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Zeeman–quadrupole cross relaxation between two nuclear spin species

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We derive an expression for the rate τ_{IS}^{-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 τ_{IS} for the case of CFCL$_2$–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 be equal to the splitting in the other. As a case in point, consider a system of I spins ($I = \frac{1}{2}$), strongly coupled to a dc magnetic field H_0 via a Zeeman interaction, and a system of S spins ($S > \frac{1}{2}$) 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[1,2] in paradichlorobenzene (I spins are ^{1}H, and S spins are ^{35}Cl and ^{37}Cl) and later was observed independently by Woessner and Gutowsky[3] in the same compound. Since then, many others[4–11] have seen this effect in a variety of experiments.

In this paper we derive an expression for the cross relaxation time τ_{IS}. We apply our result to the case of CFCl$_2$–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 τ_{IS} for CFCl$_2$–CFCl$_2$ and compare the result with experimental data. (This data was presented and discussed in detail in the preceding paper.[11])

II. GENERAL EXPRESSION FOR τ_{IS}

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

$$\mathcal{H} = \mathcal{H}_I + \mathcal{H}_S + \mathcal{H}_{IS} . \tag{1}$$

The first term $\mathcal{H}_I$ is the I-spin Zeeman interaction with $\mathbf{H}_0$. Choosing the z axis to be along $\mathbf{H}_0$, we have

$$\mathcal{H}_I = -\omega_{0I} \sum_j I_{zj} , \tag{2}$$

where $\omega_{0I} = \gamma_I H_0$ and γ_I is the gyromagnetic ratio of the I spins. The second term $\mathcal{H}_S$ in Eq. (1) is the sum of the Zeeman and quadrupole interactions for S spins. We do not give the explicit form of $\mathcal{H}_S$ here. The term $\mathcal{H}_{IS}$ is the I–S dipolar spin–spin interaction,

$$\mathcal{H}_{IS} = \sum_{j,k} \sum_{p=-2}^{2} F_{jk}^{(p)} A_{jk}^{(p)}(\mathbf{I}, \mathbf{S}) , \tag{3}$$

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

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

$$\frac{d\beta_I}{dt} = -\frac{1}{\tau_{IS}} (\beta_I - \beta_S) . \tag{4}$$

From Goldman[13] [e.g., p. 150, Eq. (6.37)], we find

$$\frac{1}{\tau_{IS}} = -\frac{1}{\mathrm{Tr}(\mathcal{H}_I)^2} \int_0^\infty d\tau \, \mathrm{Tr}\{\exp(i\tau\mathcal{H}_I + i\tau\mathcal{H}_S)$$
$$\times [\mathcal{H}_{IS}, \mathcal{H}_I]\exp(-i\tau\mathcal{H}_I - i\tau\mathcal{H}_S)[\mathcal{H}_{IS}, \mathcal{H}_I]\} . \tag{5}$$

Evaluation of the commutator gives

$$[\mathcal{H}_{IS}, \mathcal{H}_I] = -\omega_{0I}\gamma_I\gamma_S \hbar \sum_{j,k} (I_{+j}G_{jk}(S) - I_{-j}G_{jk}^\dagger(S)) , \tag{6}$$

where

$$G_{jk}(S) = \tfrac{1}{4}F_{jk}^{(0)}S_{-k} + \tfrac{3}{2}F_{jk}^{(1)}S_{zk} + \tfrac{3}{4}F_{jk}^{(2)}S_{+k}$$
$$= r_{jk}^{-3}\sqrt{\pi/5}\,[-Y_{20}(\theta_{jk}, \phi_{jk})S_{-k} + \sqrt{6}Y_{2-1}(\theta_{jk}, \phi_{jk})S_{zk}$$
$$+ \sqrt{6}Y_{2-2}(\theta_{jk}, \phi_{jk})S_{+k}] . \tag{7}$$

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

$$\exp(i\tau\mathcal{H}_I)I_{\pm j}\exp(-i\tau\mathcal{H}_I) = I_{\pm j}\exp(\mp i\omega_{0I}\tau) . \tag{8}$$

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

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$$\frac{1}{\tau_{IS}} = \frac{2\gamma_I^2\gamma_S^2\hbar^2}{N_I\,\mathrm{tr}_S(1)}\int_0^\infty d\tau \sum_{j,k,l}\{\exp(-i\omega_{0I}\tau)$$

$$\times\,\mathrm{tr}_S[\exp(i\tau\mathcal{K}_S)G_{jk}\exp(-i\tau\mathcal{K}_S)G_{jl}^\dagger]$$

$$+\exp(i\omega_{0I}\tau)\,\mathrm{tr}_S[\exp(i\tau\mathcal{K}_S)G_{jk}^\dagger\exp(-i\tau\mathcal{K}_S)G_{jl}]\}\ , \quad (9)$$

where tr_S means the trace over the S spins.

