Electron-spin relaxation and molecular dynamics in liquids. I. Solvent dependence

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Temperature-dependent ESR relaxation studies of PD-Tempone in a variety of solvents ranging from weakly interacting hydrocarbons to strongly interacting D_2O are described. The empirical molar transition energy scale \( E_T \), which is a good measure of specific solvent polarity, is found to lead to a useful interpolation method for estimating the solvent dependence of the magnetic tensors required for accurate spin-relaxation studies. The temperature-dependent results are generally well-represented by a modified Stokes–Einstein type of \( \eta/T \) dependence for \( \tau_R \), the rotational correlation time. The \( \epsilon \) parameter introduced by Freed and coworkers as an empirical correction to the nonsecular Debye spectral densities is found to correlate with \( E_T \), such that it is largest for the weakly interacting hydrocarbon solvents and approaches the Debye limit of \( \epsilon = 1 \) for D_2O solvent. This is discussed in terms of approximate fluctuating torque and slowly relaxing local structure models, and the former appears more consistent with experiment. It is also pointed out that \( \epsilon > 1 \) would result from the phenomenological feature of viscoelasticity.

I. INTRODUCTION

Hwang, Mason, Hwang, and Freed (HMHF) have shown the value of ESR relaxation studies with a relatively small and deuterated spin probe (cf. Fig. 1) in the study of molecular orientational dynamics in ordinary liquids. It is small enough that one expects and detects significant deviations from Brownian motional models. These appear as significant deviations from Debye spectral densities of the high-frequency (or nonsecular) relaxation contributions in the motional narrowing region and as line shape characteristics in the slow motional region which are particularly sensitive to reorientational model.\(^1\)\(^,\)\(^2\) These features are not usually observed with larger probe molecules such as VOAA.\(^3\)\(^,\)\(^4\) Although there are other important physical techniques for studying rotational dynamics in liquids,\(^5\)\(^,\)\(^6\) these features of ESR relaxation studies appear to be rather special.

In this work we report on further studies we have performed with PD-Tempone in a variety of isotropic solvents in recent years which amplify important aspects of the rotational dynamics of this probe. Some of this work was undertaken for comparison with studies of molecular dynamics in liquid crystalline solvents,\(^7\) and preliminary reference may be found in those reports.\(^8\)\(^,\)\(^9\) In particular, we examine in this work: (1) the solvent dependence of \( \epsilon \), which characterizes the non-Debye spectral density:

\[
\omega = \frac{\tau_R}{1 + \epsilon \omega^2 \tau_R^2},
\]

(1)

found useful in previous work\(^1\)\(^,\)\(^3\)\(^,\)\(^8\)\(^,\)\(^9\); (2) the validity of a Stokes–Einstein type of law, by which we mean a

\[
\tau_R = \frac{\eta}{T}.
\]

(2)

for this probe in a variety of solvents. Many studies in recent years have focused on the question of the applicability of modified Stokes–Einstein behavior for small molecules in liquids, and this topic has recently been extensively reviewed.\(^4\)\(^,\)\(^5\) We also consider related matters of spin-rotational relaxation and some other anomalous features of the spin relaxation.

Some interesting correlations emerge from this study of solvent dependence. In particular, we wish to emphasize the solvent polarity as an important parameter. The "effective" polarity of a solvent depends on a variety of intermolecular forces as well as specific (hydrogen) bonding between the solvent and the solute. Lin and Freed\(^10\) have employed a particular empirical method based upon the extensively studied molar transition energy scale \( E_T \).\(^6\) They found the \( E_T \) scale very useful for representing solvent variations of hyperfine splittings \( a_r \) (and \( a_d \) ), and this has now led to a comprehensive measure of solvent polarity specific to the PD-Tempone probe. The various features of rotational dynamics of this probe could then be compared with this parameter as well as more familiar ones (e.g., solvent size).

Another virtue we have found of the \( E_T \) scale for ESR studies is that the hyperfine and \( g \)-tensors, which are sensitive to solvent, scale rather well with this parameter. Thus, good estimates of these tensors can often be obtained without the necessity of performing careful simulations of rigid limit spectra in the particular solvent. The latter is often beset with poor resolution.

\[\text{FIG. 1. Perdeuterated 2,2,6,6-tetramethyl-4-piperidone N-oxide (PD-Tempone) showing molecular-fixed axis system.}\]

\(^a\)Supported by NSF Grant No. CHE 8024124.
from inhomogeneous broadening, and in many solvents the probe does not remain magnetically dilute upon freezing, because it can precipitate out. We analyze and use this scaling procedure in the present work.

The emphasis in the present work is on solvent effects on molecular dynamics from temperature-dependent studies at atmospheric pressure. In a companion work we consider the molecular dynamics of the PD-Tempone probe in a single solvent, but as a function of both temperature and density, and the matters of Stokes-Einstein behavior and non-Debye spectral densities are critically examined from that viewpoint.

II. EXPERIMENTAL CONSIDERATIONS

All ESR measurements were made at X band with a Varian E-12 Spectrometer system using 10 kHz field modulation and a Varian E-4531 multipurpose cavity. The Varian E-257 variable temperature accessory produced temperatures typically regulated to within ±0.5 °C. To determine the sample temperature, a copper-Constantan thermocouple, fixed in the active region of a standard sample tube filled with liquid solvent, was placed in the microwave cavity before and after each set of measurements. As a function of temperature, complete ESR line shapes were collected on line as described elsewhere. The effects of excessive magnetic field modulation and microwave power saturation were guarded against by frequent checks and adjustments. The nitroxide-free radical: perdeuterated 2,2,6,6-tetramethyl-4-piperidone N-oxide (PD-Tempone) shown in Fig. 2 was synthesized by Dr. Bogumił Hetnarski following procedures used previously. Solutions of PD-Tempone were prepared volumetrically in a desiccated nitrogen glove bag and transferred to conventional Pyrex sample holders for subsequent vacuum line freeze-pump-thaw degassing. After being sealed under vacuum, the sample holders were refrigerated, and solution-filled sidearms were withdrawn as needed. For each solvent, several spin-probe concentrations were tested to avoid exchange broadening. All samples demonstrated excellent stability; the same sample tubes were used more than a year later in supplemental experiments.

Di-\(\text{n}\)-butyl phthalate (DNBPT) (Eastman Organic Chemicals), \(\mathrm{D}_2\mathrm{O}\) (Aldrich Chemical Company, 99.8\% D), \(\text{n}\)-decane (Aldrich Chemical Company), and \(\text{n}\)-dodecane (Eastman Organic Chemicals) were used with PD-Tempone concentrations ranging from \(1 \times 10^{-4}\) to \(1 \times 10^{-5}\) M. Sample tubes were ordinarily made from standard 3 mm Pyrex tubing; we used 1 mm capillary Pyrex tubing for \(\mathrm{D}_2\mathrm{O}\) solutions along with careful sample positioning to minimize microwave dielectric loss and to achieve symmetric ESR line shapes.

