The Spin Lattice Relaxation of the Nuclear Dipolar Energy in Some Organic Crystals with Slow Molecular Motions

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The relaxation of nuclear dipolar energy to the lattice has been measured in three different organic solids (benzene, cyclohexane and hexamethylbenzene) as a function of temperature. In the cases of C_6H_6 and $C_6(CH_3)_6$ very slow motions associated with rather high activation energy were detected near the melting point. They are thought to be thermally activated rotations of the molecules about axes other than the hexad axis. In the case of cyclohexane the activation energy for the process of molecular diffusion was determined directly from the experimental results without the need of a model for vacancy diffusion.

A maximum in dipolar relaxation rate was always observed for correlation times of the order of the rigid lattice line width i. e. in the temperature region where the lines narrow.

1. Introduction

Important results concerning molecular motions in solid organic crystals were obtained in the past by experimental and theoretical studies of Zeeman spin lattice relaxation times and dipolar line widths. For sensitivity reasons nearly all these experiments took place in high external fields giving, typically, information about motions with correlation time $\tau_c \sim 1/\omega_0$ for the Zeeman relaxation time and $\tau_c \sim 1/\Delta\omega_{RL}$ for line width measurements (ω_0 is the Larmor frequency and $\Delta\omega_{RL}$ the rigid lattice line width). More recently new methods [1–3] have been developed which enable valuable information about much slower atomic or molecular motions to be obtained. They are based on the use of low "effective" external fields (like the rotating frame T_1 measurements) or simply on the use of the (low) local dipolar fields themselves (measurements of the relaxation of the spin spin dipolar energy). Both techniques are very powerful in the detection of long correlation time motions and furthermore do not suffer from the weak sensitivity generally associated with low field measurements.

In this paper we have used the second method for the investigation of three organic crystals namely benzene, cyclohexane and hexamethylbenzene.

Theoretically, it is supposed that the time independent part of the spin system submitted to a high external magnetic field can always be described by two temperatures [4] T_Z and T_D (the Zeeman and dipolar temperatures) and that its interaction with the lattice is weak enough to maintain a thermodynamic equilibrium inside the Zeeman and the dipolar subsystems. Any physical quantities can thus be evaluated, in the high temperature approximation, as the trace of the corresponding operator multiplied by a density matrix of the form:

$$\varrho = \frac{1}{Z}\left(1 - \frac{\mathcal{H}_0}{k\,T_Z} - \frac{\mathcal{H}'}{k\,T_D}\right) \qquad (1)$$

where $Z = \mathrm{Tr}\{1\}$ is a normalizing constant, $\mathcal{H}_0 = -\sum_i \gamma \hbar H_0 I_i^z$ is the Zeeman Hamiltonian and $\mathcal{H}'$ is the Van Vleck truncated Hamiltonian which commutes with $\mathcal{H}_0$. The spin system can be prepared in such a way that T_Z or T_D deviate from the lattice temperature T_L. The characteristic times T_{1Z} and T_{1D} to recover the lattice temperature T_L, are referred to as Zeeman and dipolar relaxation times.

2. Theory

The spin system in high external field is described by the Hamiltonian:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' + \mathcal{H}'' + \mathcal{H}_1(t) \qquad (2)$$

where $\mathcal{H}'$ and $\mathcal{H}''$ are the time independent secular and non secular parts of the dipolar interaction,

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and $\mathcal{H}_1(t)$ the time dependent term caused by the various molecular motions taking place in the sample (translation, rotation . . .). By these the dipolar interactions are modulated in time and $\mathcal{H}_1(t)$ is responsable for the exchange of energy between the lattice and the spin system.

Computation of the relaxation times under the assumption of the existence of spin temperatures during the evolution to complete equilibrium with the lattice will not be developed here. Detailed discussions can be found in refs. [1, 3]. In this paper we chiefly give the more interesting results and define their validity domain. Two cases have to be distinguished:

A. Case of short correlation time

This is the region of weak collisions and a first order time dependent perturbation calculation similar to that of BPP can be applied. The assumptions made are, as usual:

a) The lattice can be described classically.

b) The effect of $\mathcal{H}''$ can be neglected for sufficiently high external fields (no cross relaxation).

c) The correlation time of the spin lattice interaction is short enough so that

$$(1/\hbar)\,[\overline{\mathcal{H}_1^2(t)}\cdot\tau_c^2]^{1/2} \ll 1 \text{ and } \tau_c \ll T_2 .$$

d) The density matrix keeps the form of thermodynamic equilibrium during the relaxation process.

e) The high temperature approximation is valid.

