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Determination of Very Rapid Molecular Rotation by Using the Central EPR Line

Mark R. Kurban*

Department of Physics and Astronomy and The Center for Supramolecular Studies, California State University at Northridge, Northridge, CA 91330

Abstract

Picosecond rotational correlation times of perdeuterated tempone (PDT) are found in alkane and aromatic liquids by directly using the spectral width of the central electron paramagnetic resonance line. This is done by mathematically eliminating the non-secular spectral density from the spectral parameter equations, thereby removing the need to assume a particular form for it. This is preferable to fitting a constant correction factor to the spectral density, because such a factor does not fit well in the low picosecond range. The electron-nuclear spin dipolar interaction between the probe and solvent is shown to be negligible for the very rapid rotation of PDT in these liquids at the temperatures of the study. The rotational correlation times obtained with the proposed method generally agree to within experimental uncertainty with those determined by using the traditional parameters. Using the middle line width offers greater precision and smoother trends. Previous work with the central line width is discussed, and past discrepancies are explained as possibly resulting from residual inhomogeneous broadening. The rotational correlation time almost forms a common curve across all of the solvents when plotted with respect to isothermal compressibility, which shows the high dependence of rotation on liquid free volume.

Keywords

rotation; isothermal compressibility; EPR; spin-rotation

Introduction

Methods for determining molecular rotational correlation times from electron paramagnetic resonance (EPR) spectra have been known for several decades. X-band EPR studies have successfully obtained these times in ranges in which the non-secular spectral density^{1–5} has a negligible role and in some ranges in which its role is significant. However, it remains challenging to determine spin-probe rotational correlation times on the order of only a few picoseconds in X-band spectroscopy. When the atom bearing the unpaired electron on a spin probe has a spin-1 nucleus, the fast-motion Lorentzian width of an EPR line is known¹ to fit the relation

$$\Delta H(M) = A + BM + CM^2, \quad (1)$$

*mkurban@alumni.usc.edu.

Present address: Edanz Group, 2-12-13 Minato, Chuo-ku, Fukuoka, 810-0075, Japan. Phone: +81-92-715-7208. Fax: +81-92-715-7204.

Supporting Information Available: Values of *A* and *B* are provided for PDT in all eight solvents at the temperatures studied. This information is available free of charge via the Internet at <http://pubs.acs.org>.

where M is the z component of the spin of the unpaired electron's nucleus. Rotational correlation times have most commonly been found by using the equations⁵ for B and C . However, for rotation on the order of picoseconds, the correlation time obtained from C greatly diverges from linear behavior with respect to η/T and starts to level off,⁶ with η being the liquid shear viscosity and T the temperature. Furthermore, C is known⁶ to have higher uncertainties than B in this range. Therefore, C is not a reliable source for very rapid rotational times in X-band EPR.

Another difficulty is that no satisfactory form for the non-secular spectral density has been found for this region. Many studies^{6–13} have used a constant correction term, ε , for the non-secular density over a wide range of rotational times. The spectral density then assumes the non-Debye form

$$j_{L,m}(\omega_0) = \frac{\tau_{L,m}}{1 + \varepsilon \omega_0^2 \tau_{L,m}^2}, \quad (2)$$

where ω_0 is the spectrometer angular frequency, the characteristic time $\tau_{L,m}$ is associated with an element of the orientation-dependent part of the spin Hamiltonian,^{4,14} and ε is unique to each solvent. The rotational correlation time, τ_R , has sometimes been obtained by making plots of C versus B and fitting both ε and N , the ratio of rotation rate parallel to the symmetry axis to the rate transverse to it, as constant parameters.^{6–11} However, a constant ε sometimes does not fit comfortably when rotational correlation times are ~ 4 ps, such as in alkanes¹⁰ and in toluene.^{6,11}

Researchers have usually avoided determining rotation rates directly from the central line width, A , because it is difficult to isolate the broadening component arising from the dipolar interaction^{6,8,10,15} between the unpaired electron on the spin probe and the hydrogen nuclei on the solvent molecules. Although a method now exists for isolating the spectral contribution of the probe-probe electron-electron dipolar interaction in non-dilute systems,¹⁶ there is no known procedure to isolate probe-solvent electron-nuclear dipolar interaction in spectra for dilute systems.

