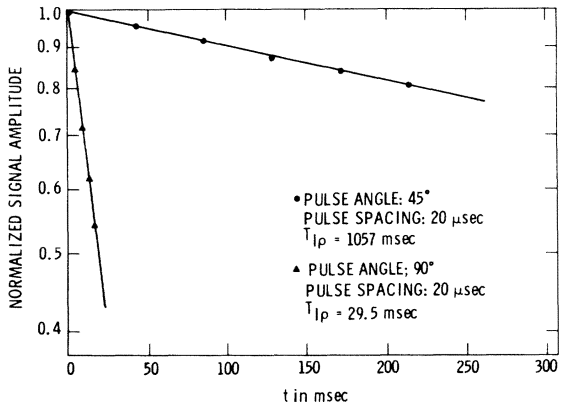

FIG. 1. Decay curves for two different pulse angles. The pulse spacing was the same for each and the decays showed good exponential behavior after a few T_2's. Note the large increase in decay constant in going from 90° to 45°. The sample was a single crystal of CaF_2 with its (111) axis approximately aligned along H_0.

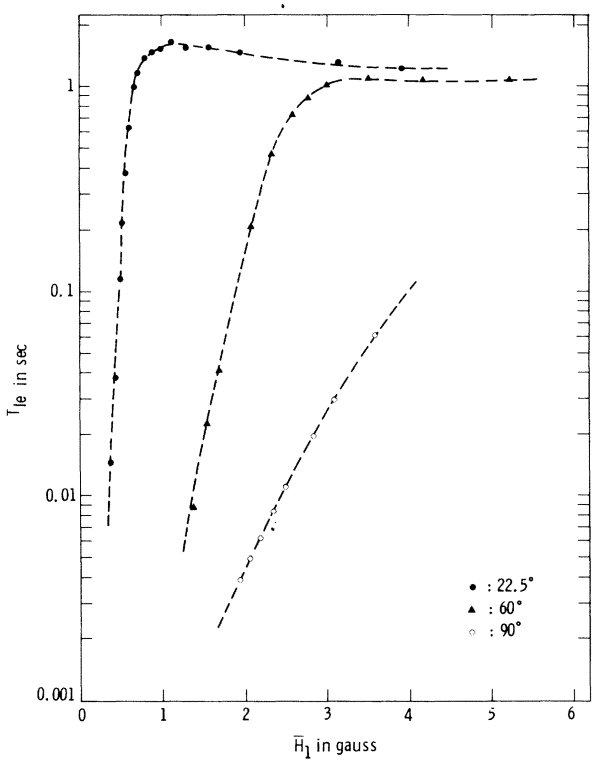

FIG. 2. The decay constant $T_{1\rho}$ as a function of average rf field $\bar{H}_1$ for three different values of pulse angle. The data points are smoothly connected by dashed lines. A CaF_2 single crystal with its (111) axis oriented approximately along H_0 was used as the sample.

spin-lattice interaction and/or the residual perturbation $\mathcal{H}_\epsilon(t)$.[6] The cross relaxation time between the Zeeman and the dipolar reservoir will be of the order of T_2 when these two Hamiltonians have comparable sizes.[5,6]

The above reasoning was tested experimentally using a CaF_2 single crystal oriented with its (111) direction approximately along the static magnetic field. Using discrete rf pulses, the spectrometer was adjusted at exact resonance to produce a conventional Ostroff-Waugh sequence[2] $\{$i.e., $(90°)_y[\tau(90°)_x\tau]^n\}$ with $\tau = 10$ μsec, and the decay time constant $T_{1e} = 29.5$ msec was observed. Under the same conditions, we reduced the pulse angle θ_x to $(45°)_x$, the only effect being to reduce the arguments of the Bessel functions in Eq. (6). The result was an astounding prolongation of $T_{1e} = 1.057$ sec (see Fig. 1). T_{1e} took on intermediate values at other pulse angles between these two.

Now, suppose only the spacing between the pulses is changed. Since $2\eta\bar{\omega}_1/\Omega = \eta\theta/\pi$ is independent of $\Omega = \pi/\tau$, increasing Ω will simply increase the frequency of the sinusoidal oscillations in $\mathcal{H}_\epsilon(t)$, resulting in a better averaging effect. Figure 2 shows this effect for three different pulse angles. The decay constant was recorded as a function of average rf field, i.e., $\bar{H}_1 = \theta\Omega/2\pi\gamma$, for three different values of θ. As can be seen in this figure, increasing Ω has a tremendous averaging effect, increasingly so for smaller values of θ. The saturation of T_{1e} above the 1-sec level is caused by the spin-lattice interaction, which was confirmed by performing a separate cw locking experiment. Thus the saturated $T_{1e} = T_{1\rho}$.