Under these conditions the relaxation times are given by the following relations:

$$\frac{1}{T_{1Z}} = \frac{1}{\hbar^2\,\mathrm{Tr}\,\mathcal{H}_0^2}\int_0^\infty \overline{\mathrm{Tr}[\mathcal{H}_0,\mathcal{H}_1(0)]\,[\tilde{\mathcal{H}}_1(\Theta),\mathcal{H}_0]}\,\mathrm{d}\Theta\,, \tag{3}$$

$$\frac{1}{T_{1D}} = \frac{1}{\hbar^2\,\mathrm{Tr}\,\mathcal{H}'^2}\int_0^\infty \overline{\mathrm{Tr}[\mathcal{H}',\mathcal{H}_1(0)]\,[\tilde{\mathcal{H}}_1(\Theta),\mathcal{H}']}\,\mathrm{d}\Theta \tag{4}$$

where the operator

$$\tilde{\mathcal{H}}_1(\Theta) = \exp\{(i\,\Theta/\hbar)\,(\mathcal{H}_0+\mathcal{H}')\}\,\mathcal{H}_1(\Theta) \cdot\exp\{-(i\,\Theta/\hbar)\,(\mathcal{H}_0+\mathcal{H}')\} \tag{5}$$

and the bar on the integrand of the second member means an average over a statistical ensemble of systems. $[A, B]$ is the commutator of A and B.

The correlation time dependence of Eqs. (3) and (4) can be made more explicit with the introduction of the following definitions and assumptions. For pure dipolar interactions, the relaxation Hamiltonian can be split in the following way:

$$\mathcal{H}_1(t) = \sum_{q,i,j}\{\mathcal{H}_1^q(t)_{ij}\,\mathcal{H}_{1;ij}^q + \mathcal{H}_1^{-q}(t)_{ij}\,\mathcal{H}_{1;ij}^{-q}\} \tag{6}$$

where the superscript q varies from 0 to 2 and refers to the type of transition involved in the dipolar operator (change of the Zeeman population by 0, ± 1 or ± 2). $\mathcal{H}_1{}^q(t)$ depends only on lattice variables and $\mathcal{H}_1{}^q$ only on spin variables. The indexes i and j refer to individual spins.

We restrict here the discussion to correlation times short as compared with T_2 so that the time dependence introduced by $\mathcal{H}'$ in (5) can be negected and:

$$\tilde{\mathcal{H}}_1{}^q = \mathrm{H}_1{}^q\cdot e^{iq\omega t}\,. \tag{7}$$

Finally, we suppose that the relaxation can be characterized by one single correlation time, that the correlation function is exponential and that the motions of the spins are isotropic and uncorrelated.

$$\overline{\mathcal{H}_1{}^q(0)_{ij}\,\mathcal{H}^{q'*}(\Theta)_{i'j'}} = \overline{|\mathcal{H}_1{}^q(0)|_{ij}^2}\exp\{-\Theta/\tau_c\}\,\delta_{ii'}\,\delta_{jj'}\,\delta_{qq'}\,. \tag{8}$$

With these simplifications Eqs. (3) and (4) may be written after integration with respect to Θ in the more familiar form:

$$\frac{1}{T_{1Z}} = C_1\,\frac{\tau_c}{1+\omega^2\tau_c^2} + C_2\,\frac{\tau_c}{1+4\,\omega^2\tau_c^2}\,, \tag{9}$$

$$\frac{1}{T_{1D}} = C_3\,\tau_c + C_4\,\frac{\tau_c}{1+\omega^2\tau_c^2} + C_5\,\frac{\tau_c}{1+4\,\omega^2\tau_c^2} \tag{10}$$

where C_1, C_2, C_3, C_4, C_5 are constants of the same order containing the strength of the dipolar interactions and the traces on the spin operators. For our experiments the evaluation of these constants is very difficult and on the other hand in cases of motional narrowing an explicit separation of the dipolar Hamiltonian into a time dependent and a time independent part results in mathematical difficulties we have not attempted to solve here. The first term in (10) comes from the transitions with $q=0$, i. e. without changes in Zeeman populations. For correlation times longer than $1/\omega_0$ it is the only one remaining in $1/T_{1D}$ justifying the fact that the dipolar relaxation rate continues to increase with τ_c in this region.

B. Case of long correlation time

This is the region of slow motions or strong collision theory where the Hamiltonian is subject to sudden jumps which can be large in amplitude. The related theory was developed by SLICHTER and AILION[1].

