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ABSTRACT

The spin temperature hypothesis is extended to a system of nuclear spins with internal magnetic dipolar interactions and subject to periodic external perturbation in the form of intense radiofrequency pulses. Preliminary results are described for the case of phase-alternated irradiation at resonance.

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The spin temperature hypothesis has provided an extremely useful tool for the understanding and development of nuclear magnetic resonance in solids.(1) The substance of the hypothesis, as related to our interest, is that a system of nuclear spins coupled by magnetic dipolar interactions in a solid approaches, in a time T_2, a state of internal equilibrium characterized by a spin temperature. Under special experimental conditions, this assumption has been shown to be invalid,(2) but we shall not be concerned with such experiments in the present case. We find that when a strong time-dependent perturbation, in the form of a sequence of intense radiofrequency pulses, is applied to such a spin

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system, the concepts of spin thermodynamics and statistical mechanics may still be employed with respect to a time-independent average Hamiltonian[3] in a frame of reference defined by the external perturbation. This is an extension of Redfield's hypothesis of spin temperature in the rotating frame[4] to a more general periodic and cyclic excitation. The form of the time-independent average Hamiltonian can be imposed by appropriate selection of the excitation, and thus, this concept constitutes a powerful means not only of treating the long term behavior of such a time-dependent system by spin thermodynamics, but also of experimentally modifying thermodynamic parameters such as spin heat capacities. This should have consequences in several areas, for example the enhancement of sensitivity in double-resonance experiments.[5]

Figure 1 depicts one of the pulse sequences used in the present experiments, performed on the ^{19}F spins in a crystal of CaF_2. An adiabatic demagnetization in the rotating frame (ADRF), or else a $(\pi/2)_y - (\pi/4)_x$ pulse pair,[6] prepares the system in a state of high inverse dipolar spin-temperature β_o, characterized by the density operator:

$$\rho_o = \frac{1}{Z_o} \exp\left(- \beta_o H_d^o\right) \tag{1}$$

where $Z = T_r\left\{\exp\left(- \beta_o H_d^o\right)\right\}$ and H_d^o is the usual truncated dipolar interaction[7] amongst ^{19}F spins. The subsequent irradiation $H_1(t)$, consists of a series of resonant rf pulses

of nutation angle θ with an alternation of phases by π every pulse. In general, the treatment of the response of the system to this excitation would be an intractable problem; however, we apply the concepts of average Hamiltonian theory, and assume that if $\tau << T_2$, then in zero order we may consider the system to behave as if under the influence of a time independent average dipolar Hamiltonian $\overline{H}_d^o$ in an interaction picture defined by $H_1(t)$,

$$\overline{H}_d^o = \frac{1}{2\tau} \int_o^{2\tau} \tilde{H}_d^o(t)\, dt \tag{2}$$

where:

$$\tilde{H}_d^o(t) = T \exp\left(\int_o^t - \frac{it'}{\hbar} H_1(t')\, dt'\right) H_d^o\, T \exp\left(\int_o^t \frac{it'}{\hbar} H_1(t')\, dt'\right) \tag{3}$$

and T is a time ordering operator. We now assume that after a sufficiently long time, the system can be described in the new picture by a canonical density matrix:

$$\rho_1 = \frac{1}{Z_1} \exp\left(- \beta_1\, \overline{H}_d^o\right) \tag{4}$$

The rf irradiation is now terminated. We can inquire into: (a) the short time behavior of the system, and (b) the dipolar spin-temperature of the final state. The time

dependent relative magnetization upon termination of the pulse sequence is given by:

$$S_1(t) = \frac{T_r \left\{ \exp\left(-\frac{it}{\hbar} H_d^o\right) \rho_1 \exp\left(\frac{it}{\hbar} H_d^o\right) I_x \right\}}{T_r \left\{ I_x^2 \right\}} \tag{5}$$

Using the high temperature approximation for ρ_1 in (4) and solving for $\overline{H}_d^o$ in the case of ideal "δ-pulses," we find after some algebra:

$$S_1(t) = - \sin\theta \cos\theta \, S_d(t) \tag{6}$$

where $S_d(t)$ is the normal dipolar free induction decay[8] observed from a system in a state described by (1), i.e.,

$$S_d(t) = \frac{T_r \left\{ \exp\left(-\frac{it}{\hbar} H_d^o\right) P_x \rho_o P_{-x} \exp\left(\frac{it}{\hbar} H_d^o\right) I_x \right\}}{T_r \left\{ I_x^2 \right\}} \tag{7}$$

and P_x is a $\left(\frac{\pi}{4}\right)_x$ pulse. This is remarkable: it predicts a transient signal, following termination of the irradiation, of shape identical to a dipolar signal. This is exactly borne out experimentally.