Viscosities were interpolated and extrapolated using available data and standard empirical relations. For temperatures below 35 °C, the viscosity of DNBPT was calculated from

\[
\ln \eta = -8.396 + \frac{966.7}{T - 151.3}
\]

(3a)

(which is in the form of a Doolittle equation), where \(\eta\) is the viscosity in poise and \(T\) is in K. From available data we found that for temperatures above 35 °C,

\[
\ln \eta = -7.790 + \frac{880.6}{T - 151.3}
\]

(3b)

The viscosity of \(\mathrm{D}_2\mathrm{O}\) was calculated from

\[
\log(\eta/1.2471) = \left[1.3580(20 - t) - 0.00067(t - 20)^2\right]/(t + 96.71)
\]

(4)

where \(\eta\) is the viscosity in cP and \(t\) is the temperature in °C. This expression was given for the 5–70 °C range, but we have compared the predictions to high temperature measurements and recent low temperature results and found less than 2% deviation across

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FIG. 2. Rigid limit spectrum of PD-Tempone in di-\(\text{n}\)-butyl phthalate. Simulation based on magnetic parameters given in Table I.
our experimental temperature range. For the hydro-
carbon solvents we used available viscosity data.\textsuperscript{17}

The Varian E-12 ESR spectrometer was interfaced to
a PRIME 400 timeshared computer, and interactive
software was developed to collect, interpret, and store
individual spectra.\textsuperscript{10} From measurements of a complete
experimental line shape (enhanced by signal averaging
when needed), the derivative peak-to-peak width and
height as well as the asymmetry of the line was deter-
mined using an efficient fifth-order polynomial curve-
fitting scheme.\textsuperscript{18} The observed line shapes include
some inhomogeneous broadening due to unresolved
super-hyperfine splitting from twelve equivalent methyl
deuterons (with smaller splittings from the ring deu-
terons). Initially, simulations of the complete line
shape were performed to obtain accurate values of $a_D$
and intrinsic homogeneous width.\textsuperscript{10} Since $a_D$ was gen-
erally found to be constant for each solvent and indepen-
dent of temperature, we then used tabulations of the in-
trinsic width, the observed width, and the observed
peak-to-peak height (where the linewidths are given in
units of $a_D$) to obtain the intrinsic widths. These in-
trinsic linewidths are expressed as a quadratic in $M_0$, the $z$
component of the $^1$H nuclear spin quantum num-
er:

$$6(\bar{M}_I) = A + B\bar{M}_I + C\bar{M}_I^2.$$  \hspace{1cm} (5)

In practice, one linewidth and two relative peak
heights were used to determine $A$, $B$, and $C$, since the
experimental error in the peak heights is typically 0.1%,
while the linewidths are uncertain by about 1%. Thus
the relative values of $A$, $B$, and $C$ are determined more
accurately than their absolute values. (The other two
measured linewidths were used to check on the accuracy
of the experimental results and the analysis). Further
details are given by Zager.\textsuperscript{10}

III. RESULTS

A. Rigid limit magnetic parameters

1. PD-Tempone in di-n-butyl phthalate

The rigid limit spectrum of PD-Tempone in DNBP
at $-150^\circ$C is shown in Fig. 2. Our best computer
simulation\textsuperscript{18} is also shown, and the resulting magnetic
parameters are given in Table I. These values are com-
parable to those found for PD-Tempone in several per-
deuterated organic solvents, being especially close to
those determined in acetone-$d_6$.\textsuperscript{1} This similarity is
also seen in the angular dependent residual Lorentzian
linewidth coefficients $\alpha = 2.22$ G and $\beta = 1.5$ G.
Although unresolved intramolecular deuteron hyperfine
interactions may be important in these widths, inter-
molecular dipolar interactions with solvent protons
should also be contributing. Consistent with this, the
deuteron hyperfine splitting constant $a_D$, obtained from
line shape simulations in the motional narrowing re-
region, appears slightly larger in this protonated solvent.

2. PD-Tempone in $D_2O$: The scaling method for
magnetic tensors

Attempts at obtaining the rigid limit spectrum of
PD-Tempone in $D_2O$ were unsuccessful. Both rapid and
slow cooling to the frozen state at several low tempera-
tures gave a broad singlet ESR spectrum. This obser-
vation is consistent with nitrooxide agglomeration; with
strong spin exchange and/or dipole–dipole interactions
collapsing the spectrum to a single line. A similar ni-
troxide radical in frozen $H_2O$ has shown this effect.\textsuperscript{15} A
proper analysis of linewidth data in the motional-
ally narrowed region depends upon accurate magnetic
parameters. Lacking the unambiguous assignment pro-
vided by a rigid limit spectral simulation, we developed
an alternate method to determine the magnetic parame-
ters for PD-Tempone in $D_2O$. We were, shortly there-
after, able to check the predictions of this method
against other results.\textsuperscript{81}

Our method is based on the observed linear relation
between the isotropic hyperfine splitting constants, $a_g$
and $a_D$, for PD-Tempone and the molar transition en-
ergy $E_T$ of the solvent,\textsuperscript{8} which is a measure of the sol-
vent polarity. PD-Tempone is chemically inert in the
solvents under consideration, but solvent complex for-
formation affects the unpaired electron density at the N–O
fragment and therefore, the measured hyperfine split-
ing constants. Indeed for PD-Tempone we found that
the individual components of both the $g$ and $A$ tensors
 correlate with the molar transition energy.

In Table I we present the data that allow one to estab-
lish these correlations. The elements of the magnetic
tensors were taken from the results of rigid limit mea-
surements and simulations of PD-Tempone in polycry-
stalline matrices. Values of $a_{2g}$, $a_D$, and $a_g$ were ob-
tained in the motional narrowing region and in the iso-
tropic phase for anisotropic liquids. The $E_T$ values
were then obtained from the linear relation between $E_T$
and $a_g$ already found for solvents for which both $E_T$ and
$a_g$ were known.\textsuperscript{8} With this extensive listing of $E_T$
values, it was possible to verify linear relations be-
 tween $E_T$ and the magnetic tensor components given in
Table I. (In examining these relations it is important
to consider the estimated experimental uncertainties
in the magnetic parameters. Some parameters showed
more scatter than others, but linear equations were
found to represent their $E_T$ dependence adequately.)

We note, in passing, that the fully protonated spin
probe Tempone has been studied in a variety of isotropic
liquids, including aqueous solutions of mixtures of hy-
drophobic solutes, 12 common organic solvents, 13 and
water–phospholipid mixtures and model systems. 14
These data could be used to perform an accurate $E_T$
analysis analogous to that which we performed for PD-
Tempone, and one would expect similar results.

