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Translational Diffusion Constants and Intermolecular Relaxation in Paramagnetic Solutions with Hyperfine Coupling on the Electronic Site

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We investigate the NMR relaxation of solvent nuclei in non viscous paramagnetic solutions, in the case where the electronic spin of the paramagnetic species is submitted to an internal hyperfine field H_{hyp}. General expressions of the intermolecular longitudinal relaxation rates $1/T_1$ are provided, and three distinct regimes corresponding to an applied external field lower, larger and much larger than H_{hyp} appear, with three distinct linear laws for the relaxation rate $1/T_1$ vs $\nu_I^{1/2}$, where ν_I is the nuclear resonance frequency. From each of these laws and mainly the third one, it is possible to derive the relative diffusion constant of the paramagnetic and solvent molecules without any model assumption for solutions with a rather high radical concentration of 10^{-1} mol L^{-1}. This is illustrated for a triglyme solution with new stable ^{15}NTMIOD free radicals at various concentrations. For this solution, T_1 measurements were performed at $\nu_I = 244$ MHz, then at low and intermediate frequencies by the field cycling technique and finally in the Earth's magnetic field. From these results and from measurements of the solvent molecule diffusion constant by the pulsed magnetic field gradient technique, a determination of the diffusion constant of the free radicals is obtained which is compared with that obtained from a direct ESR measurement at low concentration. These data are used for the interpretation of the frequency and temperature dependence of the relaxation rates in this solution.

1. Introduction

The NMR relaxation of liquid solutions has been the object of extensive work over the past decades. In particular the study of paramagnetic solutions, for which the magnetic coupling between the solvent molecules nuclei and the electronic spins of the paramagnetic molecules is the dominant relaxation process, is a powerful way for understanding the dynamical properties of these solutions.[1] Among the various applications, the dynamic nuclear polarization (DNP) by paramagnetic impurities (or Abragam−Overhauser effect[2,3]) is a very efficient method for the amplification of a NMR signal in low fields. In a solution, this amplification is obtained through the magnetic coupling between the solvent protons and the free electrons of the paramagnetic molecule after saturation of the electronic transition.[4] This effect is the basic principle for building NMR magnetometers of high sensitivity.[5] The DNP enhancement factor is strongly dependent on the nature of the paramagnetic solution, and it is known that it is considerably increased when the paramagnetic impurities have a strong hyperfine structure.[6,7] For that reason it is convenient to use free radicals with a hyperfine coupling between the free electron and a nucleus (usually ^{14}N,^{15}N, or ^{31}P) of the radical molecule.

For magnetometry purposes a new paramagnetic solution with 2×10^{-3} mol L^{-1} of 1,1,3,3-tetrakis(trideuteriomethyl)isoindolin-2-yloxyl (^{15}NTMIOD [8−10]) free radicals in triethylene glycol dimethyl ether (triglyme) was recently synthesized. This solution which is stable until 150 °C and remains efficient in rather high magnetic gradients provides enhancement factors varying between 1000 and 2000 in the 25−125 °C temperature range. No other stable solution provides comparable factors over such a wide temperature range. The experimental study and the theoretical interpretation of the DNP enhancement factor of this system was recently performed.[11] However, a crucial parameter in the theory remained unknown: the absolute diffusion constant D_S of the ^{15}NTMIOD radical, which plays an important role both in the ESR line width and in the relaxation times of the solvent protons.

It was shown that in a nonviscous liquid solution containing free radicals at room temperature the spectral densities of the magnetic dipolar coupling between the solvent nucleus and the free electron spin behave as[12−14]

$$J(\omega) = J(0) - \alpha\omega^{1/2} \tag{1}$$

in the low frequency limit ($\omega\tau \ll 1$) where τ is the translational correlation time. The important point is that α is an invariant which is independent of the local order in the liquid, of the eccentricity of the spins, and of the rotational speed of the molecules. It must be emphasized that the same value of α is obtained whichever translational diffusion model is used: diffusion equation or random finite jumps of the molecules. This

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constant is given by

$$\alpha = \frac{\sqrt{2}}{18\pi}\frac{N_S}{D^{3/2}} \qquad (2)$$

where N_S is the number density of the electronic spins S responsible for the relaxation of the solvent protons with spin I and where D is the relative translational diffusion constant of the radical and solvent molecules

$$D = D_I + D_S \qquad (3)$$

Thus the law expressed by eqs 1 and 2 for $\omega\tau \ll 1$ appears to be a characteristic property of the three-dimensional relative translational motion of the spins whatever the details of their dynamics.

This has been mathematically proved by P. H. Fries,[15] but the main reason for this feature is that, for long times, the correlation function of the magnetic dipolar coupling between I and S spins takes values arising almost completely from large interspin distance contributions for which the details of the molecular packing and the rotational motions of the molecules become irrelevant. As the longitudinal relaxation rate $1/T_{1\text{inter}}$ of the solvent nuclei can be expressed as linear combinations of the spectral densities $J(\omega_I)$, $J(\omega_S \pm \omega_I)$, where ω_I and ω_S are the angular Larmor frequencies of the nuclear I spin and of the electronic S spin, respectively, we generally obtain in low fields a linear law

$$\frac{1}{T_{1\text{inter}}} = C - B\sqrt{\omega_I} \qquad (4)$$

From the values of B, it is easy to deduce that of D. As in eq 3, the absolute diffusion constant D_I of the solvent molecule having the nuclear spin I can be measured through the usual pulse magnetic field gradient (PMFG) technique,[16] the unknown diffusion constant D_S of the free radical can be deduced by difference. This method has been successfully used for determining D_S of DTBN free radicals in neopentane solution at various temperatures.[17,18] Notice that, in eq 1, $J(0)$ is strongly model dependent[12] and that it is rather difficult to obtain reliable information from the value of C in eq 4.