To determine the long time behavior, we assume that during the pulse sequence the average dipolar energy $\langle \overline{H}_d^o \rangle$ is conserved, and that after the irradiation, $\langle H_d^o \rangle$ is conserved. The final state of the system is described by:

$$\rho_2 = \frac{1}{Z_2} \exp\left(- \beta_2 \, H_d^o\right) \tag{8}$$

Employing equations (1)-(4) and the dipolar energy conservation, we obtain after some algebra:

$$\frac{\beta_2}{\beta_o} = \frac{1}{4}\left(1 + 3\cos^2\theta\right) \tag{9}$$

These expressions are easily generalized to the case of non-ideal pulses.[9]

Figure 2 depicts the nutation angle dependence of our observed signals. $S_1(t)/S_d(t)$ is the relative intensity of the transient observed on termination of the sequence, and β_2/β_o is the final relative/inverse dipolar spin-temperature. The theoretical formulae are given in footnote 9, and are close to (6) and (9) since $\delta << 1$. The agreement indicates that despite the complexity of the problem, the assumption of quasi-equilibrium during the strong time dependent excitation is a useful one, and that quantitative predictions may be made. Details will be published elsewhere.

Interestingly, in the continuous resonant irradiation experiment of Jeener and Broekaert,[10] the average dipolar Hamiltonian is identical to our situation in which $\theta = \pi/2$. For this case, equations (6) and (9) predict no transient, and $\beta_2 = \frac{1}{4}\beta_o$ as was indeed observed by the above authors. More general excitations, particularly the case of non-resonant irradiation[11] are currently being investigated.

References and Footnotes

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9. If the pulse train does not consist of ideal "δ-pulses" then the modified expressions for equations (6) and (9) are: $S_1(t) = -\sin\theta \; p(\theta) \; S_d(t)$ and $\beta_2/\beta_o = (1 + 3\cos\theta \; p(\theta))^2/4(1 + 3p^2(\theta))$ where $p(\theta) = (1 - \delta)\cos\theta + \delta \sin\theta/\theta$ and δ is the rf duty factor.
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Figure Captions

Figure 1: Pulse sequence used in the experiment. θ_x denotes a pulse of nutation angle θ along the x axis in the rotating frame. The final $\left(\frac{\pi}{4}\right)$ pulse probes the dipolar order remaining in the system. The dotted lines depict schematically the type of transient signal observed.

Figure 2: Relative signal intensity for the two transients compared to the normal unperturbed dipolar free induction decay observed for ^{19}F spins in CaF_2 on application of pulse sequence in figure 1. S_1/S_d is the relative intensity of the first transient and β_2/β_o is the relative final imerse dipolar temperature, i.e., the relative intensity of the second transient. The solid curves are taken from footnote 9 with $\delta << 1$ variable, corresponding to the experimental conditions.

