Lawrence Berkeley National Laboratory
Recent Work

Title
DIPOLAR SPIN TEMPERATURE IN A PERIODICALLY PERTURBED NUCLEAR SPIN SYSTEM

Permalink
https://escholarship.org/uc/item/8jg2938t

Authors
Pines, A.
Waugh, J.S.

Publication Date
1973-12-01

eScholarship.org Powered by the California Digital Library
University of California

Submitted to Physics Letters A

LBL-2515
Preprint

DIPOLAR SPIN TEMPERATURE IN A PERIODICALLY PERTURBED NUCLEAR SPIN SYSTEM

A. Pines and J. S. Waugh

RECEIVED
LAWRENCE
RADIATION LABORATORY

JAN 9 1974

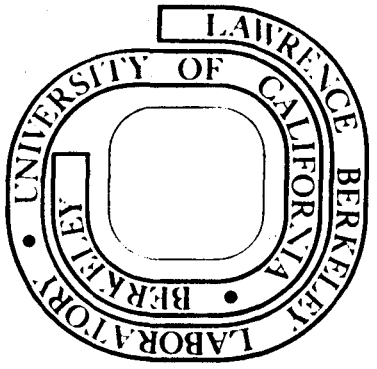
LIBRARY AND
DOCUMENTS SECTION

December 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545



LBL-2515

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-2515

DIPOLAR SPIN TEMPERATURE IN A PERIODICALLY PERTURBED NUCLEAR SPIN SYSTEM

A. Pines

Department of Chemistry, University of California
Berkeley, California 94720

and

J. S. Waugh

Department of Chemistry, Massachusetts Institute
of Technology, Cambridge, Massachusetts 02139

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.

DIPOLAR SPIN TEMPERATURE IN A PERIODICALLY PERTURBED NUCLEAR SPIN SYSTEM*

A. Pines
Department of Chemistry, University of California
Berkeley, California 94720

and

J. S. Waugh
Department of Chemistry, Massachusetts Institute
of Technology, Cambridge, Massachusetts 02139

(Received , 1973)

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

---

*Supported in part by the U. S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory and in part by the National Science Foundation.

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:

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

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 $\bar{H}_d^o$ in an interaction picture defined by $H_1(t)$,

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

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:

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

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:

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

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

$$S_1(t) = -\sin\theta \cos\theta\, S_d(t) \qquad (6)$$

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

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

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 $\langle\overline{H}_d^\circ\rangle$ is conserved, and that after the irradiation, $\langle H_d^\circ\rangle$ is conserved. The final state of the system is described by:

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

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.

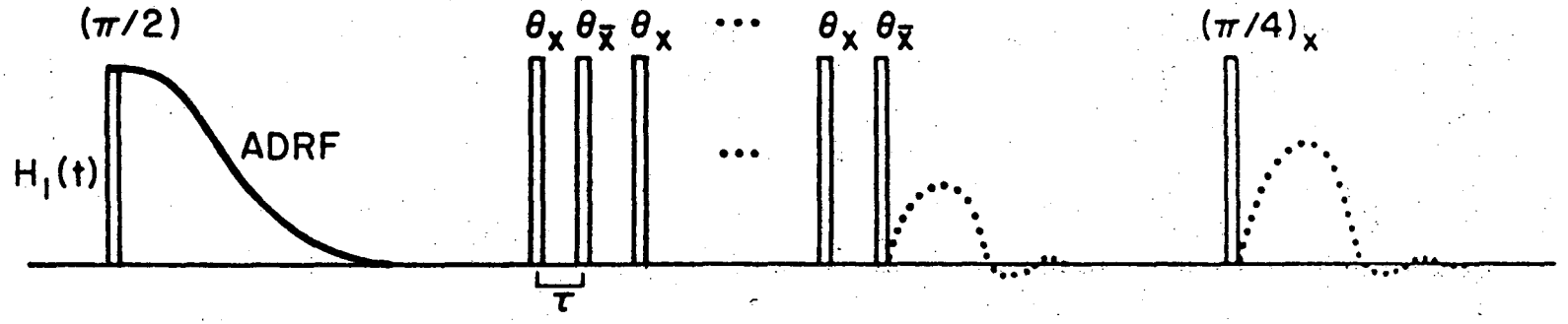
References and Footnotes

1. M. Goldman, Spin-Temperature and Nuclear Magnetic Resonance in Solids, Oxford U.P., London, 1970.
2. W-K. Rhim, A. Pines and J. S. Waugh, Phys. Rev. B3, 684 (1971).
3. U. Haeberlen and J. S. Waugh, Phys. Rev. 175, 453 (1968).
4. A. G. Redfield, Phys. Rev. 98, 1787 (1955).
5. S. R. Hartmann and E. L. Hahn, Phys. Rev. 128, 2042 (1962).
6. J. Jeener and P. Broeckaert, Phys. Rev. 157, 232 (1967).
7. J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).
8. A. G. Anderson and S. R. Hartmann, Phys. Rev. 128, 2023 (1962).
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.
10. J. Jeener, R. Dubois and P. Broekaert, Phys. Rev. 139 A1959 (1965).
11. A. Pines and J. S. Waugh, J. Mag. Res. 8, 354 (1972).