In this paper we extend the above ideas to the case of interest for us, i.e., the situation in which the electronic spin of the radical is not free, but is submitted to a hyperfine field H_{hyp} due to a nuclear spin K of the radical molecule.

In section 2 we develop the theoretical model providing the intermolecular longitudinal relaxation rate due to a dipolar magnetic coupling in this case and the ranges of validity of eq 4 is discussed. The experimental details are provided in section 3 and the method is illustrated for our solutions of triglyme with ^{15}NTMIOD free radicals in section 4.

2. Theory

Let I, S, and K be the solvent nuclear spin (proton $I = {}^1/_2$), the electronic radical spin ($S = {}^1/_2$), and the nuclear spin of the radical giving rise to an hyperfine coupling $A\ \vec{\mathrm{S}}.\vec{\mathrm{K}}$. For our system K is the ^{15}N nucleus with $K = {}^1/_2$. The static electronic Hamiltonian of the problem in presence of an applied magnetic field B_0 is

$$\hbar H = \hbar(A\vec{\mathrm{S}}.\vec{\mathrm{K}} + \omega_S S_z) \qquad (5)$$

where $\omega_S = |\gamma_S|B_0$ is the Larmor angular frequency of spin S. In eq 5 we neglected the nuclear Zeeman effect on the nuclear spin K.

The diagonalization of H gives four levels $E_i = \hbar\omega_i(i = 1 \ldots 4)$ with associated eigenstates $|i\rangle$ in the basis $|M_S, M_K\rangle$ given by

$$\begin{aligned}
\omega_1 &= \frac{\omega_S}{2} + \frac{A}{4} & |1\rangle &= |{+}{+}\rangle \\
\omega_2 &= -\frac{A}{4} + \frac{1}{2}\sqrt{A^2 + \omega_S^2} & |2\rangle &= c_1\,|+,-\rangle + c_2\,|-,+\rangle \\
\omega_3 &= -\frac{A}{4} - \frac{1}{2}\sqrt{A^2 + \omega_S^2} & |3\rangle &= -c_2|+,-\rangle + c_1|-,+\rangle \\
\omega_4 &= -\frac{\omega_S}{2} + \frac{A}{4} & |4\rangle &= |{-}\,{-}\rangle
\end{aligned} \qquad (6)$$

In eq 6, $|\pm\rangle$ are abbreviations for $|M_S = \pm{}^1/_2\rangle$, $|M_K = \pm{}^1/_2\rangle$. The coefficients c_1 and c_2 are defined by

$$c_1 = \left\{\frac{1}{2}\left[1 + \frac{\omega_S}{\sqrt{A^2 + \omega_S^2}}\right]\right\}^{1/2} c_2 = \left\{\frac{1}{2}\left[1 - \frac{\omega_S}{\sqrt{A^2 + \omega_S^2}}\right]\right\}^{1/2} \qquad (7)$$

The magnetic dipolar coupling between the spin I and the electronic spin S is

$$\hbar H_1(t) = Cr^{-3}\sum_q (-1)^q A_q^2 Y_{-q}^2(\theta,\varphi) \qquad (8)$$

where

$$C = \sqrt{\frac{24\pi}{5}}\gamma_I\gamma_S\hbar \qquad (8a)$$

$$A_0^2 = \frac{1}{\sqrt{6}}(3I_zS_z - \vec{\mathrm{I}}.\vec{\mathrm{S}}) \qquad (8b)$$

$$A_{\pm 1}^2 = \mp\frac{1}{2}(I_zS_\pm + I_\pm S_z) \qquad (8c)$$

$$A_{\pm 2}^2 = \frac{1}{2}I_\pm S_\pm \qquad (8d)$$

and r, θ, φ define the relative position vector $\vec{\mathrm{r}}$ between the interacting spins.

We define the spectral densities $J(\omega)$ of the random functions $r^{-3}\ Y_q^2(\theta,\varphi)$ as

$$J(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} g_2(t)\ \mathrm{e}^{-i\omega t}\,\mathrm{d}t \qquad (9)$$

with the correlation functions $g_2(t)$ defined by

$$g_2(t) = N_S\langle r_0^{-3}\ Y_q^2(\theta_0,\varphi_0)[r^{-3}Y_q^2(\theta,\varphi)]_t\rangle \qquad (10)$$

N_S being the free radical number density.

In these systems the electronic spins have their own relaxation processes which are much stronger than that due to the dipolar coupling with the solvent nuclei. The relevant mechanism is essentially due to the exchange coupling between free radicals. The corresponding electronic relaxation times range between 10^{-6} and 10^{-8} s according to the free radical concentration.

These times being much shorter than the relaxation times of the solvent nuclei ($10^{-2}-10$ s), the electronic spins are always in thermal equilibrium during a NMR experiment performed on the I spin.

Denoting by $\omega_I = \gamma_I B$ the resonance angular frequency of solvent nuclei $I = {}^1/_2$, the intermolecular relaxation rate $1/T_{1\text{inter}}$ due to the electronic spins is[19,20]

$$\frac{1}{T_{1\text{inter}}} = \int_{-\infty}^{+\infty} e^{i\omega_I t} k_{+-}(t)\,dt + \int_{-\infty}^{+\infty} e^{-i\omega_I t}\, k_{-+}(t)\,dt \quad (11)$$

where the quantum correlation function $k_{+-}(t)$, in which $\pm$ refer to $m_I = \pm{}^1/_2$, is the ensemble average

$$\langle\langle +|H_1(t)|-\rangle\langle -|H_1(0)|+\rangle\rangle \quad (12)$$

with a similar definition for k_{-+}. From eqs 8 and 10 we obtain

$$k_{+-}(t) = \frac{C^2}{4}\left[\langle S_+(t)S_-(0)\rangle + \langle S_z(t)S_z(0)\rangle + \frac{1}{6}\langle S_-(t)S_+(0)\rangle\right] g_2(t) \quad (13a)$$

$$k_{-+}(t) = \frac{C^2}{4}\left[\langle S_-(t)S_+(0)\rangle + \langle S_z(t)S_z(0)\rangle + \frac{1}{6}\langle S_+(t)S_-(0)\rangle\right] g_2(t) \quad (13b)$$