The main assumptions are:

a) $\tau_c > T_2$ which insures the recovering of a temperature after each jump of the Hamiltonian,

b) $\tau_c < T_1$ by which the effect of stray impurities is not considered.

In this case, the result for the dipolar relaxation rate is:

$$\frac{1}{T_{1D}} = \frac{-1}{\mathrm{Tr}\,\mathcal{H}'^2} \frac{N_0}{\tau_c} \langle \Delta E \rangle_{AV} \tag{11}$$

where $\langle \Delta E \rangle_{AV}$ is the mean change in dipolar energy in a jump averaged over al types of jump, N_0 is the number of jumping spins and τ_c the average time interval between jumps.

3. Experimental

Relaxation times were measured with a phase coherent pulse spectrometer working at 15 MHz as used in a previous paper on dipolar relaxation by impurities[5]. A sequence of two 90° pulses was used in the Zeeman case. For the dipolar one the system was first prepared in a state of low T_D by a sequence of two pulses orthogonal in phase, the first of 90° followed at time τ by a 45° one. τ is of the order of T_2 and adjusted experimentally.

A 45° "read out" pulse is then applied in phase with the first 90° one and the dipolar signal recorded as a function of the time separation between the last and the first two pulses. The Zeeman and dipolar components of the signal are separated by two orthogonal phase detectors. Details of the experimental technique can be found in ref. [6] and [7].

4. Results and Discussion

The Zeeman and dipolar relaxation rates of the three investigated substances are presented in Figs. 1, 2 and 3 as a function of the inverse temperature ($10^3/T$). In order to compare the experimental results with Eqs. (10) and (11) we suppose that the temperature variation of the correlation time can be described by an activation law of the form:

$$\tau_c = \tau_0 \cdot \exp\{E/R\,T\} \tag{12}$$

where τ_0 has only a very slight temperature dependence which we neglect here.

The following discussion will be based essentially on the behaviour of $1/T_{1D}$ since the Zeeman relaxation for all three substances was reported in earlier works.

A. Benzene (Fig. 1)

The sample used was obtained by a vacuum distillation of the Fluka puriss. 99.94 mole % product.

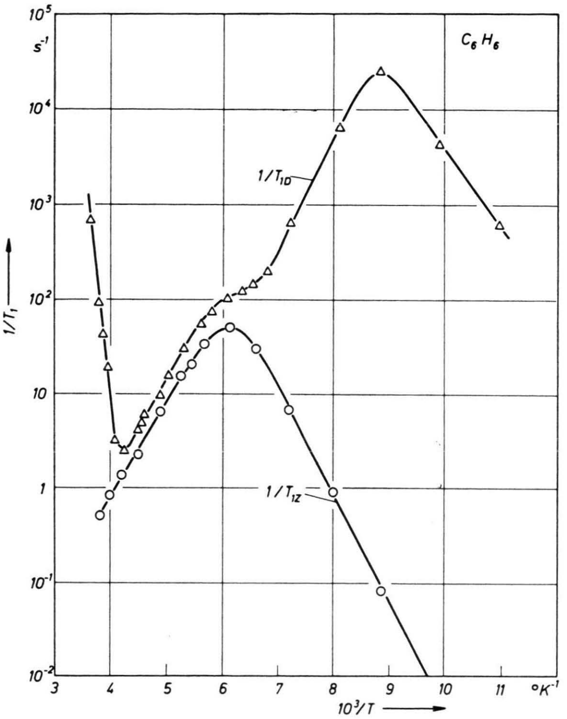

Fig. 1. Dipole-dipole and Zeeman spin-lattice relaxation rates in benzene vs. inverse of temperature

Between 125 °K and 230 °K (in the region of the Zeeman maximum relaxation rate) the correlation time corresponding to the thermally activated rotation of the molecules around their hexad axis[8] is shorter than $1/\Delta\omega_{RL}$. The behaviour of $1/T_{1D}$ can thus be interpreted with Eq. (10) and corresponds to an activation energy of 4.4 kcal/mole, a result already derived from Zeeman measurements[8, 9]. However, above 230 °K the dipolar relaxation rate

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increases suddenly and very rapidly with temperature. This fact can be interpreted only by the onset of a new type of molecular motion which is too slow to affect appreciably the Zeeman system or the line width where no changes are noticeable up to the melting point. In this region of temperature the relaxation in thus governed by Eq. (11) and the activation energy is determined by Eq. (12) to be 16 kcal/mole.