3. PD-Tempone in n-decane and in n-dodecane

We were unable to obtain rigid limit spectra for PD-
Tempone both in n-decane and n-dodecane. Instead,
single line ESR spectra were observed. In our line-
width analyses we simply utilized the magnetic param-
ters for PD-Tempone in toluene-$d_8$ given the closeness
of the $E_T$ values of these solvents (cf. Table I). (The
predicted parameters for PD-Tempone in n-decane and
n-dodecane are themselves virtually identical and would
differ from those given for PD-Tempone in toluene-$d_8$
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_T$ (kcal/mol)$^a$</th>
<th>$a_n$ (G)</th>
<th>$A_x$ (G)</th>
<th>$A_y$ (G)</th>
<th>$A_z$ (G)</th>
<th>$a_0$ (mG)</th>
<th>$\Delta q_i^b$</th>
<th>$\Delta q_x^b$</th>
<th>$\Delta q_y^b$</th>
<th>$\Delta q_z^b$</th>
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</thead>
<tbody>
<tr>
<td>n-dodecane</td>
<td>(30.6)</td>
<td>14.39 ± 0.02</td>
<td>14.39</td>
<td></td>
<td></td>
<td></td>
<td>28.7 ± 0.2</td>
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<tr>
<td>n-hexane$^e$</td>
<td>30.9</td>
<td>14.39</td>
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<tr>
<td>n-decane</td>
<td>(30.9)</td>
<td>14.40 ± 0.02</td>
<td>27.1 ± 0.2</td>
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<tr>
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<tr>
<td>CCl$_4$</td>
<td>32.5</td>
<td>14.48</td>
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<tr>
<td>toluene-$d_8$$^f$</td>
<td>(35.9)</td>
<td>14.572 ± 0.015</td>
<td>4.1 ± 0.5</td>
<td>6.1 ± 0.5</td>
<td>33.45 ± 0.2</td>
<td>20.5 ± 0.2</td>
<td>3.70 ± 0.05</td>
<td>7.28 ± 0.2</td>
<td>3.98 ± 0.2</td>
<td>-0.12 ± 0.1</td>
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<td>8CB$^g$</td>
<td>(36.6)</td>
<td>14.60 ± 0.02</td>
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<tr>
<td>di-$n$-butyl phthalate</td>
<td>(38.9)</td>
<td>14.67 ± 0.02</td>
<td>4.9 ± 0.5</td>
<td>5.5 ± 0.5</td>
<td>33.5 ± 0.3</td>
<td>22.9 ± 0.6</td>
<td>3.70 ± 0.2</td>
<td>-0.12 ± 0.3</td>
<td>-0.12 ± 0.3</td>
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<tr>
<td>40,$^a$</td>
<td>(39.4)</td>
<td>14.70 ± 0.02</td>
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<tr>
<td>BOCP$^h$</td>
<td>(40.0)</td>
<td>14.74</td>
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<tr>
<td>phase IV$^b$</td>
<td>(40.9)</td>
<td>14.75</td>
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<tr>
<td>phase 7-A$^d$</td>
<td>(41.2)</td>
<td>14.76</td>
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<tr>
<td>phase V$^b$</td>
<td>(41.7)</td>
<td>14.78 ± 0.02</td>
<td>5.61 ± 0.2</td>
<td>5.01 ± 0.2</td>
<td>33.7 ± 0.3</td>
<td>21.5 ± 0.5</td>
<td>3.69 ± 0.05</td>
<td>7.38 ± 0.2</td>
<td>3.88 ± 0.2</td>
<td>-0.17 ± 0.1</td>
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<tr>
<td>BEP$^i$</td>
<td>(42.0)</td>
<td>14.79</td>
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<tr>
<td>acetone-$d_6$$^f$</td>
<td>(42.2)</td>
<td>14.742 ± 0.015</td>
<td>4.8 ± 0.5</td>
<td>5.4 ± 0.5</td>
<td>34.0 ± 0.3</td>
<td>22.4 ± 0.2</td>
<td>3.66 ± 0.05</td>
<td>7.18 ± 0.3</td>
<td>3.88 ± 0.3</td>
<td>-0.12 ± 0.2</td>
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<td>oleic acid$^d$</td>
<td>(42.3)</td>
<td>14.80</td>
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<tr>
<td>decanoic acid$^d$</td>
<td>(46.3)</td>
<td>14.94</td>
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<td>DPL$^2$</td>
<td>(49.3)</td>
<td>15.04</td>
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<tr>
<td>egg lecithin$^d$</td>
<td>(49.5)</td>
<td>15.05</td>
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<tr>
<td>ethanol-$d_6$$^f$</td>
<td>(51.9)</td>
<td>15.173 ± 0.015</td>
<td>4.75 ± 0.6</td>
<td>5.65 ± 0.6</td>
<td>35.1 ± 0.4</td>
<td>20.2 ± 0.2</td>
<td>3.97 ± 0.05</td>
<td>6.88 ± 0.4</td>
<td>3.78 ± 0.4</td>
<td>-0.12 ± 0.3</td>
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<tr>
<td>methanol$^d$</td>
<td>(55.5)</td>
<td>15.26</td>
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<tr>
<td>85%-glycerol-$d_3$-D$_2$</td>
<td>(69.4)</td>
<td>15.740 ± 0.015</td>
<td>5.5 ± 0.5</td>
<td>5.7 ± 0.5</td>
<td>35.8 ± 0.3</td>
<td>16.0 ± 0.2</td>
<td>3.38 ± 0.05</td>
<td>6.08 ± 0.2</td>
<td>3.68 ± 0.2</td>
<td>-0.12 ± 0.1</td>
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<td>H$_2$O$^f$</td>
<td>(81.5)</td>
<td>16.17</td>
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<tr>
<td>D$_2$O</td>
<td>(81.9)</td>
<td>16.173 ± 0.05</td>
<td>(5.67)</td>
<td>(5.64)</td>
<td>36.6</td>
<td>3.28</td>
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<tr>
<td>20%-glycerol-$H_2$O$^f$</td>
<td>(82.0)</td>
<td>16.18</td>
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</tr>
</tbody>
</table>

$^a$From Ref. 8. Values in parentheses were calculated in this work from $a_n$.

$^b$$q_i = 1000 (g_i - 2.002) 32$.

$^c$W. J. Lin (unpublished results).

$^d$From Ref. 21.

$^e$J. S. Hwang (unpublished results).

$^f$From Ref. 1.

$^g$From Ref. 7(a).

$^h$From Ref. 7(a).

$^i$Interpolated magnetic parameters in parentheses.
TABLE II. Summary of results on rotational relaxation of PD-Tempone vs solvent properties.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_T$</th>
<th>$r_\epsilon$</th>
<th>$\epsilon$</th>
<th>$\tau_R \times 10^{12}$ s</th>
<th>$\epsilon$</th>
<th>$\epsilon'$</th>
<th>$N$</th>
<th>$V_s$ cm$^3$s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi$-dodecane</td>
<td>30.6</td>
<td>1.28 ± 0.02</td>
<td>0.400</td>
<td>7.3 ± 3.5</td>
<td>10</td>
<td>2y</td>
<td>227.4</td>
<td></td>
</tr>
<tr>
<td>$\pi$-decane</td>
<td>30.9</td>
<td>1.51 ± 0.02</td>
<td>0.472</td>
<td>1.6 ± 0.3</td>
<td>6.23</td>
<td>1.5y</td>
<td>194.9</td>
<td></td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>32.5</td>
<td>1.62</td>
<td>0.506</td>
<td>1.3</td>
<td>6</td>
<td>1</td>
<td>96.9</td>
<td></td>
</tr>
<tr>
<td>Toluene–d$_8$</td>
<td>35.8</td>
<td>2.0</td>
<td>0.625</td>
<td>-0.2 ± 0.3</td>
<td>5.4</td>
<td>(1–4)</td>
<td>106.3</td>
<td></td>
</tr>
<tr>
<td>SCBf</td>
<td>36.6</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>[–3–4]</td>
<td>1</td>
<td>293a</td>
<td></td>
</tr>
<tr>
<td>DNBPTf</td>
<td>38.5</td>
<td>1.47 ± 0.01</td>
<td>0.460</td>
<td>0.3 ± 0.3</td>
<td>4</td>
<td>12</td>
<td>2.1x</td>
<td></td>
</tr>
<tr>
<td>40, 8d</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...[–4.5–7]</td>
<td>[–1.0y–1]</td>
<td>...</td>
<td>365a</td>
<td></td>
</tr>
<tr>
<td>MBA*</td>
<td>42</td>
<td>~ 1.13</td>
<td>0.353</td>
<td>4.6</td>
<td>1</td>
<td>260a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone–d$_{4f}$</td>
<td>42.2</td>
<td>1.90</td>
<td>0.907</td>
<td>-6.2</td>
<td>2.5</td>
<td>1.7y</td>
<td>73.5</td>
<td></td>
</tr>
<tr>
<td>Ethanol–d$_{4f}$</td>
<td>51.9</td>
<td>2.30</td>
<td>0.721</td>
<td>-13</td>
<td>3.4</td>
<td>&gt; 1</td>
<td>3x</td>
<td></td>
</tr>
<tr>
<td>S$&amp;$ glyceral–D$_{4O}$</td>
<td>69.4</td>
<td>1.74</td>
<td>0.543</td>
<td>-21</td>
<td>...</td>
<td>~ 4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>D$_{4O}$</td>
<td>81.5</td>
<td>2.27 ± 0.01</td>
<td>0.709</td>
<td>(0.2 ± 2.8) x 10$^{-2}$</td>
<td>1.1</td>
<td>1.6x</td>
<td>18.1</td>
<td></td>
</tr>
</tbody>
</table>