Figure Captions

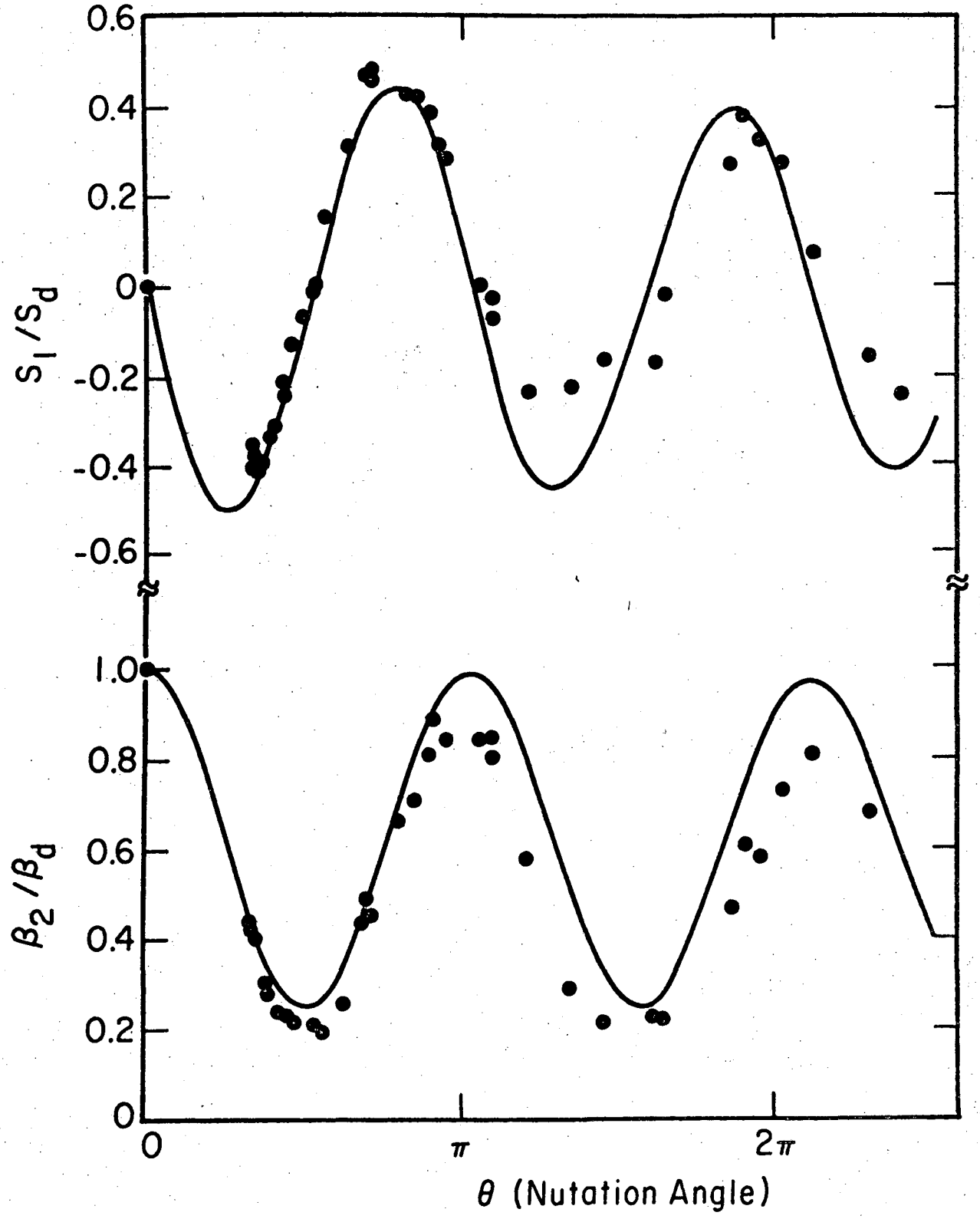
Figure 1: Pulse sequence used in the experiment. θ_x denotes a pulse of nutation angle θ along the x axis in the rotating frame. The final $\left(\frac{\pi}{4}\right)$ pulse probes the dipolar order remaining in the system. The dotted lines depict schematically the type of transient signal observed.

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.



XBL 7312-6852

Fig. 1



XBL 7312-6851

Fig. 2

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720