This motion is most probably due to a reorientation of the molecules around axes in their plane. This interpretation is also confirmed by some measurements on low frequency Raman lines[10], which were assigned to oscillatory motion perpendicular to the molecule plane. The decrease in the frequency of these lines above 240 °K suggested that the potential barriers are lowered thus allowing new types of rotation to take place near the melting point.

Between 175 °K and 230 °K the ratio of dipolar to Zeeman relaxation rate is about 2 : 1. In this region both relaxation are due to the same very short correlation times $\tau_c < 1/\omega_0$. Finally, $1/T_{1D}$ exhibits a maximum in the temperature region where the NMR line becomes motionally narrowed due to hexad rotation. Since the last two conclusions are also valid for the hexamethylbenzene case we discuss them later.

B. *Hexamethylbenzene (Fig. 2)*

At temperatures below the transition point, between 180° and 383 °K, $1/T_{1D}$ is correctly described by Eq. (10) and results in an activation energy of 6.6 kcal/mole in very good agreement with recently published results[11, 12]. The corresponding motion is attributed to a rotation of the whole molecule around the C_6 axis.

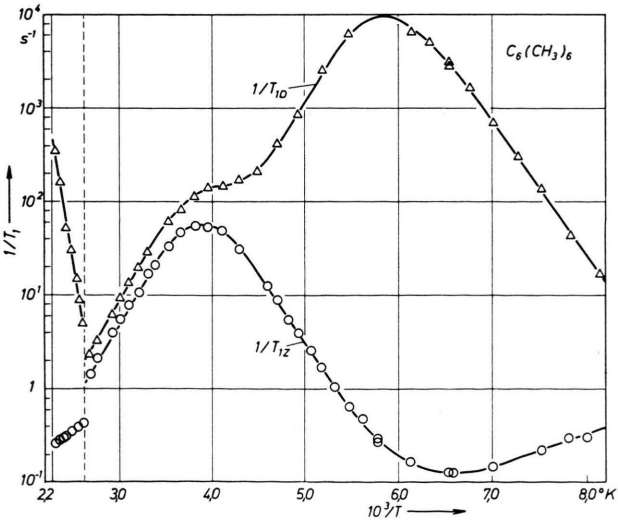

Fig. 2. Dipole-dipole and Zeeman spin-lattice relaxation rates in hexamethylbenzene vs. inverse of temperature.

The most striking and new feature of the results appears, however, in the high temperature region, above the transition point where the dipolar relaxation exhibits again a very steep increase with temperature. The motion responsible is unable to modify the Zeeman relaxation or the line width and corresponds to an activation energy of 28 kcal/mole. As in the case of benzene, the suggested interpretation is that the molecule rotates about an axis in its plane. The fact that there is a marked increase in rotational freedom above the transition point is on the other hand confirmed by the decrease of the activation energy for hexad rotation which is only 4 kcal/mole in that region as revealed by the Zeeman relaxation behaviour. Moreover as mentioned in ref. [12] dilatometric and neutron scattering experiments give some confirmation to these hypothesis.

Again in this case, the ratio of dipolar to Zeeman relaxation rates is about 2 in the extreme narrowing region ($\tau_c < 1/\omega_0$) and the maximum in $1/T_{1D}$ occurs for the temperature at which the line is motionally narrowed due to hexad rotation ($T \approx 170$ °K).

C. *Cyclohexane (Fig. 3)*

As a last example showing the value of the dipolar relaxation rate method we consider the case of cyclohexane. The sample used was obtained by a vacuum distillation of the Fluka puriss. 99.99 mole % product. Cyclohexane shows a transition point at 186 °K. Above that temperature it is known that the molecules are free to rotate about other axes beside the triad and it has even been suggested that they may diffuse through the lattice[13]. The decrease in the second moment of the resonance line at 230 °K to a value less than 0.01 G², together with the very low heat of melting, supports this hypothesis. It was however not possible to ascribe an activation energy to this diffusion process. The

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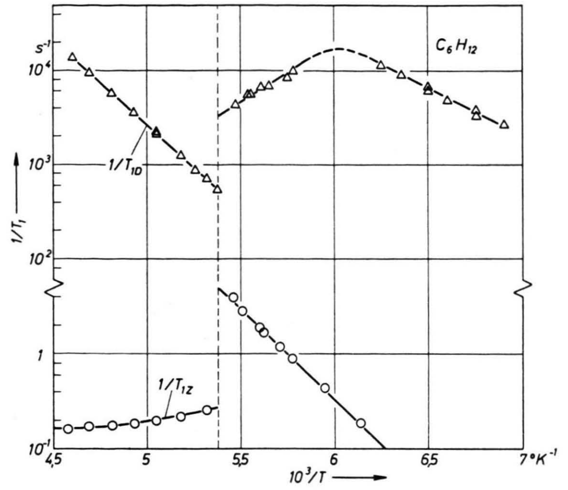