The spin dipolar interaction between a probe and its medium can give rise to a significant line-width contribution in high-viscosity systems, but there is experimental evidence that this interaction is negligible in certain low-viscosity liquids in which molecules move more rapidly. Wilson and Kivelson found that the probe-solvent dipolar contribution to the line width was negligible for vanadyl acetylacetonate^{17,18} and copper acetylacetonate¹⁹ dissolved in toluene. This raises the possibility of using A to obtain reliable rotational correlation times in a simple hydrocarbon solvent. If τ_R could be extracted with A without significant dipolar effects, it would be valuable because A is generally much larger than C and would, in principle, yield more precise results with smoother trends for reorientation times below 4 ps in X-band EPR.

Because the unpaired electron on a spin probe is not at the center of the probe, slow rotation would produce anisotropic effects on the spin interaction between the electron and solvent protons. The question then is how strong these anisotropic effects are if the probe rotates very rapidly. Studies^{20,21} on spin-exchange collisions have shown that the anisotropy averages out when the rotational correlation time is shorter than the collision duration. This is because the probe rotates significantly before translating, yielding an orientationally averaged spin-exchange interaction.²⁰ Therefore, one can safely assume that the unpaired electron is uniformly distributed over the probe molecule when rotation is very fast.

As mentioned earlier, we do not know any form for the non-secular spectral density that can apply well to systems with reorientation times within 4 ps. It is, therefore, necessary to determine very fast rotational rates without requiring any particular mathematical form for $j_{L,m}$. This can be simply achieved for isotropic rotation by algebraically eliminating $j_{L,m}$ from any two of the spectral parameters. This, then, raises the question of whether the mathematical assumption of isotropy is justified. It is known⁵ that A tends to be numerically insensitive to N , which means A would yield the same *average* rotational correlation time regardless of whether the molecule were rotating at different rates about different axes. Therefore, assuming isotropy is not likely to affect the accuracy of rotational rates determined with A . Another study,²² which determined the rotation of perdeuterated tempone (PDT) in ethanol by using B , found that varying N from 1/3 to 6 made *at most* a 3.7% difference in τ_R . In the temperature range of that study, PDT had rotational correlation times between 3 and 8 ps. Therefore, with picosecond correlation times one can assume isotropic rotation when using B without significantly affecting accuracy even if the molecule does not rotate isotropically (PDT in ethanol has been found⁶ to rotate with $N = 3$).

Given the evidence so far, this study will use the spectral parameters A and B to determine picosecond rotational correlation times of PDT in several alkane and aromatic solvents, assuming isotropy of both rotation and spin distribution. This removes the need to assume any form for the non-secular spectral densities as well as the need to include the effects of rotation on the dipolar interaction. The results will be checked by also finding the correlation times using B and C under the same assumption of isotropy. The purpose of this study, therefore, is to find out the systems for which A can yield accurate rotation times and those for which it cannot.

Theory

The determining factor in whether the spin of the unpaired electron on a spin probe can be treated as being averaged out over the molecule is whether the average duration of each spin-exchange collision is longer than the probe's rotational correlation time.^{20,21} In the contact-exchange model, the collision duration, τ_{col} , is given by²¹

$$\tau_{\text{col}} = \frac{b^2}{6D}, \quad (3)$$

where b is the distance between two probes at which spin exchange occurs, and D is the self-diffusion coefficient of each probe. The contact-exchange model is suitable for strong exchange, which is always found for uncharged nitroxides.²³ After their collision, the probes will sometimes backscatter off the surrounding solvent molecules and then re-collide with each other. The average time that elapses between their two collisions, τ_{RE} , is²⁴

$$\tau_{\text{RE}} = \frac{b^2}{2D}. \quad (4)$$

Together with Eq. (3), this implies that the average collision duration is one third of the average recollision time:

$$\tau_{\text{col}} = \frac{1}{3} \tau_{\text{RE}}. \quad (5)$$

Therefore, the collision duration can be determined by measuring the recollision time. Studies have measured τ_{RE} for PDT diffusing in alkane^{25,26} and aromatic²⁶ liquids. At all the temperatures of these experiments, τ_{RE} has ranged from about 3×10^{-11} to 5×10^{-10} s, which means that τ_{col} is one to two orders of magnitude higher than the picosecond range. This means that, for picosecond rotation, the unpaired electron spin can be treated as being averaged out over its molecule when interacting with spins on other molecules.^{20,21} If the order of the size of the solvent molecule does not exceed that of the probe, then the rotation time of the solvent will not exceed the order of the probe's rotation time, and the nuclear spins on the solvent will similarly be orientationally averaged. Therefore, the dipolar interaction can be treated from a purely translational viewpoint without significant loss of accuracy. Accordingly, here is the outline of the method used to extract rotational correlation times from the EPR spectra:

