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Citation: The Journal of Chemical Physics 70, 3572 (1979); doi: 10.1063/1.437959
View online: http://dx.doi.org/10.1063/1.437959
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/70/8?ver=pdfcov
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Zeeman–quadrupole cross relaxation between two nuclear spin species

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(Received 6 November 1978)

We derive an expression for the rate $\tau_{rs}^{-1}$ of the cross relaxation between the Zeeman splitting of one nuclear spin species ($I$ spins, $I = 1/2$) and the quadrupole splitting of another spin species ($S$ spins, $S > 1/2$) via the $I$–$S$ dipolar interaction. We calculate $\tau_{rs}$ for the case of CFCl$_3$–CFCl$_2$ ($I$ spins are $^{19}$F, and $S$ spins are $^{35}$Cl and $^{37}$Cl) and compare the results with experimental data.

I. INTRODUCTION

Cross relaxation phenomena in solid-state NMR have been observed in a wide variety of different situations. Cross relaxation between two systems generally occurs if the splitting of energy levels in one system can be made to equal to the splitting in the other. As a case in point, consider a system of $I$ spins ($I = 1/2$), strongly coupled to a dc magnetic field $H_0$ via a Zeeman interaction, and a system of $S$ spins ($S > 1/2$) strongly coupled to the crystalline electric field gradient via a quadrupole interaction. At certain values of $H_0$, the Zeeman splitting of the $I$ spins will be equal to the quadrupole splitting of the $S$ spins, and the $I$ and $S$ spins cross relax.

This phenomenon is easily observed via the spin–lattice relaxation time $T_{1I}$ of the $I$ spins. Since the quadrupole $T_{1S}$ of the $S$ spins is usually very short, cross relaxation between the $I$ and $S$ spins can cause a sharp reduction in $T_{1I}$. This effect was first observed experimentally by Goldman and Woessner and Gutowsky in paradichlorobenzene ($I$ spins are $^2$H, and $S$ spins are $^{35}$Cl and $^{37}$Cl) and later was observed independently by Woessner and Gutowsky in the same compound. Since then, many others have seen this effect in a variety of experiments.

In this paper we derive an expression for the cross relaxation time $\tau_{rs}$. We apply our result to the case of CFCl$_3$–CFCl$_2$ ($I$ spins are $^{19}$F, and $S$ spins are $^{35}$Cl and $^{37}$Cl). At low temperatures, this compound forms a glassy crystalline phase in which the molecules, sitting in a body-centered-cubic (bcc) lattice, are "frozen" into an orientationally disordered state. We calculate $\tau_{rs}$ for CFCl$_3$–CFCl$_2$ and compare the result with experimental data. (This data was presented and discussed in detail in the preceding paper.)

II. GENERAL EXPRESSION FOR $\tau_{rs}$

Consider a system of $I$ spins ($I = 1/2$) and $S$ spins ($S > 1/2$). We write the Hamiltonian,

$$\mathcal{K} = \mathcal{K}_I + \mathcal{K}_S + \mathcal{K}_{rs} .$$

The first term $\mathcal{K}_I$ is the $I$–spin Zeeman interaction with $H_0$. Choosing the $z$ axis to be along $H_0$, we have

$$\mathcal{K}_S = -\omega_{sf} \sum_{I \neq S} I_{sf} ,$$

where $\omega_{sf} = \gamma_f H_0$ and $\gamma_f$ is the gyromagnetic ratio of the $I$ spins. The second term $\mathcal{K}_S$ in Eq. (1) is the sum of the Zeeman and quadrupole interactions for $S$ spins. We do not give the explicit form of $\mathcal{K}_S$ here. The term $\mathcal{K}_{rs}$ is the $I$–$S$ dipolar spin–spin interaction,

$$\mathcal{K}_{rs} = \sum_{I \neq S} F_{2w}^I a_{\omega}^I (I, S) ,$$

where the summation over $j$ and $k$ are over the $I$ and $S$ spins, respectively. Explicit expressions for $F_{2w}^I$ and $A_{\omega}^I(I, S)$ are given in Ref. 12.

Now, the interactions $\mathcal{K}_I$ and $\mathcal{K}_S$ form energy reservoirs which can be characterized by inverse spin temperatures $\beta_I$ and $\beta_S$, respectively. The interaction $\mathcal{K}_{rs}$ is a perturbation which causes cross relaxation between them such that $\beta_I$ and $\beta_S$ evolve with time towards a common inverse spin temperature. We define the cross relaxation time $\tau_{rs}$ by the relation

$$\frac{d\beta_R}{dt} = -\frac{1}{\tau_{rs}} (\beta_I - \beta_S) .$$

From Goldman [e. g., p. 150, Eq. (6.37)], we find

$$\frac{1}{\tau_{rs}} = -\frac{1}{\text{Tr} \mathcal{K}_{rs}^2} \int_0^\infty d\tau \text{Tr} \left\{ \exp(i\mathcal{K}_I \tau + i\mathcal{K}_S \tau) \times [\mathcal{K}_{rs}, \mathcal{K}_r] \exp(-i\mathcal{K}_r \tau - i\mathcal{K}_S \tau) [\mathcal{K}_{rs}, \mathcal{K}_r] \right\} .$$

