

aid of Eq. (A3) that for the case where the nonfluorescent aggregates are dimers, essentially all the chlorophylls must belong to the nonfluorescent fraction to produce the observed self-quenching of pure chlorophyll monolayers. We conclude that the model which assumes each chlorophyll to have its excited state lifetime reduced is a much better description of the undiluted monolayers.

An important result of the fit of Eq. (A3) to the experimental data is that  $\tau_d/\tau_i=54$  to 140 and  $\tau_d/\tau_q=4.3$  to 5.7. This means that each excitation visits a large number of sites before decaying. (In this limit, each excitation can be thought of as residing on an average chlorophyll molecule, thus justifying assumption 3 above.) However, the fact that the excitation makes many transfers during its lifetime strongly suggests that the localized excitation representation of the monolayers is not the best for careful quantitative calculations. Clearly chromophore-chromophore cou-

pling interactions are strong enough so that the tendency to delocalization is pronounced. In the absence of a properly constituted collective-excitation description of the excited monolayer, the localized representation has been used here to provide semiquantitative insight into the dynamics of energy transfer.

*Note added in proof:* Since the manuscript was submitted, we have learned of an unpublished calculation by S. Lipsky [Quarterly Status Report #6, Contract # AF 19(604)-8358, 1962] describing the dynamics of a one-dimensional exciton wave packet which is relevant to the theoretical problem of this paper. It is perhaps worth noting, in addition, that experimental tests of different schemes which have been proposed for describing energy migration among the fluorescent chromophores<sup>11,12</sup> would require that the quenching process be *diffusion limited* in the localized excitation representation. Careful attention to detail is required if this condition is to be satisfied experimentally.

## Anisotropic Rotational Diffusion and Electron Spin Resonance Linewidths\*

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The recent general theory of ESR linewidths for dilute solutions of free radicals developed by Freed and Fraenkel is extended to cover the possibility that the rotational motions of the free radicals are anisotropic. The analysis is greatly simplified by expressing the solution of the rotational-diffusion equation as an expansion in Wigner rotation matrices. Only the spectral-density functions in the linewidth expressions given by Freed and Fraenkel are changed by the inclusion of anisotropic rotational diffusion. These spectral-density functions are found to depend upon five different relaxation times which are expressible in terms of the three principal values of the diffusion tensor  $\mathfrak{D}$ . It is shown how an analysis of the ESR linewidth effects, which vary from one hyperfine component to another, may be used in conjunction with calculations of the anisotropic electron-nuclear dipolar interactions to estimate the principal values of  $\mathfrak{D}$ . The experimental linewidth study on the *para*-dinitrobenzene anion radical is reanalyzed, and it is shown that an anisotropic rotational-diffusion mechanism cannot by itself explain the anomalous absence of any significant quadratic linewidth dependence on the total  $Z$  component of spin of the ring protons. While an order of magnitude estimate of  $\mathfrak{D}$  was made, further information permitting a quantitative understanding of the anomalous result (presumably due to fluctuations in isotropic hyperfine interactions) would be necessary to obtain a meaningful estimate of the principal values of  $\mathfrak{D}$  for this radical. The physical significance of  $\mathfrak{D}$  in the approximation of a Brownian particle as well as in terms of intermolecular potentials is discussed.

### I. INTRODUCTION

**I**N the recent general theory of ESR linewidths for dilute solutions of free radicals given by Freed and Fraenkel<sup>1</sup> the assumption of isotropic molecular tumbling was employed. This assumption is consistent with the isotropic Brownian rotational-diffusion mechanism frequently utilized in theories of magnetic-resonance relaxation<sup>2,3</sup> despite the fact that

the nature of molecular motions in liquids is not well understood. Thus, for example, the molecular reorientations may not be adequately represented by numerous, small, and independent elementary displacements, because the effects of larger and perhaps correlated displacements could be important. Also, the requirement of isotropic rotations is unrealistic for molecules having nonspherical shapes or nonspherically symmetric interaction potentials with surrounding molecules. We shall be mainly concerned with this latter problem.

Perrin<sup>4</sup> first developed the theory of Brownian motion (in connection with dielectric relaxation) for

\* Supported in part by the Advanced Research Projects Agency.

<sup>1</sup> J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **39**, 326 (1963). References to this work will be designated by I.

<sup>2</sup> N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

<sup>3</sup> A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

<sup>4</sup> F. Perrin, *J. Phys. Radium* **5**, 497 (1934); **7**, 1 (1936).

molecules whose shape is approximated by an ellipsoid. Favro,<sup>5</sup> in a recent independent work, demonstrated the close relationship between the solutions of the rotational-diffusion equation for a body with an anisotropic diffusion tensor and the quantum-mechanical solutions of the rigid rotor, and this relationship leads to considerable simplification of the analysis. These theories have recently been applied by Shimizu<sup>6</sup> and Woessner<sup>7</sup> to a discussion of nuclear magnetic relaxation by anisotropic rotational diffusion. Steele,<sup>8</sup> who has also studied the nuclear magnetic-relaxation problem, has re-examined the physical significance of the diffusion tensor for molecules (as opposed to Brownian particles), and has analyzed some of the effects of weakly damped classical rotational motions.

In this paper, the effects of anisotropic rotational diffusion on the theory of ESR linewidths given in I are analyzed and applied to the recent experimental linewidth study on the *para*-dinitrobenzene anion radical.<sup>9</sup> The study of ESR linewidths is complicated by the fact that there are a variety of mechanisms which can make important linewidth contributions. These may be divided into two categories: (1) the intramolecular interactions such as the electron-nuclear dipolar terms, the *g*-tensor anisotropy, and fluctuations in the electron-nuclear isotropic hyperfine terms<sup>1</sup>; (2) the intermolecular effects including dipolar interactions with neighboring molecules, and the chemical<sup>10</sup> and quantum mechanical<sup>11</sup> types of electron exchange. The experiments described in II show that at least in some cases one is able to extract out the linewidth effects of intramolecular interactions which are modulated by the rotational diffusion. This is possible because there often are many different hyperfine lines (resulting from different configurations of the nuclear spins), and the intramolecular contributions to the linewidth have an important dependence upon the nuclear-spin configurations. Then, by comparing the linewidths of the different hyperfine lines, considerable information may be obtained about these mechanisms. One purpose of this paper is to show that such studies can lead directly to the experimental determination of all the principal values of a rotational-diffusion tensor provided that other molecular parameters, such as the dipolar and *g*-tensor terms, may be calculated or obtained from independent experiments

(e.g., single crystal studies). Such ESR studies could become very useful since dielectric or nuclear magnetic-relaxation studies have not been able to supply such detailed information about the diffusion tensor.