Fig. 3. Dipole-dipole and Zeeman spin-lattice relaxation rates in cyclohexane vs. inverse of temperature.

difficulty comes from the fact that between 230 °K and the melting point both diffusion and rotation mechanisms contribute to the Zeeman relaxation and can not properly be separated ($1/T_{1Z}$ is not a straight line in that region). An estimate of the diffusion activation energy was made by ANDREW and EADES [13] with the aid of a model for vacancy diffusion [14]. They obtained a value of 8 kcal/mole, close to the latice energy which is 10 kcal/mole.

Immediately above the transition point, diffusion is, however, a very slow process giving a large contribution to the dipolar relaxation rate. Above 186 °K, Fig. 3 exhibits in fact very short dipolar relaxation times and the straight line behaviour of $1/T_{1D}$ vs. $1/T$ in that temperature region corresponds to an activation energy of 9.1 kcal/mole in good agreement with the ANDREW and EADES [13] estimation. On the other hand, the rotational motions in this region of temperature are too fast to affect the dipolar relaxation and no confusion is possible.

Below the transition point, $1/T_{1D}$ shows a maximum around 165 °K corresponding to the temperature at which the line narrows due to rotation of the molecules around their triad axis.

5. Behaviour of $1/T_{1D}$ in the region where $\tau_c \sim T_2$

For the three cases investigated the maximum dipolar relaxation rate was situated at temperatures where the respective lines motionally narrow, that is for correlation times of the order of $1/\Delta\omega_{RL}$. Experimentally this maximum was difficult to reach because T_{1D} is there always of the same order as the free decay time $t^{\times}$ ($t^{\times} \sim T_2$).

On the other hand, the description of the spin system by a dipolar temperature T_D is very dubious in these regions since the approach to internal equilibrium after the preparation pulses is also of order $t^{\times}$ so that any theory based on a density matrix of form (1) must fail.

In spite of this fact and only to give a rough justification of the experimental behaviour an extrapolation of Eq. (10) for correlation times of the order of $1/\Delta\omega_{RL}$ can be tempted. Since we are interested in values of τ_c larger than $1/\omega_0$, contributions of the terms with $q \neq 0$ to $1/T_{1D}$ will be neglected. From Eqs. (4), (6) and (8) we get:

$$\frac{1}{T_{1D}} = \frac{1}{\hbar^2 \operatorname{Tr} \mathcal{H}'^2} \int_0^\infty \mathrm{d}\Theta \sum_{i,j} \operatorname{Tr} \cdot$$
$$\cdot \overline{[\mathcal{H}', \mathcal{H}_1^0(0)_{ij} \mathcal{H}_{1;ij}^0] [\mathcal{H}_1^0(\Theta)_{ij} \tilde{\mathcal{H}}_{1;ij}^0, \mathcal{H}']} \,. \quad (13)$$

The operator $\mathcal{H}_{1;ij}^0$ does not affect the population of the Zeeman levels so that:

$$\tilde{\mathcal{H}}_{1;ij}^0 = \exp\{i\,\Theta\,\mathcal{H}'/\hbar\}\, \mathcal{H}_{1;ij}^0 \exp\{-i\,\Theta\,\mathcal{H}'/\hbar\} \,.$$

Since the mean change in energy induced by $\mathcal{H}_1^0(\Theta)_{ij}\,\mathcal{H}_{1;ij}^0$ is of the order $\Delta\omega_{RL} \cdot \hbar$ it follows that:

$$\mathcal{H}_1^0[\Theta]_{ij} \cdot \tilde{\mathcal{H}}_{1;ij}^0 \sim \mathcal{H}_1^0(\Theta)_{ij}\, \mathcal{H}_{1;ij}^0 \exp(\Delta\omega_{RL} \cdot \Theta) \,. \quad (14)$$

Putting (14) into (13) one gets after integration with respect to Θ

$$1/T_{1D} = C_3{}' \cdot \tau_c / [1 + (\Delta\omega_{RL}\, \tau_c)^2] \quad (15)$$

giving a maximum rate for $\tau_c \sim 1/\Delta\omega_{RL}$ as observed experimentally.

