Nuclear Dipolar Relaxation in Pure Solids

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Relaxation of the nuclear dipolar energy $\langle \mathscr{H}_D \rangle$ is considered. The static part of $\mathscr{H}_D$ sets up an energy reservoir, and its dynamic part is taken as the predominant cause for the spinlattice relaxation. This situation may be realized in nature in such pure solids in which molecular reorientations are frequent. Relaxation steps in which the total nuclear spin quantum number does not change are treated in detail. They are found to involve always three nuclear spins. The theory is applied to solid benzene in which the molecules are assumed to reorient about their 6fold symmetry axis. Both intra- and intermolecular interactions need to be taken into account. The theoretical results obtained are in close agreement with recent measurements of van Steenwinkel.

I. Introduction

Nuclear spin energy and spin order in solids can be transferred from the Zeeman subsystem to the dipolar subsystem by various techniques. Experiments both in the laboratory and in the rotating frame of spin coordinates have been performed[1].

Spin temperatures Θ_z and Θ_d can be assigned separately to the subsystems. The lattice, at temperature Θ_1, acts as a heat bath to both. Starting with an initial situation with Θ_z and Θ_d different from Θ_1, relaxation processes will drive Θ_z and Θ_d towards Θ_1. The Zeeman system will relax with a rate $1/T_1$ (or $1/T_{1\varrho}$ in the rotating frame), the dipolar system with a rate $1/T_{1D}$. Though both rates may be governed by the same lattice processes, e.g. molecular motions, they are numerically quite different in general. They are independent sources for information about molecular motions.

General expressions for $1/T_1$ and $1/T_{1D}$ in terms of traces of products of commutators have been given by Jeener[1]. His expression for $1/T_{1D}$ is based on the following spin Hamiltonian:

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}' + \mathscr{H}'' + \mathscr{H}_1(t) \qquad (1)$$

where $\quad \mathscr{H}_0 = -\gamma \hbar H_0 \sum_i I_{zi}$.

$\mathscr{H}'$ and $\mathscr{H}''$ are, respectively, the *time independent* secular and nonsecular parts of the dipolar Hamiltonian $\mathscr{H}_D$.

$$\mathscr{H}_D = -\sqrt{\frac{6\pi}{5}} \gamma^2 \hbar^2 \sum_{i<k} r_{ik}^{-3} (-1)^m Y_{2,-m}^{ik} T_{2m}^{ik}. \qquad (2)$$

The T_{2m}^{ik}'s are second order tensor operators formed with the components of the spin operators I^i and I^k. All other symbols have their usual meaning. The Einstein summation convention is used with respect to the index m.

$\mathscr{H}_1(t)$ is the time dependent perturbation which is the cause for the relaxation. It may represent the coupling of the nuclear spins to paramagnetic impurities or to fluctuating electric field gradients (if $I > 1/2$), but also the coupling of the spins to the lattice via time dependent nuclear dipole dipole interactions.

In a recent paper[2] van Steenwinkel has published measurements of T_1 and T_{1D} of pure solid benzene, hexamethylbenzene and cyclohexane over a wide range of temperatures.

In the theoretical analysis of his data he introduces the operator

$$\mathscr{H}_1(t) = -\gamma \hbar \sum_i H_i(t) I_i. \qquad (3)$$

While this operator often provides a good description for the coupling of nuclear spins to paramagnetic impurities with short electron spin relaxation times, $\mathscr{H}_1(t)$ can, in fact, be written in more detail for the systems measured in Ref. 2. It is known that in solid benzene, e.g., even at low temperatures substantial molecular reorientations are going on rapidly[3]. Therefore in pure solid benzene — but also in many other pure molecular crystals — nuclear dipole dipole interactions can be expected to provide the predominant spin-lattice relaxation mechanism for both the nuclear Zeeman and the dipolar energy reservoirs.

[1] J. Jeener, in: Advances in Magnetic Resonance, ed. J. Waugh, Vol. 3, New York 1968.
[2] R. van Steenwinkel, Z. Naturforsch. 24a, 1526 [1969].
[3] E. R. Andrew and R. G. Eades, Proc. Roy. Soc. London A 218, 537 [1953].

In Sect. II we show that nuclear dipole dipole interactions can set up a static energy reservoir and provide, at the same time, an effective spin-lattice relaxation mechanism. Furthermore, in this section the general expression for the dipolar relaxation rate given by Jeener is worked out in sufficient detail to enable us to calculate dipolar relaxation times for given models of molecular motions.

A very interesting feature for which a clear physical interpretation can be given is that for dipolar relaxation not only two-spin- but also three-spin-systems must be considered as smallest units. In Zeeman relaxation theory two-spin-systems are sufficient in general.

In Sect. III the results obtained in Sect. II are applied to solid benzene. For this compound a model for molecular motions is known, which accounts quantitatively (within the limits of experimental errors) for both the second moment $\overline{\Delta\omega^2}$ of the resonance line[3] and the Zeeman relaxation time T_1 over a wide range of temperatures and magnetic fields[4]. This model is used to calculate T_{1D} in order to find out if it can also account for dipolar relaxation. In Sect. IV the theoretical results are compared with the experimental results of van Steenwinkel.

