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be so for bulk properties.

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A Study on Spin-Lattice Relaxation of Methyl Protons in 2,6-Dichlorotoluene and N-Methyl Phthalimide

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Spin-lattice relaxation of methyl protons in 2,6-dichlorotoluene and N-methyl phthalimide, each dissolved in $CDCl_3$, has been studied at 34°C and the contribution from spin-rotation interaction to the relaxation process has been separated from that due to dipole-dipole interactions among methyl protons. The results show that the spin-rotational contributions to the initial rate of relaxation in 2,6-dichlorotoluene and N-methyl phthalimide amount to 18 and 31%, respectively, of the total relaxation rate at 34°C. The method of separating the spin-rotational contribution from that of dipolar interactions adopted in this paper is based on the well known fact that in an A_3 spin system such as methyl protons in liquid phase dipolar relaxation mechanism gives non-exponential decay of the z-component of total magnetization of protons while the random field fluctuation such as spin-rotational mechanism causes exponential decay.

Introduction

It is nowadays a well-established fact that the study of nuclear magnetic relaxation can provide valuable informations regarding inter- and intramolecular interactions and their dynamical characters in bulk materials.[1] Relaxation of nuclear spins in a molecule is known to be caused by randomly fluctuating magnetic fields produced at the nuclear sites by various inter- and intramolecular interactions. Among these the most pronounced are (inter- and/or intramolecular) nuclear magnetic dipole-dipole interactions, spin-rotation interactions, nuclear electric quadrupole-electric field gradient interactions, chemical shift anisotropy interactions, scalar couplings of the first and second kind, and interactions due to the presence of paramagnetic molecular species.[2]

For protons in small organic molecules dissolved in a deuterated solvent such as $CDCl_3$, it is known that only inter- and intramolecular dipole-dipole interactions and the spin-rotation interactions are the two major relaxation mechanisms to be considered and the contributions from other causes can safely be ignored.[3,4] The dipolar interactions are usually a dominating factor; however, if the molecule is of highly symmetrical shape and can undergo easy rotational motions in bulk phase, the spin-rotational contribution may be appreciable in magnitude.[5] Such seems to be the case also for protons located on a methyl group which can undergo rapid internal rotation about its own axis of symmetry with respect to the molecular frame.

Since dipolar and spin-rotational contributions are known to provide different kinds of molecular motional informations between them, it is of great importance to distinguish one from the other.[6] Many NMR investigators have probably had more or less frustrating experiences that for protons on a methyl group they did not have an easy and legitimate means at hand by which they could separate dipolar contributions from those due to spin-rotation interactions in their

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treatment of relaxation data. For ^{13}C spin located on the same methyl group it has been shown[7,8] that measured NOE data can be utillized to achieve this separation, but the same is not true for protons. Measurements of relaxation data as a function of temperature have been used as the only means for this purpose,[9,10] but the procedure is not only laborious but sometimes lacks theoretical justification as well.[11,12]

In this paper we attempt to show that the same goal may be achieved by taking advantage of the fact that spin-lattice relaxation of methyl protons usually exhibit strong nonexponential behavior.[13,14] Such nonexponential behavior was first investigated theoretically by Hubbard[15,16] and was extensively reviewed by Werbelow and Grant.[17] In this work we have confirmed that numerical fitting of predicted nonexponential behavior to the observed data for methyl proton in 2,6-dichlorotoluene and N-methyl phthalimide can provide a means by which one can extract the information of dipolar or spin-rotational contributions to the total relaxation rate in these compounds.

