SPIN TEMPERATURE IN NUCLEAR DOUBLE RESONANCE*

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Several years ago, Hahn[1] made a brilliant proposal for a type of nuclear double resonance which promised a vast increase in sensitivity. His technique was based in part on the fact that two nuclear species of widely different gyromagnetic ratios, γ, are able to couple strongly together if alternating fields are applied at resonance with both species simultaneously. The amplitudes of the two alternating fields must be adjusted so that their ratio is the inverse of the ratio of the two γ's. By making periodic phase changes in the alternating field applied to the first species, the resonance signal of the second species is destroyed. If the ordinary resonance of the second species is strong, one may in this manner observe a resonance from a first species with much greater sensitivity than is possible from a direct resonance on the first species. A full description of Hahn's technique is rather long, and requires an understanding of Redfield's[2] important work on spin temperature in the rotating reference frame. Despite the importance of Hahn's idea, there have been few papers concerning it until recently.[3,4]

In this Letter we report (1) a thermodynamic description of the technique which enables one to see simply how the effect works and to include rigorously the effects of local fields, and (2) a quantitative experimental verification of the formulas. A simplified experimental technique is employed which is closely related to one reported earlier.[5] The experiments provide further confirmation of Redfield's spin-temperature concept[2] in the rotating reference frame.[6] The quantitative agreement is important since it shows that one can determine such things as the number of nuclei giving rise to the double resonance. The experiments also demonstrate that since the instrumental adjustments to achieve double resonance are not at all critical, the technique is relatively simple.

The experiments were performed at 1.5°K on metallic Li powder. The strong resonance of the 92.6% abundant isotope Li^7 was observed directly to detect the weak resonance of the 7.4% abundant Li^6. Rotating fields $(H_1)_6$ and $(H_1)_7$ in resonance, respectively, with the Li^6 and Li^7 nuclei were applied in a field H_0 of 9060 gauss.

The procedure is as follows: With $(H_1)_6 = (H_1)_7 = 0$, H_0 is pulsed about 16 gauss above resonance by passing a current through coils placed in the magnet gap. $(H_1)_7$ is turned on at the peak of the excursion. As H_0 returns to the resonance value (a time requiring about 40 msec), the Li^7 magnetization, M_7, follows the effective field in the rotating frame,[5] ending up aligned along $(H_1)_7$ when the H_0 pulse is over. The field $(H_1)_6$ is then pulsed on for a time t_{on}, then turned off for a time t_{off}, the on-off cycle being repeated N times. At the end of the N cycles, $(H_1)_7$ is abruptly turned to zero, and the amplitude of M_7 is measured by observing the initial height of the Bloch decay on an oscilloscope photograph. The values of $(H_1)_6$ and $(H_1)_7$ were several gauss, comparable to the local field.

The experiments reported here were all conducted in times short compared to the spin-lattice relaxation times of either species. The technique is seen to be identical to that of reference 5 except for the addition of $(H_1)_6$.

The experiment is analyzed following the ideas of Redfield. Denoting the Li^7's by I and the Li^6's by S, we have a Hamiltonian, $\mathcal{H}$, in the laboratory

$$\mathcal{H} = \mathcal{H}_{ZI}(t) + \mathcal{H}_{ZS}(t) + \mathcal{H}_{dII} + \mathcal{H}_{dIS} + \mathcal{H}_{dSS}, \qquad (1)$$

where $\mathcal{H}_{ZI}(t)$ is the time-dependent Zeeman interaction of the I spins with the static field H_0 and the rotating field $(H_1)_I$, and where $\mathcal{H}_{dII}$ is the dipolar coupling of the I spins among themselves, etc. We keep only the secular parts of the dipolar terms. Generalizing Redfield's approach slightly, one eliminates the time dependence from $\mathcal{H}$ by means of the transformation T given by

$$T = \exp[-i\omega_I I_z t]\exp[-i\omega_S S_z t], \qquad (2)$$

where

$$I_z = \sum_k I_{zk}, \quad S_z = \sum_j S_{zj} \qquad (3)$$

are the total z components of spin of the two species, ω_I and ω_S are the angular frequencies of the respective rotating fields. This transformation refers the I spins to a reference frame rotating at ω_I, the S spins to one rotating at ω_S.