II. Theory

As outlined in the introduction we consider $\mathscr{H}_1(t)$ in Eq. (1) as originating from the time dependent secular and nonsecular parts of $\mathscr{H}_D$. In order to split $\mathscr{H}_D$ in time dependent and time independent parts we define quantities C_m^{ik} and $X_m^{ik}(t)$ by

$$r_{ik}^{-3}(t)\, Y_{2m}^{ik}(t) = C_m^{ik} + X_m^{ik}(t) \qquad (4)$$

where

$$C_m^{ik} = \overline{r_{ik}^{-3}(t)\, Y_{2m}^{ik}(t)}. \qquad (5)$$

The bar denotes a time average. Eqs. (4) and (5) define $X_m^{ik}(t)$. Its time average is zero by definition. Using Eqs. (4) and (5) we get straightforwardly

$$\mathscr{H}' = -\sqrt{\frac{6\pi}{5}}\,\gamma^2\hbar^2 \sum_{i<k} C_0^{ik}\, T_{20}^{ik}, \qquad (6a)$$

$$\mathscr{H}'' = -\sqrt{\frac{6\pi}{5}}\,\gamma^2\hbar^2 \sum_{i<k} (-1)^m C_{-m}^{ik}\, T_{2m}^{ik},\ m \neq 0, \qquad (6b)$$

[4] U. Haeberlen and G. Maier, Z. Naturforsch. 22 a, 1236 [1967].

$$\mathscr{H}_1(t) = -\sqrt{\frac{6\pi}{5}}\,\gamma^2\hbar^2 \sum_{i<k}(-1)^m X_{-m}^{ik}(t)\, T_{2m}^{ik}$$

$$\equiv \sum_m \mathscr{H}_1^m(t), \quad m = -2,-1,0,1,2. \qquad (6c)$$

As our starting point for calculating the relaxation rate of the dipolar energy we use the following expression[5]:

$$1/T_{1D} = \frac{1}{\hbar^2\,\mathrm{Tr}(\mathscr{H}')^2}\int_0^\infty \mathrm{d}\tau$$

$$\cdot \langle \mathrm{Tr}\{[\mathscr{H}',\widetilde{\mathscr{H}}_1(t)][\widetilde{\mathscr{H}}_1(t+\tau),\mathscr{H}']\}\rangle_{\mathrm{Av}} \quad (7)$$

where

$$\widetilde{\mathscr{H}}_1(t) = U^{-1}(t)\,\mathscr{H}_1(t)\,U(t) \qquad (8)$$

and

$$U(t) = \exp\{-i/\hbar\,(\mathscr{H}_0 + \mathscr{H}')\,t\}$$

$$= \exp\{-i/\hbar\,\mathscr{H}_0 t\}\exp(-i/\hbar\,\mathscr{H}' t). \quad (9)$$

The last equality holds because $\mathscr{H}_0$ and $\mathscr{H}'$ commute per definition.

In the regime where the correlation time τ_c of the molecular motion is short as compared to T_2 we can approximate $\exp\{-i/\hbar\,\mathscr{H}' t\}$ by unity, because then other factors under the integration sign have decayed to zero long before $\exp\{-i/\hbar\,\mathscr{H}' t\}$ deviates appreciably from unity. Here we shall restrict ourselves to this regime. A tentative ad hoc treatment for longer correlation times is given in Ref. 2.

Using $U(t) \approx \exp\{-i/\hbar\,\mathscr{H}_0 t\}$ we get

$$\widetilde{\mathscr{H}}_1^m(t) = \mathscr{H}_1^m(t)\cdot e^{im\omega_0 t} \qquad (10)$$

and

$$1/T_{1D} = \frac{1}{\hbar^2\,\mathrm{Tr}(\mathscr{H}')^2}\int_0^\infty \mathrm{d}\tau \sum_{m=-2}^{+2} e^{-im\omega_0\tau} \qquad (11)$$

$$\cdot \langle \mathrm{Tr}\{[\mathscr{H}',\mathscr{H}_1^m(t)][\mathscr{H}_1^{-m}(t+\tau),\mathscr{H}']\}\rangle_{\mathrm{Av}}.$$

Eq. (11) does not follow directly from Eqs. (7) and (10). There are more terms. However, we must suppress the additional terms in order to avoid a rapidly oscillating result.

For stochastic random molecular motions the $m=0$ term leads to a contribution proportional to τ_c, the $m=\pm 1$ and $m=\pm 2$ terms to contributions proportional to

$$\tau_c/(1+\omega_0^2\tau_c^2) \quad \text{and} \quad \tau_c/(1+4\omega_0^2\tau_c^2).$$

When the molecular motions are slow ($\omega_0\tau_c \gg 1$) the term $m=0$ will dominate the dipolar relaxation

[5] Ref. 1, Eq. (4, 43a).

rate. Here we shall mainly concentrate on this term. It is a very interesting one because it leads us to consider relaxation in three-spin-systems.