Theory

Three identical protons in a methyl group can be treated as an A_3 spin system for which the observable longitudinal component of magnetization can be represented by

$$v_1(t) = Tr[(I_z^A + I_z^{A'} + I_z^{A''})\chi(t)] \tag{1}$$

where I_z^A, $I_z^{A'}$, $I_z^{A''}$ are, respectively, the z-components of spin angular momenta of three protons A, A', A'', and $\chi(t)$ is the reduced spin deviation density operator for this system; that is,[18]

$$\chi(t) = \sigma(t) - \sigma_0 \tag{2}$$

Werbelow and Grant[17] have shown that in the extreme narrowing limit, $v_1(t)$ evolves according to the equation

$$-\frac{d}{dt}\begin{bmatrix}v_1(t)\\v_2(t)\end{bmatrix}=\begin{bmatrix}\Gamma_{11} & \Gamma_{12}\\\Gamma_{12} & \Gamma_{22}\end{bmatrix}\begin{bmatrix}v_1(t)\\v_2(t)\end{bmatrix} \tag{3}$$

where the unobservable normal mode $v_2(t)$, that is coupled to $v_1(t)$, is defined by

$$v_2(t) = (4/\sqrt{5})\; Tr\{[I_z^A(I^{A'}\cdot I^{A''})+I_z^{A'}(I^A\cdot I^{A''})+I_z^{A''}(I^A\cdot I^{A'})]\chi(t)\} \tag{4}$$

and the matrix elements Γ_{ij}'s are given by

$$\Gamma_{11} = 10J(0) + 2j(0)$$

$$\Gamma_{12} = 2\sqrt{5}\,K(0), \quad \Gamma_{22} = 4J(0) - 2K(0) + 6j(0) - 4k(0). \tag{5}$$

In Eq. (5) $J(\omega)$ and $K(\omega)$ are dipolar autocorrelation and cross correlation spectral densities defined as follows:

$$J(\omega) = \left(\frac{6\pi}{5}\right)\left(\frac{\gamma_H^2 h}{r_{HH'}^3}\right) \tag{6}$$

$$\times \int_0^\infty \langle Y_2^0(\Omega_{HH'}(0))\; Y_2^0(\Omega_{HH'}(t))\rangle \cos\omega t\; dt$$

and

$$K(\omega) = \left(\frac{6\pi}{5}\right)\left(\frac{\gamma_H^2 h}{r_{HH'}^3}\right) \tag{7}$$

$$\times \int_0^\infty \langle Y_2^0(\Omega_{HH'}(0))\; Y_2^0(\Omega_{HH'}(t))\rangle \cos\omega t\; dt$$

where

γ_H = magnetogyric ratio of a proton,

$r_{HH'}$ = internuclear distance between two methyl protons H and H',

$Y_2^0(\Omega)$ = 0 th member of the second-order spherical harmonics $Y_2^m(\Omega)$'s,

$\Omega(t)$ = spatial orientation of internuclear vector at time t. The spin-rotational auto-and cross correlation spectral densities $j(\omega)$ and $k(\omega)$ are, respectively, defined by

$$j(\omega) = \gamma_H^2\int_0^\infty \langle B_H(t)\; B_H(0)\rangle \cos\omega t\; dt \tag{8}$$

and

$$k(\omega) = \gamma_H^2\int_0^\infty \langle B_H(t)\; B_{H'}(0)\rangle \cos\omega t\; dt \tag{9}$$

where

$B_H(t)$ = z-component of the random field at the site of proton H arising from spin-rotation interaction at time t.

Eq. (3) can be solved to give the following result:

$$v_1(t)/v_1(0) = a_+ \cdot \exp(-\lambda_+ t) + a_- \exp(-\lambda_- t) \tag{10}$$

where

$$\lambda_\pm = [7J - K + 2j + 2(j-k)]$$
$$\pm\{[3J + K + 2(k-j)]^2 + 20K^2\}^{1/2} \tag{11}$$

and

$$a_\pm = 1/2\left[1\pm\frac{3J + K + 2(k-j)}{\{[3J + K + 2(k-j)]^2 + 20K^2\}^{1/2}}\right] \tag{12}$$