*aThis work.
*bJ. S. Hwang (unpublished).
*cFrom Ref. 9.
*dFrom Ref. 7(c). The limits on 40, 8 are given by the pairs $\epsilon = 4.5$ and $N = 1$ or $\epsilon = 7$ and $N = 1.6y$.
*eFrom Ref. 7(a).
*fFrom Ref. 1.
*gMolar volume for protonated solvent at 20°C. Most of entries are from Handbook of Chemistry and Physics, 54th Ed. (CRC, Cleveland, 1973–1974). See h for others.

The benzylidene liquid crystals were found to have a specific volume very close to 1 cm$^3$/g at the nematic-smectic phase transition [B. Bahadur, J. Chem. Phys. 73, 255 (1970)].

by less than twice the reported experimental error.
Over the $\tau_R$ range used this would lead to an experimentally insignificant 1%–2% increase in the theoretical values of $B$ and of $C$.

B. Linewidths and relaxation times

1. Definitions and procedures

Analysis of the ESR linewidth results in the motional narrowing region proceeds in the standard manner. The experimental linewidths were reduced to the intrinsic linewidth coefficients $A$, $B$, and $C$, (cf. previous section). Second, the resulting $B$ and $C$ values were used to determine the relaxation parameters discussed below.

The mean rotational correlation time $\tau_R$, was determined as follows: First the experimental values of $C$ were plotted against those of $B$; then, using the theoretical expressions for $B$ and $C$, parameters $N$, $\epsilon$, and $\epsilon'$ were adjusted to find the combination that best described the data. These parameters can most easily be optimized one at a time over different ranges of $\tau_R$ and their temperature independence checked. Of course only if linewidth measurements are made over a sufficiently wide range of $\tau_R$ values can $N$, $\epsilon$, and $\epsilon'$ be obtained in such a manner. Here $N$ characterizes axially symmetric rotational diffusion: $N = R_6s/R_4s$, where $R_6s$ is the principal component of the rotational diffusion tensor about the symmetry axis $z'$ and $R_4s$ is the corresponding principal component about the $x'$ and $y'$ axes. Finally, we have $\tau_\epsilon = (6 R_6s)^{-1}$, so in the limit of isotropic rotation, $N = 1$ and we let $\tau_\epsilon = \tau_R$. The local symmetry of the N−O fragment in PD-Tempone implies that the molecule-fixed $x$, $y$, $z$ axis system is (nearly) equivalent to the $x'$, $y'$, $z'$ axis system to within a permutation of the axis labels. Figure 1 shows the molecule fixed coordinate system for PD-Tempone. Both $x' = x$ and $z' = y$ assignments have been found for PD-Tempone in isotropic liquids with corresponding $N$ values ranging from 1–3 (cf. Table II).

We illustrate the analysis with the motional narrowing linewidth data for PD-Tempone in DNBPT. The determination of $\tau_R$ follows from Fig. 3. The theoretical curves of $B$ vs $C$ are sensitive to $N$ over the entire experimental range, but in the region $100 < B(mG) < 600$ they are independent of the values of $\epsilon$ and $\epsilon'$ and form a family of parallel lines for different values of $N$; (we distinguish the $\epsilon$ correction to the nonscandual and the pseudosecular spectral densities by $\epsilon$ and $\epsilon'$, respectively). Thus $N$ can be assigned from this data subset; $x$-axis orientation of the rotational diffusion tensor with $N = 2.1$ accurately represents the data. The remaining parameters are readily established, since for this choice of $N$, $\epsilon$ is important for $B(mG) < 100$ while $\epsilon'$ contributes significantly for $B(mG) > 600$. We find that $\epsilon = 4$ and $\epsilon' = 12$ are required to fit the data; larger values cause too much upward curvature, and smaller ones do not cause enough.

2. Stokes–Einstein behavior

We summarize in Figs. 3–9 our results with the solvents: DNBPT, D$_{4O}$, decane, and dodecane, and the relevant parameters may be found in Table II, where they are compared with previous results with other solvents.

For DNBPT we could study the whole motional narrowing range from $\tau_R = 5$ ps (at 118.3°C) down to $\tau_R = 1$...
ns (at −19°C). For D₂O the temperature range included the supercooled region to just below boiling (from −12°C to 96°C); the normal melting and boiling points of D₂O are 3.82°C and 101.42°C. Motionally narrowed spectra were observed for PD-Tempone in the hydrocarbon solvents for temperatures ranging from well below the normal melting point to room temperature.

In general, Stokes–Einstein-type behavior [cf. Eq. (2)] is found for these solvents provided we use a modified form to allow for a nonzero intercept:

\[ \tau_R = \frac{4 \pi \eta^2}{3 k_B T} + \tau_R^0. \]

The slopes of \( \tau_R \) vs \( \eta/T \) may be found in Table II expressed as an effective rotational radius \( \tau_R \). Alternatively, one can use a dimensionless “interaction parameter” \( \kappa = \gamma / \tau_0 \), where we take \( \tau_0 = 3.2 \text{ Å} \) as the geometric effective spherical radius of PD-Tempone. In Kivelson’s notation there is also a molecular shape parameter \( \lambda \) which is unity for spheres. For asymmetric diffusion, it is related to our asymmetry parameter \( N \). The intercepts \( \tau_R^0 \) obtained from \( \tau_R \) vs \( \eta/T \) plots are found to be negligible within experimental error for several cases, (cf. Table III), e.g., DNBPT, where it accurately describes the data over more than two orders of magnitude, as well as for D₂O where \( \tau_R^0 = -0.2 \pm 2.8 \times 10^{-14} \text{ s} \) is two orders of magnitude smaller than