Now, we denote the eigenfunctions and eigenvalues of $\mathcal{K}_S$ by $|a\rangle$ and ω_a, respectively:

$$\mathcal{K}_S|a\rangle = \omega_a|a\rangle\ . \quad (10)$$

Thus, for example,

$$\mathrm{tr}_S[\exp(i\tau\mathcal{K}_S)G_{jk}\exp(-i\tau\mathcal{K}_S)G_{jl}^\dagger]$$

$$= \sum_{a,b}\exp(i\omega_{ab}\tau)\langle a|G_{jk}|b\rangle\langle b|G_{jl}^\dagger|a\rangle\ , \quad (11)$$

where

$$\omega_{ab} = \omega_a - \omega_b\ . \quad (12)$$

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

$$\frac{1}{\tau_{IS}} = \frac{4\pi\gamma_I^2\gamma_S^2\hbar^2}{N_I\,\mathrm{tr}_S(1)}\sum_{j,k,l}\sum_{a,b}\delta(\omega_{0I}-\omega_{ab})\langle a|G_{jk}|b\rangle\langle b|G_{jl}^\dagger|a\rangle\ . \quad (13)$$

In order for $\langle a|G_{jk}|b\rangle$ to be nonzero, $|a\rangle$ and $|b\rangle$ are allowed to differ only in the state of the kth S spin. Similarly, in order for $\langle b|G_{jl}^\dagger|a\rangle$ to be nonzero, $|a\rangle$ and $|b\rangle$ are allowed to differ only in the state of the lth S spin. Thus, if the two matrix elements are to be simultaneously non-zero when $|a\rangle$ and $|b\rangle$ refer to different states (ω_{ab} nonzero), 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 $\mathcal{K}_{Sk}$ of a *single* spin S_k. Clearly, since $\mathcal{K}_S$ does not contain any S–S interactions, we can write

$$\mathcal{K}_S = \sum_k \mathcal{K}_{Sk}\ . \quad (14)$$

We denote the eigenfunctions and eigenvalues of $\mathcal{K}_{Sk}$ by $|a,k\rangle$ and ω_{ak}, respectively:

$$\mathcal{K}_{Sk}|a,k\rangle = \omega_{ak}|a,k\rangle\ . \quad (15)$$

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

$$\frac{1}{\tau_{IS}} = \frac{4\pi\gamma_I^2\gamma_S^2\hbar^2}{N_I(2S+1)}\sum_{j,k}\sum_{a,b}\delta(\omega_{0I}-\omega_{abk})|\langle a,k|G_{jk}|b,k\rangle|^2\ , \quad (16)$$

where

$$\omega_{abk} = \omega_{ak} - \omega_{bk}\ . \quad (17)$$

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 $\delta(\omega_{0I}-\omega_{abk})$ by normalized shape functions $g(\omega_{0I}-\omega_{abk})$. 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 $|a,k\rangle$ 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 $|a,k\rangle$ 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 $\langle a,k|G_{jk}|b,k\rangle$, we wish to write an expression for G_{jk} in the $x'y'z'$ coordinate system. We therefore define a coordinate transformation $xyz \to x'y'z'$ by (1) a rotation θ_k about the y axis followed by (2) a rotation ϕ_k about the new z' axis. In this new coordinate system then H_0 points in a direction defined by the spherical coordinates (θ_k, ϕ_k).

The operators S_{zk} and $S_{\pm k}$ in the xyz coordinate system can now be written in terms of the operators S'_{zk} and $S'_{\pm k}$ in the $x'y'z'$ coordinate system:

$$S_{zk} = \cos\theta_k S'_{zk} - \tfrac{1}{2}\sin\theta_k\exp(i\phi_k)S'_{+k}$$

$$-\tfrac{1}{2}\sin\theta_k\exp(-i\phi_k)S'_{-k}\ , \quad (18)$$

and

$$S_{\pm k} = \sin\theta_k S'_{zk} + \tfrac{1}{2}(\cos\theta_k + 1)\exp(\pm i\phi_k)S'_{\pm k}$$