## II. THEORETICAL CONSIDERATIONS

### A. ESR Linewidths

The theory of ESR linewidths given in I relates the linewidths to perturbing terms in the spin Hamiltonian which achieve a random, time-dependent character as a result of the random molecular-tumbling motions. This perturbing Hamiltonian  $\mathcal{H}_1(t)$  may be expressed in the form<sup>1,12</sup>

$$\mathcal{H}_1(t) = \sum_{L,m,\mu,i} F_{\mu,i}{}^{(L,m)} A_{\mu,i}{}^{(L,-m)}, \quad (2.1)$$

where both the  $F_{\mu,i}{}^{(L,m)}$  and the  $A_{\mu,i}{}^{(L,-m)}$  are irreducible (spherical) tensor components with  $L$  denoting the rank and  $m$  the component. The subscript  $\mu$  distinguishes the different types of interactions appearing in  $\mathcal{H}_1(t)$ , and the subscript  $i$  refers to the different nuclei in the radical. The primes indicate that the interactions are written in the molecule-fixed axes. The  $F_{\mu,i}{}^{(L,m)}$  are functions of molecular coordinates and may be expressed naturally in these axes. The  $A_{\mu,i}{}^{(L,m)}$  are spin operators and are quantized in the space-fixed axes. They may be transformed from space-fixed to molecule-fixed axes by means of the Wigner rotation matrices<sup>13-15</sup>  $\mathcal{D}_{m,m'}{}^{(L)}(\alpha\beta\gamma)$ , where  $\alpha$ ,  $\beta$ , and  $\gamma$  are the Euler angles for the transformation, giving

$$A_{\mu,i}{}^{(L,-m)} = \sum_{m'} \mathcal{D}_{-m,m'}{}^{(L)}(\alpha\beta\gamma) A_{\mu,i}{}^{(L,m')}, \quad (2.2)$$

where the unprimed  $A$ 's refer to space-fixed axes. The effects of the random molecular-tumbling motions are now contained in the rotation matrices. The linewidths are given by a relaxation matrix<sup>1</sup> which depends upon a spectral-density function

$$J(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} \langle \mathcal{H}_1(t) \mathcal{H}_1^*(t+\tau) \rangle \exp(-i\omega\tau) d\tau, \quad (2.3)$$

whose Fourier transform is a correlation function.<sup>16</sup> Using Eqs. (2.1) and (2.2), the correlation function

<sup>5</sup> L. D. Favro, Phys. Rev. **119**, 53 (1960).

<sup>6</sup> H. Shimizu, J. Chem. Phys. **37**, 765 (1962); **40**, 754 (1964).

<sup>7</sup> D. E. Woessner, J. Chem. Phys. **37**, 647 (1962).

<sup>8</sup> (a) W. A. Steele, J. Chem. Phys. **38**, 2404 (1963); (b) *ibid.* **38**, 2411 (1963); (c) W. B. Moniz, W. A. Steele, and J. A. Dixon, *ibid.* **38**, 2418 (1963).

<sup>9</sup> J. H. Freed and G. K. Fraenkel, J. Chem. Phys. **40**, 1815 (1964). References to this work will be designated by II.

<sup>10</sup> R. L. Ward and S. I. Weissman, J. Am. Chem. Soc. **76**, 3612 (1954); **79**, 2086 (1957); P. J. Zandstra and S. I. Weissman, J. Chem. Phys. **35**, 757 (1961).

<sup>11</sup> G. E. Pake and T. R. Tuttle, Phys. Rev. Letters **3**, 423 (1959); J. D. Currin, Phys. Rev. **126**, 1995 (1962).

<sup>12</sup> Fluctuations in the  $F_{\mu,i}{}^{(L,m)}$  due to internal rotations, solvations, etc., are being neglected to simplify the discussion. These motions were introduced in I on the assumption that they are statistically independent of the over-all rotational tumbling, and may be treated separately.

<sup>13</sup> E. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1959).

<sup>14</sup> M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

<sup>15</sup> A. K. Saha and T. P. Das, *Nuclear Induction* (Saha Institute of Nuclear Physics, Calcutta, India, 1957).

<sup>16</sup> The spectral density and correlation function as written here are still spin operators; see Ref. 1.

may be written as

$$\langle \mathfrak{C}_1(t)\mathfrak{C}_1(t+\tau) \rangle = \sum_{L,L',m,m';\mu,\nu,i,j} F_{\mu,i}{}^{(L,m)} F_{\nu,j}{}^{(L',m')} * \times \sum_{q,q'} \langle \mathfrak{D}_{-m,q}{}^{(L)}(t) \mathfrak{D}_{-m',q'}{}^{(L')*}(t+\tau) \rangle_{\Omega} \times [A_{\mu,i}{}^{(L,q)}][A_{\nu,j}{}^{(L',q')}]*, \quad (2.4)$$

where the angular brackets indicate ensemble averages. Now

$$\langle \mathfrak{D}_{-m,q}{}^{(L)}(t) \mathfrak{D}_{-m',q'}{}^{(L')*}(t+\tau) \rangle_{\Omega} = \int d\Omega_0 W(\Omega_0) D_{-m,q}{}^{(L)}(\Omega_0) \times \int d\Omega P(\Omega_0 | \Omega; \tau) \mathfrak{D}_{-m',q'}{}^{(L')*}(\Omega), \quad (2.5)$$

where  $\Omega_0$  and  $\Omega$  represent the values of the Euler angles at times  $t$  and  $t+\tau$ , respectively, ( $d\Omega_0$  and  $d\Omega$  are normalized volume elements in Euler angle space).  $W(\Omega_0)$  is just the *a priori* probability density of the molecule-fixed axes being oriented at  $\Omega_0$  and is  $(8\pi^2)^{-1}$ .  $P(\Omega_0 | \Omega; \tau)d\Omega$  is the conditional probability that if the molecular orientation is given by  $\Omega_0$  at  $\tau=0$ , it will be given by  $\Omega$  at  $\tau$ . In I it was assumed that the molecular tumbling is described by a single correlation time  $\tau_R$  (for  $L=2$ ) so that the integration over  $\Omega$  in Eq. (2.5) is replaced by  $\mathfrak{D}_{-m',q'}{}^{(L')*}(\Omega_0) \exp(-|\tau|/\tau_R)$ . We are presently concerned with a detailed evaluation of  $P(\Omega_0 | \Omega; \tau)$ .