If the fluctuation of random field $B_H(t)$ arising from the spin-rotation interaction is predominantly determined by rapid internal rotation of methyl group about its symmetry axis, it is reasonable to assume that $B_H(t)$ and $B_{H'}(t)$ are totally correlated, that is, $j = k$. In this case Eq. (10) can further be simplified to

$$R(t) \equiv v_1(t)/v_1(0)$$
$$= \exp(st)[A_1\exp(s_1 t) + (1-A_1)\exp(s_2 t)] \tag{13}$$

where

$$s = -2j,$$

$$s_1 = -(7J - K) - \{(3J + K)^2 + 20K^2\}^{1/2},$$

$$s_2 = -(7J - K) + \{(3J + K)^2 + 20K^2\}^{1/2},$$

and

$$A_1 = (1/2)[1 + (3J + K)/\{(3J + K)^2 + 20K^2\}^{1/2}]. \tag{14}$$

It is obvious from Eq. (13) that the term $\exp(st)$ represents the spin-rotational contribution and could successfully be factored out in the extreme narrowing limit which is well valid for small molecules in nonviscous solvents. The term in the square bracket on the righthand side of Eq. (13) represents the contribution from intramolecular dipolar interactions
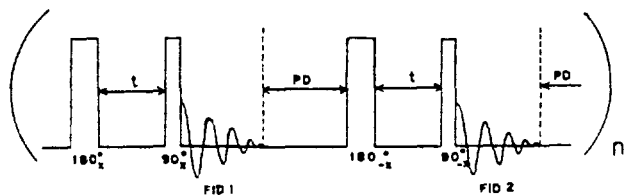
Figure 1. Two-pulse sequence used in our experiment.

Figure 2. Illustration of extrapolation to infinite dilution.

among protons which was first derived by Hubbard.[11]

For visual inspection Eq. (13) would better be drawn to the logarithmic scale, that is,

$$\ln R(t) = st + \ln[A_1 \exp(s_1 t) + (1-A_1) \exp(s_2 t)] \qquad (15)$$

Experimental

The GC grade 2,6-dichlorotoluene and N-methyl phthalimide used in our experiment were purchased from Aldrich Chemical Co. and Tokyo Kasei Co., respectively, and were used without further purifications. 2,6-Dichlorotoluene was dissolved in 100% $CDCl_3$ to prepare its 0.3, 0.2, 0.1 M and 0.08 M solutions while 0.02 M and 0.04 M solutions of N-methyl phthalimide were prepared using 100% C_6D_6 as solvent. To prevent the contamination by H_2O in the air we have prepared these solutions inside a glove box under N_2 purge. Each sample was placed in a 5 mm o.d. NMR tube and was degassed by repeating the standard freeze-pump-thaw cycle five times, and then was sealed under vacuum $(10^{-5}$ torr).