### Table III. Temperature dependence of \( \tau_R \) for PD-Tempone in several solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( a )</th>
<th>Coefficient</th>
<th>( c ) in K²</th>
</tr>
</thead>
<tbody>
<tr>
<td>85% glycerol-d3-D₂O</td>
<td>−10.3</td>
<td>−1.31 \times 10⁶</td>
<td>2.89 \times 10⁶</td>
</tr>
<tr>
<td>D₂O</td>
<td>−21.7</td>
<td>−4.51 \times 10⁶</td>
<td>1.04 \times 10⁶</td>
</tr>
<tr>
<td>di-( n )-butyl phthalate</td>
<td>−22.0</td>
<td>−5.19 \times 10⁶</td>
<td>1.40 \times 10⁶</td>
</tr>
<tr>
<td>toluene-d₈</td>
<td>−28.4</td>
<td>6.92 \times 10⁶</td>
<td>2.02 \times 10⁶</td>
</tr>
<tr>
<td>acetone-d₆</td>
<td>−29.5</td>
<td>8.40 \times 10⁶</td>
<td>4.95 \times 10⁶</td>
</tr>
<tr>
<td>ethanol-d₆</td>
<td>−30.1</td>
<td>1.18 \times 10⁷</td>
<td>8.13 \times 10⁶</td>
</tr>
</tbody>
</table>

\( a \)Coefficients of Eq. (7) obtained by least-squares-fit to the expression \( \ln \tau_R = a + (b/T) + (c/T^2) \). Here \( a = \ln \tau_R^0, b = \Delta H^0 / R, \quad c = \Delta H^0 / R \).

\( b \)From Ref. 1.
FIG. 6. $\tau_R$ vs $\eta/T$ for PD-Tempone in D$_2$O. The line is a least-squares fit.

FIG. 7. Comparison of experimental and calculated values of C vs B for PD-Tempone in n-decane. (Normal mp $-29.7^\circ$C.)
the shortest measured $\tau_R$. The values of $\tau_R^0$ for decane and dodecane are, however, different from zero within experimental error, while the results of HMHF for acetone, ethanol, and glycerol/D$_2$O reanalyzed according to Eq. (6) show negative intercepts. Rigorous Stokes–Einstein behavior would require $\tau_R^0 = 0$. We shall defer to II, a discussion of the implications of nonzero intercepts.

The modified Stokes–Einstein behavior with $\kappa < 1$ appears to fit most of our results rather well. The values of $\kappa$ show a correlation with molar volume of solvent, (cf. Table II) as would be expected from simple free-volume models. That is, the space available for reorientation of the probe should depend upon the size of holes in the solvent and this can be expected to be a function of $V_{\text{probe}}/V_s$. One might also expect that there is a correlation with $E_T$, if we regard $\kappa$ as a measure of the relative importance of intermolecular interactions. However, we do not observe a good correlation between $\kappa$ and $E_T$ in our results.

The dependence of $N$ on solvent appears to demonstrate more specific features of the interaction between probe and solvent. Thus, hydrogen bonding solvents tend to show more rapid rotation about the molecular $x$ axis, consistent with specific $H$ bonding to the N–O and/or C=O functional groups of PD-Tempone, while for the long hydrocarbon (or liquid crystalline) solvents there is a tendency to more rapid $y$-axis rotation. The standard geometric arguments for PD-Tempone as a prolate nearly axially symmetric ellipsoid (we have estimated $a_x \approx 4.2 \, \text{Å}$, $a_y \approx 2.7 \, \text{Å}$, and $a_z \approx 3.0 \, \text{Å}$) lead to the prediction of $R_x/R_y \approx 3/4$. (However, one should recall that the PD-Tempone spin-relaxation is most sensitive with respect to rotation about the $x$ and $y$ axes.) We do not find a correlation of $N$ with either $E_T$ or $V_s$. Some further comments on another mechanism which can have an apparent effect on $N$ are made in Sec. IV.

3. Non-Debye spectral densities

We next consider the results for $\epsilon$ (cf. Table II and Figs. 3, 5, 7, and 8). The most interesting observation is that while $\epsilon > 1$ for DNBPT and for the hydrocarbons, consistent with our previous results on other solvents, D$_2$O is the only case where we obtain an unequivocal result of $\epsilon \approx 1$. We also find a reasonable correlation between $\epsilon$ and $E_T$ (cf. Fig. 10), which is interesting. (The correlation with $V_s$ is not as good, but we suspect there is some correlation. There is a bias in the solvents we have used such that those with smaller $E_T$ tend to have a large $V_s$, while those with larger $E_T$ tend to have a small $V_s$.)

In general, a single $\epsilon$ is found to fit our data for each solvent rather well, but there are typical exceptions. Thus for DNBPT there is a tendency for the linewidth parameter $C$ to level off to a constant value in the region $\tau_R < 5 \, \text{ps}$, a feature previously seen for PD-Tempone in...
toluene for $\tau_R < 3$ ps, while $B$ does not show a significant deviation. No such anomaly is observed for D$_2$O solvent in this region. It was suggested by HMHF that this width anomaly in $C$ might be due to some intramolecular process which weakly modulates the hyperfine interaction. Our present results show this anomaly to be solvent dependent, perhaps due to a residual solvent modulation of the hyperfine interaction (either through direct interaction or else by affecting some intramolecular torsional motion). The absence of an anomaly for D$_2$O might be explained by a more rapid relaxation-time for such a process.

Another exception is observed for dodecane solvent where $C/B$ is unusually large in the $\tau_R \approx 1 - 3 \times 10^{-11}$ s region. The discrepancy begins at approximately the normal melting point. The same results were obtained whether samples were cooled from above or warmed from below this temperature range. Effects somewhat similar to this were previously reported near the freezing point (as a function of pressure$^{10}$) for PD-Tempone in the viscous nematic solvent, Phase V (occurring at $\tau_R \approx 10^{-9}$ s), and it was suggested that this might be due to a mechanism related to the phase transition (cf. the SRLS mechanism discussed in Sec. IV A). A similar explanation might be appropriate here.

4. Activation energies

In general, the $\tau_R$ do not show a simple logarithmic dependence with $1/T$. Instead we found that the empirical form$^{47}$:

$$\ln \tau_R = \ln \tau_R' + \Delta H_v / RT,$$

\(\text{(7a)}\)
These curves show $\Delta H_\varepsilon$ increasing with decreasing $\tau_R$. One set exhibits a very weak variation in $\Delta H_\varepsilon$ while the other shows a much stronger variation. In addition to their similarities in $\partial \Delta H_\varepsilon / \partial \tau_R$, the members of each set are similar in their respective magnitudes of $\Delta H_\varepsilon$. (The first set exhibits very similar values of $\ln \tau_R$, while those of the second set are considerably smaller.) In the case of decane and dodecane (not shown) $\Delta H_\varepsilon$ is constant except for the discontinuity at the normal melting points.

Of course, the good correlation between $\tau_R$ and $\eta/T$, means that $\eta/T$ for these solvents may also be represented by equations of the form of Eqs. (7) with behavior similar to that of Fig. 11. In fact, a variety of related expressions (including the Doolittle equation, see above), which are usually justified in terms of free-volume models, are frequently used to fit viscous behavior of liquids. A perhaps more significant point we note is that Eqs. (3) and (4) lead to values of $\Delta H_\varepsilon^{\eta/T}$ for $\eta/T$ such that the ratio $\Delta H_\varepsilon^{\eta/T}$ increases with decreasing $T$ both for DNBP and $D_2O$ solvent (e.g., for DNBP it is 0.91 at 120°C, 0.96 at 50°C, 1.01 at -20°C, while for $D_2O$ it is 0.81 at 65°C and 1.02 at -10°C). Such a gradual variation seems to cause little difficulty in obtaining good least-squares fits of the form of Eq. (2), but it does suggest some deviation from Stokes--Einstein behavior which are not apparent from Table II. These effects will be found to be more pronounced in the pressure-dependent study of II.