The evaluation of $\langle S_\pm(t)S_-(0)\rangle$ and $\langle S_z(t)S_z(0)\rangle$ is very easy in the high-temperature limit. We have in the Heisenberg representation

$$\langle S_\alpha(t)S_\beta(0)\rangle = \langle e^{iH\,t} S_\alpha e^{-iH\,t} S_\beta\rangle \quad (14)$$

or with the energy levels $E_i = \hbar\omega_i$ and eigenstates $|i\rangle$ defined by eq 6

$$\langle S_\alpha(t)S_\beta(0)\rangle = \frac{1}{4}\sum_{i,j=1}^{4} e^{i\omega_i t}\langle i|S_\alpha|j\rangle\, e^{-i\omega_j t}\langle j|S_\beta|i\rangle \quad (15)$$

We obtain, with $\omega_{ij} = \omega_i - \omega_j$,

$$\langle S_+(t)S_-(0)\rangle = \frac{1}{4}[c_2^2(e^{i\omega_{12}t} + e^{i\omega_{34}t}) + c_1^2(e^{i\omega_{13}t} + e^{i\omega_{24}t})] \quad (16a)$$

$$\langle S_-(t)S_+(0)\rangle = \frac{1}{4}[c_2^2(e^{i\omega_{21}t} + e^{i\omega_{43}t}) + c_1^2(e^{i\omega_{31}t} + e^{i\omega_{42}t})] \quad (16b)$$

$$\langle S_z(t)S_z(0)\rangle = \frac{1}{8}[1 + (c_1^2 - c_2^2)^2 + 2c_1^2c_2^2(e^{i\omega_{23}t} + e^{i\omega_{32}t})] \quad (16c)$$

Finally from eqs 11, 13, and 16, the intermolecular relaxation rate is

$$\frac{1}{T_{1\text{inter}}} = \frac{3}{20}\gamma_I^2\gamma_S^2h^2\Big\{[1 + (c_1^2 - c_2^2)^2]J(\omega_I) + 4c_1^2c_2^2J(\omega_{23}) + \frac{7}{3}c_1^2[J(\omega_{13}) + J(\omega_{24})] + \frac{7}{3}c_2^2[J(\omega_{12}) + J(\omega_{34})]\Big\} \quad (17)$$

where, as $\omega_{ij} \gg \omega_I$, $\omega_{ij} \pm \omega_I$ are replaced by ω_{ij} in the various spectral densities. A similar relation was derived by Barci, Bertini, and Luchinat [21,22] in the special case of Lorentzian spectral densities. Our expression is more general in the sense that no assumption is made about the analytical form of $J(\omega)$.

The calculation of the various $J(\omega)$ is a difficult task because the molecules are not spherical, the spins I and S are off center in their molecules (eccentricity effects), and there is a nonuniform equilibrium distribution of the interacting molecules (pair correlation effects).[12,23]

However, we will use the properties expressed by eqs 1 and 2, and for this purpose three frequency ranges are of interest.

(I) $\omega_S \gg A$. If ω_S is much larger than A, which can be neglected, the longitudinal relaxation rate $1/T_{1\text{inter}}$ of the solvent nuclear spin I is given for $S = {}^1/_2$ by the well-known[12] expression

$$\frac{1}{T_{1\text{inter}}} = \frac{3}{10}\gamma_I^2\gamma_S^2h^2\Big\{J(\omega_I) + \frac{7}{3}J(\omega_S)\Big\} \quad (18)$$

where we have replaced $J(\omega_S \pm \omega_I)$ by $J(\omega_S)$. This expression is directly obtained from the general eqs 7 and 17 with $c_1 = 1$, $c_2 = 0$, and $\omega_{13} = \omega_{24} = \omega_S$.

For example, in a model where the spin eccentricity effects and the nonuniform character of the pair correlation function are neglected, by taking correctly into account the hard sphere boundary conditions, $J(\omega)$ has an analytical expression given by eq 20b. Introducing the translational correlation time

$$\tau = b^2/D \quad (19)$$

where b is the minimal distance of approach between the centers of the molecules bearing the spins I and S, approximated as hard spheres with the same volume, and D is given by eq 3, setting

$$u = \sqrt{2\omega\tau} \quad (20a)$$

we have[24]

$$J(u) = \frac{N_S}{\pi Db}\,\frac{(3/2)u^2 + (15/2)u + 12}{u^6/8 + u^5 + 4u^4 + (27/2)u^3 + (81/2)u^2 + 81u + 81} \quad (20b)$$

Note that when $\omega\tau \ll 1$,

$$J(\omega) = \frac{N_S}{\pi Db}\,\frac{4}{27}\left[1 - \frac{3}{8}\sqrt{2\omega\tau}\right] \quad (20c)$$

which has the general form 1 and that even for $\omega\tau = 0.5$ expressions 20b and 20c differ only by 2.5%.

When $\omega\tau \gg 1$, it is clear that $J(\omega)$ behaves like $(\omega\tau)^{-2}$. So if the conditions $\omega_S\tau \gg 1$ and $\omega_I\tau \ll 1$ are satisfied, in eq 18 we can neglect $J(\omega_S)$ and replace $J(\omega_I)$ by its expression 1. This situation occurs for example for $\nu_I = 100$ MHz and $\tau = 10^{-10}$ s, for which $\omega_I\tau = 0.06$ and $\omega_S\tau = 40$. The measured relaxation rate $1/T_1$ is

$$\frac{1}{T_1} = \frac{1}{T_{10}} + \frac{1}{T_{1\text{inter}}} \quad (21)$$

where $1/T_{10}$ is the relaxation rate of the solvent nuclei in the diamagnetic solution. Then from equations 1, 2, 4, and 18 we have

$$\frac{1}{T_1} = C_1 - B_1\sqrt{\nu_I} \quad (22a)$$

with

$$C_1 = \frac{1}{T_{10}} + \frac{3}{10}\gamma_I^2\gamma_S^2 h^2 J(0) \tag{22b}$$

and

$$B_1 = \frac{1}{30\sqrt{\pi}}\gamma_I^2\gamma_S^2 h^2 \frac{N_S}{D^{3/2}} \tag{22c}$$

Consequently, in this frequency range $1/T_1$ has the general behavior given by eq 4 and D can be easily deduced from the slope B_1 of the curve $1/T_1$ vs $\sqrt{\nu_I}$ through eq 22c.