1. Rotation is extracted first with parameters A and B and then with B and C .
2. Rotation is mathematically assumed to be isotropic, which is justified by findings^{5,22} that wide variation of N makes a negligible difference in average rotational correlation time on the picosecond scale.
3. The probe-solvent electron-proton dipolar interaction is treated from a purely translational viewpoint, which is allowed because the collision times are much longer than the picosecond order.^{20,21}
4. The non-secular spectral density is eliminated by combining the equations for A and B and by combining those for B and C .

The central EPR line width A can be expressed as the sum of a component A_{mag} due to hyperfine and g tensor anisotropies and another component A' :

$$A = A_{mag} + A' \quad (6)$$

For dilute probe concentrations, one can take A' as consisting of the spin-rotational^{5,6,10,27-29} interaction, A_{SR} , and the dipolar^{6,8,10,15} interaction between the probe's unpaired electron and hydrogen nuclei on the solvent molecules, A_{dip} :

$$A' = A_{SR} + A_{dip} \quad (7)$$

The isotropic spin-rotational width is related to τ_R via^{5,6,10,27-29}

$$A_{SR} = \frac{2}{\sqrt{3}} \gamma_e \sum_i \frac{(g_{ii} - g_e)^2}{9 \tau_R}, \quad (8)$$

where the g_{ii} are the principal elements of the probe's g tensor, g_e is the free-electron g factor, and γ_e is the gyromagnetic ratio of the electron.

When the free electron on the probe interacts with a nucleus of quantum spin number I , the dipolar broadening has the form^{6,8,15}

$$A_{dip} = \frac{16\pi}{45\sqrt{3}} \gamma_I^2 \gamma_e \hbar^2 I(I+1) \frac{N}{dD} \quad (9)$$

The quantity N is the number density of spins (the number of hydrogen nuclei in one cm^3 of solvent), γ_I is the gyromagnetic ratio of the hydrogen nucleus, d is the distance of closest interaction between the free electron on the probe and the hydrogen nuclei of the solvent, and D is the average of the translational self-diffusion coefficients of the probe, D , and

solvent, D_s , i.e. $\tilde{D} = \frac{1}{2}(D + D_s)$. For simplicity, one can take d to be the Stokes radius and set $D = D_s$.⁶ In hydrodynamic theory, D for a sphere is given by

$$D = \frac{kT}{6\pi a_s \eta} \quad (10)$$

under stick boundary conditions, where a_s is the Stokes radius, and k is Boltzmann's constant. A previous paper²² showed that D could be obtained with

$$D = \left(\frac{K_e}{4000\pi N_A \sqrt{2\tau_{RE}}} \right)^{\frac{2}{3}}, \quad (11)$$

where K_e is the Heisenberg spin-exchange rate constant, and N_A is Avogadro's number. Equation (11) gives D in SI units when K_e is input with units of $\text{s}^{-1}\text{mol}^{-1}\text{L}$. Equations (9)–(11) will later be used for a first approximation of the dipolar interaction to show that it is negligibly small in the systems of this study. Because the rotation is rapid enough for spins to be averaged out over their molecules, there is no need to include a rotational term in A_{dip} here.

If A' can be well accounted for, then A becomes useful for extracting rotational correlation times with low uncertainty because it is much larger than B or C for PDT in hydrocarbon solvents at high temperatures. Although B is on the same order as C , it is often close to a factor of two higher under the conditions of this study, and is known⁶ to have lower uncertainty than C . For a radical atom with a spin-1 nucleus, taking τ_R to be isotropic and combining the standard equations^{5,30} for A and B to eliminate $j_{L,m}$ gives

$$\begin{aligned} & a_1 a_2 \left[19(\Delta a)^3 \Delta g + 57(\Delta a)^2 \delta a \delta g + 57\Delta a \Delta g (\delta a)^2 + 171(\delta a)^3 \delta g \right] \tau_R^2 \\ & + \left\{ 3a_2 (\Delta a \Delta g + 3\delta a \delta g)(A - A_{\text{dip}}) - \left[21a_1 (\Delta a)^2 + 63a_1 (\delta a)^2 + 9a_3 (\Delta g)^2 + 27a_3 (\delta g)^2 \right] B \right\} \tau_R \\ & - 3a_2 (\Delta a \Delta g + 3\delta a \delta g) \frac{2}{\sqrt{3}\gamma_e} \sum_i \frac{(g_{ii} - g_e)^2}{9} = 0 \end{aligned} \quad (12a)$$