Proton relaxation measurements were made in the pulsed FT mode on a Varian XL-100 NMR spectrometer at $34 \pm 1°C$ using a modified inversion recovery sequence, shown in Figure 1, to reduce the possible 180° pulse error. By making use of a 180° proton frequency phase shifter attached to our spectrometer we could make the phase of 180° pulse alternate as shown in Figure 1. Coaddition of FID1 and FID2 can produce a pulse-error-free FID. For a given t sufficient numbers of FID's were collected to attain the adequate S/N ratio. After obtaining the relaxation data for several different t values we repeated the entire series of measurements at least seven more times to enhance the reliability of observed data. Also paramount to this experiment is the measurement of M_0 (magnitude of equilibrium magnetization). A series of relaxation measurements for 10 different t values took more than 10 hours in our case and during such a long time interval the magnetic field homogeneity may aggravate to a certain extent even with the use of autoshim device. To check the field homogeneity we took pains to measure M_0 by letting t equal to 500 sec, a pulse delay long enough for the spin system to restore to equilibrium, every time after measurements were made for three successive t values, and took the average of thus measured M_0 to have a reliable value for this quantity.[19] Temperature in the probe was checked with an Omega digital thermometer before and after the experiment and could be maintained at $34 \pm 1°C$ by making use of the variable temperature controller attached to our spectrometer. The intensity of methyl proton signal at a given t gives the value of $M_z(t)$ and, using thus found $M_z(t)$, we calculated the normalized relaxation curve
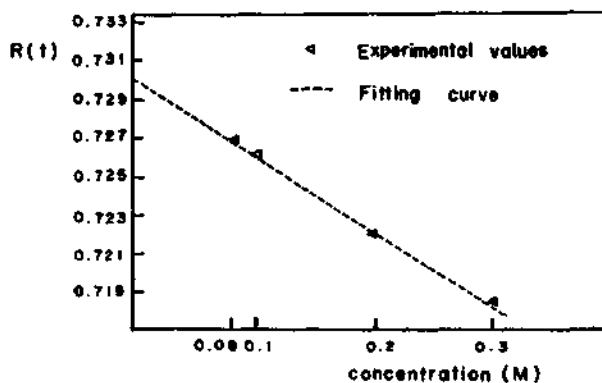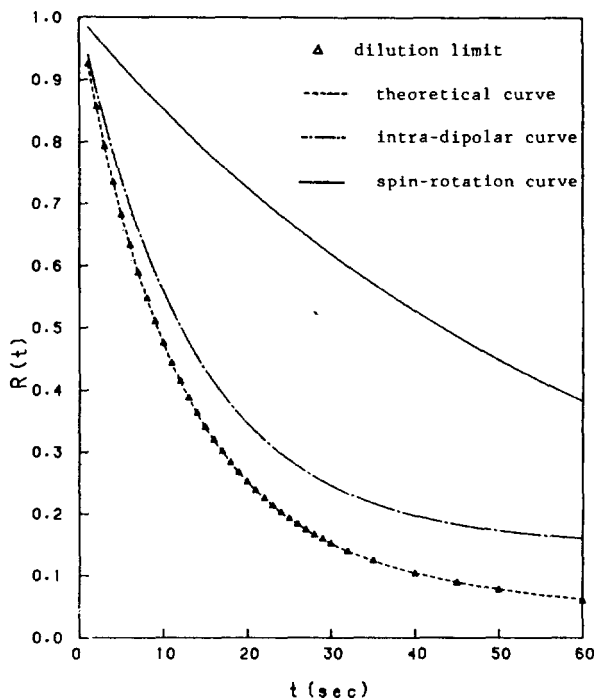

Figure 3. Infinite dilution data for $R(t)$ of 2,6-dichlorotoluene and theoretical fitting to Eq. (13).

$$R(t) = \frac{M_0 - M_z(t)}{2M_0} \qquad (16)$$

Results and Discussion

For 2,6-dichlorotoluene the $R(t)$ data for 0.3, 0.2, 0.1, and 0.08 M solution were extrapolated to infinite dilution at each t as exemplified by Figure 2. Through this extrapolation procedure intermolecular dipolar contribution to the longitudunal relaxation of methyl protons can be eliminated. Extrapolated curve $R(t)$ is shown in Figure 3. In order to manifest the strong nonexponential character of $R(t)$ we have plotted $\ln R(t)$ as a function of t for 0.3 M solution of 2,6-dichlorotoluene in Figure 4. We see from this that even in such a small molecule as 2,6-dichlorotoluene methyl protons exhibit a pronounced nonexponentiality in their relaxation behavior.