5. Spin-rotational relaxation

The experimental linewidth coefficient $A$ for PD-Tempone in $n$-butyl phthalate and in $D_2O$ are shown as a function of $\tau_R$ in Figs. 12 and 13. The calculated values $A_{44}$ based upon dipolar and $g$-tensor terms leads to the dashed curves in Figures 12(a). The difference $A - A_{44}$ is referred to as the residual linewidth $A'$, and this quantity is treated as follows.

A simplified form of the spin-rotation derivative line-

![Graph showing $\Delta H_\varepsilon$ vs $\tau_R$ for PD-Tempone in several solvents. The curves are described in Table III. Dashed segments are extrapolated results.](image-url)
width contribution for isotropic Brownian reorientation

\[ A'_{SR} = \frac{2}{3\gamma} \sum_i (g_i - g_e)^i / \tau_R , \tag{8} \]

where \( \gamma \) is the electronic magnetogyric ratio and \( g_e \) is the electron free-spin \( g \) factor. The solid curve in Fig. 12(a) is the sum \( A_{SR} + A'_{SR} \). The inclusion of the spin-rotation mechanism improves the qualitative agreement between experiment and theory, but quantitative differences are substantial, as is usually the case.\(^1\)

Figure 12(b) provides a closer look at these effects. Plotted against \( \tau_R \) the residual linewidth \( A' \) exhibits a very broad minimum. The usual analysis calls for a fit of the high temperature data to the functional form

\[ A' = A'_{SR} / \tau_R . \tag{9} \]

The short-dashed line in Fig. 12(b) is the least-squares result, \( A'_{SR} = (9.99 \pm 0.51) \times 10^{-13} \) G s for PD-Tempone in DNBPT. This is 2.05 times the corresponding coefficient calculated for spin-rotation relaxation through Eq. (8). (This value is virtually identical to that found for PD-Tempone in acetone-\( d_6 \).\(^1\))

The complete \( \tau_R \) dependence of \( A' \) can be represented by

\[ A' = \alpha / \tau_R + \beta \tau_R + \gamma , \tag{10} \]

where \( \alpha = A'_{SR} \). In view of Eq. (8), the first term in Eq. (10) should represent a spin-rotation interaction. The second term accounts for any inaccuracies in \( A_{SR} \) that result from uncertainties in the parameters \( N_i, \epsilon, \epsilon' \), and \( \tau_R \) as determined from the linewidth coefficients \( B \) and \( C \) for the rotational model used. It also includes
electron–nuclear spin dipolar interactions. The \( \tau_R \)‐
independent term should include residual inhomogeneous
broadening not accounted for by our analysis of intrinsic
widths from the observed widths (possibly from magnetic
field inhomogeneity and some residual unresolved hyper-
fine structure, see also Ref. 4). It could also include
relaxation processes that are nearly temperature inde-
dent (e.g., possible intramolecular contributions to
spin‐rotational relaxation, cf. Ref. 1 and above).

We find for DNBPT solvent: [cf. Fig. 12(b)];
\[
A' (mG) = (7.30 \pm 0.36) \times 10^{-10} / \tau_R + (1.857 \pm 0.071)
\]
\[
\times 10^{11} \tau_R + (46.9 \pm 0.33)
\]  
(11)
and for D₃O solvent (cf. Fig. 13):
\[
A' (mG) = (7.52 \pm 0.15) \times 10^{-10} / \tau_R - (1.82 \pm 0.08)
\]
\[
\times 10^{11} \tau_R + (18.2 \pm 3.0)
\]  
(12)
Thus, by means of Eq. (10) both solvents yield very
similar estimates for \( A'_R \), the effective spin‐rotation
factor of Eq. (9) and for DNBPT it is 1.5 times the pre-
diction of Eq. (8) representing an improved agreement.
The negative sign for the \( \beta \) term for D₃O solvent is sur-
prising and inconsistent with previous results; it may
simply be due to the fact that the data for PD‐Tempone
in D₂O are for \( \tau_R \approx 5.5 \times 10^{-11} \) s, so there are insufficient
results to obtain an accurate estimate of this term.
However, in our analysis, the \( \beta \)‐term, while somewhat
uncertain, is still statistically significant. It could, of
course, result from inaccuracies in \( A_W \) as noted. An-
other possibility is one that follows from previous satu-
ration measurements of the electron‐spin‐flip rate, \( W_e \)
for PD‐Tempone and PADS in other solvents. In
the high‐temperature region it was found that \( 2W_e = A' \)
consistent with a spin‐rotational mechanism, but at
lower temperatures \( A' = 2W_e \), because of the \( \beta / \tau_R \)
term. This parameter \( W_e \) did show a downsweep at
lower temperatures (in these previous studies), and if
\( A' \) for PD‐Tempone in D₂O is showing this feature, it
would be the first time that the usual positive contribu-
tions to \( \beta \) are very small.

For present purposes, the most important conclusion is
that over the motional narrowing region studied here,
the results on spin‐rotational relaxation are consistent
with the Hubbard–Einstein relation:
\[
\tau_R \tau_J = \frac{l}{6 \pi kT} = 1.45 \times 10^{-23} / T (s^2) \]  
(13)
upon which Eq. (8) is based. Then over the tempera-
ture range studied here, \( \tau_J < \tau_R \) (e.g., for D₃O the
smallest \( \tau_R = 3.5 \) ps at 96 °C, so from Eq. (13) \( \tau_J =
0.11 \) ps). Thus inertial effects are negligible over the
range of rotational correlation times we have stud-
ied, and this justifies our neglect of them in our analysis
of \( \tau_R \) in terms of modified Stokes–Law models.

6. Slow‐motional spectra
In HMFH it was shown that analysis of slow‐mo-
tional line shapes of PD‐Tempone can be used to dis-
tinguish the microscopic model for reorientation, i.e.,
whether the motion is Brownian, or jump, or an approx-
imate “free diffusion” one. Only in the case of DNBPT
did we observe in the present work slow motional line
shapes which were amenable to analysis. These were
studied in the manner of HMFH, and it was found from
simulations in the model–sensitive region (\( \tau_R \approx 10^{-8} \) s)
that while none of the models gave nearly as good agree-
ment with experiment as HMFH obtained, the best
agreement was found to be with the approximate free
diffusion or with the moderate jump [with an \( RT \sim 2 \), cf.
Ref. 2(a)], a result that is consistent with the results
of HMFH on PD‐Tempone in toluene=\( d_8 \) and glycerol-
\( d_1 = D_2 \) solvent.