(II) $\omega_S > A$. $\omega_S\tau < 1$. Now we assume that the electronic Zeeman effect is larger than the hyperfine coupling, in such a way that the latter can be treated as a first-order perturbation $\hbar A S_z K_z$. Neglecting terms of the order of A^2/ω_S^2, we still have $c_1 = 1$, $c_2 = 0$, $\omega_{13} = \omega_S + A/2$, $\omega_{24} = \omega_S - A/2$, and from eq 17

$$\frac{1}{T_{1\text{inter}}} = \frac{3}{10}\gamma_I^2\gamma_S^2 h^2\left\{J(\omega_I) + \frac{7}{6}\left[J\left(\omega_S + \frac{A}{2}\right) + J\left(\omega_S - \frac{A}{2}\right)\right]\right\} \tag{23}$$

It is seen that for the limiting case where $A = 0$, we have the expected result given by eq 18. Moreover, according to the fact that the spectral densities $J(\omega_S + A/2)$ and $J(\omega_S - A/2)$ have the same weight in the above expression and that the spectral densities have a rather smooth frequency dependence, we see that the simplified expression 18 of $1/T_{1\text{inter}}$ can be used even for values of A which are not much lower than ω_S. In addition if $\omega_S\tau < 1$, using relations 1, 2, 18, and 21

$$\frac{1}{T_1} = C_2 - B_2\sqrt{\nu_I} \tag{24a}$$

with

$$C_2 = \frac{1}{T_{10}} + \gamma_I^2\gamma_S^2 h^2 J(0) \tag{24b}$$

and

$$B_2 = \frac{1}{30\sqrt{\pi}}\gamma_I^2\gamma_S^2 h^2 \frac{N_S}{D^{3/2}}\left(1 + \frac{7}{3}\sqrt{\frac{\gamma_S}{\gamma_I}}\right) \tag{24c}$$

In this frequency range $1/T_1$ has still the general behavior given by eq 4 and D can be determined independently from the slope B_2 of the curve $1/T_1$ vs $\sqrt{\nu_I}$ through eq 24c.

(III) $\omega_S < A$. $\omega_S\tau < 1$. Now we assume that the electronic Zeeman term effect is lower than the hyperfine coupling $\omega_S < A$. This situation occurs in low fields and in particular in the Earth's magnetic field. The Zeeman term in the expression 5 of H is treated as a first-order perturbation. Neglecting terms of the order of ω_S^2/A^2, we have $c_1 = c_2 = 1/\sqrt{2}$, $\omega_{23} = A$, $\omega_{13} = A + \omega_S/2$, $\omega_{43} = A - \omega_S/2$, and $\omega_{12} = \omega_{24} = \omega_S/2$. The intermolecular relaxation rate $1/T_{1\text{inter}}$ of the solvent nuclei is, according to eq 17

$$\frac{1}{T_{1\text{inter}}} = \frac{3}{20}\gamma_I^2\gamma_S^2 h^2\left\{J(\omega_I) + \frac{7}{3}J\left(\frac{\omega_S}{2}\right) + J(A) + \frac{7}{6}\left[J\left(A + \frac{\omega_S}{2}\right) + J\left(A - \frac{\omega_S}{2}\right)\right]\right\} \tag{25}$$

It is seen that in the extreme narrowing case where all the spectral densities can be approximated by $J(0)$, we have

$$\frac{1}{T_{1\text{inter}}} = \gamma_I^2\gamma_S^2 h^2 J(0) \tag{26}$$

We find the known result that the hyperfine coupling has no effect on $T_{1\text{inter}}$ in the extreme narrowing case.[25] Moreover as $J(A + \omega_S/2)$ and $J(A - \omega_S/2)$ have the same weight in eq 25, which can be safely replaced by the simplified expression 27 which will be valid even if ω_S is not much smaller than A.

$$\frac{1}{T_{1\text{inter}}} = \frac{3}{20}\gamma_I^2\gamma_S^2 h^2\left\{J(\omega_I) + \frac{7}{3}J\left(\frac{\omega_S}{2}\right) + \frac{10}{3}J(A)\right\} \tag{27}$$

In addition if $\omega_S\tau < 1$, a condition very easily satisfied in this frequency range, using relations 1, 2, 21, and 27, we have

$$\frac{1}{T_1} = C_3 - B_3\sqrt{\nu_I} \tag{28a}$$

with

$$C_3 = \frac{1}{T_{10}} + \frac{1}{2}\gamma_I^2\gamma_S^2 h^2[J(0) + J(A)] \tag{28b}$$

and

$$B_3 = \frac{1}{60\sqrt{\pi}}\gamma_I^2\gamma_S^2 h^2 \frac{N_S}{D^{3/2}}\left(1 + \frac{7}{3\sqrt{2}}\sqrt{\frac{\gamma_S}{\gamma_I}}\right) \tag{28c}$$

In this frequency range, $1/T_1$ has once more the general behaviour given by eq 4 and D can be determined from the slope B_3 of the curve $1/T_1$ vs $\sqrt{\nu_I}$ through eq 28c. To summarize, we have three frequency ranges for which $1/T_1 = \mathrm{C}_i - \mathrm{B}_i\sqrt{\nu_I}$ where B_i is model independent and is given by equations 22c, 24c, and 28c for $\omega_S \gg A$, $\omega_S\tau \gg 1$; $\omega_S > A$, $\omega_S\tau < 1$ and $\omega_S < A$, $\omega_S\tau < 1$, respectively. These three laws provide independent experimental determinations of the relative diffusion constant D between the radical and the solvent molecules carrying the nuclear spin I. Note that in first approximation, one has $B_2/B_1 = 61$ and $B_3/B_2 = 1/2\sqrt{2}$.