In calculating relaxation times T_1, T_2, $T_{1\varrho}$ etc. we have got used to treat two-spin-systems. However, for a two-spin-system the spin parts of both $\mathscr{H}'$ and $\mathscr{H}_1^0(t)$ are T_{20}^{ik} with the same pair of indices i and k and hence the commutators in Eq. (11) vanish.

By taking a three-spin-system as the basic relaxing unit we do get a non-zero result, and, as our example will show, we are able to explain experimental results quite well.

At this point we should perhaps ask ourselves: How about four-spin-systems in dipolar relaxation? How about a possible contribution of three-spin-systems to the relaxation rate of the Zeeman energy? Answering the first question we remark that both $\mathscr{H}'$ and $\mathscr{H}_1(t)$ are bilinear in the spin operators, therefore the commutators in Eq. (11) vanish when four different spins occur in a single one and the *trace* will vanish unless every spin from one commutator finds a partner in the other one. Thus we arrive easily at the result that *only* three-spin-systems contribute to the $m = 0$ term in Eq. (11).

Turning now to the second question we note that we know from *experiments* that no terms proportional to τ_c, which might possibly arise from three-spin-systems, contribute to the Zeeman relaxation rate.

Examining the expression for $1/T_1$ which corresponds to Eq. (11) (see Eq. (3) from Ref. 2) one can show by a similar argument as used above that indeed only spin pairs contribute to the relaxation rate of the Zeeman energy[6].

Checking the $m = 1$ and $m = 2$ terms in Eq. (11) one finds that spin pairs do contribute to the dipolar relaxation rate. It is interesting to note that the $m = 2$ part does so for $I > 1/2$ only.

These results are easily understood on a physical basis: The $m = 0$, ± 1, ± 2 terms in Eq. (11) represent, respectively, spin processes with $\Delta m = 0$, ± 1, ± 2 where Δm is the change of the spin quantum number of the total system in an elementary relaxation step.

For $\Delta m = 0$ in an elementary relaxation step one spin "flips up" another "flops down". The dipolar energy remains unchanged in a two-spin-system because the *relative* spin directions have not changed (for $I = 1/2$) in this flip-flop process. By supplementing the two-spin-system by a third spin the flip-flop process, while leaving unaffected the third spin, does result in a change of the total dipolar energy because the two flipping spins change their spin directions with respect to the third spin.

In a two-spin-system with $I = 1/2$ an elementary step with $\Delta m = \pm 2$ can only flip both spins in the same direction leaving their *relative* directions and their dipolar energy unchanged. For spins with $I > 1/2$, however, even in a two-spin-system there are $\Delta m = \pm 2$ processes in which relative spin directions do change. They always change in $\Delta m = \pm 1$ processes, hence these contribute to the dipolar relaxation rate even for two-spin-systems with $I = 1/2$.

Experimental evidence for an essential difference between two-spin- and more-than-two-spin-systems have been obtained by EISENDRATH et al. from measurements on gypsum[7].

Returning to the term $m = 0$ in Eq. (11), restricting ourselves to a single three-spin-system, dropping all indices $m = 0$ as redundant, and denoting the corresponding relaxation rate by $1/T_{1D}'$ we find by inserting Eqs. (6a—c) into Eq. (11)

$$1/T_{1D}' = \frac{6\pi}{5} \frac{\gamma^4 \hbar^2}{\mathrm{Tr}\{T_{20}^{ik}\}^2 \sum (C^{ij})^2} \int_0^\infty \mathrm{d}\tau \langle \mathrm{Tr}\{[\sum C^{ij} T_{20}^{ij}, \sum X^{kl}(t) T_{20}^{kl}][\sum X^{k'l'}(t+\tau) T_{20}^{k'l'}, \sum C^{i'j'} T_{20}^{i'j'}]\}\rangle_{\mathrm{Av}}. \quad (12)$$

The sums $\sum A^{\alpha\beta}$ always mean $\sum\limits_{\alpha<\beta}^{3} A^{\alpha\beta}$.

The first commutator K_1 under the integral gives

$$K_1 = [T_{20}^{12}, T_{20}^{13}]\{C^{12} X^{13}(t) - C^{13} X^{12}(t)\} + [T_{20}^{12}, T_{20}^{23}]\{C^{12} X^{23}(t) - C^{23} X^{12}(t)\}$$
$$+ [T_{20}^{13}, T_{20}^{23}]\{C^{13} X^{23}(t) - C^{23} X^{13}(t)\}. \quad (13)$$

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[6] One should not confuse the three-spin relaxing units as they are introduced here with the three or more spin-systems which must be treated as an entity with regard to spin relaxation because the molecule to which they belong moves as an entity.

[7] H. EISENDRATH, W. STONE, and J. JEENER, quoted in Ref. 1, page 214.