where

$$a_1 = \frac{2\gamma_e}{45\sqrt{3}}, \quad a_2 = \frac{2\omega_0}{15\sqrt{3}}, \quad \text{and} \quad a_3 = \frac{\omega_0^2}{90\sqrt{3}\gamma_e}. \quad (12b)$$

The quantities Δa and δa represent the hyperfine tensor anisotropies given by

$$\Delta a = a_{z'z'} - \frac{1}{2}(a_{x'x'} + a_{y'y'}) \quad (12c)$$

and

$$\delta a = a_{x'x'} - a_{y'y'} \quad (12d)$$

when rotation is assumed to be axially symmetric. The g tensor anisotropies, Δg and δg , are defined in parallel manner.

Combining the equations⁵ for B and C , assuming rotational isotropy, and eliminating $J_{L,m}$ yields

$$\tau_R = \frac{4\Omega B + 24\Gamma C}{19\Gamma\Omega} \quad (13a)$$

with

$$\Gamma = \frac{8\omega_0}{45\sqrt{3}}(\Delta a \Delta g + 3\delta a \delta g) \quad (13b)$$

and

$$\Omega = \frac{8\gamma_e}{45\sqrt{3}}[(\Delta a)^2 + 3(\delta a)^2]. \quad (13c)$$

Equation (13) can be used to check the rotation rate found with Eq. (12).

Experimental Method

The 9.5-GHz EPR spectra used to extract rotational correlation times in this paper were obtained in the experiments of Refs. 25 and 26 on PDT in several organic solvents (see those references for full experimental details). Those two studies only determined translational diffusion from the experiments and did not deal with rotation. The present study takes the spectra of dilute concentrations from those experiments to determine the rotational diffusion rates. These PDT concentrations were 0.08 mM for decane, 0.05 mM for hexadecane, and 0.1 mM for hexane, tridecane, cyclohexane, benzene, toluene, and *p*-xylene. The static magnetic field and microwave radiation were stable to within 0.02 G and 1 MHz, respectively. It is known that unresolved hyperfine interactions and other causes give rise to inhomogeneous broadening that produces a Gaussian component to the line shape, so the spectra were fitted with a Lorentzian-Gaussian sum function by using a non-linear least-squares routine.³¹ The method described in Ref. 31 has also been used to fit EPR spectra very well in many other studies.^{16,22,25,26,32–37} After the Lorentzian and Gaussian components were extracted, the Lorentzian width of the middle line was taken to be A , while B and C were found in the standard way with the line-height ratios.

Results

Figure 1 shows the fitted EPR spectrum for the PDT concentration of 0.08 mM in decane at 283 K, and focuses on the middle line, which yields A . Because of the fit's high quality, it is virtually indistinguishable from the experimental spectrum. All spectra were found to be virtually completely described by Lorentzian and Gaussian components for these liquids at the temperatures of this study, so any effects that cannot be modeled by either component are negligible in these particular systems. The fitting will be further discussed later.

To get an idea of the magnitude of A_{dip} , we substitute the experimental spin-exchange and recollision rates from Refs. 25 and 26 into Eq. (11) to find D , and then use Eqs. (9) and (10) by setting $D_s = D$ and $d = a_s$ as first approximations⁶. This yields an estimate of A_{dip} that is below 1% of A for the majority of spectra and reaches a maximum of 3% of A . Hence, A_{dip} appears to be generally within experimental uncertainty. Although D_s and d here are first approximations, there is no reason to believe that their exact magnitudes differ so much from these estimates as to make A_{dip} alter the results significantly. We can be reasonably confident, therefore, in these low estimates of A_{dip} , and they have been used in Eq. (12) when calculating τ_R .