3. Experimental Section

Sample Preparation. The synthesis of the nitroxide free radical (1,1,3,3-tetrakis(trideuteriomethyl)isoindolin-2-yloxyl) ^{15}-NTMIOD has been described.[9] Triethylene glycol dimethyl ether (triglyme) was provided by Aldrich and was distilled twice at low pressure (120 °C, 50 Torr) over NaH. Solutions of ^{15}NTMIOD 10^{-3} mol L^{-1}, 2×10^{-3} mol L^{-1}, 10^{-1} mol L^{-1} in triglyme were degassed in appropriate flasks and then vacuum sealed.

NMR Experiments. *High-Frequency Experiment.* The longitudinal relaxation time T_1 of the protons of the diamagnetic and paramagnetic solutions were measured with the usual inversion recovery sequence ($\pi - t - \pi/2$). We used a superconducting magnet (5.7 T) and a homemade spectrometer working at 244 MHz. The temperature regulation was performed with a BVT 1000 Bruker variable temperature unit allowing a temperature accuracy better than 0.5 °C. The diffusion coefficients D_I of the protons of the solvent triglyme molecule were measured at various temperatures through the usual pulsed magnetic field gradient technique (PMFG) using the sequence described by Stejskal and Tanner.[16] In our experiment the magnitude g of the two gradient pulses was varied between 0 and 0.3 T m^{-1}, the time interval Δ between these pulses and their duration δ were fixed as 53×10^{-3} and 3×10^{-3} s, respectively. This allowed us to observe the attenuation of a spin echo amplitude providing good accuracy (5%) of the values determined for the self-diffusion constants. In fact the presence of a static gradient $\mathbf{g}_0$, due to the direct field $\mathbf{B}_0$ inhomogeneities in the coil, leads with the above values of δ to a nonnegligible interference term proportional to $\mathbf{g}_0 \cdot \mathbf{g}$. We were able to get rid of this term by alternating an even number of sequences with $\mathbf{g}$ parallel and antiparallel to $\mathbf{B}_0$. With an accumulation procedure, the interference term cancels.

Intermediate Frequency Experiment. T_1 measurements of protons in the solution were performed with the usual technique on a MSL Bruker spectrometer working at various frequencies 17 MHz $< \nu_I <$ 90 MHz in Grenoble.

Low Field Experiment. T_1 measurements of protons in the solution have been performed in Stuttgart using the field cycling technique[26,27] for 100 Hz $< \nu_I <$ 28 MHz. The nuclear spins are polarized in a 3900 Gauss magnetic field, then the field is decreased to a lower value in a time much shorter than T_1; after a time t, the field is restored to its original value and the amplitude of the free precession signal of protons is immediately recorded. The value of T_1 in low field is deduced from the variation of the amplitude of the signal as a function of time t, spent in low field. This technique allows measurements of T_1 in magnetic field as low as 2×10^{-6} T with good sensitivity.

ESR Experiments. The translational diffusion constant for TMIO (it was not necessary to use the isotopically-labeled version, NTMIOD, of the radical) in triglyme was measured using the ESR capillary method.[28,29] A 10 cm long thin-walled capillary of internal diameter 1.3 mm was filled to a depth of 7 cm with air-saturated triglyme. To the top of the liquid column was introduced 5 μL of a millimolar solution of TMIO in triglyme. The capillary was located centrally inside a standard 5 mm o.d. NMR tube: ESR spectra were recorded at known intervals along the capillary as the sample tube was pushed with a calibrated screw into the spectrometer cavity. It takes several days to obtain a complete set of data, but each set only takes about 30 min. Spectra were recorded with a Varian E4 spectrometer, which was interfaced to a personal computer with the aid of a Real Time Devices analog/digital card, and the spectra were written to disk using the EW program supplied by Scientific Software Services. The EW program was also used to obtain the heights (taken to be equivalent to concentrations) of one of the three lines in the TMIO spectrum: because of the presence of air, no hyperfine structure of the protons was resolved. The sampling function of the cavity was determined using an experiment similar to that used for the diffusion experiments. This was done with the aid of a single crystal of lithium phthalocyanine (which has a single sharp line) mounted at the tip of a cocktail stick which was placed centrally inside a 5 mm o.d. NMR tube that was pushed through the cavity with the calibrated screw. The data were processed using the corrected-zero method as described in ref 29 (note that in this reference there are three errors (i) the slopes referred to after eqs 8 and 15 should be $(4Dt)^{-1}$, (ii) eq 16 should read $a = (4 \ln 2)/W_a^2$, (iii) W_b in Figure 2 should be $W_b/2$).

4. Results and Discussion

Diffusion Constants of TMIO Molecules. Some of the data obtained through ESR capillary experiments are plotted in Figure 1. The diffusion constants derived from them give for TMIO with $N_S = 10^{-3}$ mol L^{-1} in triglyme at 298 K, a mean value of D_S of $(5.5 \pm 0.2) \times 10^{-6}$ (cm^2 s^{-1}). This value was obtained from measurements made at times varying between 8.77×10^4 and 52.18×10^4 s.

