Rate of establishment of a spin temperature in a rotating coordinate system

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An experimental study was made of the process of thermal mixing of the Zeeman and secular spin-spin subsystems in a rotating coordinate system using rf field intensities exceeding the local field intensity. An original sequence of pulses was applied to the system of the ^{19}F nuclear spins in CaF$_2$ in a static field oriented along the [111] axis. The Gaussian approximation was found to be incapable of describing the dependence of the mixing rate on the rf field intensity. A signal due to nonsecular dipole-dipole interactions in the density matrix was observed. Measurements were made of the spin-lattice relaxation time of the dipole reservior in the presence of an alternating field.

Although the rate of establishment of a common spin temperature T_m^{-1} is of fundamental importance, the process of thermal mixing of the Zeeman and dipole subsystems has not yet been investigated sufficiently on the experimental side. In particular, we know only of one study[1] in which measurements of T_m in a regular homonuclear magnetic material were made in a rotating coordinate system (RCS). The measurements reported in Ref. 1 were carried out under field detuning conditions and rf field amplitude H_1 varied within the limits of the NMR linewidth. As the field H_1 increased, the agreement between the theory and experiment in Ref. 1 deteriorated.

Our aim was to investigate the dependence of T_m on H_1 for values of H_1 exceeding the NMR linewidth under exact resonance conditions: $\omega = \omega_0 = 2\pi \times 22.5$ MHz. Measurements were carried out on CaF$_2$ samples with the field oriented along the [111] axis at ~ 300 K.

The sequence of pulses employed is shown in Fig. 1. Initially the spin system was in a state of equilibrium at the lattice temperature. The adiabatic demagnetization method in an RCS was used to transfer the system to a state with a very high value of the reciprocal of the temperature of the secular spin-spin subsystem and zero reciprocal temperature of the Zeeman subsystem. Then, after an interval of 300 μsec an rf field of the resonance frequency was applied for a time t_m. Exchange of energy with Zeeman subsystem lowered the reciprocal temperature β of the secular subsystem. The value of β was measured by the application of a 45°_y pulse.

During the action of the rf field the Hamiltonian of the system in the RCS is

$$\mathscr{H} = \omega_1 I_x + \mathscr{H}_d', \quad \omega_1 = \gamma_F H_1,$$
$$\mathscr{H}_d' = \sum_{i<j} a_{ij}\left[I_{zi} I_{zj} - {}^1/_4 (I_{+i} I_{-j} + I_{-i} I_{+j})\right], \tag{1}$$

where γ_F is the gyromagnetic ratio of the fluorine nuclei; I_{zi} and $I_{\pm i}$ are the spin operators.

Adopting a tilted RCS (TRCS) by transformation carried out using an operator $R = \exp(\frac{1}{2} i \pi I_y)$, we find that after a 90°_{-y} pulse, up to the moment of application of the rf field, the density matrix is

$$\sigma' = 1 - \beta \mathscr{H}_d', \quad \beta = H_0 \beta_L / H_L', \tag{2}$$

where H_L' is the local field in the RCS.

The Hamiltonian of the system expressed in the TRCS becomes

$$\mathscr{H}' = \omega_1 I_z + {}^3/_8 P - {}^1/_2 \mathscr{H}_d', \quad P = \sum_{i<j} a_{ij} (I_{+i} I_{+j} + I_{-i} I_{-j}). \tag{3}$$

It is known that the process of thermal mixing of the Zeeman and nonsecular spin-spin subsystems occurs in a time of the order of several T_2. Consequently, after several T_2, we have

$$\sigma' = 1 - \beta_1 (\omega_1 I_z + {}^3/_8 P) + {}^1/_2 \beta_2 \mathscr{H}_d'. \tag{4}$$

Application of the 90°_{-y} pulse yields in the RCS

$$\sigma = \sigma' \tag{4'}$$

and by the instant of application of the 45°_y pulse we have

$$\sigma = 1 - \beta_1 \omega_1 I_z + {}^1/_2 \beta_2 \mathscr{H}_d'. \tag{5}$$

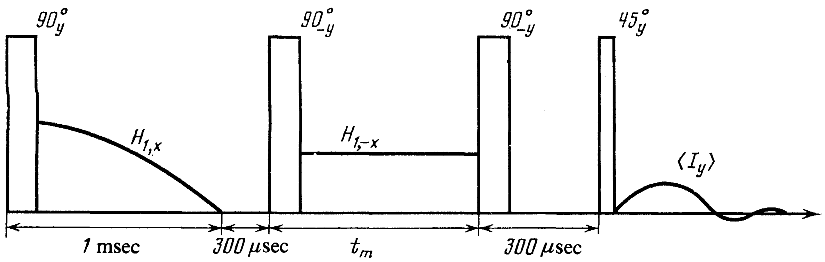

FIG. 1. Sequence of pulses used to determine T_m and T_{1dp}. The designations 90°_x, 90°_{-x} 90°_y, and 90°_{-y} indicate that the amplitude H_1 and the duration of the pulse τ are related by $\gamma H_1 \tau = \pi/2$. The subscripts x, y, $-x$, and $-y$ are the axes of the RCS relative to which the pulses are applied.