6. Ratio of Dipolar to Zeeman Relaxation Rates for $\tau_c < 1/\omega_0$

Another point we discuss now is the factor of order 2 between dipolar and Zeeman relaxation rates in regions where both of them are governed by the same, short corerlation time as happens in the case of C_6H_6 and $C_6(CH_3)_6$.

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[14] F. SEITZ, Phase Transformation in Solids, ed. R. SMOLUCHOWSKI et al., N.Y.: John Wiley and Sons Inc., New York 1951.

For simplicity we will examine the case where the relaxing Hamiltonian is a linear function of the spin variables and can be written in the form:

$$\mathcal{H}_1(\Theta) = -\sum_i \gamma \hbar \, \boldsymbol{h}_i(\Theta) \cdot \boldsymbol{I}_i \qquad (16)$$

where $\boldsymbol{h}_i(\Theta)$ is the fluctuating field at site i and time Θ.

Since we are interested in short correlation times $\tau_c < 1/\omega_0$, the exponential in Eq. (5) can be equalized to 1 and $\widetilde{\mathcal{H}}_1(\Theta) = \mathcal{H}_1(\Theta)$.

Equations (9) and (10) are thus written:

$$\frac{1}{T_{1Z}} = \frac{3\,\gamma^2}{I(I+1)\,(2\,I+1)^N N} \int \mathrm{d}\Theta \sum_i \mathrm{Tr} \cdot \qquad (17)$$
$$\cdot\, [I_i^z, \boldsymbol{h}_i(0) \cdot \boldsymbol{I}_i]\, [\boldsymbol{h}_i(\Theta) \cdot \boldsymbol{I}_i, I_i^z]$$

and (18).

The traces in (17) and (18) are readily evaluated.

Furthermore we suppose that the fields at sites i and j are completely uncorrelated and distributed isotropically:

$$\frac{1}{T_{1D}} = \frac{5\,\gamma^2}{9 \sum u_{ij}^2\, I^2 (I+1)^2\, (2\,I+1)^N} \times \int_0^\infty \mathrm{d}\Theta \; \mathrm{Tr} \left[\sum_{i \neq j} u_{ij} (\mathbf{I}_i \cdot \mathbf{I}_j - 3\, I_i^z\, I_j^z), \sum_k \boldsymbol{h}(0)_k\, \mathbf{I}_k \right] \qquad (18)$$
$$\left[\sum_k \boldsymbol{h}_k(\Theta)\; \mathbf{I}_k\,,\; \sum_{i \neq j} u_{ij} (\mathbf{I}_i \cdot \mathbf{I}_j - 3\, I_i^z\, I_j^z) \right] \text{ where } u_{ij} = \tfrac{1}{2}\, (\gamma^2\, \hbar^2 / r_{ij}^3)\, (1 - 3 \cos^2 \Theta_{ij}).$$

$$\overline{h_i^\alpha(0)\; h_j^\beta(\Theta)} = \overline{h_i^\alpha(0)\; h_j^\beta(\Theta)}\; \delta_{\alpha\beta}\, \delta_{ij}$$

and $\overline{h_i^\alpha(0)\; h_i^\alpha(\Theta)} = \overline{h_i^\beta(0)\; h_i^\beta(\Theta)}$

where $\alpha, \beta = x, y, z$.

It is then easily found that:

$$1/T_{1Z} = 2\,\gamma^2 \int_0^\infty h^z(0)\; h^z(\Theta)\; \mathrm{d}\Theta$$

and

$$1/T_{1D} = 4\,\gamma^2 \int_0^\infty h^z(0)\; h^z(\Theta)\; \mathrm{d}\Theta$$

the dipolar rate of relaxation being twice as fast as the Zeeman one. The observed ratios were respectively 1.7 in the case of benzene and 1.8 in the case of hexamethylbenzene, an agreement which is not too bad in view of the approximations made. (The perturbation is not a linear but a bilinear form of the spin variable.)

7. Conclusions

The three examples we have investigated show that the method of dipolar relaxation is nicely able to extend the amount of information one can obtain about molecular motions in organic solids. The main interest lies of course in the extreme sensitivity to long correlation times where, as in the case of benzene and hexamethylbenzene, it gave evidence for new types of motion near the melting point.

On the other hand, the technique is also able to give information complementary to Zeeman relaxation and dipolar line width. This was the case in cyclohexane where the substance melts before an appreciable effect of diffusion can be observed in the Zeeman rate of relaxation preventing any direct measurement of the activation energy for that process.

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