Dipole temperature in heteronuclear systems in a rotating coordinate system

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The dipole temperature in heteronuclear systems is studied experimentally for a combined dipole reservoir of Li and F nuclei in an LiF single crystal. The spin system in LiF was perturbed by applying different sequences of pulses. In all cases the experimental results are described by a statistical operator which is diagonal in the energy representation. Signals corresponding to both the secular and the nonsecular terms in the statistical operator were observed. The cooling of the dipole subsystem was studied by applying an rf field whose frequency was shifted by Δ from the resonance frequency for Li. The oscillations in the dipole signal were measured as a function of the rf pulse length for a given mismatch Δ.

Resonance in heteronuclear systems is an important special case of NMR which has wide practical application. The concept of spin temperature is used to interpret NMR experiments in solids,[1] and the choice of the statistical operator for calculating the spin temperature is an important problem which has not yet been solved. In this paper we experimentally investigate the dipole temperature and the form of the statistical operator in heteronuclear systems for a combined Li, F dipole reservoir in an LiF crystal, which was chosen because of its strong heteronuclear interaction.[2] The experiments were carried out in a constant $H_0 = 5618$ Oe at $T = 300$ K with the magnetic field pointing along the second-order crystallographic axis.

We will consider the dynamic response of the spin system in LiF to various pulse sequences from a unified point of view.

1. Pulse sequence 1 (Fig. 1) perturbed the LiF spin system at the resonance frequency 22.5 MHz of the F nuclei. We cooled the system by adiabatically demagnetizing it in a rotating coordinate system. Figure 2 shows the experimental dependence on the amplitude H_1 of the applied rf field after the application of a 45°_y pulse.

In order to describe how the sequence 1 affects the spin system we use the operator

$$U_t = \exp\left(i\frac{\pi}{2}I_y\right)\exp[i(\omega_0^I I_z + \omega_0^S S_z)t]$$

to pass to a tilted doubly rotating coordinate system (which we call CS1). The Hamiltonian of the system in the rf field is then

$$\mathcal{H} = \omega_1 I_z + {}^3/_8 P_I - Q_{IS}{}^I - {}^1/_2 \mathcal{H}_{DI}' + \mathcal{H}_{DS}', \qquad (1)$$

where

$$P_I = \sum_{i<j} \alpha_{ij}{}^I (I_i^+ I_j^+ + I_i^- I_j^-), \quad Q_{IS}{}^I = \sum_{k,l} a_{kl}{}^{IS} I_k^x S_l^z.$$

Since the statistical operator σ is required to be diagonal in the energy representation, we express it in the form

$$\sigma = 1 - \beta_1(\omega_1 I_z + {}^3/_8 P_I - Q_{IS}{}^I) - \beta_2(\mathcal{H}_{DS}' - {}^1/_2 \mathcal{H}_{DI}') \qquad (2)$$

after the spin temperature has relaxed in system CS1 in the presence of the rf field.

We thus assume rapid thermal mixing of the Zeeman and nonsecular reservoirs in the coordinate system CS1, while the secular subsystem is at a single temperature. (It was first shown in Ref. 3 that the secular subsystem is described by a single temperature in the laboratory frame. Although the assumption of a single temperature for the secular subsystem in CS1 is a natural one, it nevertheless required experimental verification). The Zeeman and nonsecular reservoirs are known to be rapidly mixed for homonuclear molecules[1]; however, the influence of this mixing on the form of σ has been debated.[4,5,6] Thermal mixing of the Zeeman and nonsecular reservoirs has not been studied in detail for heteronuclear systems in rotating coordinate systems.