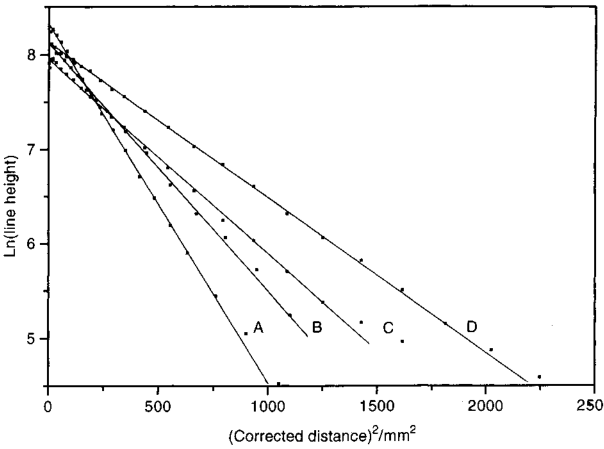

Figure 1. Some typical plots of the logarithm of the height of an ESR line against the square of the corrected distance, for the diffusion of TMIO in triglyme at 298 K with $N_S = 10^{-3}$ mol L^{-1}. Measurements were made at the times: $A = 10.57 \times 10^4$ s, $B = 19.39 \times 10^4$ s, $C = 28.03 \times 10^4$ s, $D = 52.18 \times 10^4$ s. Note that the intercepts have no significance.

TABLE 1: Experimental Values of $10^6 \times D_I$ (cm^2 s^{-1}) for the Triglyme Solution with ^{15}NTMIOD Free Radicals at Various Temperatures

T (K)	pure solvent	$N_S = 10^{-1}$ mol L^{-1}	$N_S = 10^{-3}$ mol L^{-1}
298	6.06	4.61	5.83
308	7.06	6.07	7.06
323	9.14	8.00	8.64
338	11.66	8.72	10.84
353	13.92	10.95	13.52
373	17.3	15.41	17.3

Diffusion Constants of Triglyme Molecules. These constants were measured by the PMFG method described in section 3 for various free radical ^{15}NTMIOD concentrations and different temperatures. The results are displayed in Table 1. As expected there is a strong increase of D_I with temperature, but between the diamagnetic and the paramagnetic solution with $N_S = 10^{-3}$ mol L^{-1} which is used for dynamic nuclear polarization purpose, D_I varies less than 7%, which means that it remains approximately constant according to the experimental uncertainty (±5%). Even for radical solution concentrations reaching 10^{-1} mol L^{-1}, D_I decreases by less than 25% at $T = 298$ K and 10% at $T = 373$ K. This means that the viscosity of the solution slowly increases with the presence of ^{15}NTMIOD molecules. Note that even for $N_S = 10^{-1}$ mol L^{-1} there are 55 triglyme molecules for one ^{15}NTMIOD radical.

High Frequency T_1 Relaxation Times. We have measured the solvent proton longitudinal relaxation times at a frequency $\nu_I = 244$ MHz both for the diamagnetic solution and the paramagnetic solution with $N_S = 10^{-1}$ mol L^{-1} at various temperatures. These results are displayed in Table 2.

Low and Intermediate Frequency T_1 Relaxation Times. We display on Figure 2 the measured relaxation rates $1/T_1$ obtained by the field cycling method in the frequency range $100 < \nu_I < 30$ MHz and by the usual method for $17 < \nu_I < 90$ MHz for the paramagnetic solutions with $N_S = 10^{-1}$ mol L^{-1} at $T = 298$ K. On this figure the values of $1/T_1$ obtained in the Earth's magnetic field and at $\nu_I = 244$ MHz at 298 K are also reported.

Relative Diffusion Constants D. We consider the values of $1/T_1$ measured by the usual method between $\nu_I = 17$ and 90 MHz for a solution with $N_S = 10^{-1}$ mol L^{-1} at $T = 298$ K. The

TABLE 2: Measured Proton Longitudinal Relaxation Times T_{10} of the Triglyme Diamagnetic Solution and T_1 of the ^{15}NTMIOD Paramagnetic Solution with $N_S = 10^{-1}$ mol L^{-1} for Various Temperatures (Frequency Resonance $\nu_I = 244$ MHz)[a]

T (K)	T_{10} (s) (pure solvent)	T_1 (s) (10^{-1} mol L^{-1})	$1/T_{1\text{inter}}$ (s^{-1}) experimental	$1/T_{1\text{inter}}$ (s^{-1}) theoretical
298	2.5	0.15	7.0	6.8
323	3.9	0.185	5.15	4.6
338	4.9	0.23	4.15	4.3
353	5.25	0.25	3.81	3.6
373	5.75	0.287	3.31	2.8

[a] $T_{1\text{inter}}$ is defined by eq 21. The theoretical values of $1/T_{1\text{inter}}$ are discussed in section 4.

