

Estimating Slow-Motional Rotational Correlation Times for Nitroxides by Electron Spin Resonance¹

by S. A. Goldman, G. V. Bruno, and J. H. Freed*

Department of Chemistry, Cornell University, Ithaca, New York 14850 (Received January 3, 1972)

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A simple method of estimating slow-motional rotational correlation times τ_R for nitroxides by esr, which is based on the rigorous theory of Freed, Bruno, and Polnaszek, is discussed. The results can be fit to the expression $\tau_R = a(1 - S)^b$, where S is the ratio of the separation of the outer hyperfine extrema to that for the rigid limit value. The parameters a and b depend upon intrinsic line width, rotational model, and hyperfine parameters, and appropriate results are given.

Recently, there has been considerable interest in the slow-motional esr spectra of nitroxide free radicals.² In this motional region, which corresponds to rotational correlation times 10^{-9} sec $\lesssim \tau_R \lesssim 10^{-6}$ sec, the line shape can no longer be described by the earlier relaxation theories.³ Slow-motional nitroxide spectra have been observed in viscous liquids, solids, and in the hindered rotation of spin-labeled molecules.^{2,4}

Using the methods developed by Freed, *et al.*,⁵ it is possible to interpret these line shapes in terms of the relevant spin parameters to learn about the dynamics of the molecular reorientational process. This was demonstrated for peroxyamine disulfonate (PADS), $(\text{SO}_3)_2\text{NO}^{2-}$, where the detailed line shapes were analyzed in terms of their dependence on \mathbf{A} , \mathbf{g} , an intrinsic line width, and the rotational correlation time, τ_R .⁴ It was also shown that the proper analysis of the observed spectra depends on whether the molecule is undergoing anisotropic rotational reorientation and whether there are significant deviations from a Brownian diffusion model.

The ability to interpret these esr line shapes in terms of molecular dynamics would be particularly useful in the spin-label technique where changes in line shape resulting from variations in molecular size, structure, location of paramagnetic site, etc., could yield information on the nature of the local molecular environment. In principle this can be done for any slow-motional nitroxide spectrum. However, in practice, many of the expected line shape changes are obscured by inhomogeneous line broadening resulting from intramolecular or intermolecular (solvent) hyperfine and dipolar interactions. These interactions decrease the spectral resolution and consequently increase the difficulty in obtaining useful information from the observed line shapes.

From single crystal studies on a variety of nitroxides, it is known that their \mathbf{A} and \mathbf{g} tensors are only slightly dependent on the detailed molecular structure and that

$A_z \gg A_x \approx A_y$, where the z axis is along the $2p-\pi$ orbital of nitrogen, the x axis is along the N-O bond, with the y axis perpendicular to these.⁶ Thus a typical nitroxide slow-motional spectrum has two well separated outer hyperfine extrema with an overlapped central region. A useful parameter for describing these spectra is $S = A_z'/A_z$, where A_z' is one-half the separation of the outer hyperfine extrema and A_z is the rigid limit value for the same quantity.⁷ The very detailed experimental results for PADS⁴ demonstrated that S is a sensitive, monotonically increasing, function of τ_R and this general type of behavior is also characteristic of other nitroxides as studied in this laboratory as well as in others.^{2,6,7} Thus, if we know how S is affected by changes in the (1) spin parameters, (2) line width, and (3) rotational diffusion model, then the variation of S with τ_R could generally be applied to nitroxides, and it would be possible to estimate τ_R without the necessity of making detailed line shape calculations and comparisons.

Slow-motional line shapes were calculated for completely asymmetric \mathbf{A} and \mathbf{g} tensors as well as for axially symmetric models where the z axis was chosen as the symmetry axis.⁸ Spectra simulated under these

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(7) R. C. McCalley, E. J. Shimshick, and H. M. McConnell (to be published) discuss parameters closely related to S (*i.e.*, the deviations of high-field and low-field line positions from their respective rigid limit values) in work on spin-labeled oxyhemoglobin.

latter simplifying assumptions showed qualitative agreement with those calculated with the asymmetric parameters with the major differences occurring in the central region of the spectra. For isotropic diffusion, the separation between the outer hyperfine extrema was unaffected (within the accuracy of our computer calculations) by the approximation of axially symmetric A and g . Thus, for simplicity, axial symmetry was assumed in many of the calculations. The value of S was also found to be insensitive to variations in A_{\perp} , g_{\parallel} , and g_{\perp} , typical of nitroxide, as long as A_z is kept constant. Changes in the magnitude of A_z , however, do affect the value of S , and this dependence can be approximately expressed in the functional form $S = S(\tau_R A_z)$, *i.e.*, S is simply dependent on the product $\tau_R A_z$. This functional dependence permits scaling our results given below over the range of values of A_z typical for nitroxides (27–40 G) with an error of less than 3%.