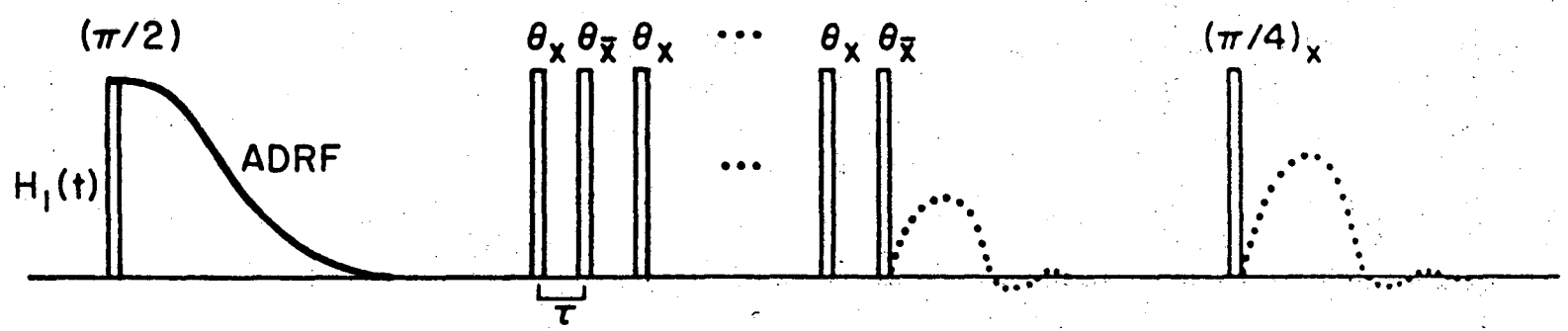

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Fig. 1

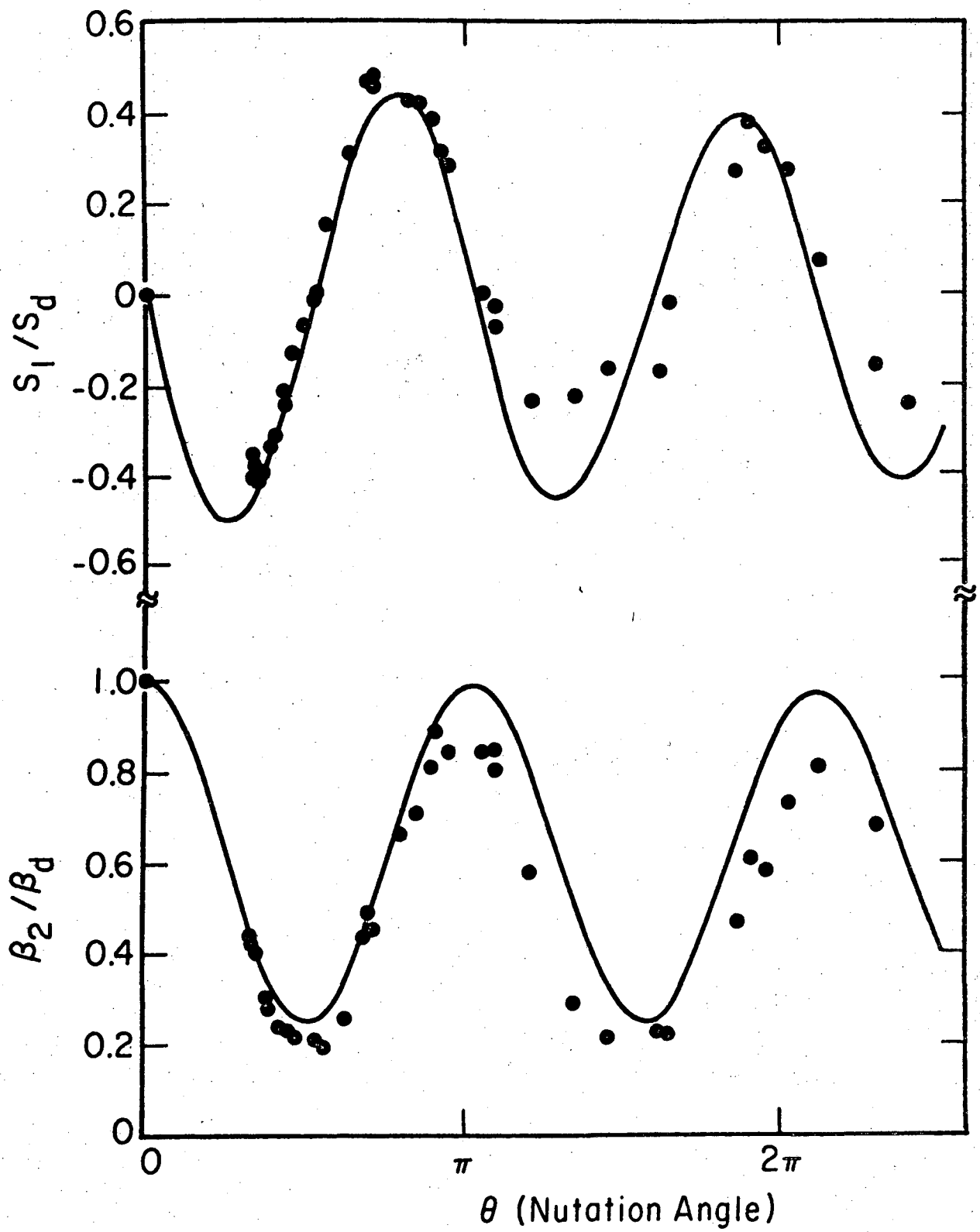

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Fig. 2

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