IV. FURTHER DISCUSSION
A. Non‐Debye spectral densities
We wish to consider the observed correlation between
\( \epsilon \) and \( E_T \). HMFH\(^1\) presented an approximate theory for
\( \epsilon \), in which the fluctuating (or random) torques acting on the probe molecule were explicitly included in either a generalized or an augmented Fokker–Planck equation for the probe molecule. They could obtain a simplified expression for \( \epsilon \) in the limit where \( \tau_1 / \tau_R \ll 1 \) (i.e., neglect of the usual inertial terms) but where \( \tau_R \), the relaxation time of the torques is not necessarily much faster than \( \tau_R \). In particular, they obtained:

\[
\epsilon = \left( 1 + \frac{\tau_1}{\tau_R} \right)^2,
\]

with

\[
\tau_R = \tau_R \left( \frac{IV^2}{\delta k_B T} \right),
\]

and

\[
\tau_1^2 = \frac{V^2}{\tau_R},
\]

so that the Hubbard–Einstein relation Eq. (13) is obeyed. Here \((\delta k_B T) V^2\) is the mean-square value of the fluctuating torques. Hwang and Freed\(^{\text{30a}}\) presented a more detailed derivation of this result using a projection operator approach to generate the generalized rotational Fokker–Planck operator and then a functional derivative method to produce the lowest order contribution of the fluctuating torques to a Smoluchowski equation. The method of the augmented Fokker–Planck equation outlined by HMHF yielded similar results, but illustrated some significant weaknesses of these results. Recently Stillman and Freed\(^{\text{30b}}\) have considered the approach of augmented Fokker–Planck equations in detail, and have established a self-consistent method for creating and studying them. It is clear from these works that the above expressions for \( \epsilon \) are really just lowest order results (in an expansion of \( l V \tau_R \)) for a very simple model, even though they are then applied to results for which lowest order results are not really applicable. It is our belief that, while Eqs. (14)–(16) cannot be taken as quantitatively valid over the range to which we apply them, they provide a certain “qualitative insight” in examining experimental trends, and we use them in this spirit.\(^{31}\)

Polnassek and Freed\(^{1(1)}\) in studies on liquid–crystalline solvents found that they required \( \tau_1 / \tau_R > 1 \) (for \( \epsilon^1 \)) for PD-Tempone, and this appears to be unphysical. Therefore, they introduced a modified point of view that they refer to as the slowly relaxing local structure (SRLS) model. In this model, the slowly fluctuating components of the anisotropic intermolecular potential are regarded as a local structure which persists for a mean time \( \tau_R \), and with respect to which the probe rotates, since \( \tau_1 > \tau_R \). Then, on this longer time scale \( \tau_R \), the local structure relaxes. This SRLS model was found to be particularly useful in dealing with PD-Tempone in liquid crystalline solvents.\(^7\) It leads to a prediction that spectral densities become \( \epsilon^1(1,1), \epsilon^1, \epsilon^2, \epsilon^2 \) for PD-Tempone.

\[
\epsilon^1(\omega) = j_\epsilon(\omega)(1 - S_{1,\epsilon}^2) + \frac{S_{1,\epsilon}^2}{1 + \omega^2 \tau_1 / \tau_R} \tau_1 / \tau_R,
\]

where \( j_\epsilon(\omega) \) are the Debye-type spectral densities:

\[
j_\epsilon(\omega) = \frac{\tau(K)[1 + \omega^2 \tau(K)^2]}{\tau(K)}.
\]

Here \( S_{1,\epsilon} \) is the \( \epsilon \)th irreducible component of the local ordering tensor for the probe in the instantaneous potential of interaction with neighboring solvent molecules, and for our present purposes \( K = 0 \) or \( \pm 2 \) corresponding to a unique principal axis system for the molecular properties of PD-Tempone (cf. Fig. 1) for this fluctuating order parameter.\(^{32}\) Also \( \tau(K)^2 = 6\tau_{0}, \tau(K) = \tau_{0} \). Under conditions we can most simply write as \( \tau_1 / \tau_R < 1 \), we have \( \epsilon^1(1) \) for each \( K \)

\[
j_\epsilon(\omega) = j_\epsilon(0)/[1 + \epsilon_k \omega^2 \tau(K)]^2,
\]

[with \( j_\epsilon(\omega = 0) = \tau(K) \)]

\[
\epsilon_k = \frac{1}{1 + \tau_k/\tau(K)} \left[ \frac{1 + \omega^2 \tau_k/\tau(K)}{1 + \omega^2 \tau_k/\tau(K)} \right]^2 \left[ 1 + \left( \frac{\tau_k}{\tau(K)} \right) S_{1,\epsilon}^2 \right]^{-2}
\]

\[
\omega^2 \tau_k^2 \ll 1 \left[ 1 + \tau_k/\tau(K) \right]^{-1} \left[ 1 + \tau_k/\tau(K) \right]^{-1}
\]

[with \( \tau_k = \tau_0 \) for PD-Tempone (cf. Fig. 1)].

We do wish to point out that spectral densities of the form of Eq. (17) with Eq. (18) may be written down quite generally for any relaxation process whose correlation function is expressed as the sum of two exponential decays (with e.g., decay constants \( \tau(K) \) and \( \tau_1 \)). The SRLS model is one such model but one that we emphasize because we believe it to be physically relevant.\(^{1,30,32}\)

We now inquire whether we can distinguish an \( \epsilon \) from the form of Eqs. (14)–(16) (e.g., fluctuating torque model) from an \( \epsilon \) from the form of Eqs. (19) (e.g., SRLS) on the basis of our experimental results. Equations (14)–(16) for the fluctuating torque model will lead to a nearly constant value of \( \epsilon \) over the whole temperature range provided \( kT/IV^2 \) is only weakly temperature dependent compared to \( \tau_0 \) or \( \tau(0) \) and \( \tau(2) \). Equations (17)–(19) for the SRLS model will lead to different results for \( \epsilon \) in the two limits of extreme narrowing:

\[
\tau_1 \ll \tau_R \ll \omega, \quad \text{and of slower tumbling (but still motional narrowing)} \quad \tau_1 \gg \tau_R \gg \omega^2,
\]

with a more complex behavior between these two limits. It was suggested by Polnassek and Freed\(^{1(1)}\) that both \( \tau_R \) and \( \tau_1 \) are coupled to the same viscous modes represented by the shear viscosity \( \eta_s \), so that \( \tau_0 / \tau_R \) should only be weakly temperature dependent, and the same might be expected for \( S_{1,\epsilon}^2 \) (based on mean ordering of nematics and their temperature dependence).

We thus see that while both models lead to values of \( \epsilon > 1 \) required by our observations on \( \epsilon \) in this work (and that of HMHF), there is a constancy in \( \epsilon \) over the full range of \( \Omega \tau_R \) observed in most solvents that is best fit with Eq. (14). (More precisely, when \( \omega^2 \tau(K)^2 \gg 1 \), the SRLS model predicts \( \epsilon < 1 \), but \( \epsilon > 1 \) for faster motions.)

In the case of dodecane, an \( \epsilon \approx 10 \) would yield from Eq. (14) a \( \tau_R > \tau_R \), which does not seem satisfactory. However, \( \epsilon \) for a SRLS model should be decreasing with decreasing \( \tau_R \) except perhaps for an anomalous increase in \( \tau_0 / \tau_R \) with decreasing temperature (cf. Eq. (19b)). Also, it is likely that the SRLS mechanism affects \( j_\epsilon(0) \) and \( j_\epsilon(0) \) differently (that is, in general \( S_{1,\epsilon}^2 \neq S_{1,\epsilon} \), and in particular for axial local ordering of the probe one has \( S_{1,\epsilon} = 0 \)). This can lead to large apparent anisotropy.
points. Nevertheless there are clear indications of a phase transition in the observed \( \tau_N \) as shown in Fig. 9. Thus for PD-Tempone in \( n \)-decane there is a discontinuity in \( \tau_N \) at about the melting point (-29.7 °C), but \( \Delta H_p \) is constant and equal to 3.00 ± 0.16 kcal/mol above and 5.1 ± 0.4 kcal/mol below the melting point. For PD-Tempone in \( n \)-dodecane there is only a discontinuous change in slope of \( \tau_N \) vs 1/T at the melting point (-9.6 °C) with constant values of \( \Delta H_p \) of 3.01 ± 0.14 and 5.36 ± 0.09 kcal/mol above and below the melting point, respectively. From this we can conclude that the local environment sampled by the PD-Tempone molecule is very much the same in the two solvents in the same phase. The increase in activation energy upon freezing can be understood in terms of a change in the solvent cavity within which the spin probe rotates. Since the density of the solid hydrocarbon is greater than that of the liquid, simple compression of the solvent cavity should restrict rotational motion and increase its activation energy.