The experimental spectra for PADS have been compared to simulated spectra calculated for models of (1) Brownian diffusion, (2) strong jump diffusion, and (3) an approximation to a free-diffusion model (which gives essentially the same results as a moderate jump model). It was shown that the calculated line shapes were very sensitive to the choice of rotational model, and that the spectra simulated with the approximate free-diffusion model came closest to the observed spectra. Slow-motional spectra observed for nitroxides attached to larger molecules in solution exhibit line shapes which, as expected, are more characteristic of Brownian diffusion.⁷ In Figure 1, the variation of S with τ_R is shown for Brownian, approximate free, and strong jump-diffusion models,⁴ isotropic diffusion, $A_z = 32$ G and peak-to-peak derivative Lorentzian line widths of 0.3 and 3.0 G. It can be seen that S is model sensitive and for an equivalent value of τ_R ,⁹ S increases from Brownian to free to a jump reorientational model. We have found that these curves can be fit to the expression

$$\tau_R = a(1 - S)^b$$

to within 2, 3, or 5% in the value of τ_R for a given S , for jump, Brownian, or free diffusion, respectively, with the values of a and b given in the figure caption. It should be noted that for $\tau_R \lesssim 7 \times 10^{-9}$ sec, S is undefinable since the outer lines begin to converge to the motionally narrowed spectrum. For longer τ_R 's than shown in Figure 1, the spectrum approaches the rigid limit, and the value of $1 - S$ become comparable to experimental uncertainties.

As previously noted, the detailed esr slow-motional line shape can be greatly affected by the presence of a large intrinsic line width resulting from unresolved inhomogeneous line broadening. It is often difficult to estimate the size of this intrinsic width directly from the slow-motional spectra without detailed spectral

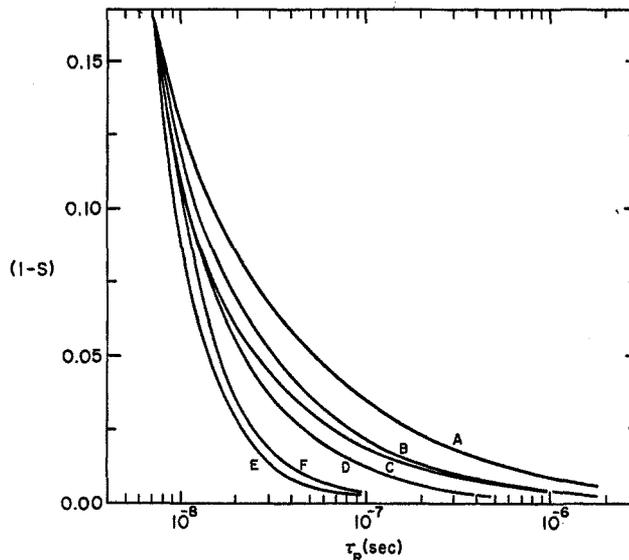


Figure 1. Graph of $(1 - S)$ vs. τ_R for nitroxides for different models of isotropic rotational reorientation (from computer simulation). Curves A and B are for Brownian diffusion and derivative widths $\delta = 0.3$ and 3.0 G, respectively, curves C and D are for a moderate jump diffusion and $\delta = 0.3$ and 3.0 G, respectively, and curves E and F are for strong jump diffusion and $\delta = 0.3$ and 3.0 G, respectively. Curves may be approximated by $\tau_R = a(1 - S)^b$ with (A) $a = 2.57 \times 10^{-10}$ sec, $b = -1.78$; (B) $a = 5.4 \times 10^{-10}$, $b = -1.36$; (C) $a = 6.99 \times 10^{-10}$, $b = -1.20$; (D) $a = 1.10 \times 10^{-9}$, $b = -1.01$; (E) $a = 2.46 \times 10^{-9}$, $b = -0.589$; (F) $a = 2.55 \times 10^{-9}$, $b = -0.615$.

simulations. Moreover, in many experimental situations, the magnitude of the inhomogeneous line broadening may increase as the rotation slows. Some estimate of the intrinsic line width and its variation with τ_R can be obtained from line width measurements in both the motional-narrowing and rigid limits. In the studies on PADS, the intrinsic line width, for $\tau_R \lesssim 7 \times 10^{-8}$ sec, was only slightly larger than for the motional-narrowing region, and only for longer τ_R the line width increases to the rigid limit value. The effect of line width on the value of S is shown in Figure 1. For Brownian and free diffusion models, S increases with increasing line width, while for jump diffusion a decrease in S is observed. The uncertainty in estimating τ_R , due to an uncertainty in intrinsic line width, for a given value of S , increases for longer τ_R . Thus for a Brownian diffusion model, and a 1.5 G uncertainty in the intrinsic width, the uncertainty in calculating τ_R for a given value of S increases from about 5% for $\tau_R \approx 1 \times 10^{-8}$ sec, to about 50% for $\tau_R \approx 1 \times 10^{-7}$ sec to

(8) Cf. ref 4 and 5 for the method. Typical axial-symmetry simulation times for Brownian diffusion on an IBM 360/65 computer are $\lesssim 6$ sec for $\tau_R \lesssim 3 \times 10^{-8}$ sec to 40 sec for $\tau_R \sim 3 \times 10^{-7}$ sec when a rapid diagonalization subroutine developed by Messenger and Gordon (to be published) is utilized. Asymmetric simulations are longer, *e.g.*, $\lesssim 70$ sec for $\tau_R \lesssim 3 \times 10^{-8}$ sec including nonisotropic diffusion. Our nitroxide programs are available upon request.