Clearly K_1 does not vanish in general. A similar expression is obtained for the second commutator K_2. With

$$T_{20}^{ik} = \sqrt{2/3}\,(3\,I_Z^i\,I_Z^k - \mathbf{I}^i \cdot \mathbf{I}^k) \tag{14}$$

we find

$$[T_{20}^{ik},\,T_{20}^{il}] = [T_{20}^{ki},\,T_{20}^{li}] = 2/3\,i\,\{i\,k\,l\} \tag{15}$$

where

$$\{i\,k\,l\} = 2\,I_y^i(I_x^k\,I_z^l - I_z^k\,I_x^l) + 2\,I_x^i(I_z^k\,I_y^l - I_y^k\,I_z^l) + I_z^i(I_x^k\,I_y^l - I_y^k\,I_x^l). \tag{16}$$

Inserting Eqs. (13), (15) and (16) into Eq. (12) we get for the integral in Eq. (12):

$$\frac{4}{9}\int_0^\infty \mathrm{d}\tau \,\langle \mathrm{Tr}\,\{[C^{12}\,X^{13}(t) - C^{13}\,X^{12}(t)]\,\{123\}$$
$$+ [C^{12}\,X^{23}(t) - C^{23}\,X^{12}(t)]\,\{213\} + [C^{13}\,X^{23}(t) - C^{23}\,X^{13}(t)]\,\{312\}\}$$
$$\times \{[C^{12}\,X^{13}(t+\tau) - C^{13}\,X^{12}(t+\tau)]\,\{123\} + [C^{12}\,X^{23}(t+\tau) - C^{23}\,X^{12}(t+\tau)]\,\{213\} \tag{17}$$
$$+ [C^{13}\,X^{23}(t+\tau) - C^{23}\,X^{13}(t+\tau)]\,\{312\}\}\rangle_{\mathrm{Av}}.$$

We now introduce the following correlation functions

$$K_{ik}(\tau) = \langle X^{ik}(t)\,X^{ik}(t+\tau)\rangle_{\mathrm{Av}} \tag{18a}$$

and

$$k_{ik,\,mn}(\tau) = \langle X^{ik}(t+\tau)\,X^{mn}(t) + X^{mn}(t+\tau)\,X^{ik}(t)\rangle_{\mathrm{Av}}. \tag{18b}$$

For the traces we get

$$\mathrm{Tr}\,(\{i\,k\,l\}\{i\,k\,l\}) = 18\,(\mathrm{Tr}\,I_Z^2)^3$$
$$= 18\left(\frac{I(I+1)(2\,I+1)}{3}\right)^3, \tag{19}$$

$$\mathrm{Tr}\,(\{i\,k\,l\}\{k\,i\,l\}) = \mathrm{Tr}\,(\{i\,k\,l\}\{l\,i\,k\}) = 0 \tag{20}$$

and

$$\mathrm{Tr}\,(T_{20}^{ik})^2 = 4\left(\frac{I(I+1)(2\,I+1)}{3}\right)^2(2\,I+1). \tag{21}$$

The extra factor $(2\,I+1)$ in Eq. (21) arises because this trace as the former ones has to be evaluated for a three-spin system.

By inserting Eqs. (17) through (21) into Eq. (12) we get our final result

$$1/T_{1\mathrm{D}}' = \frac{4\pi}{5}\,\frac{\gamma^4\,\hbar^2\,I(I+1)}{\sum(C^{ik})^2}\int_0^\infty \mathrm{d}\tau$$
$$\cdot\{(C^{12})^2\,[K_{13}(\tau) + K_{23}(\tau)]$$
$$+ (C^{13})^2\,[K_{12}(\tau) + K_{23}(\tau)]$$
$$+ (C^{23})^2\,[K_{13}(\tau) + K_{12}(\tau)] \tag{22}$$
$$- C^{12}\,C^{13}\,k_{12,\,13}(\tau) - C^{12}\,C^{23}\,k_{12,\,23}(\tau)$$
$$- C^{13}\,C^{23}\,k_{13,\,23}(\tau)\}.$$

For the sake of clarity we didn't contract — as is possible — the two different types of terms into sums with running indices. Eq. (22) is easily generalized for many-spin systems. The expression in the curly brackets has to be replaced by a sum of such expressions, one for each different three-spin system $(i\,k\,l)$, $i < k$, $i < l$, which can be selected from the many-spin system. In the denominator of Eq. (22) the sum has to be extended over all spins of the whole system.

The generalization in question will be used in the example to be treated in the next section.

III. Application to Benzene

A model for the molecular motions in solid benzene has been described in the literature [3,4,8] which accounts very well for the observed behaviour of the Zeeman spin lattice relaxation and the second moment of the resonance line. According to this model the benzene molecules always stay at their equilibrium lattice sites but jump randomly around their sixfold symmetry axes into any of the six equivalent equilibrium positions with equal probabilities. We shall use this model to calculate $1/T_{1\mathrm{D}}'$.

First we consider *intra*molecular interactions only. Later on we shall turn to *inter*molecular ones also.

We begin by separating the secular dipolar intramolecular Hamiltonian of a randomly chosen benzene molecule into its time dependent and time independent parts (see Fig. 1).

The argument Θ^{ik} of $Y_{20}^{ik}(t) = Y_{20}(\Theta^{ik}(t))$ in Eq. (4) is defined with respect to a frame of reference in which H_0 points along the z-direction. Y_{20} is

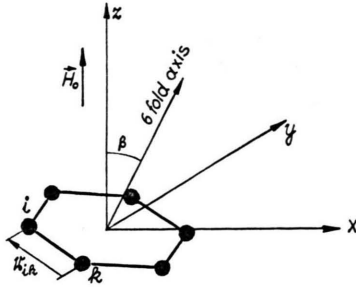[8] J. E. Anderson, J. Chem. Phys. **43**, 3575 [1965].

