DIPOLAR SPIN TEMPERATURE IN A PERIODICALLY PERTURBED NUCLEAR SPIN SYSTEM[☆]

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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.

The spin temperature hypothesis has provided an extremely useful tool for the understanding and development of nuclear magnetic resonance in solids [1]. We find that when a strong time-dependent perturbation, in the form of a sequence of intense radiofrequency pulses, is applied to a spin system, the concepts of spin thermodynamics and statistical mechanics may still be employed with respect to a time-independent average Hamiltonian [2] 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 [3].

Fig. 1 depicts one of the pulse sequences used in present experiments. An adiabatic demagnetization in the rotating frame (ADRF) prepares the system in a state of high inverse dipolar spin-temperature $\bar{\beta}_0$, characterized by the density operator:

$$\rho_0 = \frac{1}{Z_0} \exp(-\beta_0 \mathcal{H}_d^0), \tag{1}$$

where $Z = \mathrm{Tr}\,\{\exp(-\beta_0 \mathcal{H}_d^0)\}$ and $\mathcal{H}_d^0$ is the usual truncated dipolar interaction amongst ^{19}F spins. The subsequent irradiation $\mathcal{H}_1(t)$, consists of a series of resonant rf pulses of nutation angle θ with an alternation of phases by π every pulse. We assume that if $\tau \ll T_2$, we may consider the system to behave as if under the influence of a time independent average dipolar Hamiltonian $\bar{\mathcal{H}}_d^0$ in an interaction picture defined by $\mathcal{H}_1(t)$,

$$\bar{\mathcal{H}}_d^0 = \frac{1}{2\tau}\int_0^{2\tau} T \exp\left(\int_0^t -\frac{it'}{\hbar}\, \mathcal{H}_1(t')\,\mathrm{d}t'\right)\mathcal{H}_d^0 \tag{2}$$

$$\times\; T \exp\left(\int_0^t \frac{it'}{\hbar}\, \mathcal{H}_1(t')\,\mathrm{d}t'\right)\mathrm{d}t,$$

and T is a time ordering operator. We now assume that after a sufficiently long time, the system can be de-

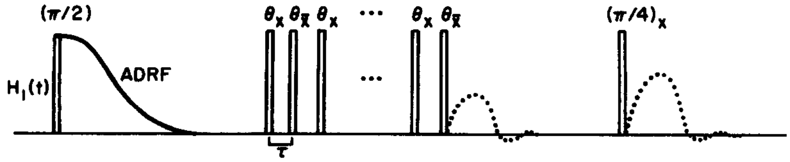

Fig. 1. Pulse sequence used in the experiment. The dotted lines depict schematically the type of transient signal observed.

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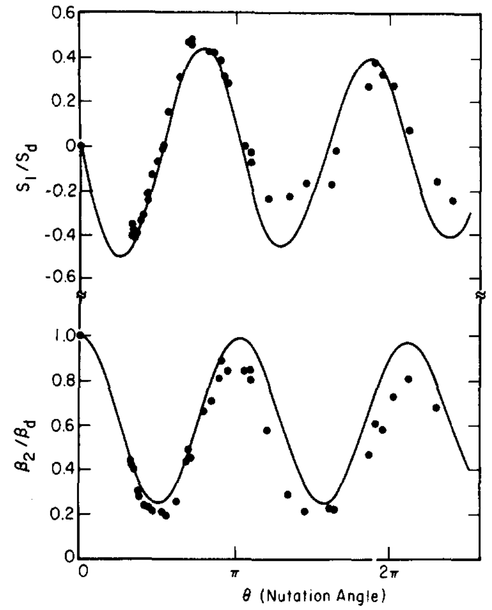

Fig. 2. Relative signal intensity for the two ^{19}F transient in CaF_2 on application of pulse sequence in fig. 1. S_1/S_d is the relative intensity of the first transient and β_2/β_0 is the relative final inverse dipolar temperature, i.e., the relative intensity of the second transient. The theoretical solid curves are taken from footnote ‡.

scribed in the new picture by a canonical density operator:

$$\rho_1 = \frac{1}{Z_1}\exp(-\beta_1 \bar{H}_d^0). \qquad (3)$$

The rf irradiation is now terminated. The time dependent relative magnetization upon termination of the pulse sequence is given by:

$$S_1(t) = \frac{\mathrm{Tr}\{\exp(-\mathrm{i}t\, \bar{H}_d^0/\hbar)\rho_1 \exp(\mathrm{i}t\, \bar{H}_d^0/\hbar) I_x}{\mathrm{Tr}\{I_x^2\}}. \qquad (4)$$

Using the high temperature approximation for ρ_1 in (3) and solving for $\bar{H}_d^0$ in the case of ideal "δ-pulses", we find:

$$S_1(t) = -\sin\theta\cos\theta\, S_d(t), \qquad (5)$$

where $S_d(t)$ is the normal dipolar free induction decay [4] observed from a system in a state described by (1) after a $(\pi/4)_x$ pulse. This is exactly borne out experimentally.

To determine the long time behavior, we assume that during the pulse sequence the average dipolar energy $\langle \bar{H}_d^0 \rangle$ is conserved, and that after the irradiation, $\langle H_d^0 \rangle$ is conserved. The final state of the system is described by (3) with subscript 1 replaced by 2. Employing eqs. (1) – (3) we obtain with some trival algebra:

$$\beta_2/\beta_0 = \tfrac{1}{4}(1 + 3\cos^2\theta). \qquad (6)$$

These expressions are easily generalized to the case of non-ideal pulses.‡

Fig. 2 depicts the nutation angle dependence of our observed signals in CaF_2. $S_1(t)/S_d(t)$ is the relative intensity of the transient observed on termination of the sequence, and β_2/β_0 is the final relative inverse dipolar spin-temperature. The agreement indicates that the assumption of quasi-equilibrium during the strong time dependent excitation is a useful one, and that quantitative predictions may be made.

Interestingly, in the continuous resonant irradiation experiment of Jeener and co-workers [5] the average dipolar Hamiltonian is identical to our situation in which $\theta = \pi/2$. For this case, eqs. (5) and (6) predict no first transient and $\beta_2 = \frac{1}{4}\beta_0$, as was indeed observed by the above authors.

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‡ The general expressions for (6) and (7) are: $S_1(t) = -\sin\theta\, p(\theta)\, S_d(t)$ and $\beta_2/\beta_0 = (1+3\cos\theta\, p(\theta))^2/4(1+3p^2(\theta))$ where $p(\theta) = (1-\delta)\cos\theta + \delta\sin\theta/\theta$ and δ is the rf duty factor.

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