The statistical operator in the rotating coordinate system had the form

$$\sigma = 1 - \beta_0 \mathcal{H}_D' = 1 - \beta_0(\mathcal{H}_{DI}' + \mathcal{H}_{DS}' + \mathcal{H}_{DIS}') \qquad (3)$$

just before the rf pulse sequence 1 was applied. Together with energy conservation, Eqs. (2) and (3) imply that

$$\beta_0 \operatorname{tr}(\mathcal{H}_D'^2) = \beta_1[\omega_1^2 \operatorname{tr}(I_z^2) + {}^3/_4 \operatorname{tr}(\mathcal{H}_{DI}'^2) + \operatorname{tr}(\mathcal{H}_{DIS}'^2)] + \beta_2[{}^1/_4 \operatorname{tr}(\mathcal{H}_{DI}'^2) + \operatorname{tr}(\mathcal{H}_{DS}'^2)]. \qquad (4)$$

Our calculations yield the following values for the trace ratios in (4):

$$\frac{\operatorname{tr}(\mathcal{H}_{DI}'^2)}{\gamma_I^2 \operatorname{tr}(I_z^2)} = 3.43\ \text{Oe}^2, \quad \frac{\operatorname{tr}(\mathcal{H}_{DS}'^2)}{\gamma_I^2 \operatorname{tr}(I_z^2)} = 2{,}49\text{Oe}^2,$$

$$\frac{\operatorname{tr}(\mathcal{H}_{DIS}'^2)}{\gamma_I^2 \operatorname{tr}(I_z^2)} = 8.1\ \text{Oe}^2 \qquad (5)$$

In our experiments the time interval from the termination of the rf field to the application of the 45°_y pulse was several times greater than T_2; in this case the off-diagonal terms of σ in the energy representation do not contribute to the observables (this follows from the general observation that the off-diagonal terms in σ vanish over times comparable to the relaxation time[7]). Immediately after the rf field terminates in the rotating coordinate system, we have

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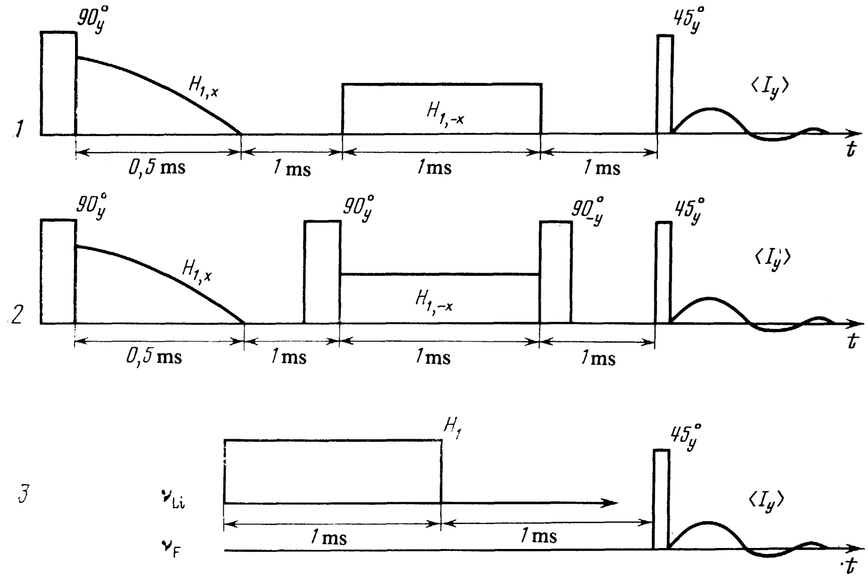

FIG. 1. Pulse sequences.

$$\sigma=1-\beta_1\left(\omega_1 I_x+\frac{3}{16}P_I+\frac{3}{4}\mathscr{H}_{DI}'+\mathscr{H}_{DIS}'\right)$$
$$-\beta_2\left(\frac{1}{4}\mathscr{H}_{DI}'-\frac{3}{16}P_I+\mathscr{H}_{DS}'\right), \tag{6}$$

so that by the above discussion we have

$$\sigma=1-\beta\mathscr{H}_D', \tag{7}$$

at the instant the 45°_y pulse is applied, and the conservation law gives

$$\beta\ \mathrm{tr}\,(\mathscr{H}_D'^2)=\beta_1[{}^3/_4\ \mathrm{tr}\,(\mathscr{H}_{DI}'^2)+\ \mathrm{tr}\,(\mathscr{H}_{DIS}'^2)\,]$$
$$+\beta_2[{}^1/_4\ \mathrm{tr}\,(\mathscr{H}_{DI}'^2)+\mathrm{tr}\,(\mathscr{H}_{DS}'^2)\,], \tag{8}$$

where β_1 and β_2 correspond to the time when the rf field is discontinued.