Fig. 1. Definition of frames and reference.

invariant under rotations around the z-axis, so we can choose the x-axis, without loss of generality, such that it lies in the plane defined by the z-axis and the sixfold symmetry axis of the molecule.

A rotation through β around the y-axis brings the frame of reference into a new position with z_{new} along the symmetry axis of the molecule.

$$r_{ik}^{-3} Y_{20}(\Theta^{ik}(t)) = r_{ik}^{-3} \sum_{m'} \mathbf{D}_{om'}^{2}(0, \beta, 0)\, Y_{2m'}(\vartheta^{ik}, \varphi^{ik}).$$
$$(23)$$

The $\mathbf{D}_{mm'}^{2}(\alpha, \beta, \gamma)$'s are Wigner rotation matrices in the notation of EDMONDS [9]; r_{ik}, ϑ^{ik} and φ^{ik} are the spherical coordinates of the internuclear vector $\mathfrak{r}_{ik}$ in the new frame. For intramolecular interactions all r_{ik} are constant in time. The model described above tells us that ϑ^{ik} is also independent of time and equals $\pi/2$ for all i, k. φ^{ik} *is* dependent on time and jumps randomly between the six values

$$\varphi_g = \varphi_0 - g \cdot \pi/3, \quad g = 0, 1, 2, 3, 4, 5.$$

By noting that for this model of molecular motions $\bar{Y}_{2m} = 0$ except for Y_{20} which is independent of φ we get

$$C^{ik} \equiv \overline{r_{ik}^{-3}(t)\, Y_{20}(\Theta^{ik}(t))} = r_{ik}^{-3}\, \mathbf{D}_{00}^{2}\,(0, \beta, 0)\, Y_{20}\left(\frac{\pi}{2}\right)$$
$$= r_{ik}^{-3}\,\frac{3\cos^2\beta - 1}{2}\left(-\frac{1}{4}\,\sqrt{\frac{5}{\pi}}\right). \quad (24)$$

Because

$$Y_{2,\pm1}\left(\frac{\pi}{2}, \varphi\right) = 0, \quad Y_{22}\left(\frac{\pi}{2}, \varphi\right) + Y_{2,-2}\left(\frac{\pi}{2}, \varphi\right)$$
$$= \frac{1}{4}\,\sqrt{\frac{15}{2\pi}}\,(e^{2i\varphi} + e^{-2i\varphi}),$$

and

$$\mathbf{D}_{0,\pm2}^{2}(0, \beta, 0) = \sqrt{\tfrac{3}{8}}\,\sin^2\beta$$

[9] A. R. EDMONDS, Angular Momentum in Quantum Mechanics, Princeton University Press 1957.

we find by subtracting Eq. (24) from Eq. (23)

$$X^{ik}(t) = r_{ik}^{-3} \cdot \tfrac{3}{8}\,\sqrt{5/\pi}\,\sin^2\beta\,\cos 2\,\varphi(t). \quad (25)$$

By use of the absolute and conditional probabilities p and P defined in Ref. 4 we get by straightforward calculation

$$K_{ik}(\tau) = \frac{45}{128\,\pi}\,r_{ik}^{-6}\,\sin^4\beta\,e^{-\tau/\tau_c} \quad (26)$$

and

$$k_{ik,mn}(\tau) = \frac{45}{64\,\pi}\,r_{ik}^{-3}\,r_{mn}^{-3}\,\sin^4\beta\,\cos 2\,\Delta\varphi_{ik,mn}\,e^{-\tau/\tau_c}$$
$$(27)$$

where

$$\cos\Delta\varphi_{ik,mn} = \frac{\mathfrak{r}_{ik}\cdot\mathfrak{r}_{mn}}{r_{ik}\,r_{mn}}. \quad (28)$$

For a single benzene molecule which we consider here the sum $\sum_{i<k}(C^{ik})^2$ in the denominator of Eq. (22) has 15 terms of three types as indicated in Table 1.

Type		#	r_{ik}
1)		6	d
2)		6	$d\sqrt{3}$
3)		3	$2d$

Tab. 1. r_{ik}'s in the benzene molecule; d is the distance of nearest neighbour protons.

With the aid of Table 1 and Eq. (24) we get

$$\sum_{i<k}(C^{ik})^2 = \frac{5}{64\,\pi}\,(3\cos^2\beta - 1)^2\,\frac{1}{d^6}\left\{6 + \frac{6}{27} + \frac{3}{64}\right\}. \quad (29)$$

From the six protons of a benzene ring twenty different three-spin systems may be selected and divided into three groups (Table 2). Every three-spin system in a group contributes the same amount to the dipolar relaxation rate.

Group	Members	#
1	(123), (234), (345), (456), (156), (126)	6
2	(124), (236), (136), (145), (146), (256)	12
	(125), (235), (356), (245), (134), (346)	
3	(135), (246)	2

Tab. 2. Intramolecular three-spin systems in a benzene molecule.