$$+\tfrac{1}{2}(\cos\theta_k - 1)\exp(\mp i\phi_k)S'_{\mp k}\ . \quad (19)$$

Also, from Gottfried[14] we find that

$$Y_{2m}(\theta_{jk}, \phi_{jk}) = \sum_{m'} Y_{2m'}(\theta'_{jk}, \phi'_{jk})D^{(2)}_{m'm}(-\phi_k, -\theta_k, 0)$$

$$= \sum_{m'} Y_{2m'}(\theta'_{jk}, \phi'_{jk})\exp(im'\phi_k)d^{(2)}_{mm'}(\theta_k)\ , \quad (20)$$

where θ'_{jk} and ϕ'_{jk} are the spherical coordinates of $\mathbf{r}_{jk}$ in the new coordinate system $x'y'z'$. Explicit expressions for $d^{(2)}_{mm'}(\theta_k)$ are found in Ref. 15.

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

$$G_{jk} = \tfrac{1}{2}r_{jk}^{-3}\sqrt{\frac{\pi}{5}}\sum_m Y_{2m}(\theta'_{jk}, \phi'_{jk})\exp(im\phi_k)$$

$$\times[\exp(i\phi_k)f_{+m}(\theta_k)S'_{+k} + \exp(-i\phi_k)f_{-m}(\theta_k)S'_{-k} + f_{zm}(\theta_k)S'_{zk}]\ , \quad (21)$$

where

$$f_{\pm m}(\theta_k) = -(\cos\theta_k \mp 1)d^{(2)}_{0m}(\theta_k) - \sqrt{6}\sin\theta_k d^{(2)}_{-1m}(\theta_k)$$

$$+\sqrt{6}(\cos\theta_k \pm 1)d^{(2)}_{-2m}(\theta_k)\ , \quad (22)$$

and

$$f_{zm}(\theta_k) = -2\sin\theta_k d^{(2)}_{0m}(\theta_k) + 2\sqrt{6}\cos\theta_k d^{(2)}_{-1m}(\theta_k)$$

$$+2\sqrt{6}\sin\theta_k d^{(2)}_{-2m}(\theta_k)\ . \quad (23)$$

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 α transition involves energy levels split by an amount

$$\omega_{abk} = \omega_{QS} - \tfrac{1}{2}\cos\theta_k[3 - (1 + 4\tan^2\theta_k)^{1/2}]\omega_{0S}\ , \quad (24)$$

where ω_{QS} is the pure quadrupole splitting of the S spins in zero field ($H_0 = 0$) and $\omega_{0S} = \gamma_S H_0$. Using the following relations for the α transition,

$$\langle a, k \,|\, S'_{+k} \,|\, b, k\rangle = \sqrt{\tfrac{3}{2}}\,[1 + (1 + 4\tan^2\theta_k)^{-1/2}]^{1/2}\,, \qquad (25)$$

$$\langle a, k \,|\, S'_{-k} \,|\, b, k\rangle = 0\,, \qquad (26)$$

and

$$\langle a, k \,|\, S'_{zk} \,|\, b, k\rangle = 0\,, \qquad (27)$$

we obtain from Eqs. (16) and (21),

$$\frac{1}{\tau_{IS\alpha}} = \frac{3\pi}{160}\,\gamma_I^2\gamma_S^2\hbar^2 N_I^{-1}\sum_{j,k} r_{jk}^{-6}\delta(\omega_{0I} - \omega_{abk})$$

$$\times [1 + (1 + 4\tan^2\theta_k)^{-1/2}]\sum_{m,m'} 4\pi Y_{2m}(\theta'_{jk}, \phi'_{jk})$$

$$\times Y^*_{2m'}(\theta'_{jk}, \phi'_{jk})\exp[i(m - m')\phi_k]f_{+m}(\theta_k)f_{+m'}(\theta_k)\,. \qquad (28)$$