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Therefore, the above sequence of pulses makes it possible to observe (after the 45°_y pulse) a signal proportional to the reciprocal temperature β_2 of a dipole system secular in the TRCS. Determination of the change in the signal proportional to β_2 as a function of the duration t_m of application of the rf field gives the value of T_m. This method of determination of T_m has obvious advantages over the method based on measurements of the magnetization $\langle I_z \rangle$ (Ref. 1).

The problem of establishment of a spin temperature in the TRCS with the Hamiltonian (3) is equivalent to the same problem in a laboratory coordinate system considered in Ref. 2. A solution of the system of equations for the reciprocal temperatures β_1 and β_2 under the initial conditions corresponding to our pulse sequence has the following form when $\omega_1 > D$:

$$\beta_2=\beta_{20}\exp(-t/T_d), \quad T_d^{-1}=T_m^{-1}+T_{1d\rho}^{-1}, \qquad T_m^{-1}=W(4\omega_1^2/D^2),\ D=\gamma_F H_L'. \tag{6}$$

It follows that the time dependence of β_2 is a single exponential function.

It is clear from the system (6) that the rate of relaxation T_d^{-1} of the dipole reservior considered in the TRCS is governed by the rate of establishment of a common spin temperature T_m^{-1} and also by the spin-lattice relaxation rate of the dipole reservior $T_{1d\rho}^{-1}$ considered in the TRCS, which differs from the spin-lattice relaxation rate T_{1d}^{-1} in the RCS. The need to introduce $T_{1d\rho}^{-1}$ arises because in the RCS the density matrix (4) is

$$\sigma=1-\beta_1[\omega_1 I_x+{}^3/_8({}^1/_2P+2\mathscr{H}_d')]+{}^1/_2\beta_2({}^3/_8P-{}^1/_2\mathscr{H}_d'). \tag{7}$$

Consequently, in the presence of an alternating field we should speak of relaxation of the dipole system which has an energy operator

$$\exp\left(-i\frac{\pi}{2}I_y\right)\mathscr{H}_d'\exp\left(i\frac{\pi}{2}I_y\right)=\frac{3}{8}P-\frac{1}{2}\mathscr{H}_d',$$

whereas in discussing the dipole relaxation in the RCS the Hamiltonian of the dipole subsystem is assumed to be $\mathscr{H}_d'$ even in the presence of an alternating field.[2] The expressions for the time $T_{1d\rho}$ can in many cases be obtained by a simple replacement of the operator $\mathscr{H}_d'$ with

$$\exp\left(-i\frac{\pi}{2}I_y\right)\mathscr{H}_d'\exp\left(i\frac{\pi}{2}I_y\right)$$

in the appropriate formulas for T_{1d} (Ref. 2). The value of $T_{1d\rho}$ was first introduced for heteronuclear systems in Ref. 3. We shall now give the values of T_{1d} and $T_{1d\rho}$ found by us experimentally for different CaF_2 samples in the [111] orientation:

T_{1d}, sec	0,36	13,0	5,3	2,7	1,8
$T_{1d\rho}$, sec	0,30	8,8	7,6	3,2	1,5

If we follow Ref. 2, we find that W is given by [see Eq. (6.39) in Ref. 2]:

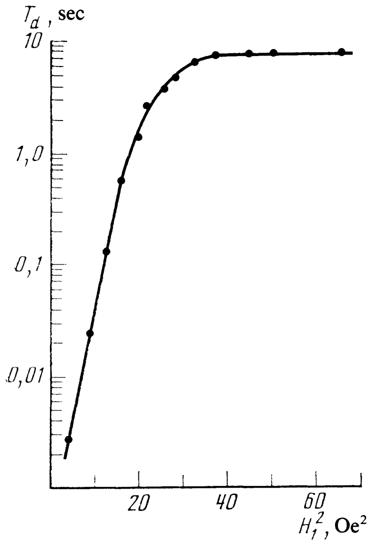

FIG. 2. Experimental dependence of T_d on H_1^2.

$$W=f_2(2\omega_1)\frac{4\pi\,\mathrm{Tr}\{(E+F)^2\}}{\mathrm{Tr}(I_z^2)},$$

$$f_2(\omega_1)=\frac{1}{(2\pi M_2^{(2)})^{1/2}}\exp\left(-\frac{\omega_1^2}{2M_2^{(2)}}\right), \tag{8}$$

$$M_2^{(2)}=\frac{2\,\mathrm{Tr}\{[{}^1/_2\mathscr{H}_d',F][E,{}^1/_2\mathscr{H}_d']\}}{\mathrm{Tr}\{(E+F)^2\}}$$

$$E={}^3/_8\sum_{i<j}a_{ij}I_{+i}I_{+j}, \quad F={}^3/_8\sum_{i<j}a_{ij}I_{-i}I_{-j}.$$