Let us take spin systems (123), (124) and (135) as representatives of their groups. The $\Delta\varphi_{ik,mn}$'s re-

quired for the evaluation of the $k_{ik,mn}$'s are as follows:

System (123):
$$\Delta\varphi_{12,23} = 120°; \quad \Delta\varphi_{12,13} = \Delta\varphi_{13,23} = 30°;$$

System (124):
$$\Delta\varphi_{12,14} = 60°; \quad \Delta\varphi_{12,24} = 90°; \quad \Delta\varphi_{14,24} = 30°;$$

System (135):
$$\Delta\varphi_{13,15} = \Delta\varphi_{13,35} = \Delta\varphi_{15,35} = 60°. \tag{30}$$

Eqs. (24), (26), (27) and (30) and Table 1 yield with a little algebra for the contribution of three-spin system (123) to the integrand of Eq. (22) the expression

$$\text{const}\{r_{12}^{-6} r_{23}^{-6}(1 - \cos 240°) + r_{12}^{-6} r_{13}^{-6}(1 - \cos 60°) + r_{13}^{-6} r_{23}^{-6}(1 - \cos 60°)\} = 1.537\, d^{-12} \cdot \text{const} \tag{31}$$

where

$$\text{const} = \frac{225}{\pi^2}\, 2^{-12}\, (3\cos^2\beta - 1)^2 \sin^4\beta\, e^{-\tau/\tau_c}. \tag{32}$$

Similarly, three-spin systems (124) and (135) contribute, respectively,

$$\text{const}\{r_{12}^{-6} r_{24}^{-6}(1 - \cos 180°) + r_{12}^{-6} r_{14}^{-6}(1 - \cos 120°) + r_{14}^{-6} r_{24}^{-6}(1 - \cos 60°)\} = 0.101\, d^{-12}\, \text{const}, \tag{33}$$

and

$$3\, \text{const}\{r_{13}^{-6} r_{15}^{-6}(1 - \cos 120°)\} = 0.006\, d^{-12}\, \text{const}.$$

We have chosen to present the contributions of the various spin systems in the form of Eqs. (31) ... (34) in order to show how rapidly the contributions drop off with increasing distances between the spins involved.

Carrying out the integration — which replaces $\exp\{-\tau/\tau_c\}$ in Eq. (32) simply by τ_c — and adding up the various contributions we get

$$1/T'_{1D}(\text{intra}) = \gamma^4 \hbar^2 I(I+1) \tag{35}$$
$$\cdot \frac{\tau_c}{d^6}\, \frac{9}{16}\, \sin^4\beta\, \frac{6 \cdot 1{,}537 + 12 \cdot 0{,}101 + 2 \cdot 0{,}006}{6{,}269}.$$

Note that the factors $(3\cos^2\beta - 1)^2$ in the numerator and denominator cancel. The three addends of the numerator in Eq. (35) arise from the three types of three-spin systems. For a poly-crystalline sample $\sin^4\beta$ must be averaged over a sphere with the result $\langle\sin^4\beta\rangle_{\text{av}} = 8/15$ and our final result for the intramolecular contributions to the dipolar relaxation rate is thus

$$1/T'_{1D}(\text{intra}) = \gamma^4 \hbar^2 I(I+1)\, \frac{\tau_c}{d^6}\, \frac{3}{10} \cdot \frac{10{,}444}{6{,}269}. \tag{36}$$

Turning now to the dipolar relaxation rate due to *inter*molecular interactions we note first that for a given model of molecular motions it can be treated also fully but such a treatment cannot reasonably be done by hand. Here we present an approximate treatment only. We intend to do a computer calculation of the intermolecular relaxation rate, its main motivation being a test how close simple approximate methods approach the exact result.

Let us first extend the system considered by a second (primed) molecule. For a powder sample $\text{Tr}\{\mathscr{H}'(\text{intra})\}^2$ in the denominator of Eq. (7) just doubles and so does the intramolecular part of the numerator. Three-spin systems of the types (ikl') and $(ik'l')$. $i, k, \ldots, l' = 1, 2, \ldots, 6$ will "couple" the two molecules. It is now very important to note that *inter*molecular interactions contribute only very little to $\text{Tr}\{\mathscr{H}'\}^2$, because the time average of all distances $r_{ik'}$ is much larger than d. Whereas the static intermolecular interactions are vital for establishing a common spin temperature among the various molecules they can and will be neglected in our present considerations. Dropping now one half of the coupling three-spin systems, say all $(ik'l')$ systems, enables us to restrict the summation for $\text{Tr}\{\mathscr{H}'\}^2$ still over the protons of the first molecule only. From the remaining (i, k, l') systems we keep only the most important ones which are those for which i and k are nearest neighbours.

There are 36 such (i, k, l') spin systems. They all relax the unprimed (reference) benzene molecule equally. Hence we shall consider only one such spin system, say the $(123')$ spin system, and multiply the result by 36.