This expression can be simplified considerably by taking a powder average. (In the glassy crystalline phase of $CFCl_2$–$CFCl_2$, for example, where the molecular orientations are disordered, we would expect the anisotropy of τ_{IS} to be rather small. Thus, in this case, taking a powder average probably does not affect the results significantly.) Therefore, we average Eq. (28) over θ_k and ϕ_k. Since ω_{abk} is independent of ϕ_k [see Eq. (24)], the integration is trivial, and we obtain

$$\left\langle\frac{1}{\tau_{IS\alpha}}\right\rangle = \frac{1}{160}\,\pi\gamma_I^2\gamma_S^2\hbar^2\omega_{0S}^{-1}N_I^{-1}\sum_m [\,f_{+m}(\theta)]^2$$

$$\times \sum_{j,k} r_{jk}^{-6}4\pi\,|\,Y_{2m}(\theta'_{jk}, \phi'_{jk})\,|^2\,, \qquad (29)$$

where θ is the solution of

$$\omega_{QS} - \tfrac{1}{2}\cos\theta[3 - (1 + 4\tan^2\theta)^{1/2}]\omega_{0S} = \omega_{0I}\,. \qquad (30)$$

Solving Eq. (30), we find that θ is double valued, i.e.,

$$\theta = \cos^{-1}\left\{-\frac{1}{2}\frac{\gamma_I}{\gamma_S}\left(1 - \frac{\omega_{QS}}{\omega_{0I}}\right) \pm \left[\frac{1}{3} - \frac{1}{12}\frac{\gamma_I^2}{\gamma_S^2}\left(1 - \frac{\omega_{QS}}{\omega_{0I}}\right)^2\right]^{1/2}\right\}\,. \qquad (31)$$

and is restricted to the range,

$$\frac{\gamma_I}{\gamma_S}\left|1 - \frac{\omega_{QS}}{\omega_{0I}}\right| \leq 1\,. \qquad (32)$$

This restriction results from the requirement that the solution must also satisfy Eq. (24).

Similarly, expressions can be derived for the α', β, and β' transitions. Adding together the contributions to τ_{IS}^{-1} from each transition, we finally obtain

$$\left\langle\frac{1}{\tau_{IS}}\right\rangle = \frac{1}{160}\,\pi\gamma_I^2\gamma_S^2\hbar^2\omega_{0S}^{-1}(N_S/N_I)a_0^{-6}\sum_{p=0}^{1}\sum_{q=0}^{1}\sum_{m=-2}^{2}\left\{-[\cos\theta_{pq} - (-1)^q]d_{0m}^{(2)}(\theta_{pq})\right.$$

$$\left. -\sqrt{6}\sin\theta_{pq}d_{-1m}^{(2)}(\theta_{pq}) + \sqrt{6}[\cos\theta_{pq} + (-1)^q]\,d_{-2m}^{(2)}(\theta_{pq})\right\}^2 N_S^{-1}\sum_{j,k}\left(\frac{a_0}{r_{jk}}\right)^6 4\pi\,|\,Y_{2m}(\theta'_{jk}, \phi'_{jk})\,|^2\,, \qquad (33)$$

where

$$\theta_{pq} = \cos^{-1}\left\{-\frac{1}{2}(-1)^q\frac{\gamma_I}{\gamma_S}\left(1 - \frac{\omega_{QS}}{\omega_{0I}}\right)\right.$$

$$\left. + (-1)^p\left[\frac{1}{3} - \frac{1}{12}\frac{\gamma_I^2}{\gamma_S^2}\left(1 - \frac{\omega_{QS}}{\omega_{0I}}\right)^2\right]^{1/2}\right\}\,. \qquad (34)$$

The summations over the indices p and q arise from the need to sum over all four transitions; however, there is not a one-to-one correspondence between p, q, and any particular transition.

IV. APPLICATION TO CFCl$_2$–CFCl$_2$

In the glassy crystalline phase of $CFCl_2$–$CFCl_2$, the molecules sit in a bcc lattice but are randomly oriented relative to each other. They are "frozen" into an orientationally disordered state. The lattice sum in Eq. (33) can thus be written,

$$S_m = N_S^{-1}\sum_{j,k}\left(\frac{a_0}{r_{jk}}\right)^6 4\pi\,|\,Y_{2m}(\theta'_{jk}, \phi'_{jk})\,|^2$$

$$= \sum_j\left\langle\left(\frac{a_0}{r_{jk}}\right)^6 4\pi\,|\,Y_{2m}(\theta'_{jk}, \phi'_{jk})\,|^2\right\rangle\,, \qquad (35)$$

where the summation is over all I spins (j) relative to a given S spin (k). The lattice parameter a_0 is defined to be the distance between lattice points along the [100] direction. Since the S spins are not in equivalent positions, we average each j-k pair over all possible orientations of their respective molecules. Note that

$|\,Y_{2m}(\theta'_{jk}, \phi'_{jk})\,|^2$ is independent of ϕ'_{jk} and depends only on θ'_{jk}, the angle between $\mathbf{r}_{jk}$ and the symmetry axis of the electric field gradient at S_k. (We assume this symmetry axis, the z' axis, to be along the C–Cl bond.)