Having seen that $\mathcal{H}_\epsilon(t)$ can easily be made much smaller than the inverse cross relaxation time between the Zeeman and dipolar reservoirs, we can now test whether the system truly achieves a common spin temperature after a few θ_x pulses following the initiating $(90°)_y$ pulse. If this is the case, the magnetization M_z of this semi-equilibrium state should obey the formula

$$M_z/M_0 = \bar{H}_1^2/(\bar{H}_1^2 + H_{1oc}^2), \tag{8}$$

which is identical in its form to the cw locking experiment with a 90° prepulse. Here M_0 is the equilibrium magnetization before the initiating $(90°)_y$ pulse is applied and $H_{1oc}^2 = \mathrm{Tr}(\mathcal{H}_D^{(s)})^2/\gamma^2\mathrm{Tr}(I_z^2)$. The actual variation of $\bar{H}_1$ was accomplished by changing the pulse angle as well as the pulse spacing. The measured magnetization is shown in Fig. 3, together with the theoretical curve from Eq. (8) with $H_{1oc} \approx 1.1$ G. Considering the uncertainty in crystal orientation, this figure

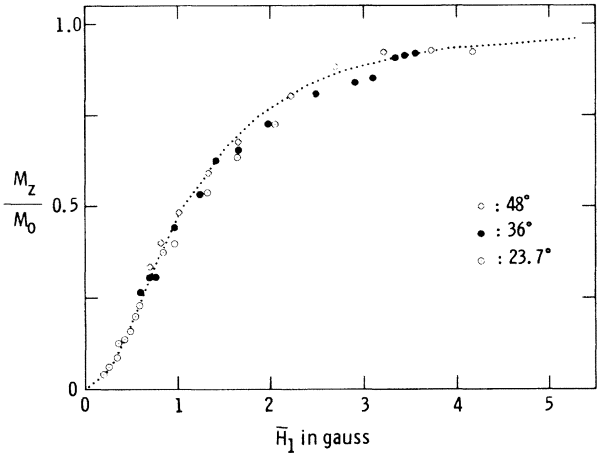

FIG. 3. Initial semi-equilibrium values of the magnetization as a function of average rf field strength. The dotted line is the theoretical curve [Eq. (9)], with H_{loc} = 1.1 G. Various $\bar{H}_1$ values were achieved by changing both the spacing and the angles of the pulses. A CaF_2 single crystal with its (111) axis oriented approximately along H_0 was used as the sample.

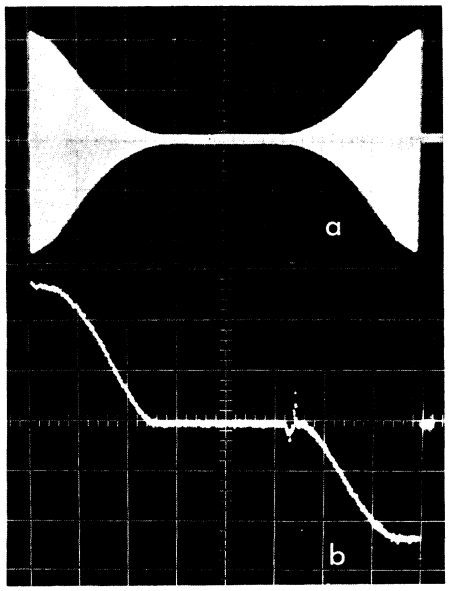

FIG. 4. Demonstration of adiabatic demagnetization in the rotating frame: (a) the modulation envelope of the rf burst; (b) the corresponding signal sampled between rf pulses. The maximum $\bar{H}_1 \approx 2$ G and the horizontal scale is 5 msec/cm. In the remagnetization process the rf phase was changed by 180°, producing inverse remagnetization.

provides convincing evidence that the spin-temperature hypothesis is well justified for this pulsed spin-locking case.

We can also impose a slow modulation on the values of θ_x in the same pulse sequence, and thus cause the spin system to follow $\bar{H}_1$ isentropically, which is analogous to the cw case. By sampling the signal between rf pulses, we observed the adiabatic demagnetization and inverse remagnetization process almost instantly. Figure 4(a) shows the slow amplitude modulation of the rf burst, and Fig. 4(b) is the result obtained during such an adiabatic process. In the remagnetization process the rf carrier phase was changed by 180° compared to the demagnetization process, producing inverse remagnetization. In this experiment the magnetization was proportional to $\bar{H}_1/(\bar{H}_1^2+H_{loc}^2)^{1/2}$ as expected for an adiabatic process.[5]

One obvious practical advantage of the discrete rf pulse excitation technique over the conventional cw technique in dipolar solids is the fact that it enables us to observe the dynamic variation of the spin system during a single rf burst. Application of this technique to the measurement of the rotating frame spin-lattice relaxation times of spin systems with various correlation times and to NMR double resonance is underway. These and a more rigorous theoretical analysis will be published elsewhere.

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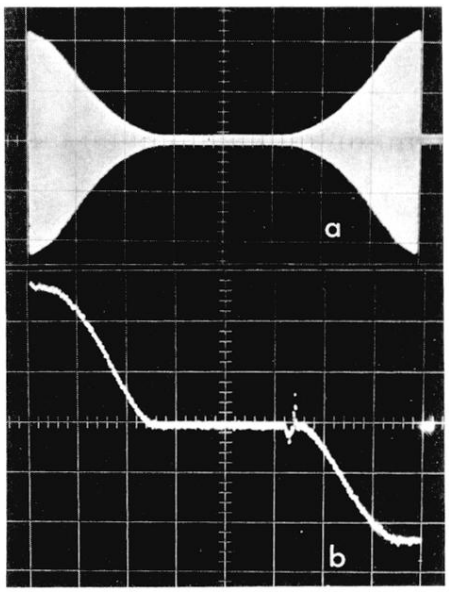

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