Evaluation of the commutator gives

$$[\mathcal{K}_{rs}, \mathcal{K}_r] = -\omega_{sf} I_{rs} R \sum_{I \neq S} (L_j G_{1j}(S) - L_j G_{1j}(S)) ,$$

where

$$G_{1j}(S) = \frac{1}{2} F_{1j}^{(1)} S_a + \frac{3}{2} F_{1j}^{(2)} S_a + \frac{\gamma_f}{3} \frac{\sqrt{2}}{5} \left[ \sqrt{3} Y_{20}(\theta_{ja}, \phi_{ja}) S_a + \sqrt{6} Y_{2-1}(\theta_{ja}, \phi_{ja}) S_a + \sqrt{6} Y_{21}(\theta_{ja}, \phi_{ja}) S_a \right] .$$

In the above equation $Y_{2\ell}(\theta_{ja}, \phi_{ja})$ refers to spherical harmonics. Also,

$$\exp(i\mathcal{K}_r) I_{rs} \exp(-i\mathcal{K}_r) = I_{rs} \exp(i\omega_{sf} \tau) .$$

We obtain from Eq. (5), using Eqs. (6) and (8) and taking the traces over the $I$ spins,

$$\tau_{rs}^{-1} = \omega_{sf} R \sum_{I \neq S} |L_j G_{1j}(S)|^2 ,$$

where $R$ is the component of angular momentum along the $I$–$S$ axis.

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\[
\frac{1}{\tau_{gS}} = \frac{2\gamma_2^2 \hbar^2}{N_2 \tau_{S}} \int_0^\infty dt \sum_{l, h, k} \{ \exp(-i\omega_{2h} t) 
\times \text{tr} \left[ \exp(i\tau G_{k}) G_{l} \exp(-i\tau G_{h}) G_{k} \right] 
+ \exp(i\omega_{2h} t) \text{tr} \left[ \exp(i\tau G_{k}) G_{l} \exp(-i\tau G_{h}) G_{k} \right], \tag{9}\]
\]
where \(\text{tr}\) means the trace over the \(S\) spins.

Now, we denote the eigenfunctions and eigenvalues of \(\mathcal{K}_{s}\) by \(|a, k\rangle\) and \(\omega_{ak}\), respectively:

\[
\mathcal{K}_{s} |a, k\rangle = \omega_{ak} |a, k\rangle. \tag{10}\]

Thus, for example,

\[
\text{tr}_{S}[\exp(i\tau G_{k}) G_{l} \exp(-i\tau G_{h}) G_{k}] = \sum_{a, b} \exp(i\omega_{at} t) \langle a | G_{k} | b \rangle \langle b | G_{l} | a \rangle, \tag{11}\]

where

\[
\omega_{ab} = \omega_{a} - \omega_{b}. \tag{12}\]

Putting this into Eq. (9) and performing the integration over \(t\), we obtain

\[
\frac{1}{\tau_{gS}} = \frac{4\gamma_2^2 \hbar^2}{N_2 \tau_{S}} \sum_{l, h, k} \sum_{a, b} \delta(\omega_{at} - \omega_{ab}) \langle a | G_{k} | b \rangle \langle b | G_{l} | a \rangle. \tag{13}\]

In order for \(\langle a | G_{k} | b \rangle\) to be nonzero, \(|a\rangle\) and \(|b\rangle\) are allowed to differ only in the state of the \(k\)th \(S\) spin. Similarly, in order for \(\langle b | G_{l} | a \rangle\) to be nonzero, \(|a\rangle\) and \(|b\rangle\) are allowed to differ only in the state of the \(l\)th \(S\) spin. Thus, if the two matrix elements are to be simultaneously non-zero when \(|a\rangle\) and \(|b\rangle\) refer to different states \((\omega_{ab} \neq 0)\), then we must have \(k = l\). Physically, this means that the cross relaxation proceeds via a transition of an \(I\) spin accompanied by a transition of a single \(S\) spin.

