PHYSICAL REVIEW B VOLUME 22, NUMBER 11 1 DECEMBER 1980

Quasistationary magnetization in pulsed spin-locking experiments in dipolar solids

D. Suwelack* and J. S. Waugh
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 27 May 1980)

The quasistationary magnetization in dipolar solids for pulsed spin-locking experiments is calculated. A temporary equilibrium after several pulses is assumed to develop under a Hamiltonian obtained with average Hamiltonian theory from the terms for the rf field and the dipolar interaction. The effect of finite pulse width is discussed. Experimental data from a CaF_2 sample support the theoretical results. It is shown that pulse flip angles $\phi_x = 180° \pm \epsilon$ have the same effect as the flip angle ϵ.

I. INTRODUCTION

Ever since the first multiple-pulse experiment on dipolar solids[1] showed a dramatically prolonged decay of the nuclear magnetization, a number of papers[2–5] have treated the so-called short- and long-time behavior of the magnetization under pulsed spin-locking conditions of the more general $90_y - (\tau - \phi_x - \tau)^N$ type. (This notation means a 90° pulse polarized along the y axis of the rotating frame followed by a train of x-polarized pulses of flip angle ϕ and spacing 2τ.) The short-time behavior is characterized by a quasiequilibrium which is reached after a few times T_2, the normal transverse relaxation time. For longer times a slow exponential decay becomes evident, given by a time constant T_{2e} which has an upper bound of $T_{1\rho}$, the relaxation time in the rotating frame. In this paper we focus our attention on the short-time behavior.

Rhim *et al.*[3] showed that preliminary data for the magnetization in the quasiequilibrium state could be described by the formula

$$\frac{M_{st}}{M_0} = \frac{\overline{H}_1^2}{\overline{H}_1^2 + H_L'^2} , \tag{1}$$

with $\overline{H}_1$ as the average rf field and H_L' the local dipolar field. This formula is well known to apply to cw spin-locking experiments[9] but is not directly applicable to the special conditions of pulsed spin locking and hence does not account for different values for ϕ_x and the effect of nonzero pulse width. More recently Erofeev and Shumm[4(a)] and Ivanov, Provotorov, and Fel'dman[4(b)] presented new data for this multiple-pulse experiment, gave a different theoretical approach to describe their results, and questioned the applicability of average Hamiltonian theory[6] to these kinds of NMR experiments in dipolar solids. While the question of the scope of validity of the average Hamiltonian theory will be discussed in a more general fashion in a forthcoming paper,[7] some of their criticisms are easily answered. Concerning the long-time behavior, the authors of Ref. 4 show that T_{2e} is often not proportional to a negative integer power of τ, as had been suggested by an earlier analysis,[2] and state that this fact contradicts the predictions of average Hamiltonian theory. In fact, that theory makes no such predictions.

Other arguments concerning the short-time behavior will be discussed in Sec. II of this paper, where we shall outline a calculation for obtaining an equation for the quasiequilibrium magnetization using the average Hamiltonian theory and the spin temperature concept. Aspects of finite pulse widths and pulses near 180° will also be discussed. The third section describes the experimental details and the fourth section shows the experimental results.

II. THEORY

We begin our calculation with the secular part of the dipolar Hamiltonian in a high magnetic field (in the rotating frame)

$$\mathcal{H}_R = \mathcal{H}_d^0 , \tag{2}$$

with

$$\mathcal{H}_d^0 = C^d \sum_{i<j} R_{20}^{ij} T_{20}^{ij} , \tag{3}$$

using Haeberlen's[8] definitions and notations for the constant C^d and the irreducible tensor elements $R_{l,m}$ and $T_{l,m}$ for the spatial and spin dependence of $\mathcal{H}_d$, respectively. At $t=0$ a $\frac{1}{2}\pi$ rotation about the y axis is applied, and the spin components T transform into T' according to

$$T_{lm}' = \sum_{m'} D_{m'm}^{l}(0, \tfrac{1}{2}\pi, 0) T_{lm'} ; \tag{4}$$

D is the usual Wigner rotation matrix. The dipolar Hamiltonian in this titled rotating frame reads then as

$$\mathcal{H}_d^{0\prime} = C^d \sum_{i<j} R_{20}^{ij} [-\tfrac{1}{2} T_{20}^{ij} + \sqrt{3/8} (T_{22}^{ij} + T_{2-2}^{ij})] \ . \tag{5}$$