Equation (7) shows that the observed signal is proportional to the dipole temperature β, and the average $\langle I_y\rangle$ is given by the expression on p. 132 of Ref. 1.

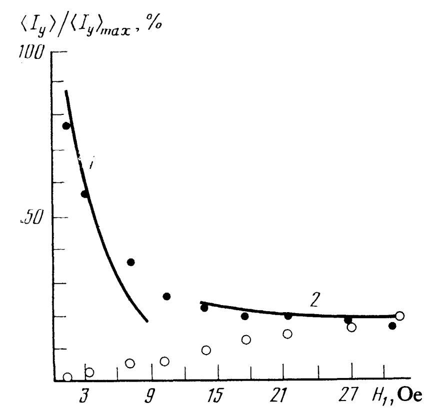

FIG. 2. Dependence of the dipole signal amplitude on H_1; the dark and open circles show values for pulse sequences 1 and 2, respectively.

We did not measure the relaxation rate T_m^{-1} of the overall spin temperature during the rf pulse sequence as a function of the pulse amplitude. However, it is clear that relaxation to a single spin temperature can occur in weak rf fields if the fields are applied long enough (large τ), and (4) gives

$$\beta=\beta_1=\beta_2=\beta_0\frac{\mathrm{tr}\,(\mathscr{H}_D'^2)}{\omega_1^2\ \mathrm{tr}\,(I_z^2)+\ \mathrm{tr}\,(\mathscr{H}_D'^2)}. \tag{9}$$

If we recall that $\beta_2\approx\beta_0$ and use the fact that

$$\frac{{}^3/_4\ \mathrm{tr}\,(\mathscr{H}_{DI}'^2)+\mathrm{tr}\,(\mathscr{H}_{DIS}'^2)}{{}^1/_4\ \mathrm{tr}\,(\mathscr{H}_{DI}'^2)+\mathrm{tr}\,(\mathscr{H}_{DS}'^2)}=3{,}12, \tag{10}$$

for strong rf fields when the mixing time is long ($\tau<T_m$), we find from (8) that

$$\beta=\beta'\left[\frac{{}^3/_4\ \mathrm{tr}\,(\mathscr{H}_{DI}'^2)+\mathrm{tr}\,(\mathscr{H}_{DIS}'^2)}{\omega_1^2\ \mathrm{tr}\,(I_z^2)+\mathrm{tr}\,(\mathscr{H}_D'^2)}\right.$$
$$\left.+\frac{{}^1/_4\ \mathrm{tr}\,(\mathscr{H}_{DI}'^2)+\mathrm{tr}\,(\mathscr{H}_{DS}'^2)}{\mathrm{tr}\,(\mathscr{H}_D'^2)}\right], \tag{11}$$

where $\beta_0'\approx\beta_0$.

The statistical operator for a system with two types of spins is given by[1]

$$\sigma=1-\beta_I\omega_I I_z-\beta_S\omega_S S_z-\beta_d\mathscr{H}_d'. \tag{12}$$

We can also derive an expression of the type (12) by replacing the term $3/8P_I-Q_{IS}^I$ in (2) $\omega''I_z$, as in Ref. 5. We note that it was asserted in Ref. 1 that allowance for the nonsecular terms is equivalent to adding corrections of higher order in the ratio ω_4/ω_1, and the nonsecular terms in Ref. 4 are not replaced by corrections to the Zeeman terms.

If we omit the nonsecular terms in (2) or replace them by $\omega''I_z$ as in Ref. 5, we find

$$\beta=\beta_2[{}^1/_4\ \mathrm{tr}\,(\mathscr{H}_{DI}'^2)+\mathrm{tr}\,(\mathscr{H}_{DS}'^2)]/\mathrm{tr}\,(\mathscr{H}_D'^2) \tag{13}$$

in place of (8); for the case corresponding to Eq. (9), β_2 is given by Eq. (9), while $\beta_2 \approx \beta_0$ for strong fields [case (11)].