### B. Anisotropic Diffusion

Perrin<sup>4</sup> and Favro<sup>5</sup> showed that the probability distribution for a classical particle undergoing random anisotropic rotational reorientations may be described by a diffusion equation. (A discussion of some of the assumptions of such a model is deferred to Sec. IV.) This diffusion equation is quite similar to the time-dependent Schrödinger equation for a quantum-mechanical rigid rotor, where the rotational constants for the rigid rotor in units of Planck's constant  $\hbar$ <sup>17</sup> are replaced by the principal values of the molecular-diffusion tensor  $\mathfrak{R}$ . It may be shown to yield as an expression for  $P(\Omega_0 | \Omega; \tau)$ , the expansion<sup>5</sup>

$$P(\Omega_0 | \Omega; \tau) = \sum_n \varphi_n^*(\Omega_0) \varphi_n(\Omega) e^{-E_n \tau}, \quad (2.6)$$

where the  $\varphi_n(\Omega)$  constitute a complete orthonormal set of rigid rotor wavefunctions with eigenvalues  $E_n$ .

#### 1. Axially Symmetric Rotational Diffusion

It is convenient to choose the molecule-fixed coordinates  $x', y', z'$  in Eq. (2.1) as the three principal axes of  $\mathfrak{R}$  with principal values of  $\mathfrak{R}_1, \mathfrak{R}_2, \mathfrak{R}_3$ . When

<sup>17</sup> C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

$\mathfrak{R}_1 = \mathfrak{R}_2$ , the diffusion equation resembles the Schrödinger equation of the symmetric rotor, whose symmetry axis corresponds to the  $z'$  axis. The  $\varphi_n$  are then the well-known symmetric-rotor wavefunctions which may be classified in terms of the quantum numbers  $L, K$ , and  $M$ , i.e.,  $\varphi_n \rightarrow \varphi_{KM}{}^L(\Omega)$ .<sup>17</sup> It is useful to identify the wavefunctions with the Wigner rotation matrices. Thus,<sup>13,14</sup>

$$\varphi_{KM}{}^L(\Omega) = (-1)^{K-M} [(2L+1)/8\pi^2]^{\frac{1}{2}} \mathfrak{D}_{KM}{}^L(\Omega), \quad (2.7)$$

and

$$E_n \rightarrow E_{L,K} = \mathfrak{R}_1 L(L+1) + (\mathfrak{R}_3 - \mathfrak{R}_1) K^2. \quad (2.8)$$

Now Eq. (2.4) is easily evaluated using Eqs. (2.5), (2.7), (2.8), and the orthogonality of the rotation matrices<sup>13,14</sup>

$$\int d\Omega \mathfrak{D}_{m_1,q_1}{}^{(L_1)*}(\Omega) \mathfrak{D}_{m_2,q_2}{}^{(L_2)}(\Omega) = (2L_1+1)^{-1} \delta_{L_1 L_2} \delta_{m_1 m_2} \delta_{q_1 q_2}. \quad (2.9)$$

One obtains

$$J(\omega) = \sum_{\mu,\nu;i,j} \sum_{L,q} [A_{\mu,i}{}^{(L,q)}][A_{\nu,j}{}^{(L,q)}]* j_{ij}{}^{(\mu\nu;L)}(\omega), \quad (2.10)$$

where

$$j_{ij}{}^{(\mu\nu;L)}(\omega) = (2L+1)^{-1} \sum_m F_{\mu,i}{}^{(L,m)} F_{\nu,j}{}^{(L,m)*} \hat{\tau}_{L,m}, \quad (2.11)$$

and

$$\hat{\tau}_{L,m} = E_{L,m}^{-1} / (1 + E_{L,m}^{-2} \omega^2). \quad (2.11a)$$

For the interactions usually of interest in ESR,  $L=0$  or 2. Isotropic terms, which are represented by  $L=0$ , are unaffected by rotations ( $\hat{\tau}_{0,0}=0$ ). When  $\omega E_{L,m}^{-1} \ll 1$ , then  $\hat{\tau}_{L,m} \cong E_{L,m}^{-1} \equiv \tau_{L,m}$ , where  $\tau_{L,m}$  is a "relaxation time." For  $L=2$  there are three different relaxation times.

When Eqs. (2.10) and (2.11) are compared with Eqs. (4.8) and (4.9) of I it is found, as expected, that the only effect of introducing anisotropic relaxation is to change the spectral-density functions  $j_{ij}{}^{(\nu;L)}(\omega)$ . However, for isotropic rotational relaxation,  $\mathfrak{R}_1 = \mathfrak{R}_3$ , the three relaxation times obtained from Eqs. (2.8) and (2.11a) become identical, and Eqs. (2.10) and (2.11) go over into Eqs. (4.8) and (4.9) of I with  $\tau_R = 6\mathfrak{R}_1$ . The advantage of using the irreducible tensor components is now apparent because according to Eq. (2.11) each component  $F_{\mu,i}{}^{(L,m)}$  is "relaxed" with its own characteristic time  $E_{L,|m|}^{-1}$ , and for a particular rotational model it is easy to determine which terms will be important in Eq. (2.11). Thus for axially symmetric rotational diffusion, the irreducible tensor components are the "normal modes" of relaxation of that tensor. It should be noted that in general the principal axes of the  $\mathbf{F}_{\mu,i}$  will not coincide with those of  $\mathfrak{R}$ . But it is possible to express the  $F_{\mu,i}{}^{(L,m)}$

TABLE I. Asymmetric rotor functions.