The transformed Hamiltonian $\mathcal{H}'$ then becomes

$$\mathcal{H}' = T^{-1}\mathcal{H}T = -\gamma_I\hbar\{[H_0 - (\omega_I/\gamma_I)]I_z + (H_1)_I I_x\}$$
$$-\gamma_S\hbar\{[H_0 - (\omega_S/\gamma_S)]S_z + (H_1)_S S_x\}$$
$$+\mathcal{H}_{dII} + \mathcal{H}_{dIS} + \mathcal{H}_{dSS}$$
$$+\text{time-dependent terms we ignore.} \quad (4)$$

The secular dipolar terms are unaffected, but the Zeeman terms become independent of time (for notational simplicity we use $\mathcal{H}_{dII}$, etc., to stand for the secular terms only). Following Redfield, we postulate that this system will come to a common spin termperature after an adequate time. In the process, energy will be exchanged among the parts represented by different terms in Eq. (4) by cross relaxation. If the local fields could be neglected and $\gamma_I H_0 = \omega_I$, $\gamma_S H_0 = \omega_S$, the I and S spins would exchange Zeeman energy via the term $\mathcal{H}_{dIS}$, the exchange being fastest when $\gamma_I(H_1)_I = \gamma_S(H_1)_S$, Hahn's condition. As in all cross-relaxation experiments, however, this condition can be violated if one waits long enough, or if the local fields are large enough. Since typical local fields are several gauss, they can only be neglected if one uses very large H_1's, a condition violated in our experiments.

Assuming that during t_{on} or t_{off} a common spin temperature is reached, and following the analysis of reference 5 for sudden switching, one can show that the magneitzation of Li^7 after N pulses, $M_7(N)$, obeys the equation

$$M_7(N) = M_7(0)\exp[-N\epsilon], \quad (5)$$

where ϵ (assumed small) is

$$\epsilon = C_6(H_1)_6^2/C_7[(H_1)_7^2 + H_L^2], \quad (6)$$

where C_6 and C_7 are the respective Curie constants, and H_L^2 is

$$H_L^2 = (1/3)\langle\Delta^2 H\rangle_{II} + \langle\Delta^2 H\rangle_{IS}$$
$$+(1/3)\frac{\gamma_S^2 f_S S(S+1)}{\gamma_I^2 f_I I(I+1)}\langle\Delta^2 H\rangle_{SS}, \quad (7)$$

where $\langle\Delta^2 H\rangle_{IS}$ is the contribution in gauss of the S spins to the second moment of the I spins, f_I the fraction of spins of species I, etc. (an incorrect expression for H_L^2 was given in reference 5). H_L can be calculated exactly, and is 1.20 gauss for our experiments.

In our experiments the amplitudes of $(H_1)_6$ and $(H_1)_7$ were calibrated at room temperature by use of 180° pulses on (1) the Li^7 nuclei, and (2) the protons in the oil suspension surrounding the metal particles. At helium temperatures, a small vial containing liquid He^3 was inserted, and the He^3 resonance used to detect a 180° pulse. The three answers agree within ±3%.

Equation (5) can be studied by varying N or ϵ. In testing the theory, there are no adjustable constants, since $(H_1)_6$ and $(H_1)_7$ can be measured and C_6, C_7, and H_L^2 can be calculated exactly.

Figure 1 shows the variation of $\ln M_7$ vs N, holding ϵ constant for H_1's satisfying the Hahn condition. $(H_1)_7 = 2.14$ gauss. The theoretical slope, calculated using Eq. (6), is seen to agree well with the data. We have proven that the curvature is due to slight inhomogeneities in $(H_1)_6$ and $(H_1)_7$. Figure 2 shows $\ln M_7$ vs $(H_1)_6^2$ for fixed N. Since $\epsilon \propto (H_1)_6^2$, this should be a straight line. The experimental curves for $t_{on} = t_{off} = 1$, 2, and 10 msec show that (a) a common spin temperature is reached for certain values of $(H_1)_6$; (b) the range in $(H_1)_6$ about the Hahn condition over which a spin temperature is established is quite great if one waits long enough.

Equation (6) suggested that $(H_1)_7$ can even be

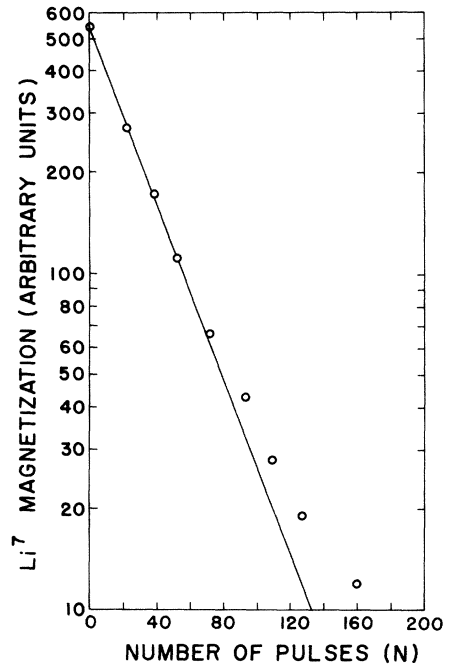

FIG. 1. $\ln M_7$ vs N. $(H_1)_7 = 2.14$ gauss, $(H_1)_6 = 5.4$ gauss, nearly satisfying the Hahn condition. $t_{on} = t_{off} = 4$ msec. The solid line is calculated using Eqs. (5) and (6). $H_L = 1.20$ gauss in lithium metal.