For N-methyl phthalimide $R(t)$'s for 0.04 and 0.02 M solution have been plotted in Figure 5. Virtually no difference
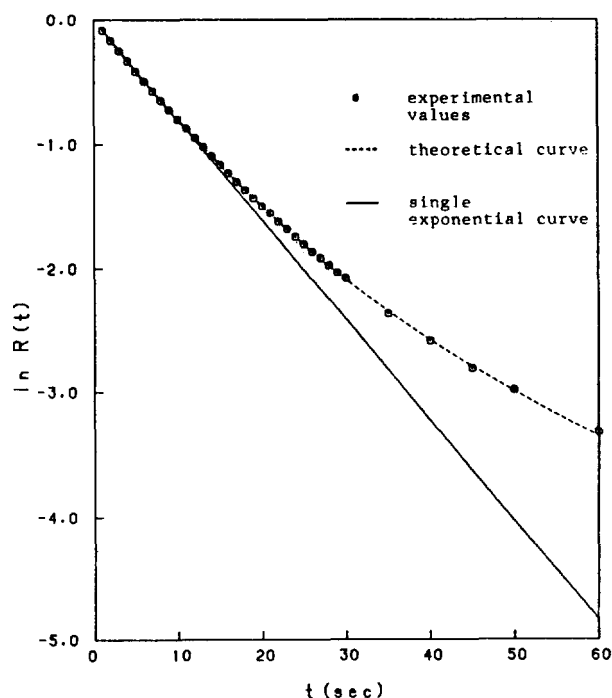
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Figure 4. Plot of ln $R(t)$ as a function of t for 0.3 M solution of 2,6-dichlorotoluene.
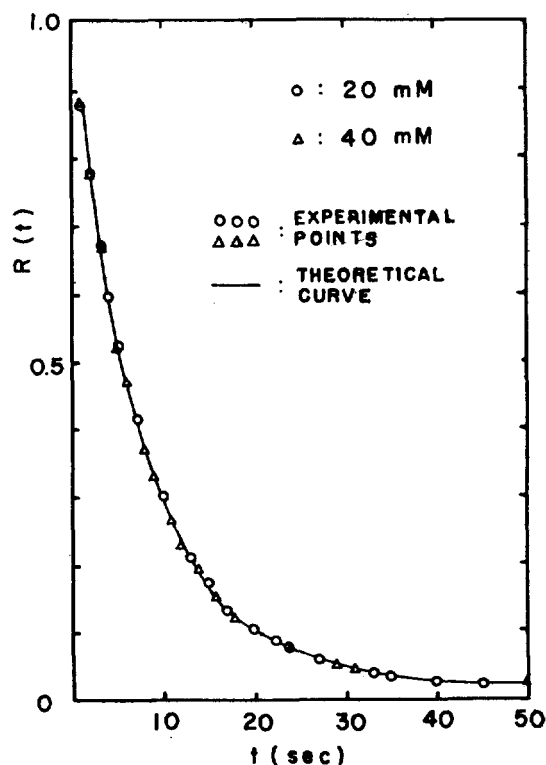

Figure 5. Relaxation data $R(t)$ for 0.02 and 0.04 M solutions of N-methyl phthalimide.

can be seen between these two data, which means the $R(t)$ for 0.02 M solution may be taken as that for infinitely dilute solution.

For theoretical interpretation of thus obtained infinite dilution data we first tried the dipolar-only expression
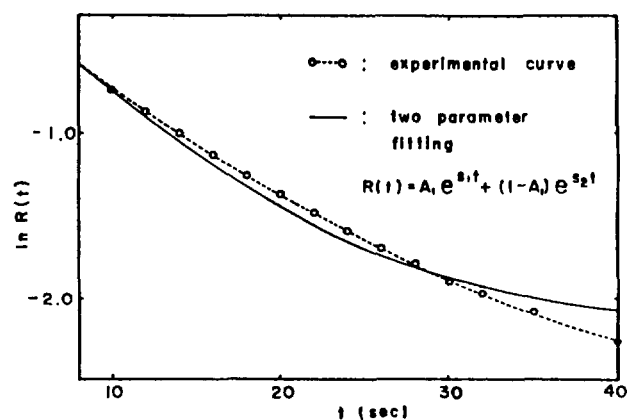

Figure 6. Least-square fitting of dipolar-only expression, Eq. (17), to the infinite dilution data for 2,6-dichlorotoluene.
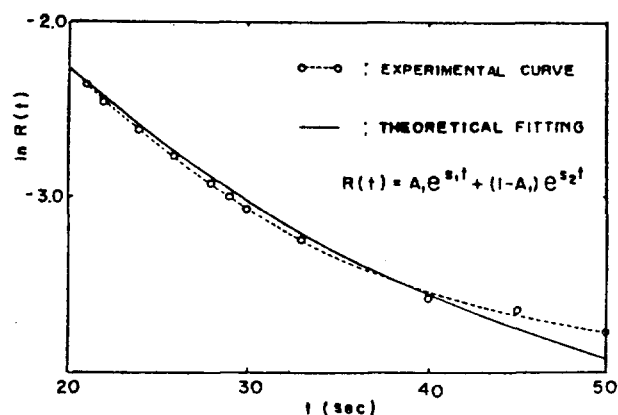