The calculation of the intramolecular contribution to S_m is straightforward since r_{jk} and θ'_{jk} are independent of molecular orientation in this case. The calculation of the intermolecular contribution to S_m, on the other hand, is more complicated. For this calculation, we find it convenient to use a coordinate system $x''y''z''$ such that the z'' axis points from the center of the molecule (the midpoint of the two carbon atoms) through the Cl atom on the same molecule. (This Cl atom is the one whose interactions are now being calculated.) Thus we define a coordinate transformation $x'y'z' \rightarrow x''y''z''$ by (1) a rotation 19° about the y' axis (chosen to be perpendicular to the C–C–Cl plane) followed by (2) a rotation ϕ about the new z'' axis. (19° is thus the angle between the old z' axis and the new z'' axis.) Using relations such as Eq. (20) and averaging over ϕ, we obtain

$$S_m^{\text{inter}} = \sum_{m'} [d_{mm'}^{(2)}(19°)]^2\sum_j\left\langle\left(\frac{a_0}{r_{jk}}\right)^6 4\pi\,|\,Y_{2m'}(\theta''_{jk}, \phi''_{jk})\,|^2\right\rangle\,, \qquad (36)$$

where θ''_{jk} and ϕ''_{jk} are spherical coordinates of $\mathbf{r}_{jk}$ in the new coordinate system $x''y''z''$.

The average over all orientations of the two molecules containing the j and k sites is done by integrating over the surfaces of two spheres generated by rotating
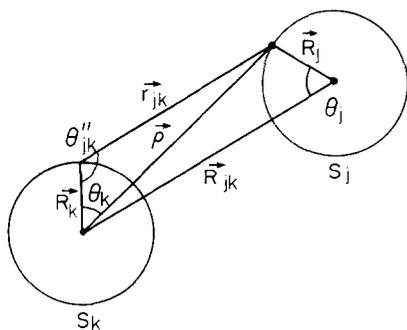
FIG. 1. Integration over the surfaces of spheres S_j and S_k.

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

$$\cos\theta_k = \frac{R_k^2 + \rho^2 - r_{jk}^2}{2R_k\rho} , \tag{37}$$

and

$$\cos\theta_{jk}'' = \frac{r_{jk}^2 + R_k^2 - \rho^2}{2R_k r_{jk}} . \tag{38}$$

Holding ρ fixed, we have

$$\oint_{S_k} dS_k \left(\frac{a_0}{r_{jk}}\right)^6 f(\cos\theta_{jk}'') = \frac{1}{2}\int_{-1}^{1} d(\cos\theta_k)\left(\frac{a_0}{r_{jk}}\right)^6 f(\cos\theta_{jk}'')$$

$$= \frac{1}{2}\frac{a_0^6}{R_k\rho}\int_{\rho-R_k}^{\rho+R_k} r_{jk}^{-5}\,dr_{jk}\,f\left(\frac{r_{jk}^2 + R_k^2 - \rho^2}{2R_k r_{jk}}\right) , \tag{39}$$