Consider then the Hamiltonian \(\mathcal{K}_{s}\) of a single spin \(S\). Clearly, since \(\mathcal{K}_{s}\) does not contain any \(S-S\) interactions, we can write

\[
\mathcal{K}_{s} = \sum_{a, b} \mathcal{K}_{a, b}. \tag{14}\]

We denote the eigenfunctions and eigenvalues of \(\mathcal{K}_{a, b}\) by \(|a, k, b\rangle\) and \(\omega_{ab}\), respectively:

\[
\mathcal{K}_{a, b} |a, k, b\rangle = \omega_{ab} |a, k, b\rangle. \tag{15}\]

We then write Eq. (13), setting \(k = l\),

\[
\frac{1}{\tau_{gS}} = \frac{4\gamma_2^2 \hbar^2}{N_2 \tau_{S}} \sum_{a, b} \delta(\omega_{at} - \omega_{ab}) \langle a, k | G_{k} | b, k \rangle \langle b, k | G_{l} | a, k \rangle, \tag{16}\]

where

\[
\omega_{ab} = \omega_{a} - \omega_{b}. \tag{17}\]

Note that this result predicts infinitely sharp rates (Dirac delta functions) which arise from the omission of line-broadening terms in the Hamiltonian. The effects of such terms can be incorporated into Eq. (16) by replacing the Dirac delta functions \(\delta(\omega_{at} - \omega_{ab})\) by normalized shape functions \(g(\omega_{at} - \omega_{ab})\). However, as we shall see, introduction of these shape functions would have negligible effect on the result as long as their line-width is reasonably narrow.

The eigenfunctions \(|a, b\rangle\) are well known. To simplify the calculation, we assume that the electric field gradient is axially symmetric at each \(S\) spin. Under this assumption, the eigenfunctions \(|a, b\rangle\) take on a particularly simple form in a reference frame \(x' y' z'\) such that the \(z'\) axis points along the axis of symmetry. Thus, in order to calculate the matrix elements \(\langle a, k | G_{s} | b, h \rangle\), we wish to write an expression for \(G_{s}\) in the \(x' y' z'\) coordinate system. We therefore define a coordinate transformation \(xyz \rightarrow x'y'z'\) by (1) a rotation \(\phi_{h}\) about the \(y\) axis followed by (2) a rotation \(\phi_{k}\) about the new \(z'\) axis. In this new coordinate system the \(G_{s}\) points in a direction defined by the spherical coordinates \((\phi_{h}, \phi_{k})\).

The operators \(S_{a, b}\) and \(S_{a, b}'\) in the \(x'y'z'\) coordinate system can now be written in terms of the operators \(S_{a, b}\) and \(S_{a, b}'\) in the \(x' y' z'\) coordinate system:

\[
S_{a, b} = \cos \theta_{s} S_{a, b}' - \frac{1}{2} \sin \theta_{s} \exp(-i\phi_{s}) S_{a, b}'', \tag{18}\]

and

\[
S_{a, b}' = \sin \theta_{s} S_{a, b} + \frac{1}{2} (\cos \theta_{s} + 1) \exp(i\phi_{s}) S_{a, b}''. \tag{19}\]

Also, from Gottfried\(^{14}\) we find that

\[
Y_{mn}(\phi_{s}, \psi_{s}) = \sum_{n} Y_{mn}(\phi_{s}', \psi_{s}) D_{m}^{(2)}(\phi_{s}', \theta_{s}, -\theta_{s}, 0), \tag{20}\]

where \(\phi_{s}'\) and \(\theta_{s}'\) are the spherical coordinates of \(S_{a, b}'\) in the new coordinate system \(x'y'z'\). Explicit expressions for \(d_{m}^{(2)}(\phi_{s})\) are found in Ref. 15.

Using Eqs. (19) and (20), we write Eq. (7) as

\[
C_{s} = \frac{1}{2} \tau_{gS} \int \frac{d^3}{6 \pi} \sum_{x, y, z} Y_{mn}(\phi_{s}, \psi_{s}) \exp(i\phi_{s}') D_{m}^{(2)}(\phi_{s}', \theta_{s}, -\theta_{s}, 0) \times \left[ \exp(i\phi_{s}) f_{m}(\phi_{s}) S_{a, b}'' + \exp(-i\phi_{s}) f_{m}(\phi_{s}) S_{a, b}'' + f_{m}(\phi_{s}) S_{a, b}'' \right], \tag{21}\]

where

\[
f_{m}(\phi_{s}) = - (\cos \theta_{s} + 1) d_{m}^{(2)}(\phi_{s}) - \sqrt{6} \sin \theta_{s} d_{m}^{(2)}(\phi_{s}) \tag{22}\]

and

\[
f_{m}(\phi_{s}) = - 2 \sin \theta_{s} d_{m}^{(2)}(\phi_{s}) + 2 \sqrt{6} \cos \theta_{s} d_{m}^{(2)}(\phi_{s}) \tag{23}\]

III. \(S = \frac{3}{2}\) CASE

For the case \(S = \frac{3}{2}\), there are four transitions of interest to us. (Reference 16 gives a detailed discussion of these transitions and their associated eigenfunctions and eigenvalues.) For example, the \(\alpha\) transition involves energy levels split by an amount

\[
\omega_{ab} = \omega_{Qz} - \frac{1}{2} \cos \theta_{s} \left[ 3 - (1 + 4 \tan^2 \theta_{s}) \right] \omega_{Qz}, \tag{24}\]

where \(\omega_{Qz}\) is the pure quadrupole splitting of the \(S\) spins in zero field \((h_{0} = 0)\) and \(\omega_{Qz} = y_{s} h_{0}\). Using the following relations for the \(\alpha\) transition,
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the two molecules (see Fig. 1). The radii \( R_j \) and \( R_k \) of the two spheres are the distances from the \( j \) and \( k \) sites to the centers of their respective molecules. \( R_{jk} \) is the distance between the centers of the two molecules.