Curve 1 in Fig. 2 was calculated using (9). The theoretical and experimental values are nearly equal for small H_1. The discrepancy as H_1 increases is a consequence of the longer mixing time T_m. Curve 2 in Fig. 2 corresponds to expression (11) while $\beta_0' = 0.75\beta_0$. The fact that β_0' is not equal to β_0 might be attributable to the effect of energy exchange on the initial conditions during spin temperature relaxation. A detailed study of these effects would clearly be of great interest.

The results found by the methods in Refs. 1 and 5 must be compared with experimental data for weak fields, for which Eqs. (9) and (13) lead to substantially different results. Since

$$[{}^1/_4 \operatorname{tr}(\mathscr{H}_{DI}'^2)+\operatorname{tr}(\mathscr{H}_{DS}'^2)]/\operatorname{tr}(\mathscr{H}_D'^2)=0.24,$$

while Eq. (9) agrees closely with experiment for weak fields, (13) must clearly disagree sharply with experiment. This conflict was resolved in Ref. 1 by treating the nonsecular terms; by contrast, the approach in Ref. 5 cannot lead to agreement with experiment.

It is important to note that the amplitude of the observed Zeeman signal and its dependence on H_1 for long durations τ are essentially identical to the dependences for shorter $\tau \sim (1\text{–}10)T_2$. This behavior, which follows from (4) and (10), indicates that the Zeeman and nonsecular subsystems relax quickly to a common temperature in the rotating coordinate system.

2. The pulse sequence 2 in Fig. 1 was used to observe signal proportional to the reciprocal temperature of the secular term in CS1. This was achieved by employing a 90°_y pulse, which maximizes the cooling of the secular subsystem.

Figure 2 shows how the signal amplitude depends on the field strength H_1 for pulse sequence 2.

Immediately after the 90°_y pulse terminates in sequence 2, the statistical operator in CS1 is given by

$$\sigma=1-\beta_0\mathscr{H}_D'; \tag{14}$$

after the spin temperature has relaxed, σ takes the form (2). At the instant a 45°_y pulse is applied in the rotating coordinate system

$$\sigma=1-\beta_1\omega_1 I_z-\beta'\mathscr{H}_D', \tag{15}$$

and

$$\beta' \operatorname{tr}(\mathscr{H}_D'^2)=\beta_2[\operatorname{tr}(\mathscr{H}_{DS}'^2)-{}^1/_2 \operatorname{tr}(\mathscr{H}_{DI}'^2)]. \tag{16}$$

As in Ref. 1, we observe a signal proportional to β'.

If the rf fields are weak, relaxation to a common spin temperature can occur while the rf field is applied. Moreover, as in the case of pulse sequence 1, β_2 is given by Eq. (9), and by (16)

$$\beta'=\beta_0[\operatorname{tr}(\mathscr{H}_{DS}'^2)-{}^1/_2 \operatorname{tr}(\mathscr{H}_{DI}'^2)]/[\omega_1^2 \operatorname{tr}(I_z^2)+\operatorname{tr}(\mathscr{H}_D'^2)]. \tag{17}$$

Because the observed dipole signal is weak in this case [cf. (11) and (17)], it is not possible to compare Eq. (17) with experimental data.

Figure 2 shows that when $\omega_1 > \omega_L$, the signal for sequence 2 grows with the field amplitude H_1. This is because the coupling between the secular subsystem and the combined Zeeman + nonsecular subsystem in CS1 becomes weaker, as in the heteronuclear case. The secular subsystem in CS1 thus remains cool longer, so that the signal is stronger.