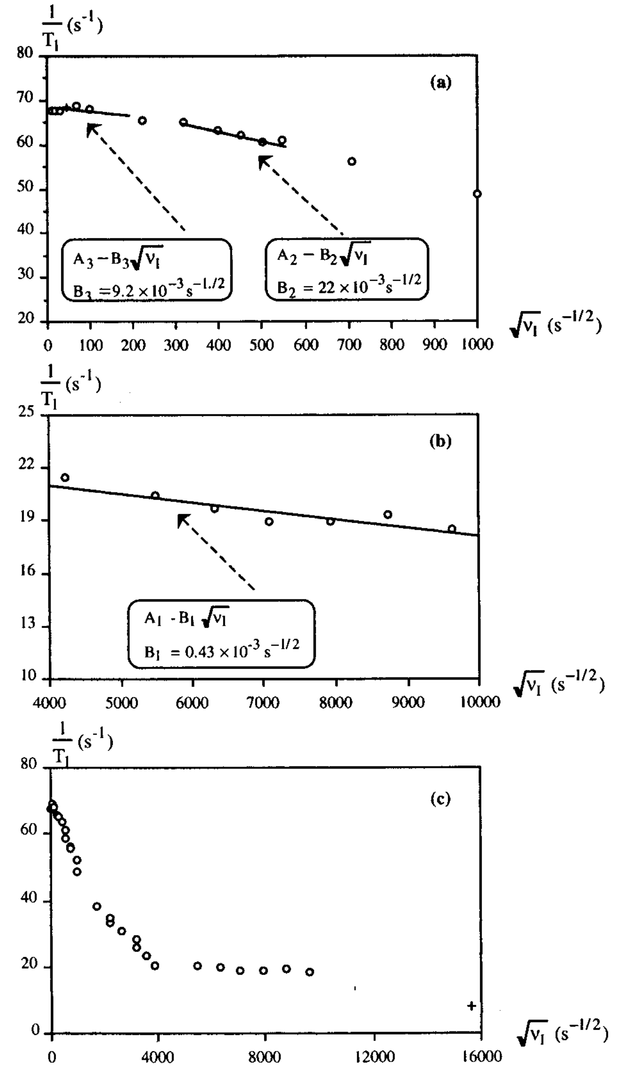

Figure 2. Proton nuclear relaxation rates $1/T_1$ vs $\nu_I^{1/2}$ for a paramagnetic solution of ^{15}NTMIOD radicals in triglyme with $N_S = 10^{-1}$ mol L^{-1} at $T = 298$ K. (a) Low-frequency range $100 < \nu_I < 1$ MHz obtained by field cycling technique. The cross represents the measured value in the Earth's magnetic field ($\nu_I = 2$ kHz). (b) Intermediate frequency range $17 < \nu_I < 90$ MHz obtained by the usual inversion recovery method. (c) Variation over the whole frequency range. The cross corresponds to the high-frequency data ($\nu_I = 244$ MHz).

corresponding points in a diagram $1/T_1$ vs $\nu_I^{1/2}$ fit a linear law with a slope $B_1 = (4.3 \pm 0.15) \times 10^{-4}$ s$^{-1/2}$. From eq 22c we deduce the relative diffusion constant $D = (8.8 \pm 0.2) \times 10^{-6}$ cm^2 s^{-1}. The minimal distance of approach of the ^{15}NTMIOD and triglyme molecules has been estimated through CPK model to be $b = 7.3 \times 10^{-8}$ cm. From the above value of D, the translational correlation time $\tau = b^2/D$ is $\tau = 6 \times 10^{-10}$ s. It is noted that, with this value of τ, the corresponding value of $\omega_S\tau$ for the investigated frequencies vary between 42 and 225. Consequently the condition $\omega_S\tau \gg 1$ allowing to use relation 22a is fully satisfied.

From ESR measurements in the liquid solution at $T = 298$ K, the isotropic hyperfine constant between the electronic spin and the ^{15}N nucleus of the ^{15}NTMIOD radical was determined: $A/2\pi = 55$ MHz. Then we have $A\tau = 0.2$. The condition $\omega_S\tau = 1$ is obtained for $\nu_I = 400$ kHz. The results corresponding to the section 2.II are reasonably satisfied for $0.4 < \omega_S\tau < 0.8$, i.e., for $160 < \nu_I < 320$ kHz or for $400 < \nu_I^{1/2} < 566$ (s$^{-1/2}$). From Figure 2 it is seen that the measured values of $1/T_1$ vs $\nu_I^{1/2}$ fit a linear law with a slope $B_2 = (2.2 \pm 0.2) \times 10^{-2}$ s$^{-1/2}$. From eq 24c we deduce $D = (9.6 \pm 0.7) \times 10^{-6}$ cm^2 s^{-1} in excellent agreement with the high-frequency determination.

Finally, the results corresponding to the section 2.III are reasonably satisfied for $\omega_S/A < 0.5$, i.e., for $\nu_I < 40$ kHz or $\nu_I^{1/2} < 200$ (s$^{-1/2}$). As expected in this frequency range, the experimental results displayed in Figure 2 show a very small frequency variation. The dispersion of the experimental points due to the uncertainty in the measurements cannot provide a reliable value of the slope of the linear law predicted by the theory for the variation of $1/T_1$ vs $\nu_I^{1/2}$. However our best determination gave a slope $B_3 = 9.2 \times 10^{-3}$ s$^{-1/2}$. From eq 28c we deduce $D = 8.8 \times 10^{-6}$ cm^2 s^{-1} still in very good agreement with both above determinations. At this temperature for this solution, the diffusion constant of the triglyme molecule given in Table 1 is $D_I = (4.6 \pm 0.2) \times 10^{-6}$ cm^2 s^{-1} and we deduce the value of the absolute diffusion constant of the ^{15}NTMIOD radical $D_S = (4.3 \pm 0.3) \times 10^{-6}$ cm^2 s^{-1} . Note that by using the Stokes formula with the effective radius of ^{15}NTMIOD ($a_S = 3.67 \times 10^{-8}$ cm) and triglyme ($a_I = 3.61 \times 10^{-8}$ cm), we obtain, from the measured values of D_I, $D_S = 4.5 \times 10^{-6}$ cm^2 s^{-1} and $D = 9.1 \times 10^{-6}$ cm^2 s^{-1}, a value very close to that obtained through our method.

Direct measurement of D_S in the 10^{-3} mol L^{-1} solution at $T = 298$ K by ESR spectroscopy using the capillary method gave $D_S = (5.5 \pm 0.2) \times 10^{-6}$ cm^2 s^{-1}.

If we refer to Table 1 for solutions with $N_S = 10^{-1}$ mol L^{-1} and 10^{-3} mol L^{-1} of TMIO radicals, we measured $D_I = 4.61 \times 10^{-6}$ cm^2 s^{-1} and $D_I = 5.83 \times 10^{-6}$ cm^2 s^{-1}, respectively. Assuming that the ratio D_S/D_I remains constant, we obtain in the 10^{-1} mol L^{-1} solution $D_S = (4.34 \pm 0.2) \times 10^{-6}$ cm^2 s^{-1} in remarkable agreement with our determination through the relaxation method ($D_S = (4.3 \pm 0.3) \times 10^{-6}$ cm^2 s^{-1}).