Now we are facing again the problem of splitting a Hamiltonian ($\mathscr{H}_{\text{Dip, sec}}$ $(123')$) into its time dependent and time independent parts. From Eq. (24) we *know* that

$$C^{12} = \frac{1}{d^3}\, \overline{Y_{20}^{12}(t)} = -\frac{1}{4}\sqrt{\frac{5}{\pi}}\, \frac{1}{d^3}\, \frac{3\cos^2\beta - 1}{2}, \tag{37}$$

and because of the large time average distances we approximate $C^{13'}$ and $C^{23'}$ by zero. A rough assessment of the various factors and terms entering Eq. (22) indicates that this approximation will not entail errors bigger than about 20%. Putting $C^{13'} = C^{23'} = 0$ simplifies further calculations significantly: Only $K_{12'}(\tau)$ and $K_{23'}(\tau)$ are needed of all

the many K_{ik}'s and $k_{ik, mn}$'s. In accordance with our previous policies we approximate $K_{i3'}$ $(i = 1, 2)$ by

$$\langle r_{i3}^{-3}(t)\, r_{i3}^{-3}(t+\tau)\, Y_{20}^{i3'}(t)\, Y_{20}^{i3'}(t+\tau)\rangle_{\mathrm{Av}}$$
$$= \sum_{\mu} \sum_{\nu} p_{\mu} r_{\mu}^{-3} Y_{20}^{\mu} P(\mu, t;\, \nu, t+\tau)\, r_{\nu}^{-3} Y_{20}^{\nu}. \quad (38)$$

$p_{\mu} = 1/36$ is the absolute probability of finding the primed and unprimed benzene molecules in the μ'th combined equilibrium position at time t;

$$P(\mu, t;\, \nu, t+\tau)$$

is the conditional probability of finding the two molecules in position ν at time $t+\tau$ when they are *known* to have been in position μ at time t; r_{μ} is the distance of protons i and $3'$ when the two molecules are in position μ, and r_{ν}, Y_{20}^{μ} and Y_{20}^{ν} have a similar meaning. According to Ref. 4

$$P(\mu, t;\, \nu, t+\tau) = 1/36\,(1 + 5\, e^{-\tau/\tau_c})^2 \quad \text{for} \quad \mu = \nu,$$
$$= 1/36\,(1 + 5\, e^{-\tau/\tau_c})\,(1 - e^{-\tau/\tau_c})$$

for $\mu \neq \nu$ but *one* of the two molecules in same position at times t and $t+\tau$.

$$= 1/36\,(1 - e^{-\tau/\tau_c})^2$$

for $\mu \neq \nu$ and both molecules in different positions at times t and $t+\tau$.

The sum in the right hand expression of Eq. (38) contains $36^2 = 1296$ terms. They differ greatly in size because of both the r's and the dependence on μ and ν of $P(\mu, t;\, \nu, t+\tau)$. Inspection of the various terms in Eq. (38) shows that dropping all of them except those for which $\mu = \nu$ yields a result which comes fairly close to the exact one. Hence

$$K_{i3'} \approx 1/36 \sum_{\mu} r_{\mu}^{-6} (Y_{20}^{\mu})^2\, 1/36\,(1$$
$$+ 10\, e^{-\tau/\tau_c} + 25\, e^{-2\tau/\tau_c}). \quad (39)$$

The one in the bracket of Eq. (39) reveals a (small) error we made above, when we put $C^{13'} = C^{23'} = 0$ and approximated $K_{i3'}$ by the expression (38). To be consistent we must drop the one here. Note that $K^{13'} = K^{23'}$ which can be taken care of in Eq. (22) by a factor of 2 and keeping only $K_{13'}$.

Inserting Eqs. (29), (37) and (39) into Eq. (22), integrating over τ and taking into account the factors 2 and 36 mentioned above yields the following expression for the contribution of the primed molecule to the relaxation rate of the unprimed one

$$1/T_{1\mathrm{D}}'(\text{primed}) = \pi\, \gamma^4 \hbar^2 I\,(I+1) \frac{\tau_c}{6{,}269} \sum_{\mu} r_{\mu}^{-6} (Y_{20}^{\mu})^2. \quad (40)$$

The *powder average* of all $(Y_{20}^{\mu})^2$ is $1/4\pi$.

Summing expression (40) over all molecules $\varkappa$ with which the reference molecule is interacting generalizes expression (40) to yield the dipolar relaxation rate due to intermolecular spin interactions in a powder sample:

$$1/T_{1\mathrm{D}}'(\text{inter}) = \gamma^4 \hbar^2 I\,(I+1) \frac{\tau_c}{25} \sum_{\varkappa} \sum_{\mu} (r_{\mu}^{-6})_{\varkappa}. \quad (41)$$

The approximate nature of this equation should be kept in mind. Now we are ready to insert numbers.