Asymmetric rotor functions	Linear combination of symmetric rotor functions	Eigenvalue
$\Phi_{+1,M}^{(2)}$	$(1/\sqrt{2})[\phi_{1,M}^{(2)} + \phi_{-1,M}^{(2)}]$	$3(\mathfrak{R}_s + \mathfrak{R}_1) = E_{2,1}$
$\Phi_{-1,M}^{(2)}$	$(1/\sqrt{2})[\phi_{1,M}^{(2)} - \phi_{-1,M}^{(2)}]$	$3(\mathfrak{R}_s + \mathfrak{R}_2) = E_{2,-1}$
$\Phi_{-2,M}^{(2)}$	$(1/\sqrt{2})[\phi_{2,M}^{(2)} - \phi_{-2,M}^{(2)}]$	$3(\mathfrak{R}_s + \mathfrak{R}_3) = E_{2,-2}$
$\Phi_{2,M}^{(2)}$	$(a/N_+) \phi_{0,M}^{(2)} + (b_+/N_+) (1/\sqrt{2})[\phi_{2,M}^{(2)} + \phi_{-2,M}^{(2)}]$	$6\mathfrak{R}_s + 2\Delta = E_{2,2}$
$\Phi_{0,M}^{(2)}$	$(a/N_-) \phi_{0,M}^{(2)} + (b_-/N_-) (1/\sqrt{2})[\phi_{2,M}^{(2)} + \phi_{-2,M}^{(2)}]$	$6\mathfrak{R}_s - 2\Delta = E_{2,0}$

$$\mathfrak{R}_s = \frac{1}{3}(\mathfrak{R}_1 + \mathfrak{R}_2 + \mathfrak{R}_3)$$

$$\Delta = \pm [3\mathfrak{R}_-^2 + 9/4(\mathfrak{R}_3 - \mathfrak{R}_s)^2]^\dagger$$

$$a = 2\sqrt{3}\mathfrak{R}_- \quad b_\pm = 3(\mathfrak{R}_3 - \mathfrak{R}_s) \pm 2\Delta \quad a^2 = -b_+b_-$$

$$N_\pm = 2[2\Delta^2 \pm 3\Delta(\mathfrak{R}_3 - \mathfrak{R}_s)]^\dagger$$

in terms of their principal values  $F_{\mu,i}{}''^{(L,m)}$  by

$$F_{\mu,i}{}'{}^{(L,m)} = \sum_{m'} \mathfrak{D}_{m,m'}{}^{(L)}(\alpha'\beta'\gamma') F_{\mu,i}{}''^{(L,m')}, \quad (2.12)$$

and  $\alpha'$ ,  $\beta'$ , and  $\gamma'$  are the Euler angles for the rotation of the  $x''$ ,  $y''$ ,  $z''$  axes into the  $x'$ ,  $y'$ ,  $z'$  axes.

2. Asymmetric Rotational Diffusion

When  $\mathfrak{R}_1 \neq \mathfrak{R}_2 \neq \mathfrak{R}_3$ , then the eigenfunctions of Eq. (2.6) become rather complex, but they may be expressed as linear combinations of the symmetric rotor eigenfunctions.<sup>5</sup> Since only spherical tensors of rank  $L=2$  are of interest, we need only find the eigenfunctions corresponding to  $L=2$ . These are given in Table I.<sup>18</sup> When  $\mathfrak{R}_- = 0$ , the asymmetric rotor functions reduce to symmetric rotor functions (or simple linear combinations of the degenerate functions), e.g.,  $\Phi_{0,M}^{(2)} \rightarrow \varphi_{0,M}^{(2)}$ , etc.<sup>19,20</sup> When Table I is used in place of Eqs. (2.7) and (2.8), the evaluation of Eq. (2.4) results in a replacement of Eq. (2.11) by

$$j_{ij}{}^{(\mu\nu;2)}(\omega) = \frac{1}{5} \sum_{m,m'} F_{\mu,i}{}'{}^{(2,m)} F_{\nu,j}{}'{}^{(2m')} * \lambda_{mm'}(\omega), \quad (2.13)$$

where

$$\lambda_{0,0} = (4\Delta)^{-1} [b_+\hat{\tau}_0 - b_-\hat{\tau}_2], \quad (2.14a)$$

$$\lambda_{\pm 1,1} = \frac{1}{2} [\hat{\tau}_1 \pm \hat{\tau}_{-1}], \quad (2.14b)$$

$$\lambda_{\pm 2,2} = \frac{1}{2} [\pm \hat{\tau}_{-2} + (4\Delta)^{-1} (b_+\hat{\tau}_2 - b_-\hat{\tau}_0)], \quad (2.14c)$$

$$\lambda_{0,2} = [(6)^{1/2} \mathfrak{R}_- / 4\Delta] [\hat{\tau}_2 - \hat{\tau}_0], \quad (2.14d)$$

$$\lambda_{0,1} = \lambda_{1,2} = 0, \quad (2.14e)$$

<sup>18</sup> Favro<sup>6</sup> gives  $N_\pm = (4\Delta)^{-1}$  which would not normalize  $\Phi_{2,M}^{(2)}$  and  $\Phi_{0,M}^{(2)}$ .

<sup>19</sup> Actually in order for  $\Phi_{0,M}^{(2)} \rightarrow \varphi_{0,M}$  and

$$\Phi_{2,M}^{(2)} \rightarrow (1/\sqrt{2})[\phi_{2,M}^{(2)} + \phi_{-2,M}^{(2)}],$$

the sign of  $\Delta$  must be so chosen that  $\Delta \rightarrow (D_3 - D_1)$  when  $\mathfrak{R}_- \rightarrow 0$ .

<sup>20</sup> Another simplification for the asymmetric diffusion case occurs when  $\mathfrak{R}_s \gg \mathfrak{R}_\pm$ . This corresponds to rotational relaxation about the molecular  $z'$  axis being much more rapid than about the other two axes. The solutions for asymmetric diffusion in Table I are then approximated by the axially symmetric diffusion solutions with  $E_{2,\pm 1} \cong \mathfrak{R}_s$ ,  $E_{2,\pm 2} \cong 4\mathfrak{R}_s$ , and  $E_{2,0} \cong \mathfrak{R}_+$ .

and

$$\lambda_{i,j} = \lambda_{j,i} = \lambda_{-i,-j}, \quad (2.14f)$$

where  $L=2$  has been dropped in the above  $\hat{\tau}_{L,m}$ .