(9) τ_R is normalized so that in the motional narrowing region, all models give the same line widths for the same value of τ_R ; cf. ref 4.

an order of magnitude for $\tau_R \gtrsim 1 \times 10^{-6}$ sec. We find that linear interpolations along the vertical line between the curves A and B (or C and D, or E and F) give the correct results for intermediate line width values.

The curves in Figure 1 were calculated for isotropic rotational reorientation. For anisotropic diffusion, the approximation of axial symmetry for the spin parameters may no longer be valid and the anisotropic parameters must be used. For simplicity, the rotational diffusion tensor can often be assumed to be axially symmetric with its symmetry axis $z' = x, y,$ or z of the molecular fixed axis.¹⁰ Thus $R_{||}$ and R_{\perp} are the components of the rotational diffusion tensor about the z' and the x' and y' axes, respectively. For $z' = z$ and $R_{||} > R_{\perp}$, *i.e.*, fast rotation about the molecular z axis, the results are relatively straightforward. This type of rotation preserves the approximate axial symmetry of the spin parameters, and the observed value of S is the value expected for isotropic diffusion and $\tau_R = (6R_{\perp})^{-1}$. For relatively more rapid diffusion about the x or y axes, the results are more complicated. For small anisotropies about these axes, *i.e.*, $R_{||} \cong$

$3R_{\perp}$, the value of S is very slightly changed from the value calculated for isotropic diffusion and $\tau_R = (6\bar{R})^{-1} = 1/6(R_{\perp}R_{||})^{1/2}$, but this corresponds to a decrease of about 8% in the apparent value of τ_R obtained from Figure 1. For larger anisotropies, a decrease in the value of S is observed (*e.g.*, for $\tau_R = 3.0 \times 10^{-8}$, Brownian diffusion, and a line width = 0.3 G, S decrease from 0.931 for $R_{||}/R_{\perp} = 1$ to 0.897 for $R_{||}/R_{\perp} = 20$ or an apparent decrease in τ_R obtained from Figure 1 by a factor of 2). The magnitude of this decrease is independent of whether the x or y axis is the symmetry axis. However, in general, if the axis of rotation is unknown, or does not correspond to a molecular coordinate axis, or if the rotation is completely asymmetric, then estimates of the components of the rotational diffusion tensor can only be obtained from detailed spectral simulations.⁸ Further detailed studies of other nitroxides in terms of the general theory^{4,5} and the simplified method discussed here are of interest and are being pursued in part in our laboratories.

(10) This is a good approximation for $R_z' \gg R_x', R_y'$ with R_{\perp} defined as $R_{\perp} = (R_x' + R_y')/2$.

The Monoisotopic Mass Spectra of Borane Derivatives¹

by Eileen McLaughlin and R. W. Rozett*

Chemistry Department, Fordham University, New York, New York 10458 (Received November 2, 1971)

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The monoisotopic mass spectra of borane derivatives are calculated by a least-squares computer technique from polyisotopic information. Alkyl boranes, carboranes, and borane derivatives containing bromine, chlorine, sulfur, nitrogen, oxygen, deuterium, many metals and any monoisotopic element can be handled. Elemental formulas for ions can be established. As examples we investigate the following borane derivatives: $B_{10}H_8N_4$, $C_2B_4H_8$, $CH_3CB_5H_8$, $(CH_3)_2C_2B_6H_8$, $(CH_3)_2C_2B_7H_7$, and $(CH_3)_2C_2B_8H_8$. Finally the sources of error in the procedure are discussed.

Introduction

The mass spectra of borane derivatives which contain elements with a significant fraction of a second or third isotope are even more complex than the polyisotopic mass spectra of the boranes, B_nH_m . For example, in the mass spectrum of decaborane-14, in the mass region of ten boron ions, 165 isotopic variants occur if one takes into account only the boron isotope combinations. If in addition the deuterium variants are counted, 1254 ions could be found. The small natural abundance of deuterium makes the hydrogen case trivial, but the same cannot be said for the pres-

ence of ^{13}C in alkyl boranes and carboranes, or for ^{37}Cl and ^{81}Br in haloboranes (see Table IX).

If the mass spectrum is taken to study kinetic or mechanistic details of reactions, the complicated polyisotopic data may be looked upon as a mask hiding monoisotopic information. But from another point of view, the isotopic variation contains additional information which may be used to identify the ions present

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