The rotational correlation times were calculated both with Eq. (12) and Eq. (13). The precise published³⁸ values of the a and g tensor components for PDT in toluene are $a_{xx} = 4.1$ G, $a_{yy} = 5.1$ G, $a_{zz} = 33.6$ G, $g_{xx} = 2.00936$, $g_{yy} = 2.00633$, and $g_{zz} = 2.00233$. It is reasonable to use the same values for the related solvents benzene and *p*-xylene. Zager and Freed¹⁰ found that the values for PDT in toluene were also appropriate for PDT in decane and dodecane, showing their applicability to simple alkanes. Since the magnetic tensor components for PDT in toluene are not expected to be significantly different from those in other simple hydrocarbon solvents, these values have been used for all of the alkane and aromatic liquids in this study. The permutation $z' \rightarrow y$ from the diffusion tensor axes to the molecular frame is done for all of these solvents because it has been found appropriate for PDT in toluene^{6,11} and in decane and dodecane.¹⁰ The range of τ_R is found to be entirely below 4 ps in all of these solvents at these temperatures.

The τ_R values from B and C tend to confirm those from A and B to within experimental error. As examples, Figure 2 shows comparisons between τ_R from A and B and from B and C for toluene, decane, and hexadecane, and shows the standard deviations. For toluene (Figure 2a), τ_R from B and C levels off at high temperature. This is because of C 's known tendency to level off at high temperature,^{6,11} perhaps due to an unknown relaxation. Away from the high-temperature end, the τ_R values from both methods agree very well in toluene and are virtually identical. Decane (Figure 2b) may also be showing a leveling off at high temperature for τ_R from B and C , though overall there is no clear difference between the two τ_R sets. In hexadecane (Figure 2c), τ_R values from both methods are in general agreement.

In all solvents, the resultant τ_R values from B and C have larger uncertainties and less smooth trends with temperature. Overall, B had more stable trends than C and lower uncertainties, which is consistent with previous findings.⁶ Using A with B yields smooth τ_R trends for all solvents, as well as lower uncertainties. The overall agreement between the τ_R values from both methods is further evidence that the dipolar interaction is negligible in these systems at these temperatures.

A notable feature of the correlation time is that it is more linear with respect to $1/T$ than to η/T in all the solvents at the temperatures studied here, as shown in Figure 3. The coefficients of correlation are better than 0.999 for the lines of almost all of the solvents. The aromatics, in particular, form a strong common line, which is shown in the inset of Figure 3 for clarity. It should be noted, however, that these are mainly high-temperature ranges, and this linear behavior likely does not extend far below them. A plot of τ_R vs. η/T (not shown) still forms a strong common aromatic curve but is less linear. The trend for τ_R vs. η/T in the alkanes (not shown) is significantly less linear than for τ_R vs. $1/T$.

Studies have suggested that free volume within a liquid, which can also be represented by compressibility, strongly influences molecular rotation.^{11,39,40} This is because the available space around a molecule affects the ease with which it can rotate. The isothermal compressibility, κ_T , is given by

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \quad (14)$$

where V is the liquid volume and P the pressure. Previous studies^{25,26} have already shown that PDT recollision forms common alkane and aromatic curves as a function of isothermal compressibility, with ethanol joining the alkanes at high temperature.²² Figure 4 shows τ_R as a function of κ_T in all solvents (see Refs. 25 and 26 and references therein for details on how compressibilities were obtained). All of the aromatics and alkanes are very near to each other and almost form a common curve. It is remarkable that the aromatics are clustered together with the n -alkanes and cyclohexane. The previous study in this series determined τ_R for PDT in ethanol.²² The τ_R - κ_T curve for ethanol generated from the data of that study lies significantly far from the alkane and aromatic curves of Figure 4, and is not shown here. It seems that the known tendency of PDT to form hydrogen bonds with ethanol⁶ greatly affects the relationship between rotation and compressibility. Nevertheless, it is experimentally clear from Figure 4 that liquid compressibility is a major determinant of molecular rotation.

Discussion

Hwang *et al.*⁶ studied PDT rotation in several solvents, including toluene and toluene- d_8 . They determined τ_R from B and C by assuming a constant ε even in the lower half of the picosecond range. They then used these τ_R values to calculate A_{mag} , subtracted A_{mag} from the experimental A to find A' , then fitted A' to Eq. (8). They found while that the spin-rotational contribution calculated from Eq. (8) accounted for most of A' , there was still an excess broadening, with A' being 32% more than A_{SR} for toluene and 23% more than A_{SR} for toluene- d_8 . The question to ask is how this bears upon the results of this study. The first remark to be made is that their fit to Eq. (8) is an average that encompasses their full range of temperatures from low to high. It is not clear from that paper how much of the excess A' was found specifically at the high temperatures. However, setting this point aside, the excess A' may be due to the type of line-width analysis used, as will now be discussed.