3. The field frequency ω of pulse sequence 3 (Fig. 1) was close to the resonance frequency for the Li nuclei, and the signal from the dipole system was recorded at the resonance frequency for the F nuclei. After a reading pulse was applied, we observed a signal whose amplitude depended on H_1 and Δ as shown in Figs. 3 and 4. In terms of the inclined doubly rotating coordinate system CS2 obtained using the operator

$$U_2=\exp(i\theta S_y)\exp[i(\omega S_z+\omega_0{}^I I_z)t],$$
$$\theta=\arcsin(\omega_1/\omega_{eff}),\quad \omega_{eff}=(\Delta^2+\omega_1^2)^{1/2},$$
$$\Delta=\omega-\omega_0,$$

the Hamiltonian of the system in the rf field is given by

$$\begin{aligned}\mathscr{H}=&\omega_{eff}S_z+{}^1/_2(3\cos^2\theta-1)\mathscr{H}_{DS}'\\&+{}^3/_8 P_S\sin^2\theta-{}^3/_4 Q_S\sin\theta\cos\theta\\&+\mathscr{H}_{DIS}'\cos\theta-Q_{IS}{}^S\sin\theta+\mathscr{H}_{DI}',\end{aligned} \tag{18}$$

where

$$Q_S=\sum_{i<j}a_{ij}[S_i^z(S_j^++S_j^-)+S_j^z(S_i^++S_i^-)],$$
$$Q_{IS}{}^S=\sum_{k,l}a_{kl}{}^{IS}S_k{}^x\tilde{I}_l{}^z.$$

We use the expression

$$\begin{aligned}\sigma=1&-\beta_1[\omega_{eff}S_z+{}^3/_8 P_S\sin^2\theta-{}^3/_4 Q_S\sin\theta\cos\theta-Q_{IS}{}^S\sin\theta]\\&-\beta_2[{}^1/_2(3\cos^2\theta-1)\mathscr{H}_{DS}'+\mathscr{H}_{DIS}'\cos\theta+\mathscr{H}_{DI}']\end{aligned} \tag{19}$$

for the statistical operator in CS2 after the spin temperature has relaxed. The conservation law gives

$$\begin{aligned}\beta_L[\omega_0\Delta &\operatorname{tr}(S_z^2)+\operatorname{tr}(\mathscr{H}_D'^2)]\\&=\beta_1\{\omega_{eff}^2 \operatorname{tr}(S_z^2)+[1-{}^1/_4(3\cos^2\theta-1)^2]\\&\quad\times\operatorname{tr}(\mathscr{H}_{DS}'^2)+\operatorname{tr}(\mathscr{H}_{DIS}'^2)\sin^2\theta\}\\&\quad+\beta_2\{{}^1/_4(3\cos^2\theta-1)^2 \operatorname{tr}(\mathscr{H}_{DS}'^2)\\&\quad+\operatorname{tr}(\mathscr{H}_{DIS}'^2)\cos^2\theta+\operatorname{tr}(\mathscr{H}_{DI}'^2)\}.\end{aligned} \tag{20}$$

If $\omega_{\text{eff}} \sim \omega_L$ then $\beta_1 = \beta_2$; if we neglect $\operatorname{tr}(\mathscr{H}_D'^2)$ in the left-hand side of (20) in favor of $\omega_0\Delta \operatorname{tr}(S_z^2)$, we get

$$\beta_1=\beta_2=\beta_L\omega_0\Delta \operatorname{tr}(S_z^2)/[\omega_{eff}^2 \operatorname{tr}(S_z^2)+\operatorname{tr}(\mathscr{H}_D'^2)]. \tag{21}$$

Equation (21) is similar to expression (2.31) in Ref. 1 for the reciprocal of the temperature of the spin system during cooling (homonuclear case, nonresonant rf field).