The multiple-pulse sequence of the $90_y - (\tau - \phi_x - \tau)^N$ experiment consists of a burst of identical rf pulses at exact resonance polarized along the new z axis of this frame. We can therefore write the total Hamiltonian as

$$\mathcal{H}_{TR} = -\omega_1(t) I_z + \mathcal{H}_d^0 \ , \tag{6}$$

where the time-dependent $\omega_1(t)$ can be split in a constant term $\overline{\omega}_1$ and an rf field $\omega_p(t)$ with zero average. In the next step we perform a canonical transformation on $\mathcal{H}_{TR}$ and arrive in a "switched" frame by applying a rotation about I_z with

$$\psi(t) = \int_0^t \omega_p(t') dt' \ . \tag{7}$$

Following Eq. (4) we obtain

$$\mathcal{H}_{SRT} = -\overline{\omega}_1 I_z + C^d \sum_{i<j} R_{20}^{ij} [-\tfrac{1}{2} T_{20}^{ij} + \sqrt{3/8} (T_{22}^{ij} e^{i2\psi(t)} + T_{2-2}^{ij} e^{-i2\psi(t)})] \ . \tag{8}$$

The phase factor in the nonsecular terms $T_{2\pm 2}$ is periodic and can therefore be expanded into a Fourier series

$$e^{2i\psi} = \sum_{n=-\infty}^{\infty} c_n \exp(in 2\pi t / 2\tau) \ . \tag{9}$$

The calculation up to this point is very similar to the one shown in Ref. 4(b) and the main difference is that so far we have made no assumption for the pulse shape. For the observation of the short-time behavior of the magnetization we are interested in a stroboscopic sampling of the signal once every cycle. Hence, $\mathcal{H}_{SRT}$ is now treated by the average Hamiltonian method. To lowest order,

$$\overline{\mathcal{H}}^{(0)} = \frac{1}{t_c} \int_0^{t_c} \mathcal{H}_{SRT}(t)\, dt \ , \tag{10}$$

and we obtain

$$\overline{\mathcal{H}}^{(0)} = -\overline{\omega}_1 I_z + C^d \sum_{i<j} R_{20}^{ij} [-\tfrac{1}{2} T_{20}^{ij} + \sqrt{3/8}\, c_0 (T_{22}^{ij} + T_{2-2}^{ij})] \ . \tag{11}$$

The nominal criterion for being able to omit higher-order terms in $\overline{\mathcal{H}} = \sum_n \overline{\mathcal{H}}^{(n)}$ is that $\overline{\omega}_1 t_c = \overline{\omega}_1 2\tau << 1$. Since $\overline{\omega}_1 2\tau$ represents the angle ϕ_x through which the magnetization is flipped by each pulse, this criterion is the same as $\phi_x << 1$; i.e., we may expect Eq. (11) to be valid in the limit of small flip angles. In Ref. 4 it is stated that the average Hamiltonian does not account for the shape of the magnetization signal between pulses. Of course this is true: as remarked above, $\overline{\mathcal{H}}$ claims to describe only the behavior of the system as observed stroboscopically, once following each pulse. They however also make the more substantial criticism that $\overline{\mathcal{H}}$ does not predict the proper approach of the stroboscopically observed signal to a quasistationary state over several T_2, but before the slow exponential decay is evident. We now proceed using $\overline{\mathcal{H}}^{(0)}$ from Eq. (11) to show that this is not the case. We assume that the spin system approaches a (temporary) thermal equilibrium under $\overline{\mathcal{H}}^{(0)}$, beginning from an initial condition $M_z = M_0$. The standard apparatus of spin thermodynamics for a sudden change in Hamiltonian[9] gives the stationary magnetization M_{st} as

$$\frac{M_{st}}{M_0} = \frac{(\overline{\omega}_1)^2}{(\overline{\omega}_1)^2 + D_{eff}^2} \ , \tag{12}$$

where D_{eff}^2, the trace over the squared dipolar part of $\overline{\mathcal{H}}^{(0)}$, is calculated to be

$$D_{eff}^2 = (\gamma H_L')^2 (\tfrac{1}{4} + \tfrac{3}{4} c_0^2) \ , \tag{13}$$

yielding

$$\frac{M_{st}}{M_0} = \frac{1}{1 + (H_L'/\overline{H}_1)^2 (\tfrac{1}{4} + \tfrac{3}{4} c_0^2)} \ , \tag{14}$$

with the dipolar local field H_L'. The result Eq. (14) differs from Eq. (1) given by Rhim *et al.*[3] in that it takes into account the multiple-pulse conditions of the spin-locking experiment and from the one given in Ref. 4 which fails for small values of $\overline{H}_1$ in that it predicts a finite stationary magnetization even in the limit $\overline{H}_1 \to 0$ (or $\tau \to \infty$).