A possible cause of the excess broadening in Ref. 6 is found in the study by Zager and Freed¹⁰ on PDT rotation in solvents such as decane and di- n -butyl phthalate (DNBPT). They modeled A' according to

$$A' = \frac{\alpha}{\tau_R} + \beta \tau_R + \gamma, \quad (15)$$

where the first term on the right side is essentially the spin-rotational contribution of Eq. (8), the second term ($\beta \tau_R$) includes A_{dip} , and γ includes residual inhomogeneous broadening. While that paper does not give the coefficients α , β , and γ for decane, it does give them for DNBPT. If one substitutes $\tau_R = 4 \times 10^{-12}$ s for PDT in DNBPT, the result is a negligible $\beta \tau_R$ (0.4 % as large as A_{SR}) with γ being 26% as large as the spin-rotational width. The latter is comparable to the 32% and 23% excess in A' over A_{SR} found for PDT in toluene and toluene- d_8 in Ref. 6. Both of those studies used essentially the same method of extracting intrinsic line widths by simulating the ^{14}N lines arising from the radical's interaction with PDT's 12 methyl deuterons while neglecting its ring deuterons. It seems likely that if the excess in A' over A_{SR} in Ref. 6 existed also at high temperatures, it too was due largely to residual inhomogeneous broadening left over from the line-width analysis. It may be that the analyses of Refs. 6 and 10 did not account for the full methyl contributions, or that the ring deuterons contributed non-negligibly to the line broadening. This shows the importance and

usefulness of instead fitting the spectra with a Lorentzian-Gaussian sum function and fully extracting inhomogeneous broadening with the Gaussian component. The success of the fit in Figure 1 shows that this broadening is now very well accounted for, yielding an accurate Lorentzian width to use in calculating the spectral parameters of Eq. (1). Also, the negligible $\beta\tau_R$ for very fast PDT rotation in DNBPT is further evidence that the probe-solvent electron-nuclear dipolar interaction is negligible when τ_R is in the low picosecond range.

It is interesting to compare A for PDT in toluene- d_8 obtained in the variable-pressure study of Ref. 11 with A found in the present study for non-deuterated toluene. The temperature of Ref. 11 that comes nearest to a temperature for toluene in this study is 51.6 °C, at which their value for A at atmospheric pressure is 0.2631 G. The present study's value of A for PDT in non-deuterated toluene is 0.22828 G at 50.0 °C, which is significantly lower. This difference is far wider than can be accounted for by the slight temperature difference. What makes this especially significant is that the extracted line width would actually be expected to be greater for the non-deuterated solvent if the line-width analysis did not properly account for inhomogeneous broadening. The fact that A in this study is instead smaller even with non-deuterated toluene seems another indication that the excess in A found in the other studies results from not fully accounting for the broadening.

The question now is how much of A in the present systems arises from the magnetic tensor anisotropies and how much is due to spin-rotation. In the picosecond rotation range in these solvents, A_{SR} is almost all of A , with A_{mag} being much smaller than A_{SR} . Figure 5 shows the fraction of A consisting of the spin-rotational contribution for benzene as an example. These results are consistent with results for PDT in heavy water,¹⁰ in which A' was almost all of A for rotational correlation times within 4 ps.

Thus far, this paper has examined non-polar organic solvents. The study of Ref. 22 on PDT diffusion in ethanol determined the rotational correlation time by only using B with the known⁶ value of ε for this system. That study avoided using C because it levels out in this system at high temperature, just as it does for organic solvents. If A and B from that study are used in Eq. (12) to find τ_R for PDT in ethanol, the resulting values are all much lower (by as much as a factor of two or more) than τ_R from B alone or from B and C together using Eq. (13). This is likely because of the significant hydrogen bonding between PDT and ethanol.⁶ Such association would keep the spins on the probe close to those on the solvent and affect their relative orientation, thereby increasing the strength of interactions between them, including dipolar interactions. It may, therefore, be necessary to modify Eq. (9) and well as models of other interactions to account for probe-solvent association. The reason unaccounted-for broadening would decrease τ_R from A and B instead of increase it is that A_{SR} is much larger than A_{mag} in the picosecond range. Because A_{SR} is inversely proportional to τ_R , excessive broadening not included in Eq. (9) would decrease τ_R in this range. Therefore, the conditions under which A can be properly used to extract τ_R are both rapid rotation and non-association between the probe and solvent.