Figure 7. Similar fitting of Eq. (17), as in Figure 6, for N-methyl phthalimide.

$$R(t)_{dd} = A_1 \ \exp(s_1 t) + (1-A_1) \ \exp(s_2 t) \tag{17}$$

to reproduce the experimental data, Nonlinear least-square fitting of Eq. (17), using J and K as two adjustable parameters, to the observed infinite dilution data are shown in Figure 6 and 7. Obviously, the dipolar-only expression alone does not suffice for our purpose. Figure 3 and 8 show that Eq. (13), which is a full expression including the spin-rotational contribution as well, gives excellent agreement with experimental data when J, K, and j are treated as three adjustable parameters. Numerically found values of the parameters involved are listed in Table 1. From these parametric data we can see that the spin-rotational contribution to the initial rate of relaxation in 2,6-dichlorotoluene and N-methyl phthalimide, respectively, amounts to 18 and 31%.

Thus far we have successfully demonstrated a semiempirical method of separating the spin-rotational contribution from that due to the dipole-dipole interactions on the basis of a theoretically predicted relaxation curve $R(t)$[Eq. (13)]. The method described in this paper obviously has a distinct advantage over the conventional temperature variation method in that we do not have to toil to measure the relaxation at many temperatures as required by the latter method. Furthermore, we do not have to introduce any awkward assumption regarding temperature dependence of the so-called "cor-
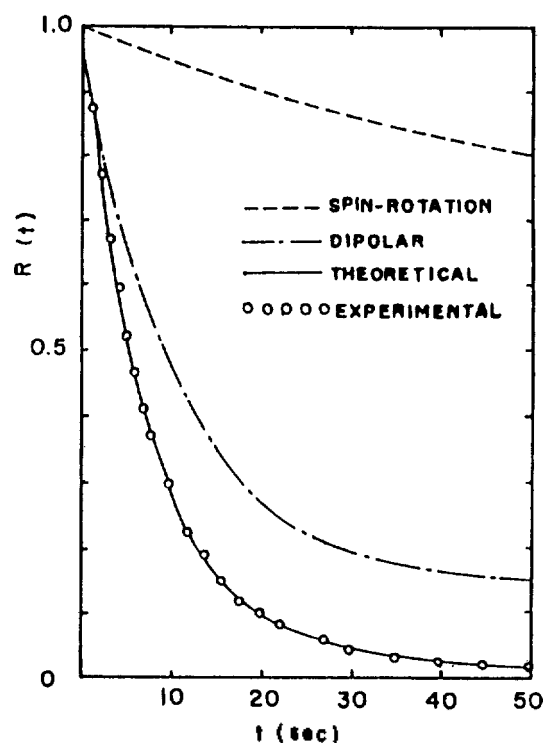
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Figure 8. Theoretical fitting of infinite dilution data to Eq. (13) for N-methyl phthalimide.

Table 1. Values of Parameters Determined by Nonlinear Least Square Fitting of Eq.(13) to Experimental Data

	2, 6-dichlorotoluene	N-methyl phthalimide
A_1	0.838	0.84
s_1	−0.0746	−0.10
s_2	−0.0011	−0.002
$s(= -2j)$	−0.016	−0.047
J	6.27×10^{-3}	8.37×10^{-3}
K	6.05×10^{-3}	7.98×10^{-3}

relation times". However, one should keep in mind the fact that Eq.(13), on which our discussion is based, is valid only under the assumptions of extreme narrowing limit and total correlation of the random magnetic fields arising from spin-rotation interactions and violation of either of these assumptions may lead to the failure of validity of Eq. (13). We believe that it is indeed the case for large molecules such as proteins, etc.[13,20]

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