The existence of cross terms between the irreducible components of different  $m$  values in Eq. (2.13) indicates that the "normal mode" components of the  $F_{\mu,i}$  are now complex linear combinations of irreducible components.<sup>21</sup> Nevertheless, there are only three independent physical quantities describing the anisotropic motion, namely the three principal values of  $\mathfrak{R}$ .

III. AN EXAMPLE: PARA-DINITROBENZENE LINEWIDTHS

The application of the theory in Sec. II to specific cases can be demonstrated in reanalyzing the experimental results of linewidth studies on the *p*-dinitrobenzene anion given in II. The linewidth data are sufficiently detailed to encourage such an investigation. Furthermore, it was shown in II that an isotropic rotational-diffusion model could not properly account for all of the experimental results. While the possibility that time-dependent fluctuations in the isotropic hyperfine interactions was suggested as a mechanism which might account for the anomalous results, it would be interesting to estimate the extent to which only an anisotropic rotational-tumbling mechanism might be able to explain them.

The theoretical and experimental studies of I and II have shown that the variation in linewidth from one

<sup>21</sup> It is not difficult to obtain the "normal modes." Thus, if we rewrite the  $\Phi_{K'M}{}^{(L)}$  of Table I as  $\Phi_{K'M}{}^{(L)} = \sum_{K''K'} c_{K''K'} \Phi_{K''M}{}^{(L)}$  (where the  $c_{K''K'}$  form a unitary matrix), the "normal modes" are

$$\mathfrak{F}_{\mu,i}{}'{}^{(L,M')} = \sum_{M''M} c_{M''M} F_{\mu,i}{}'{}^{(L,M'')}$$

and

$$j_{ij}{}^{(\mu\nu;L)}(\omega) = (2L+1)^{-1} \sum_M \mathfrak{F}_{\mu,i}{}'{}^{(L,M)} \mathfrak{F}_{\nu,j}{}'{}^{(L,M)} * \hat{\tau}_{L,M}$$

While this result is neater than Eq. (2.23), it has the disadvantage that the  $\mathfrak{F}_{\mu,i}{}'{}^{(L,M)}$  are not only functions of the principal axes and values of  $F_{\mu,i}{}'{}^{(L,M)}$ , but also of the rotational diffusion coefficients via the  $c_{K''K'}$ . Separation of these terms as in Eq. (2.23) is desirable especially when the principal axes of  $F_{\mu,i}{}'{}^{(L)}$  and  $\mathfrak{R}$  are known or can be inferred from molecular symmetries (see Sec. III).

hyperfine component to another should be describable in terms of modulations of  $g$  tensor and electron-dipolar interactions by the molecular-tumbling motion<sup>22</sup> when isotropic terms are neglected. As we have seen in Sec. II, the anisotropic relaxation will only affect the spectral densities. Thus, the following linewidth equation derived from II is still applicable:

$$[T_2(M_N; M_H)_{Av}]^{-1} = j_N^{(D)}(0)\eta(M_N) + \frac{1}{8}j_N^{(DG_2)}(0)B_0M_N + \frac{8}{3}j_H^{(D)}(0)[0.794]M_H^2 + \frac{1}{8}j_H^{(DG_2)}(0)B_0M_H + \frac{1}{8}j_{NH}^{(D)}(0) + X, \quad (3.1)$$

where  $M_N$  and  $M_H$  are the total  $z$  components of spin angular momentum for the two nitrogen nuclei and four protons, respectively;  $B_0$  is the magnetic field strength in gauss; the function  $\eta(M_N)$  has values  $\eta(\pm 2) = 10$ ,  $\eta(\pm 1) = 3$ ,  $\eta(0) = 0$ . The relaxation time  $T_2$  is a function of  $M_N$  and  $M_H$  and, as expressed in Eq. (3.1), is an average over the different components of a composite hyperfine line.<sup>1,9</sup> The term  $X$  contains all other contributions to the linewidth which are independent of  $M_H$  and  $M_N$ . Equation (3.1) is based upon the assumption that  $\omega_0^2\tau_i^2 \gg 1$  (see below), where  $\omega_0/2\pi$  is the Larmor frequency of the unpaired electron. The experimental values of the spectral densities were found to be (in reciprocal seconds)<sup>9</sup>

$$j_N^{(D)}(0) = 3.32 \times 10^4, \quad (3.2a)$$

$$j_H^{(D)}(0) \lesssim 0.09 \times 10^4, \quad (3.2b)$$

$$j_{NH}^{(D)}(0) = -0.708 \times 10^4, \quad (3.2c)$$

$$j_N^{(DG_2)}(0)B_0 = -4.32 \times 10^4, \quad (3.2d)$$

$$j_H^{(DG_2)}(0)B_0 = 0.71 \times 10^4. \quad (3.2e)$$

The superscripts  $D$  and  $DG_2$  refer to the pure dipolar and dipolar- $g$ -tensor cross terms, respectively; the subscripts N, H, and NH refer to the nitrogen nuclei, the proton nuclei, and the cross term between nitrogen and proton nuclei. The three pure-dipolar spectral densities were estimated theoretically in II assuming an isotropic rotational model with a single correlation time  $\tau_R$ , and using formulas for the anisotropic dipolar interaction given by McConnell and Strathdee.<sup>23</sup> Comparison of these calculated values with the first three of Eqs. (3.2) lead to the predictions for  $\tau_R$  of  $2.01 \times 10^{-10}$  sec,  $\lesssim 0.35 \times 10^{-10}$  sec, and  $1.36 \times 10^{-10}$  sec, respectively, where the second value is anomalously low. In re-estimating the results for anisotropic relaxation, it is first necessary to obtain irreducible tensor components in the principle axis system of the  $\mathfrak{H}$  tensor, which, because of the  $D_{2h}$  molecular symmetry, coincides with the principle axes of the  $g$  tensor. Thus, from II these are for the dipolar interactions (sub-