where f is some function of $\cos\theta_{jk}''$. In our particular case, we have

$$f(\cos\theta_{jk}'') = 4\pi\,|\,Y_{2m'}(\theta_{jk}'', \phi_{jk}'')\,|^2 \tag{40}$$
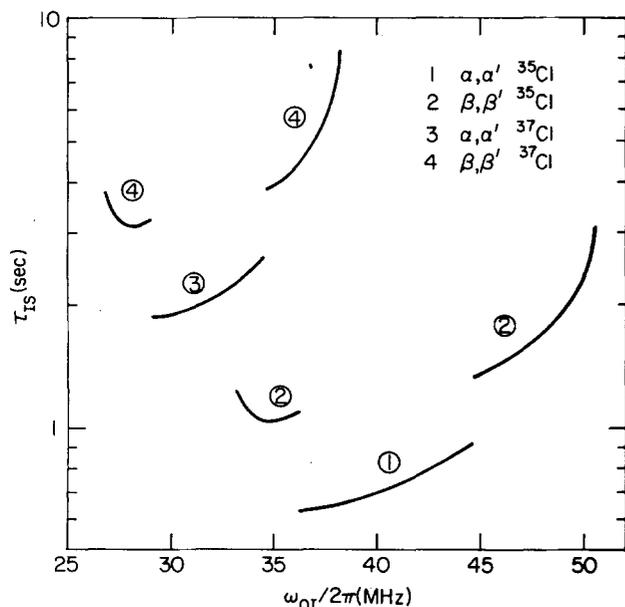
FIG. 2. Contribution to τ_{IS} of the ^{35}Cl and ^{37}Cl isotopes in CFCl$_2$–CFCl$_2$.
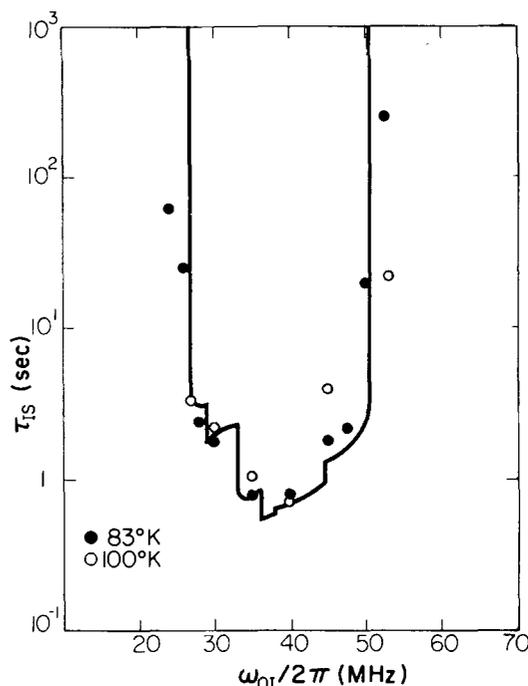

FIG. 3. Total cross relaxation time τ_{IS} in CFCl$_2$–CFCl$_2$ calculated from Eq. (33). Experimental points are from Ref. 11.

Similarly, we integrate over the sphere S_j, using

$$\cos\theta_j = \frac{R_{jk}^2 + R_j^2 - \rho^2}{2R_{jk}R_j} , \tag{41}$$

and obtain

$$\oint_{S_j} dS_j \oint_{S_k} dS_k \left(\frac{a_0}{r_{jk}}\right)^6 f(\cos\theta_{jk}'')$$

$$= \frac{a_0^6}{4R_jR_kR_{jk}}\int_{R_{jk}-R_j}^{R_{jk}+R_j} d\rho \int_{\rho-R_k}^{\rho+R_k} r^5\,dr\,f\left(\frac{r^2 + R_k^2 - \rho^2}{2R_k r}\right) . \tag{42}$$

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

$$S_m^{\text{inter}} = \sum_{m'}[d_{mm'}^{(2)}(19°)]^2\,2\sum_j \frac{a_0^6}{4R_jR_kR_{jk}}$$

$$\times \int_{R_{jk}-R_j}^{R_{jk}+R_j} d\rho \int_{\rho-R_k}^{\rho+R_k} r^{-5}\,dr\,4\pi\,|\,Y_{2m'}(\theta_{jk}'', \phi_{jk}'')\,|^2 , \tag{43}$$

where $|\,Y_{2m'}(\theta_{jk}'', \phi_{jk}'')\,|^2$ is evaluated at $\cos\theta_{jk}'' = (r^2 + R_k^2 - \rho^2)/2rR_k$. 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 τ_{IS} for CFCl$_2$–CFCl$_2$. All the physical constants needed for the calculations are well known except for the pure quadrupole splitting ω_{QS} of ^{35}Cl and ^{37}Cl. From NQR measurements in other chlorinated ethanes[17-19] we find that, generally, $\omega_{QS}/2\pi \cong 40$ MHz

TABLE I. Evaluation of the lattice sum S_m in $CFCl_2-CFCl_2$.

m	Isomer	Intramolecular	Intermolecular	Total
0	*trans*	931	234	1165
	gauche	988		1222
±1	*trans*	1063	195	1258
	gauche	930		1125
±2	*trans*	184	156	340
	gauche	136		292

for ^{35}Cl in these compounds. Thus we used this value (and hence 31.5 MHz for ^{37}Cl) in the calculation of τ_{IS}.

In Fig. 2 we plot the results of the calculation, showing the separate contributions to τ_{IS}^{-1} from the ^{35}Cl and ^{37}Cl isotopes. Adding them together, we obtain the resultant τ_{IS}^{-1} 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.[11]) As can be seen, the agreement between theory and experiment is quite good.

ACKNOWLEDGMENTS

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