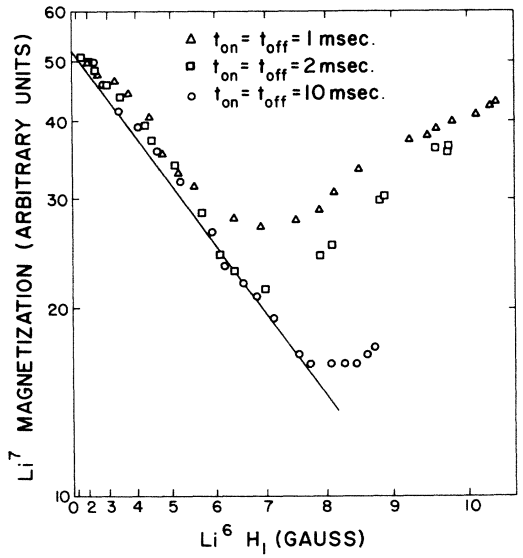

FIG. 2. $\ln M_7$ vs $(H_1)_6^2$ for $N = 22$, for $t_{on} = t_{off} = 1$, 2, and 10 msec. $(H_1)_7 = 2.31$ gauss. The solid line is calculated using Eqs. (5) and (6). $(H_1)_6 = 6.1$ gauss satisfies the Hahn condition.

turned to zero, in which case one can use lower values of $(H_1)_6$, an important advantage experimentally. The same idea has occurred independently to Hartmann and Hahn,[3] and Anderson and Hartmann,[3] and is similar to the technique of reference 4. The results of such measurements are shown in Fig. 3. [For these experiments, $(H_1)_7$ was turned slowly to zero following the H_0 pulse, then the $(H_1)_6$ pulses were applied, then $(H_1)_7$ was turned up slowly. The M_7 Bloch decay was then observed following the rapid turnoff of $(H_1)_7$.]

The agreement of the data, not only with the form of Eq. (5), but also with the actual magnitudes predicted by Eq. (6), demonstrates convincingly the validity and usefulness of the thermodynamic approach. The experimental technique is seen to be very simple, and the broad minima of Figs. 2 and 3 show that precise settings of the amplitude of the second alternating field are quite unnecessary in searching for unknown resonances.

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[6]A related set of experiments are those of M. Goldman and A. Landesman, Compt. Rend. 252, 263 (1961).

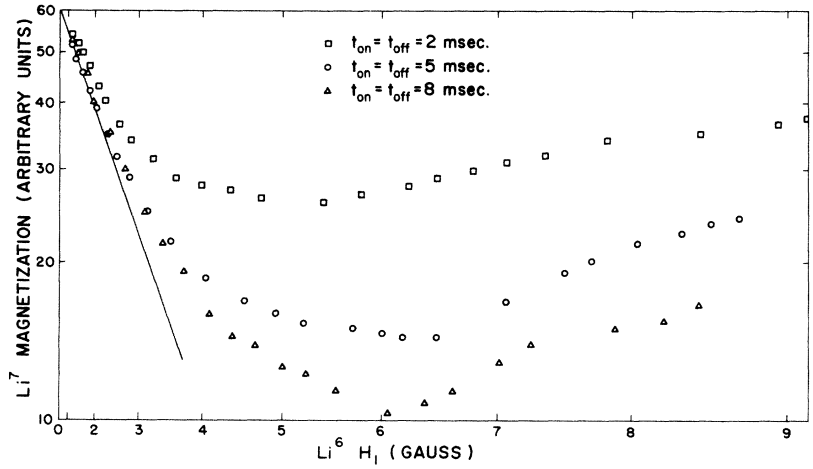

FIG. 3. $\ln M_7$ vs $(H_1)_6^2$ for $(H_1)_7 = 0$. $t_{on} = t_{off} = 2$, 5, and 8 msec. The solid line is calculated using Eqs. (5) and (6). Note the very broad minimum as a function of $(H_1)_6$.