script  $D$ ) expressed as angular frequencies

$$F_{D,N}{}^{(0)} = 28.76 \times 10^6 \text{ sec}^{-1}, \quad (3.3a)$$

$$F_{D,N}{}^{(\pm 2)} = -0.396 \times 10^6 \text{ sec}^{-1}, \quad (3.3b)$$

$$F_{D,H}{}^{(0)} = -0.9142 \times 10^6 \text{ sec}^{-1}, \quad (3.3c)$$

$$F_{D,H}{}^{(\pm 2)} = -(3.512 \pm 3.135i) \times 10^6 \text{ sec}^{-1}, \quad (3.3d)$$

and for the  $g$ -tensor interactions with the magnetic field  $B_0$  (subscript  $G_2$ )

$$F_{G_2}{}^{(0)} = -[1/2(6)^{1/2}](2g_3 - g_1 - g_2)\beta_e\hbar^{-1}, \quad (3.4a)$$

$$F_{G_2}{}^{(\pm 2)} = -\frac{1}{4}(g_1 - g_3)\beta_e\hbar^{-1}, \quad (3.4b)$$

where  $g_1$ ,  $g_2$ , and  $g_3$  are the principal values of the  $g$  tensor along the molecule-fixed axes, and  $\beta_e$  is the Bohr magneton. The tensor components of  $\pm 1$  vanish for a planar radical. Equations (3.4) and (3.5) are given for a right-handed molecule-fixed axis system with origin at the center of the molecular plane and with the  $x'$  axis passing through the nitrogen atoms.

If terms in  $F_{D,N}{}^{(\pm 2)}$  are neglected compared to those in  $F_{D,N}{}^{(0)}$  [see Eqs. (3.3)], then the relevant spectral densities are found from Eqs. (2.13), (2.14), and (3.3) to be in reciprocal seconds:

$$j_N^D(0) = 1.65 \times 10^{14} \lambda_{00}(0), \quad (3.5a)$$

$$j_H^D(0) = [0.167\lambda_{00}(0) + 0.0886\lambda_{22}(0) + 0.0100\lambda_{-2,-2}(0) + 0.257\lambda_{0,2}(0)] \times 10^{14}, \quad (3.5b)$$

$$j_{NH}^D(0) = -[0.526\lambda_{0,0}(0) + 0.404\lambda_{0,2}(0)] \times 10^{14}, \quad (3.5c)$$

$$j_N^{(DG_2)}B_0 = 3.388(6)^{1/2}g_N^{(0)}\lambda_{00}(0) \times 10^{16}, \quad (3.5d)$$

$$j_H^{(DG_2)}B_0 = -\{1.081g_H^{(0)}\lambda_{00}(0) + 0.827g_H^{(2)}\lambda_{22}(0) + [0.827g_H^{(0)} + 2.162g_H^{(2)}]\lambda_{02}(0) + 0.827g_H^{(2)}\lambda_{-2,-2}(0)\} \times 10^{16}. \quad (3.5e)$$

Also the  $\lambda_{i,j}(0)$  may be reduced to

$$\lambda_{0,0}(0) = A/[AB - 2C^2], \quad (3.6a)$$

$$\lambda_{\pm 2,2}(0) = \frac{1}{2}(B/[AB - 2C^2] \pm 1/A), \quad (3.6b)$$

$$\lambda_{0,2}(0) = -C/[AB - 2C^2], \quad (3.6c)$$

where

$$A = 4\mathfrak{R}_3 + 2\mathfrak{R}_+, \quad (3.6d)$$

$$B = 6\mathfrak{R}_+, \quad (3.6e)$$

$$C = (6)^{1/2}\mathfrak{R}_-, \quad (3.6f)$$

and

$$\lambda_{-2,2}(0) = [\lambda_{0,2}(0)]^2/\lambda_{0,0}(0). \quad (3.6g)$$

When Eqs. (3.5a, b, c) are equated to Eqs. (3.2a, b, and c) the unique<sup>24</sup> solution is  $\mathfrak{R}_1 = -0.26 \times 10^{10} \text{ sec}^{-1}$ ,

<sup>24</sup> That the solution of these equations is unique may be seen as follows: Equation (3.5a) determines  $\lambda_{0,0}(0)$  uniquely; then Eq. (3.5c) gives  $\lambda_{0,2}(0)$ ;  $\lambda_{-2,2}(0)$  is found from Eq. (3.6g), and  $\lambda_{2,2}(0)$  from Eq. (3.5b). Then  $C = -A[\lambda_{0,2}(0)/\lambda_{0,0}(0)]$  and  $B = [A/\lambda_{0,0}(0)][\lambda_{2,2}(0) + \lambda_{-2,2}(0)]$ . In order for  $A$  and  $B$  to be positive the condition  $\lambda_{2,2} > \lambda_{-2,2}$  must be fulfilled.

<sup>22</sup> In II it was shown that electric quadrupole effects may be neglected.

<sup>23</sup> H. M. McConnell and J. Strathdee, Mol. Phys. 2, 129 (1959).

$\mathfrak{R}_2=0.25 \times 10^{10} \text{ sec}^{-1}$ , and  $\mathfrak{R}_3=-0.36 \times 10^{10} \text{ sec}^{-1}$ . The appearance of negative diffusion coefficients is physically unsound and clearly demonstrates that an anisotropic diffusion model cannot by itself account for the anomalously low value in Eq. (3.2b).