This behavior is reminiscent of observations made for PD-Tempone in several liquid crystalline solvents,\(^{165}\) and we can take the point of view offered there to discuss the present results. The nematic-smectic A phase transition in the liquid crystals (40,6) and (40,8) was found to lead to a discontinuity in \( \tau_N \) in the manner of \( n \)-decane in Fig. 9, while \( \tau_N \) for PD-Tempone in the liquid crystal 8 CB showed a kink at this transition much like that seen for \( n \)-dodecane at its melting point. Arguing by analogy to the mechanism of expulsion of the spin probe observed in the \( N \rightarrow S_A \) transition, frozen \( n \)-decane and \( n \)-dodecane must involve different molecular packing efficiencies at the phase transition. The more dramatic effect at the phase transition is shown by the smaller solvent \( n \)-decane which is more likely to freeze into a regular crystalline form that differs greatly from the liquid. The larger \( n \)-dodecane molecule probably freezes more amorphonously with a reduced packing effect on the PD-Tempone. These results are of some interest in comparing with results on liquid crystals [cf. Ref. 7(c)].

V. CONCLUSIONS

(1) Our temperature-dependent results on rotational correlation time, \( \tau_N \) for PD-Tempone in a variety of solvents appear to be consistent with a simple Stokes-Einstein type of \( \eta/T \) dependence but with nonzero intercept for some solvents, and it can be either positive or negative. Also inertial effects should be negligible over the range of \( \tau_N \) studied.

(2) The parameter \( \epsilon \) introduced by Freed and co-workers to correct the Debye-type nonsecular spectral densities is generally found to represent the results very well for \( \tau_N \geq 5 \) ps, i.e., a single \( \epsilon \) is required for each solvent. A reasonable correlation between \( \epsilon \) and the solvent molar transition energy \( E_T \) (which is a good measure of specific solvent polarity) was found. That is, as solute-solvent interactions become weaker, \( \epsilon \) increases from its Debye limit of unity. Only in the case of D2O solvent has this limit been observed so far.
for PD-Tempone. These results appear consistent with the fluctuating-torque model previously used by Freed and co-workers, although the model must be regarded as a very approximate one.

(3) A useful method of interpolation to obtain the solvent dependence of the PD-Tempone magnetic tensors is described. It is based on the good correlation of these tensor components with the molar transition energy $E_T$. This method should be useful for other spin probes (e.g., nitroxides, vanadyl complexes, etc.), and it reduces the need for extensive rigid limit simulations.

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8. C. Reichardt, Angew. Chem. Internat. Edit. 4, 29 (1965). The $E_T$ scale is based upon the use of pyridinium $N$-phenol-betaine, which exhibits a very large displacement of its solvatochromic band in different solvents. Thus $E_T$ (real/mol) $= 2.86 \times 10^4 \Delta \varepsilon$, where $\Delta \varepsilon$ is the absorption maximum in cm$^{-1}$.
24. In special cases where this analysis fails then $\tau_a$ is simply given as the value calculated from the $B$ linewidth coefficient, since it is found to be less sensitive to the details of the model used (Refs. 1, 2, and 7); (b) CRC Handbook of Chemistry and Physics, edited by R. C. Weast (CRC, Cleveland, 1973).
25. X-ray studies summarized by J. Lajzerowicz-Bonneau in Spin Labeling Theory and Applications, edited by L. J. Berliner (Academic, New York, 1976), Chap. 5, shows that Tempone is planar in the solid state. (More precisely, the N-O and C=O fragments lie in the mean plane, i.e., the N-O bond makes $\tau$ angle with the CNC plane, although the six-member ring is in a twisted boat conformation). Bullock and Howard [J. Chem. Soc. Faraday Trans 1, 76, 1296 (1980)] have concluded from an analysis of $\rho_2/d\tau$ that Tempone (and other nitroxides) which are planar in the solid state seem also to be planar in solution, although they cannot rule out a pyramidal distortion with a very low barrier to inversion from studying $\rho_2/d\tau$ alone.
26. Observation that might contradict the $\epsilon$ analysis was a linewidth study for $^{13}$C labeled PDS (peroxyazide disulfonate) anion in H$_2$O (Ref. 2b). In that work the analysis of O$^{13}$ linewidths suggested that $\epsilon \approx 1$ while that for the N$^{14}$ hfs linewidths suggested that $\epsilon \approx 4$. However, the $\epsilon$ hfs tensor is large enough that one must use higher-order perturbation corrections in the manner of Wilson and Kivelson [Ref. 3a], but this was not done in the previous study. We have reanalyzed the $B_2$ and $C_4$ terms using such higher-order corrections, and we find that they yield $4.5 \times 10^{-6} < 8 < 4.6 \times 10^{-6}$ which is in reasonably good agreement with the N$^{14}$ values of $N = 4$, $\ell = 1, \epsilon = 4$. We also believe that the $A_1$ linewidth parameter was not obtained very accurately by Goldman et al. [Ref. 2b] because of extra spin-exchange broadening of the rather concentrated O$^{13}$ labeled sample versus the more dilute unlabeled sample. The details of this reanalysis may be found in Ref. 10.
29. We wish to thank Mr. Yishay Manssen for his extensive help with these simulations.
33. In our earlier work (Refs. 7 and 32) we have usually assumed cylindrically-symmetric local ordering of the probe, so $S_{a,a}$ $= S_{b,b}$. However, Lin and Freed [cf. Ref. 7c, Appendix (B)] have generalized this result. Equations (21) and (22) are actually for $S_{a,a} \leq 1$ (Ref. 32) and we have neglected cross terms of type: $S_{a,a}S_{b,b}$ for $k \neq k''$ (Ref. 7c).
37. Actually these forms for $\tau_a$ and $\epsilon$ are based upon having $\tau_2$ $\approx \epsilon$, so inertial effects are negligible in the rotational reorientation. We have already shown this to be true for the experiments reported here. More precisely the approximation used is that the frequency-dependent rotational diffusion
The coefficient

\[ D_R(\omega) = \frac{kT}{\beta(\omega)} [\beta(\omega) - i\omega]^{-1} \]

\[ = \frac{kT}{i\beta(\omega)} \sum_{n=0}^{\infty} \left( \frac{i\omega}{\beta(\omega)} \right)^n, \quad \text{for} \ |\omega| \ll \beta(\omega), \]

\[ \approx \frac{kT}{i\beta(\omega)}, \quad \text{for} \ |\omega| \ll \beta(\omega), \]

[where \( \beta(\omega) \) is the frequency-dependent friction coefficient and \( \beta(0) = \tau_0 \). This is the approximation made by HMHF and by Hwang and Freed (Ref. 29).]