The rotational correlation time is believed to obey the general form

$$\tau_R = \frac{V_p \eta}{kT} f Q + \tau_0 \quad (16)$$

where V_p is the Stokes volume of the probe, f is a factor based on slip and stick conditions, Q is based on geometric considerations of both the probe and solvent, and τ_0 is the zero-viscosity correlation time. In the Stokes-Einstein-Debye (SED) model, which does not account for solvent free volume, f and Q are both unity and τ_0 is zero. Using the SED model and calculating V_p from a_S in Eq. (10) yields τ_R values that are much higher than the

measured times in this study, often by an order of magnitude. It is clear from results such as Figure 4 that rotation is largely governed by the free volume within the solvent. The Dote-Kivelson-Schwartz model³⁹ and its modified version by Anderton and Kauffman⁴⁰ treat Q from a free-volume/compressibility viewpoint. While each of those models has had success in some systems in the past, it is difficult to determine the values of f and Q that are appropriate for each situation. Nevertheless, experimental results such as those of Fig. 4 should motivate further development of free-volume/compressibility-based models of rotational diffusion.

Conclusions

The central line width can be directly used to extract reliable rotational correlation times in X-band EPR under certain conditions. These conditions are: 1) Rotation is very rapid, and 2) the probe and solvent do not form significant association with each other. Multiple lines of evidence, including independent confirmation from B and C , have shown that the probe-solvent electron-nuclear dipolar interaction is negligibly small for $\tau_R \approx 4$ ps in organic solvents. Values of τ_R in this range obtained by using A and B instead of B and C have smaller uncertainties, and, hence, higher precision. Furthermore, τ_R from A and B does not level off at high temperature as τ_R from B and C sometimes does. The proposed method also removes the problem of fitting a constant correction factor to the non-secular spectral density on a time scale where it cannot always be comfortably fitted. The study has also found a close relationship between rotation and liquid compressibility, thereby providing further experimental basis for developing free-volume/compressibility-based models of rotational diffusion.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References and Notes

1. Kivelson D. J Chem Phys. 1960; 33:1094.
2. Freed JH, Fraenkel GK. J Chem Phys. 1963; 39:326.
3. Freed JH. J Chem Phys. 1965; 43:1710.
4. Nordio, PL. General Magnetic Resonance Theory. In: Berliner, LJ., editor. Spin Labeling: Theory and Applications. Academic Press; New York: 1976. p. 5
5. Goldman SA, Bruno GV, Polnaszek CF, Freed JH. J Chem Phys. 1972; 56:716.
6. Hwang JS, Mason RP, Hwang L-P, Freed JH. J Phys Chem. 1975; 79:489.
7. Goldman SA, Bruno GV, Freed JH. J Chem Phys. 1973; 59:3071.
8. Polnaszek CF, Freed JH. J Phys Chem. 1975; 79:2283.
9. Kowert BA. J Phys Chem. 1981; 85:229.
10. Zager SA, Freed JH. J Chem Phys. 1982; 77:3344.
11. Zager SA, Freed JH. J Chem Phys. 1982; 77:3360.
12. Jones LL, Schwartz RN. Molec Phys. 1981; 43:527.
13. Lepock JR, Cheng K-H, Campbell SD, Kruuv J. Biophys J. 1983; 44:405. [PubMed: 6318842]
14. Freed, JH. Theory of Slow Tumbling ESR Spectra for Nitroxides. In: Berliner, LJ., editor. Spin Labeling: Theory and Applications. Academic Press; New York: 1976. p. 53