The coefficients of the Fourier series[9] are given by

$$c_n = \frac{1}{t_c} \int_0^{t_c} \psi(t) \exp(-in 2\pi t / t_c)\, dt \tag{15}$$

with $\psi(t)$ from Eq. (7). For δ pulses we obtain

$$c_0^2 = \left[\frac{\sin\phi_x}{\phi_x} \right]^2 \ , \tag{16}$$

and the result for a finite pulse width is

$$c_0^2 = \left[\frac{\sin[2\phi_x(1-\zeta)]}{2\phi_x(1-\zeta)} \right]^2 + \left[\frac{1-\cos[2\phi_x(1-\zeta)]}{2\phi_x(1-\zeta)} \right]^2 \tag{17}$$

with the duty factor ζ. The function Eq. (17) is plotted in Fig. 1 for several ϕ_x values. Since c_0^2 does not change over a wide range for small flip angles, the

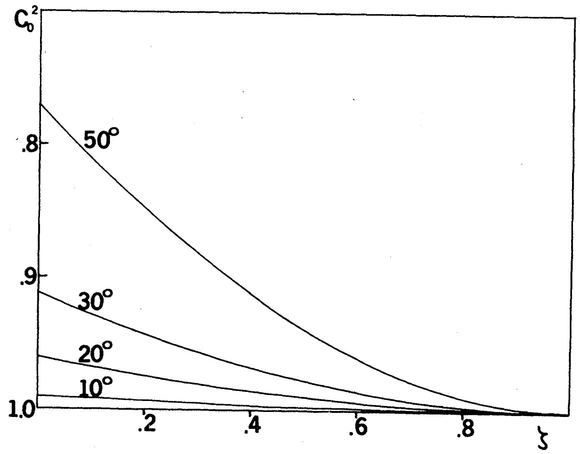

FIG. 1. Squared zero-order Fourier coefficient calculated from Eq. (17) as a function of the duty factor of the multiple-pulse cycle for various flip angles ϕ_x.

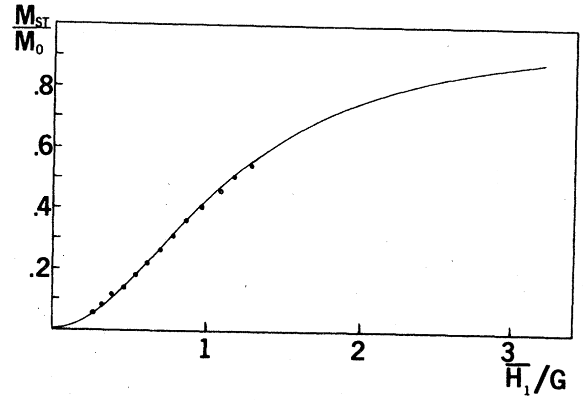

FIG. 2. Normalized stationary magnetization as a function of the average rf field $\bar{H}_1$ for a flip angle of $\phi_x = 10.8°$. The experimental data (points) agree with the behavior predicted from Eqs. (14) and (17) (solid line).

stationary magnetization will not be strongly affected by variations in ζ.

III. EXPERIMENTAL

As in the previously published investigations[3,4] we chose a CaF_2 crystal to test the theoretical results and oriented its [111] axis approximately parallel to the H_0 field direction. A home-built spectrometer with a superconducting magnet at $H_0 = 4.0$ T and a 1 kW rf amplifier was used. The probe consists of a R-L-C series resonance circuit with a quality factor Q of about 10 to avoid phase glitch effects.[10] The magnetization M_0 at $t = 0$ after the $\frac{1}{2}\pi y$ pulse and the local field H_L' were obtained from a plot of $M(t)$ as a function of t^2 for small times t using the moment expansion for $M(t)$

$$M(t) = M_0(1 - \tfrac{1}{2}M_2 t^2 + \cdots) \qquad (18)$$

and

$$H_L' = \sqrt{M_2/3} \ . \qquad (19)$$

Here M_2 is the second moment of the CaF_2 spectrum in this orientation. The point $t = 0$ lies in the middle of the finite-width $\frac{1}{2}\pi y$ pulse and a local field of $H_L' \simeq 1.17$ G resulted. The peak value of the rf field H_1 and the flip angle ϕ_x were obtained from a plot of the magnetization M_0 as a function of the pulse width t_p

$$M_0(t_p) = M_0 \sin(\omega_1 t_p) \ . \qquad (20)$$

The average rf field of the multiple-pulse experiment $\bar{H}_1$ was varied by changing the time 2τ between pulses. The average magnetization between the pulses was measured between about three to five T_2's. Thus all experimental parameters for Eq. (14) were determined.