If $\omega_{\text{eff}} > \omega_L$ and the spin system does not have time to

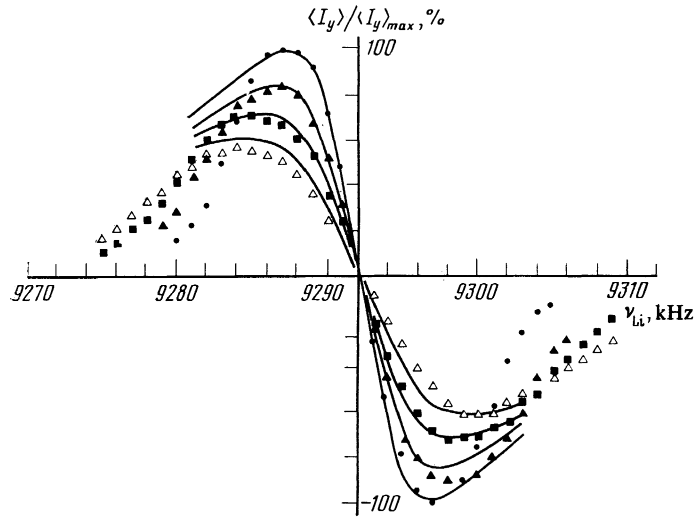

FIG. 3. Dipole signal amplitude as a function of the mismatch Δ for four fields $H_1 = 3.5, 4.9, 6.3$, and 7.7 Oe (corresponding to the dark circles and triangles and the open squares and triangles, respectively). The curves plot the theoretical values of $\langle I_y \rangle / \langle I_y \rangle_{\max}$.

relax during the time τ the rf field is applied, then $\beta_2 \ll \beta_1$ (20) gives

$$\beta_1 \approx \beta_L \omega_0 \Delta / \omega^2_{eff}. \tag{22}$$

The statistical operator in the rotating coordinate system takes the form

$$\sigma = 1 - \beta_1 \Delta S_z - \beta'' \mathcal{H}_D' \tag{23}$$

at the instant the 45°_y pulse is applied. The conservation law implies that

$$\beta''\ \mathrm{tr}\,(\mathcal{H}_D'^2) = \left[\beta_1 \frac{3\omega_1^2}{\omega^4_{eff}}\left(\frac{\omega_1^2}{4} + \Delta^2\right) + \beta_2 \frac{(2\Delta^2 - \omega_1^2)^2}{4\omega^4_{eff}}\right] \mathrm{tr}\,(\mathcal{H}_{DS}'^2) + \left(\beta_1 \frac{\omega_1^2}{\omega^2_{eff}} + \beta_2 \frac{\Delta^2}{\omega^2_{eff}}\right) \mathrm{tr}\,(\mathcal{H}'^2_{DIS}) + \beta_2\ \mathrm{tr}\,(\mathcal{H}_{DI}'^2), \tag{24}$$

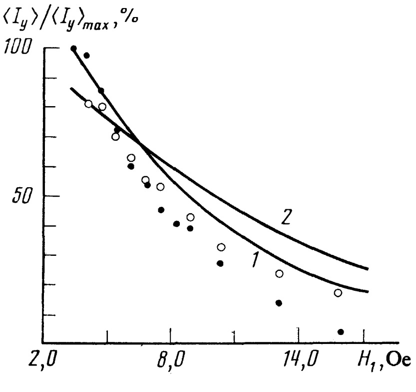

FIG. 4. Dependence of the amplitude of the dipole signal on H_1 for different mismatches. The dark and light circles correspond to $\Delta/\gamma = 3.14$ Oe (theoretical curve 1) and $\Delta/\gamma = 9.8$ Oe (theoretical curve 2), respectively.

where β_1 and β_2 are the reciprocal spin temperatures at the instant the rf field terminates.

If $\omega_{\rm eff} \sim \omega_L$ then

$$\beta'' = \beta_1 = \beta_2 = \beta_L \frac{\omega_0 \Delta\ \mathrm{tr}\,(S_z^2)}{\omega^2_{eff}\ \mathrm{tr}\,(S_z^2) + \mathrm{tr}\,(\mathcal{H}_D'^2)}. \tag{25}$$

Figures 3 and 4 show that the theoretical dipole signal amplitudes calculated from (19) and (24) agree closely with the experimental data for weak rf fields. As in the case of pulse sequence 1, the discrepancy as H_1 increases reflects the fact that for strong fields, the thermal mixing of the subsystems is not complete before the rf field terminates.