Strictly speaking, the comparison of the self-diffusion coefficient D_S determined from the relaxation rates with the diffusion coefficient from the ESR capillary method is subject to caution, since in the capillary method diffusion occurs in a concentration gradient and represents mutual diffusion. Only in the limit of zero concentration one obtains the real tracer diffusion coefficient, which is equal to the self-diffusion coefficient. The correct way would be to measure at different low concentrations and extrapolate to zero concentrations. But with the low TMIO concentration (10^{-3} mol L^{-1}) this error is expected to be small and lower than the experimental uncertainty as shown by the coherence between both determinations.

For our solutions, as we have measured D_I for various temperatures; assuming that the ratios D/D_I is constant, we approximately know the temperature dependence of D and D_S.

Temperature Dependence of $1/T_{1\text{inter}}$ at High and Low Frequency. For the solution with $N_S = 10^{-1}$ mol L^{-1}, the measured values of $1/T_{1\text{inter}}$ of the solvent protons at $\nu_I = 244$ MHz are provided for various temperatures in Table 2. As we know from the above discussion the corresponding values of D, it is possible to calculate the theoretical dependence of $1/T_{1\text{inter}}$

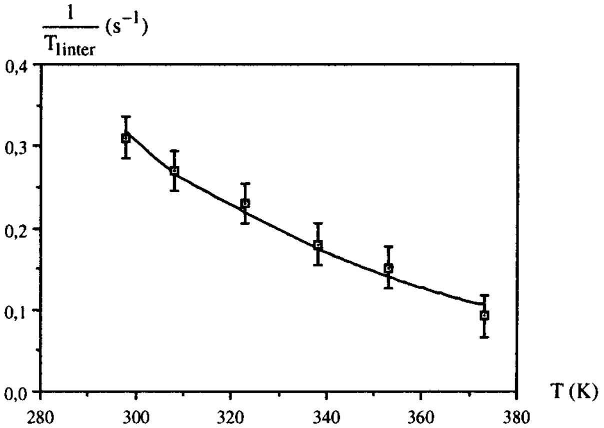

Figure 3. Experimental (points) and theoretical (continuous curve) temperature dependences of the solvent protons intermolecular relaxation rate $1/T_{1\text{inter}}$ in the Earth's magnetic field of the radical solution with $N_S = 10^{-3}$ mol L^{-1}.

through eqs 19, 20, and 21. We obtain the results given in the last column of Table 2. The difference between the experimental and theoretical values never exceeds 15%. According to the experimental uncertainties (5% on D_I, 5% on T_1), despite our assumption concerning the temperature variation of D_S and the fact that we neglected any pair correlation effects in $J(\omega)$, the agreement is very satisfactory.

In a high-performance hydrogenated paramagnetic solution for use in the Earth's field NMR magnetometers based on nuclear dynamic polarization effect, a solution with $N_S = 10^{-3}$ mol L^{-1} of ^{15}NTMIOD free radicals was selected. For this purpose we have measured the T_1 relaxation time of the solution in the Earth's magnetic field at various temperatures. Indeed, the T_1 values of protons are essential for determining the efficiency factor of the solution. The results concerning $1/T_{1\text{inter}}$ are displayed in Figure 3 and are compared to the theoretical values obtained from eqs 28a and 28b with $\nu_I = 0$

$$\frac{1}{T_{1\text{inter}}} = \frac{1}{2}\gamma_I^2\gamma_S^2\hbar^2[J(0) + J(A)] \qquad (29)$$

where $J(0)$ and $J(A)$ are given by eqs 20c with the values of D deduced from that of D_I given in Table 1. We obtain a good agreement on the whole temperature range.

5. Conclusion

We have considered paramagnetic solutions in which the electronic spins of the paramagnetic species is submitted to an internal hyperfine coupling $\hbar A\vec{S}.\vec{K}$ with a nucleus K belonging to the paramagnetic molecule. But instead of studying the relaxation properties of this molecule, we were interested in the solvent nuclei relaxation process, which is dominated by the intermolecular dipolar coupling between these nuclei and the electronic spin S. Various expressions for the intermolecular relaxation rates in terms of the spectral densities $J(\omega_I)$, $J(\omega_S)$, and $J(A)$ where ω_I, ω_S are the nuclear and electronic angular Larmor frequencies have been derived according to the values of the ratio ω_S/A and of $\omega_I\tau$, where τ is the translational correlation time. We extensively used the general linear dependence of $J(\omega)$ vs $\sqrt{\omega}$, which is valid for $\omega\tau < 1$, with a slope which is model independent, to derive the relative translational diffusion constant D between the solvent molecule carrying the nuclear spin I and the paramagnetic molecule. Rather accurate values of D are obtained in this way and can be checked by several independent determinations at low-, intermediate-, and high-resonance frequencies. In the particular case of ^{15}NTMIOD free radicals in triglyme solutions, only two independent reliable determinations of D could be achieved which were shown to be coherent. Moreover, the value of D_S, the absolute diffusion constant of the radical, was shown to be consistent with that obtained through ESR capillary method. It should be pointed out that the ESR technique is limited to rather dilute paramagnetic solutions (10^{-3} mol L^{-1}) due to electronic relaxation effects, while the method based on frequency dependence of the solvent nuclei is appropriate to more concentrated solutions (10^{-1} mol L^{-1}) in order to have significant slopes in the $1/T_1$ vs $\sqrt{\nu_I}$ curves. In systems where the hyperfine constant A is much larger such as for phosphorus-centered free radicals in solution,[30] three independent determinations of D are expected to be possible. But practically D can be determined from the highest frequency range which is by far the easiest to be investigated and which provides the most accurate results. Finally, at very low fields, we have been able to interpret the temperature dependence of the proton relaxation rate with good accuracy, a result which is very useful in the application of this solution in a magnetometer utilizing the dynamic polarization effect for amplifying the nuclear signal.[11]

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