IV. RESULTS AND DISCUSSION

Representative results for two different flip angles are shown in Figs. 2 and 3. The solid lines were calculated from Eqs. (14) and (17) (using the measured local field H_L' and the flip angle ϕ_x) and describe the experimental data (points) rather nicely. The broken line in Fig. 3 displays the behavior of the stationary magnetization as given by the equation in Ref. 4.

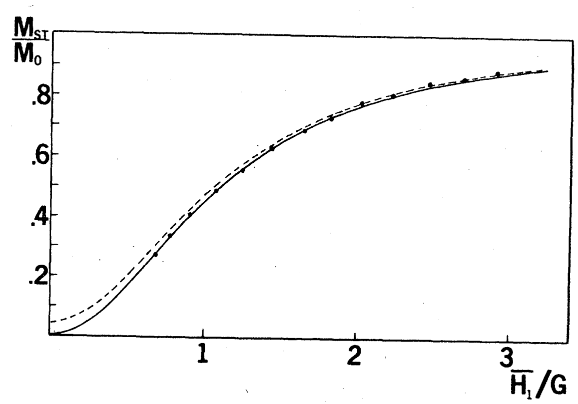

FIG. 3. Normalized stationary magnetization vs the average rf field $\bar{H}_1$ for a flip angle $\phi_x = 32.2°$. The solid line was calculated from Eqs. (14) and (17). The broken line was obtained from Ref. 4 with parameters that were used in this experiment. For small fields $\bar{H}_1$ it deviates slightly from our results.

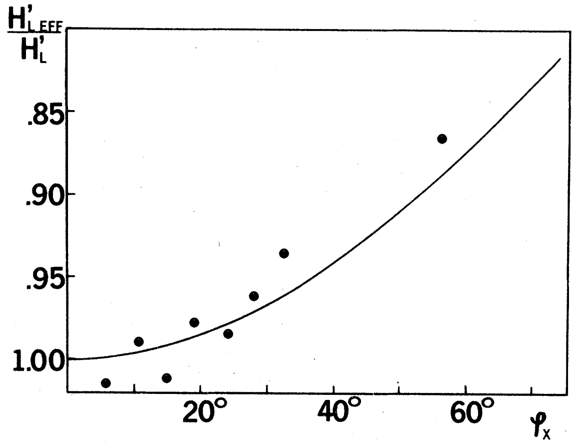

FIG. 4. Normalized effective field vs pulse angle. The experimental points were obtained from a fit of the data for each angle to Eq. (12). The theoretical curve follows $(\frac{1}{4}+\frac{3}{4}c_0^2)$ and describes the data within their experimental errors (mean deviation 1.6%).

Deviations from our results are clearly visible in the low-field ($\bar{H}_1$) part of the plot, especially for the limit $\bar{H}_1 \rightarrow 0$, where the broken line predicts a finite stationary magnetization. Another way of presenting the data was chosen for Fig. 4. With the knowledge of the average rf field $\bar{H}_1$, one can fit the experimental data to Eq. (12) and obtain an effective local field, which should follow the field that can be calculated from Eq. (13)

$$H'_{L_{\rm eff}} = H'_L(\tfrac{1}{4}+\tfrac{3}{4}c_0^2)^{1/2} \ . \tag{21}$$

Figure 4 now shows the ratio $H'_{L_{\rm eff}}/H'_L$ for all experiments (points) and for Eq. (21). Considering the mean deviation of only 1.6% the experimental points are well represented by the calculated line, even for relatively large values of ϕ_x where $\phi_x \sim 1$ holds.