Thus far, linewidth effects due to fluctuations in isotropic hyperfine interactions have not been considered in the analysis. Such a mechanism has been found to be very important in the spectra of a number of substituted dinitrobenzenes, where it leads to the alternating linewidth phenomenon.<sup>25</sup> While it is clear that this mechanism is not very important in the *para*-dinitrobenzene spectrum, it still may be making a small contribution.<sup>9</sup> A likely possibility<sup>9</sup> is that there are small fluctuations in the ring-proton hyperfine splittings such that the splittings of protons *ortho* to one another are out-of-phase correlated,<sup>1</sup> while for protons *meta* to each other they are in-phase correlated.<sup>1</sup> It was shown in II that the coefficient of  $M_H^2$  in Eq. (3.1) must for this case be replaced by

$$\frac{1}{3} \{ 8j_H^{(D)}(0)[0.794] - j_H^{(1)}(0) \},$$

where  $j_H^{(1)}(0)$  is the spectral density generated by fluctuations in the isotropic hyperfine interactions of a proton. Thus if  $j_H^{(1)}(0)$  is sufficiently large, the coefficient of  $M_H^2$  can be made negligibly small as required by the experimental result, although  $j_H^{(D)}(0)$  is not negligible. All the other values in Eqs. (3.2) would also be somewhat affected by such a mechanism. Assuming, however, that only the experimental value of  $j_H^{(D)}$  is appreciably in error, then in order to obtain positive values of the diffusion tensor, the anisotropic relaxation model requires that  $j_H^{(D)}(0) > 0.151 \times 10^4 \text{ sec}^{-1}$ ; thus  $j_H^{(1)}(0) > 0.4 \times 10^4 \text{ sec}^{-1}$ , which is reasonable.<sup>25</sup> A reasonable guess of the value of  $j_H^{(D)}(0)$  would be one that gives a prediction of  $\tau_R$  (using an isotropic model) of the same order of magnitude as the other two values. Thus for  $j_N^D = 0.36 \times 10^4$  (equivalent to a value of  $\tau_R = 1.4 \times 10^{-10} \text{ sec}$ ), the values

$$\mathfrak{R}_1 = 0.18 \times 10^{10} \text{ sec}^{-1}, \quad (3.7a)$$

$$\mathfrak{R}_2 = 0.034 \times 10^{10} \text{ sec}^{-1}, \quad (3.7b)$$

$$\mathfrak{R}_3 = 0.052 \times 10^{10} \text{ sec}^{-1}, \quad (3.7c)$$

are obtained. The relatively large value of  $\mathfrak{R}_1$  would imply that the fastest reorientational rate is occurring about the molecular axes passing through the nitrogen atoms. The correlation times using Eqs. (3.7) are

$$\tau_0 = 3.9 \times 10^{-10} \text{ sec}, \quad (3.8a)$$

$$\tau_2 = 1.2 \times 10^{-10} \text{ sec}, \quad (3.8b)$$

$$\tau_{-2} = 2.4 \times 10^{-10} \text{ sec}, \quad (3.8c)$$

which do not differ appreciably from the results  $\tau_R$  for an isotropic model. For these correlation times and

<sup>25</sup> J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1156 (1962); J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *ibid.* **37**, 1881 (1962); J. H. Freed and G. K. Fraenkel, *ibid.* **41**, 699 (1964); J. H. Freed, thesis, Columbia University, New York (1962).

a resonance frequency of 9.2 kMc/sec,  $\omega_0^2 \tau_i^2 \cong 100 \gg 1$  consistent with our original assumption.

It should be emphasized that the quantitative results just obtained cannot be taken too seriously as they are based upon a rough guess of the correct value of  $j_H^{(D)}(0)$ . Another uncertainty involves the estimates of the dipolar terms which depend upon highly-approximate values for the pi-electron spin densities,<sup>9</sup> as well as the approximations inherent in the McConnell-Strathdee formula. It would, of course, also be helpful to have reasonably accurate values of the  $g$  tensor, so Eqs. (3.2d, e) and (3.5d, e) could be used to give further information on  $\mathfrak{R}$ .<sup>26,27</sup> The main point to be made, however, is that information of the sort obtained by linewidth studies can lead to a complete specification of the principal values of  $\mathfrak{R}$ .

Generalizing to the case of the spectrum of a radical with  $N$  nonequivalent groups of magnetic nuclei which give rise to distinguishable hyperfine splittings: there are in principle  $N$  different  $j_i^{D2}(0)$ ,  $N(N-1)/2$  different  $j_{ij}^{D}(0)$  for  $i \neq j$ , and  $N$  different  $j_i^{DG2}(0)$ . If the  $j_i^{D}(0)$  can be calculated then there are  $N(N+1)/2$  independent facts, all of which depend only upon the three principal values of  $\mathfrak{R}$ . Sufficient independent information is obtained when  $N=2$ , while for  $N>2$  it may be possible to extract out effects of fluctuations in hyperfine interactions, etc., which may be present. A knowledge of the  $g$  tensor increases the information to  $N(N+3)/2$  independent facts.

#### IV. DISCUSSION—FRICTION TENSOR

The derivation of the diffusion equation by Perrin and Favro essentially applies the method of the Fokker-Planck equation<sup>28</sup> for translational diffusion to the angular orientations of the molecule. In neglecting the effects of initial velocity on orientations, the formulation is appropriate only to times much greater than the time required for the initial angular velocity to be damped out, and then, only if the angular reorientations which occur during this velocity damping time are very small. (These conditions, taken together, are consistent with the requirements of the spin-relaxation theory as long as appreciable molecular reorientations occur in times short compared to the spin-relaxation times.) When the elementary angular reorientations are very small, the effects of noncommutativity and periodicity of the rotational motions become negligible. Under these conditions the diffusion tensor is time-independent and is related to the friction

<sup>26</sup> If the results Eqs. (3.7) are assumed, then using  $g_{av} = 2.00510$ ,<sup>9</sup> the  $g$  values are found to be  $g_1 = 2.0074$ ,  $g_2 = 2.0049$ ,  $g_3 = 2.0030$  and are almost identical to the values found in II for an isotropic model using  $\tau_R = 2 \times 10^{-10} \text{ sec}$ .

<sup>27</sup> A theory for the calculation of  $g$  tensors of aromatic free radicals has recently been developed by A. J. Stone, *Proc. Roy. Soc. (London)* **A271**, 424 (1963); *Mol. Phys.* **6**, 509 (1963); **7**, 311 (1964).