ANDREW and EADES[3] obtained from proton magnetic resonance studies of solid benzene $d = 2.495 \pm 0.018$ Å. The crystal structure of benzene has been determined by Cox et al.[10]. The unit cell is orthorhombic with a; b; $c = 7.460$; 9.666; 7.034 Å and contains four benzene molecules. Any reference molecule is surrounded by 12 direct neighbours. By using Cox' data and summing only over the protons of direct neighbour benzene molecules we get

$$\sum_{\varkappa} \sum_{\mu} (r_{\mu}^{-6})_{\varkappa} = 7{,}6 \cdot 10^{-2}\, \text{Å}^{-6}. \quad (42)$$

For comparison we give

$$d^{-6} = 0{,}413 \cdot 10^{-2}\, \text{Å}^{-6}. \quad (43)$$

Inserting these numbers into Eqs. (36) and (41) yields

$$1/T_{1\mathrm{D}}'(\text{intra}) = \gamma^4 \hbar^2 I\,(I+1)\, \tau_c \cdot \{0{,}21 \cdot 10^{-2}\, \text{Å}^{-6}\} \quad (44)$$

and

$$1/T_{1\mathrm{D}}'(\text{inter}) = \gamma^4 \hbar^2 I\,(I+1)\, \tau_c\, \{0{,}30 \cdot 10^{-2}\, \text{Å}^{-6}\}. \quad (45)$$

Whereas for our model of molecular motions the *intra*molecular spin spin interactions are predominant in setting up the dipolar energy reservoir, the *inter*molecular interactions are more important for relaxation.

Molecular motions consisting of rapid 180° jumps around some fixed molecular axis represent an extreme in this respect: Despite of the motion the total of the intramolecular interactions remains

[10] E. G. COX, D. CRUICKSHANK, and J. SMITH, Proc. Roy. Soc. London A 247, 1 [1958].

static and sets up the dipolar energy reservoir. Relaxation takes place only via intermolecular interactions. Such motions are likely to be responsible for dipolar spin relaxation in crystals of a number of organic molecules such as naphthalene, diphenyl and others.

IV. Comparison with Experiment

Van Steenwinkel[2] has measured T_{1D} and T_1 (for which he uses the symbol T_{1z}) of solid polycrystalline benzene over a wide range of temperatures. His results are reproduced in Fig. 2 together with an extrapolation. The correlation time τ_c can be deduced from the T_1 data: At the temperature Θ_m where $1/T_1$ goes through its maximum ($\Theta_m = 164\,°K$) ω_0 and τ_c are related by[4]

$$\omega_0 \tau_c = 0{,}86. \qquad (46)$$

With $\omega_0 = 2\pi \cdot 15 \cdot 10^6$ Hz (the frequency used by van Steenwinkel) we obtain

$$\tau_c = 0{,}914 \cdot 10^{-8}\,\text{sec at } \Theta = \Theta_m = 164\,°K. \quad (47)$$

In order to get $1/T'_{1D}$ at Θ_m we extrapolate to Θ_m — as indicated in Fig. 2 — the low temperature data of $1/T_{1D}$ for which $T'_{1D} = T_{1D}$
The result is

$$1/T'_{1D} = 25\,\text{sec}^{-1} \text{ at } \Theta = 164\,°K.$$

Inserting numbers for γ, $\hbar$, I, and τ_c (from Eq. (47)) into Eqs. (44) and (45) we get as out theoretical result

$$1/T'_{1D} = 1/T'_{1D}(\text{intra}) + 1/T'_{1D}(\text{inter}) = 20\,\text{sec}^{-1}$$
$$\text{at } \Theta = 164\,°K.$$

In view of all the approximations introduced the close agreement between theoretical and experimental results is, perhaps, beyond significance. It
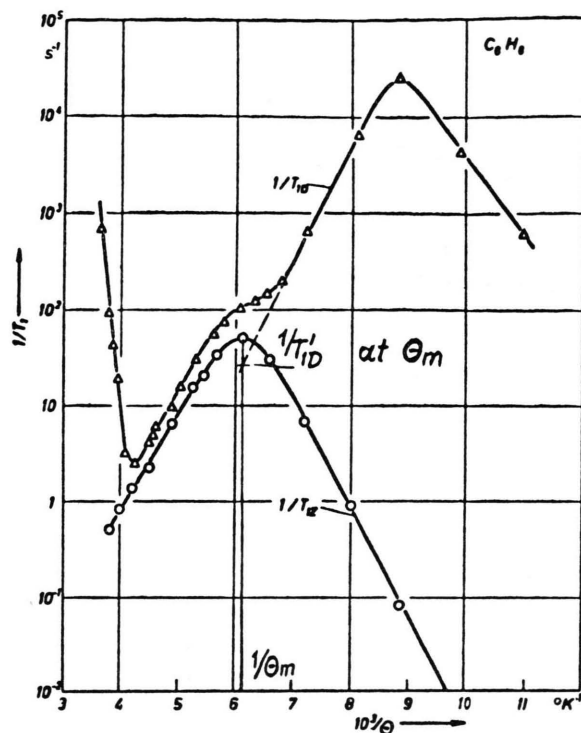

Fig. 2. Dipole dipole and Zeeman spin-lattice relaxation rates in benzene (from Ref. 2).

nevertheless confirms that (a) the model of molecular motions in benzene which is so successful in explaining $T_1(\Theta, H)$ and $\overline{\Delta\omega^2}(\Theta)$ measurements can also account for the relaxation of the dipolar energy and (b) threespin relaxation as considered here can be the essential mechanism for the $\Delta m = 0$ dipolar relaxation processes.