Also data were taken for flip angles $\phi_x = \pi \pm \epsilon$ with small ϵ. When performing these experiments we observed a decrease and subsequent increase of the stationary magnetization as a function of ϕ_x by raising ϕ_x up to π and going higher. In fact, by separating the π part from ϕ_x one can perform the transformation as for Eq. (8) and obtain the Hamiltonian H_{STR}, where only the ϵ part survives since H_{TR} does not change under a π rotation as can be confirmed with Eq. (4). The data for an experiment with $\phi_x = 180° + 16.6°$ and $\phi_x = 180° - 16.1°$ are therefore well described by Eq. (14) where c_0 is calculated for an angle of 16.6° and 16.1°, respectively, as is shown in Fig. 5.

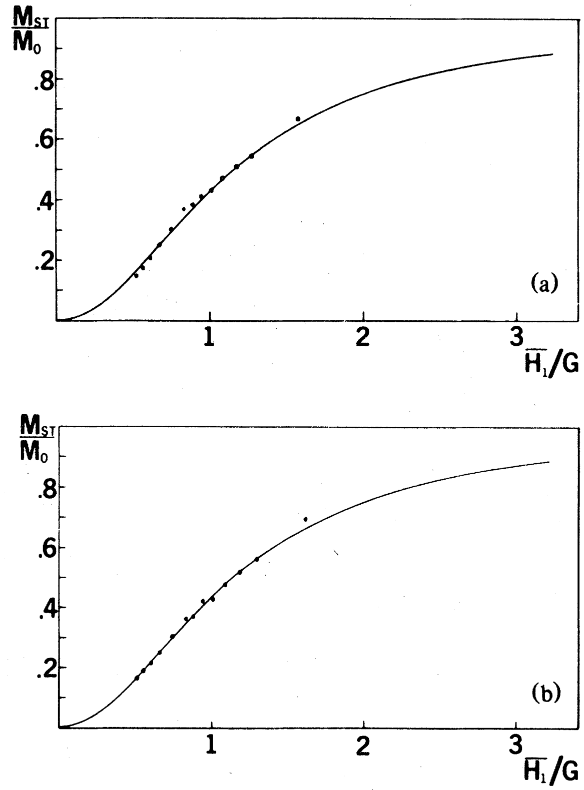

FIG. 5. Normalized stationary magnetization vs the average rf field $\bar{H}_1$ for flip angles (a) $\phi_x = 180° + 16.6°$ and (b) $\phi_x = 180° - 16.1°$. The solid line was calculated from Eqs. (14) and (16) by using flip angles and pulse times that resulted from the difference between the actual values and the π-pulse condition.

We have shown that the short-time behavior in the pulsed spin-locking experiment for dipolar solids can be understood in terms of spin thermodynamics, where the quasistationary state is approached under a Hamiltonian that can be calculated with average Hamiltonian theory. The experimental data are in good agreement with our theoretical results.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation.

*Present address: Institut für Physik, Universität Dortmund, 46 Dortmund, Federal Republic of Germany.

[1]E. D. Ostroff and J.S. Waugh, Phys. Rev. Lett. 16, 1097 (1966).
[2]J. S. Waugh and C. H. Wang, Phys. Rev. 162, 209 (1967).
[3]W. K. Rhim, D. P. Burum, and D. D. Elleman, Phys. Rev. Lett. 37, 1764 (1976).
[4](a) L. N. Erofeev and B. A. Shumm, Pis'ma Zh. Eksp. Teor. Fiz. 27, 161 (1978) [JETP Lett. 3, 149 (1978)]; (b) Yu. N. Ivanov, B. N. Provotorov, and E. B. Fel'dman, Pis'ma Zh. Eksp. Teor. Fiz. 27, 164 (1978) [JETP Lett. 3, 153 (1978)].
[5]L. N. Erofeev, B. A. Shumm, and G. B. Manelis, Zh. Eksp. Teor. Fiz. 75, 1837 (1978) [Sov. Phys. JETP 48, 925 (1979)]; Yu. N. Ivanov, B. N. Provotorov, and E. B. Fel'dman, Zh. Eksp. Teor. Fiz. 75, 1847 (1978) [Sov. Phys. JETP 48, 930 (1979)].
[6]U. Haeberlen and J. S. Waugh, Phys. Rev. 175, 453 (1968).
[7]M. Goldman and J. S. Waugh (unpublished).
[8]U. Haeberlen, *High Resolution NMR in Solids* (Academic, New York, 1976).
[9]M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Oxford Univ. Press, Oxford, 1970).
[10]J. D. Ellett, M. G. Gibby, U. Haeberlen, L. M. Huber, M. Mehring, A. Pines, and J. S. Waugh, Adv. Magn. Reson. 5, 117 (1971).