<sup>28</sup> The translational Brownian-motion case is treated in several review articles appearing in *Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, Inc., New York, 1954).

tensor  $\beta$  by

$$\mathfrak{R}_i = kT/\beta_i, \quad (4.1)$$

where  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. Now in the hydrodynamic limit when the particle in question is much larger than the fluid molecules and exhibits no slip with the fluid as it rotates, then the friction tensor depends only on the particle shape. The Stokes-Einstein relation for a sphere may be generalized to ellipsoids where  $a_1$ ,  $a_2$ , and  $a_3$  are the lengths of  $x'$ ,  $y'$ ,  $z'$  semi-axes and  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  are the principal values of the diffusion tensor about these axes in a medium of effective viscosity  $\eta^{4,5}$ :

$$\beta_i = \frac{16\pi\eta(a_j^2 + a_k^2)}{3(a_j^2 Q_j + a_k^2 Q_k)}, \quad (4.2)$$

where  $i \neq j \neq k$ , and  $Q_j$  is the elliptic integral

$$Q_j = \int_0^\infty (a_j^2 + s)^{-3/2} [(a_i^2 + s)(a_k^2 + s)]^{-1/2} ds. \quad (4.3a)$$

Also,

$$\sum_i Q_i = \frac{2}{a_i a_j a_k} \quad (4.3b)$$

and

$$\sum_i a_i^2 Q_i = \int_0^\infty \prod_j (a_j^2 + s)^{-1/2} ds. \quad (4.3c)$$

For an axially symmetric ellipsoid, letting  $a_2 = a_3$ , then the  $\beta_i$  become:

$$\beta_2 = \beta_3 = \frac{32\pi\eta(a_1^4 - a_2^4)}{3[(2a_1^2 - a_2^2)S - 2a_1]}, \quad (4.4a)$$

$$\beta_1 = \frac{32\pi\eta a_2^2(a_1^2 - a_2^2)}{3(2a_1 - a_2^2 S)}. \quad (4.4b)$$

When  $a_1 > a_2$ ,

$$S = 2(a_1^2 - a_2^2)^{-1/2} \ln \{ [a_1 + (a_1^2 - a_2^2)^{1/2}] / a_2 \}, \quad (4.4c)$$

and when  $a_1 < a_2$ ,

$$S = 2(a_2^2 - a_1^2)^{-1/2} \tan^{-1} [(a_2^2 - a_1^2)^{1/2} / a_1]. \quad (4.4d)$$

Utilizing the x-ray crystal-structure data for the neutral *para*-dinitrobenzene molecule,<sup>29</sup> the distance between oxygen nuclei at opposite ends of the molecule is 6.66 Å, and adding the van der Waals radii of the oxygens<sup>30</sup> gives 9.46 Å as  $2a_1$ . The  $y'$  axis length ( $2a_2$ ) taken as the distance between two protons *meta* to each other plus the projection of their van der Waals radii (a C-H bond length of 1.08 Å is assumed) gives 6.34 Å. The thickness of the  $\pi$  system ( $2a_3$ ) is taken as 3.40 Å. In order to employ the simpler equations for an axially symmetric ellipsoid the values of  $a_1 \cong 5$  Å, and  $a_2 \cong a_3 \cong 2.5$  Å are used. Then at  $-55^\circ\text{C}$ , where

<sup>29</sup> S. C. Abrahams, *Acta Cryst.* **3**, 194 (1950).

<sup>30</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed.

$\eta = 3$  cP,<sup>31</sup>  $\mathfrak{R}_1 = 0.16 \times 10^{10}$  sec<sup>-1</sup>, and  $\mathfrak{R}_2 = 0.085 \times 10^{10}$  sec<sup>-1</sup>, which are of the same order of magnitude as the values given in Eq. (3.7). Any more detailed comparison of these values is not justified due to the very large uncertainty in Eqs. (3.7).

Another, and perhaps more adequate interpretation may be given to  $\beta_i$ . Steele<sup>8a</sup> has shown, starting from the rotational analog to the Langevin equation,<sup>28</sup> that  $\beta_i$  for a molecule whose three principal moments of inertia  $I_i$  are equal may be approximated by

$$\beta_i^2 = (2I/\pi) \langle \partial^2 V / \partial \psi_i^2 \rangle, \quad (4.5)$$

where  $V$  is the intermolecular potential of a molecule with the surrounding molecules in the liquid, and  $\psi_i$  is the angle of orientation about the  $i$ th molecular axis. While Eq. (4.5) may not be readily useful for a quantitative calculation of  $\beta_i$ , it allows for the possibility of rotational slip. That is, if  $V$  is approximately symmetric about some molecular axis  $x$ , then  $\beta_x$  will be small, implying more rapid reorientations about that axis. If  $\beta_i$  becomes very small, then there is appreciable reorientation during the velocity damping time and the diffusion equation as we have used it will no longer be valid.<sup>8</sup> For the case of charged ions such as the *para*-dinitrobenzene anion there are large interactions of the ion with the solvent, and appreciable energy changes upon molecular reorientation are expected. Thus, ion radicals lacking a symmetric charge distribution should be characterized by well damped motions, although, reorientations about some axes may well occur more rapidly than about others. If there are strong solvent interactions with the oxygen atoms of the nitro groups, as implied in several recent ESR studies,<sup>25,32</sup> then a sensible diffusion model for the *para*-dinitrobenzene anion would call for rapid reorientations about the molecular axis passing through the nitrogen nuclei and much slower rotational diffusion about the other axes. Unfortunately, the data available for the present analysis did not permit an experimental verification of such a model.

It would be useful to obtain accurate information on the  $g$  tensor and dipolar interactions as well as to estimate the effects of fluctuations in spin density for the *para*-dinitrobenzene anion radical in order to permit a realistic comparison of an anisotropic diffusion model with the ESR linewidths in the manner described in this paper. The advent of high-resolution and sharp-line ESR should lead to improved linewidth studies on a variety of radicals, and thereby permit this technique to become a new source of information on the mechanism of molecular and ionic rotations in liquids.

<sup>31</sup> This value was obtained by a logarithmic extrapolation of  $\eta$  vs  $T^{-1}$  [C. P. Smyth, *Dielectric Behavior and Structure* (McGraw-Hill Book Company, Inc., New York, 1955), p. 119] using the viscosity data in *Physical Properties of Chemical Compounds—III*, edited by R. F. Gould (American Chemical Society, Washington, D. C., 1961), p. 444.

<sup>32</sup> J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.* **37**, 2832 (1962); P. H. Rieger and G. K. Fraenkel, *ibid.* **39**, 609 (1963).