Using Eq. (8), we obtain

$$T_m^{-1}=\frac{12\pi^{1/2}}{(2M_2^{(2)})^{1/2}}\gamma_F H_1^2\exp\left[-\frac{(2H_1)^2}{2M_2^{(2)}}\right]. \tag{9}$$

In agreement with the system (6), in our experiments the value of β_2 decayed with time in accordance with one-exponential equation. Figure 2 shows the experimental dependence of T_d on H_1^2. Our calculations give the value $M_2^{(2)} = 0.854$ Oe² for the [111] orientation. Line 1 in Fig. 3 corre-

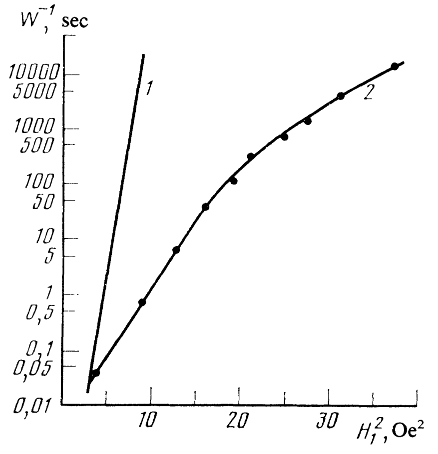

FIG. 3. Dependence of W^{-1} on H_1^2.

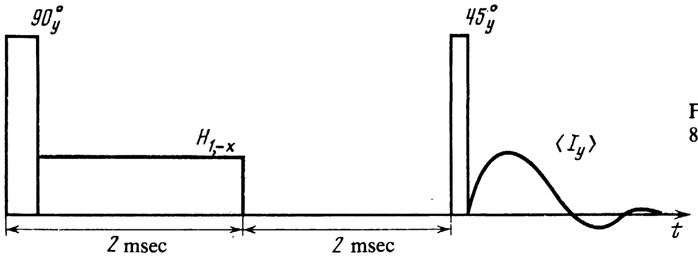

FIG. 4. Sequence of pulses used to observe a signal due to the term $(3/8)\beta_1 P$ in the density matrix.

sponds to the theoretical dependence of W^{-1} on H_1^2 calculated from Eq. (9) using our value of $M_2^{(2)}$. Curve 2 in Fig. 3 is plotted employing the experimental values for a sample characterized by $T_{1d\rho} = 8.3$ sec. It is clear from Fig. 3 that the theory of establishment of a spin temperature proposed in Ref. 2 fails to describe our results.

A change in the Zeeman signal was observed in the experiments that confirm rapid thermal mixing of the Zeeman and nonsecular energy reserviors. However, we could observe a signal due to the term $(3/8)\beta_1 P$ in the density matrix (4). This was done using a pulse sequence shown in Fig. 4. The density matrix (4) yields the following expression for the dipole signal observed after the 45°_y pulse:

$$\langle I_y \rangle = {}^1/_8 (3\beta_1 + \beta_2)\,\mathrm{Sp}\,(I_y^2)\, dG(t)/dt, \tag{10}$$

where $G(t)$ is the profile of the free induction signal. Measurements were carried out employing a locking pulse of 2 msec duration and the amplitude H_1 was varied from 3 to 10 Oe. Under these conditions the reciprocal temperature β_2 became equal to β_L, because $\beta_1 = \beta_L H_0 (H_1^2 + H_L'^2)^{-1/2}$. Figure 5 shows the dependence of the observed signal on H_1. The experimental values can be seen to agree completely with those calculated from Eq. (10), where it is assumed that $\beta = \beta_L = 0$.

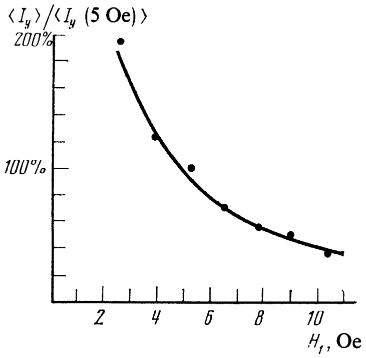

FIG. 5. Dependence of the signal determined using Eq. (10) on H_1 ($H_0 \| [111]$).

The problem of the rate of establishment of a spin temperature is very important not only in the dynamics of spin systems and related applications (various aspects of high-resolution NMR, double resonance, etc.). Nonequilibrium spin systems provide convenient theoretical and experimental models of nonequilibrium systems from statistical physics and the results obtained for the former may be of fairly general validity. Consequently, it would be desirable to continue investigations of the rate of establishement of a spin temperature, extending them particularly to higher values of the ratio ω_1/ω_L.

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