First, we integrate over the sphere \( S_k \). From geometry, we have

\[
\cos \theta_k = \frac{R_j^2 + R_k^2 - \rho^2}{2R_j \rho},
\]  

(37)

and

\[
\cos \theta_{jk}' = \frac{r_{jk}^2 + R_j^2 - \rho^2}{2R_j r_{jk}}.
\]  

(38)

Holding \( \rho \) fixed, we have

\[
\int_{S_k} dS_k \left( \frac{d_S}{r_{jk}} \right)^4 f(\cos\theta_k') = \frac{1}{2} \int_{-1}^{1} d(\cos\theta_k) \left( \frac{d_S}{r_{jk}} \right)^4 f(\cos\theta_k'),
\]  

(39)

where \( f \) is some function of \( \cos\theta_k' \). In our particular case, we have

\[
f(\cos\theta_k') = 4\pi |Y_{1m} ' (\phi_{jk}, \phi_{jk}')|^2
\]  

(40)

Similarly, we integrate over the sphere \( S_j \), using

\[
\cos \theta_j = \frac{R_j^2 + R_k^2 - \rho^2}{2R_k \rho}.
\]  

(41)

and obtain

\[
\int_{S_j} dS_j \int_{S_k} dS_k \left( \frac{d_S}{r_{jk}} \right)^4 f(\cos\theta_j')
\]  

\[
= \frac{1}{4} \int_{-1}^{1} \int_{-1}^{1} d(\cos\theta_j) \left( \frac{d_S}{r_{jk}} \right)^4 f(\cos\theta_j')
\]  

(42)

Since \( r_{jk} \) is a dummy variable, we have omitted the indices \( j, k \). Putting this into Eq. (36), we obtain

\[
S_{\text{inter}} = \sum_{m} \left[ d_{mn} (19') \right]^2 \sum_{r} \frac{d_r^2}{4R_j R_k r_{jk}}
\]  

(43)

where \( |Y_{2m} ' (\phi_{jk}, \phi_{jk}')|^2 \) is evaluated at \( \cos\theta_k' = (r^2 + R_j^2 - \rho^2)/2R_j \rho \). The summation over \( j \) is now over molecular sites \( j \). Hence, the factor 2 in Eq. (43) accounts for two fluorine atoms per molecule. The integrals were evaluated numerically. The results for both the intramolecular and intermolecular contributions to \( S_{m} \) are given in Table I. As can be seen, the intramolecular contribution is isomer dependent. However, the dependence is not great, so we just used the average of the two.

Using Eq. (33) and the lattice sums in Table I, we can now calculate \( \tau_{15} \) for CFCl\(_2\)–CFCl\(_2\). All the physical constants needed for the calculations are well known except for the pure quadrupole splitting \( \omega_{QS} \) of \( ^{35}\text{Cl} \) and \( ^{37}\text{Cl} \). From NQR measurements in other chlorinated ethanes\(^{17-19} \) we find that, generally, \( \omega_{QS}/2\pi \approx 40 \text{ MHz} \).
TABLE I. Evaluation of the lattice sum $S_m$ in CFCl$_2$–CFCl$_2$.

<table>
<thead>
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<th>Intermolecular</th>
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<td>gauche</td>
<td>136</td>
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</table>

for $^{35}$Cl in these compounds. Thus we used this value (and hence 31.5 MHz for $^{35}$Cl) in the calculation of $\tau_{IS}$.

In Fig. 2 we plot the results of the calculation, showing the separate contributions to $\tau_{IS}$ from the $^{35}$Cl and $^{37}$Cl isotopes. Adding them together, we obtain the resultant $\tau_{IS}$ which we plot in Fig. 3. The experimental points were obtained from $^{19}$F $T_1$ data at two different temperatures. (A detailed discussion of the data is given in the preceding paper.) As can be seen, the agreement between theory and experiment is quite good.

ACKNOWLEDGMENTS

This work was supported by the NSF under Grant DMR 76-18966. We wish to thank T. A. Case for assisting with the computer work. We appreciate helpful discussions with Dr. J. Piott and Dr. C. E. Hayes.