15. Eastman MP, Kooser RG, Das MR, Freed JH. *J Chem Phys.* 1969; 51:2690.
16. Bales BL, Meyer M, Smith S, Peric M. *J Phys Chem A.* 2009; 113:4930. [PubMed: 19385676]
17. Wilson R, Kivelson D. *J Chem Phys.* 1966; 44:154.
18. Wilson R, Kivelson D. *J Chem Phys.* 1966; 44:4440.
19. Wilson R, Kivelson D. *J Chem Phys.* 1966; 44:4445.
20. Zientara GP, Freed JH. *J Phys Chem.* 1979; 83:3333.
21. Nayeem A, Rananavare SB, Sastry VSS, Freed JH. *J Chem Phys.* 1989; 91:6887.
22. Kurban MR. *J Chem Phys.* 2011; 134:034503. [PubMed: 21261364]
23. Molin, YN.; Salikhov, KM.; Zamaraev, KI. *Principles and Applications in Chemistry and Biology.* Springer-Verlag; New York: 1980. Spin Exchange; p. 8
24. Salikhov KM. *J Magn Reson.* 1985; 63:271.
25. Kurban MR, Peric M, Bales BL. *J Chem Phys.* 2008; 129:064501. [PubMed: 18715079]
26. Kurban MR. *J Chem Phys.* 2009; 130:104502. [PubMed: 19292536]
27. Atkins PW, Kivelson D. *J Chem Phys.* 1966; 44:169.
28. McClung RED, Kivelson D. *J Chem Phys.* 1968; 49:3380.
29. Kooser RG, Volland WV, Freed JH. *J Chem Phys.* 1969; 50:5243.
30. For the pseudosecular spectral densities given by $j_m(\omega_a) = \tau_m / (1 + \omega_a^2 \tau_m^2)$, where $\omega_a = 8.8 \times 10^6(a_{xx} + a_{yy} + a_{zz})/3$ represents the nuclear-spin-transition rate, $\omega_a^2 \tau_m^2 \ll 1$ for $\tau_m < 10^{-10}$ s, and can thus be neglected for relaxation times on the order of picoseconds.
31. Bales, BL. Inhomogeneously Broadened Spin-Label Spectra. In: Berliner, LJ.; Reuben, J., editors. *Biological Magnetic Resonance.* Vol. 8. Plenum Publishing; New York: 1989. p. 77
32. Halpern HJ, Peric M, Yu C, Bales BL. *J Magn Reson A.* 1993; 103:13.
33. Bales BL, Peric M. *J Phys Chem B.* 1997; 101:8707.
34. Bales BL, Peric M. *J Phys Chem A.* 2002; 106:4846.
35. Bales BL, Peric M, Dragutan I. *J Phys Chem A.* 2003; 107:9086.
36. Bales BL, Meyer M, Smith S, Peric M. *J Phys Chem A.* 2008; 112:2177. [PubMed: 18278887]
37. Alves M, Peric M. *Biophys Chem.* 2006; 122:66. [PubMed: 16517048]
38. Budil DE, Earle KA, Freed JH. *J Phys Chem.* 1993; 97:1294.
39. Dote JL, Kivelson D, Schwartz RN. *J Phys Chem.* 1981; 85:2169.
40. Anderton RM, Kauffman JF. *J Phys Chem.* 1994; 98:12117.

Figure 1. Fitted EPR spectrum for PDT in decane (0.08 mM) at 283 K. (a) All three spectral lines; (b) $M = 0$ line magnified horizontally. The blue curve is the raw spectrum, and the red is the fit

with the Lorentzian-Gaussian sum function. The horizontal green line running through the middle of each spectral line is the difference between the experimental spectrum and the fit.

Figure 2. Rotational correlation time from A and B (squares) and from B and C (circles) vs. $1/T$ for (a) toluene, (b) decane, and (c) hexadecane. Each error bar is $\pm$ one standard deviation.

Figure 3.

Measured rotational correlation time vs. $1/T$ for PDT in hexane (hollow squares), decane (blue solid circles), tridecane (green triangles), hexadecane ($\times$'s), cyclohexane (hollow diamonds), benzene (hollow circles), toluene (red triangles), and *p*-xylene (purple solid squares). The coefficients of correlation for the lines of best fit are 0.99932 for hexane, 0.99919 for decane, 0.99868 for tridecane, 0.99957 for hexadecane, 0.99945 for cyclohexane, 0.99912 for benzene, 0.99995 for toluene, and 0.99978 for *p*-xylene. The inset shows the common line formed by benzene, toluene, and *p*-xylene. Each error bar is $\pm$ one standard deviation.

Figure 4.

Measured rotational correlation time vs. solvent isothermal compressibility for PDT in hexane (hollow squares), decane (blue solid circles), tridecane (green triangles), hexadecane (x's), cyclohexane (hollow diamonds), benzene (hollow circles), toluene (red triangles), and *p*-xylene (purple solid squares). Each error bar is $\pm$ one standard deviation.

Figure 5.
 A (diamonds) and A_{SR} (triangles) vs. T for benzene.