If we apply energy conservation to the statistical operator (12) (with the operator $3/8 P_s \sin^2\theta - 3/4 Q_s \sin\theta \times \cos\theta - Q^S_{IS} \sin\theta$ replaced by $\omega'' S_z$ as in Ref. 5), we get the expression

$$\beta'' = \beta_L \frac{\omega_0 \Delta\ \mathrm{tr}\,(S_z^2)}{\omega^2_{eff}\ \mathrm{tr}\,(S_z^2) + \mathrm{tr}\,(\mathcal{H}_D'^2)} \times \left[\frac{\Delta^2}{\omega^2_{eff}}\ \mathrm{tr}\,(\mathcal{H}'^2_{DIS}) + \frac{(2\Delta^2 - \omega_1^2)^2}{4\omega^4_{eff}}\ \mathrm{tr}\,(\mathcal{H}_{DS}'^2) + \mathrm{tr}\,(\mathcal{H}_{DI}'^2)\right] [\ \mathrm{tr}\,(\mathcal{H}_D'^2)\,]^{-1}, \tag{26}$$

for weak rf fields. This result does not agree with the experimental data.

It is clear from (20), (24), and the experimental data that sequence 3 gives the highest β for the a heteronuclear spin system; moreover, the maximum signal (corresponding to maximum cooling of the dipole system during sequence 3) occurred for $\Delta/\gamma = 3.14$ Oe and $H_1 = 3.5$ Oe. In addition, and unlike the other cooling methods using sequences 1 and 2, sequence 3 can alter the sign of β'' for certain mismatches Δ.

Figure 5 shows how the signal recorded during sequence 3 depended on the time τ the rf field was applied.

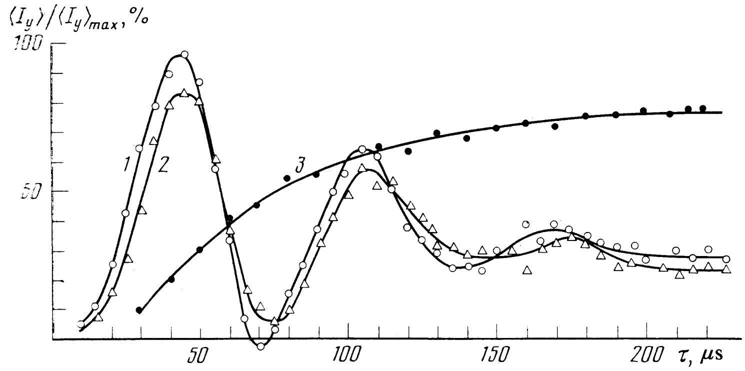

FIG. 5. Dependences of the recorded signal on the time τ the rf field was applied (mismatch $\Delta/\gamma = 3.14$ Oe). The experimental curves 1 and 2 correspond to $H_1 = 8$ Oe; curve 3 was recorded for $H_1 = 3$ Oe.

Curve 1 was recorded for a reading pulse applied $t_1 = 1$ ms after the rf field had terminated; curve 2 corresponds to $t_1 = 0$. The recorded signal was proportional to β_d for $t_1 = 1$ ms because the spin temperature was able to relax by the time the 45°_y pulse was applied. However, for $t_1 = 0$ and τ less than the time $\tau_1 = nT_2$ at which the oscillations in the dipole signal terminated, the observed signal cannot be regarded as proportional to the reciprocal dipole temperature, because in this case the spin temperature did not relax. This accounts for the difference between curves 1 and 2. Curve 3 in Fig. 5 corresponds to the field $H_1 = 3$ Oe; in this case $\omega_{\text{eff}} \sim \omega_L$ and there are clearly no oscillations in the dipole signal. We note that as in Ref. 8, the spin-spin relaxation time in our experiments was $\tau_1 = nT_2$, where n is ≈ 4.

We used various pulse sequences and coordinate systems to analyze the LiF heteronuclear spin system. In all cases the experimental results could be described in the spin temperature formalism by using a statistical operator diagonal in the energy representation, i.e., containing all the terms in the Hamiltonian. Thermal mixing of the Zeeman and nonsecular reservoirs (including the term Q_{IS}) occurred more rapidly in the inclined doubly rotating coordinate systems which we employed; this mixing was followed by relaxation to a common spin temperature (the relaxation was slow when $H_1 \gg H_L$). The nonsecular terms in the statistical operator frequently determine the amplitude of the signal proportional to the dipole temperature; it is therefore not legitimate to discard them or replace them by a correction to the Zeeman term.

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