

A general theory of the spectroscopic properties of partially ordered ensembles. I. One vector problems

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(Received 24 July 1979; accepted 28 September 1979)

We have developed a method for determining the response of a static, partially ordered ensemble of molecules to various types of electromagnetic probes. In our formalism a physical model is constructed for the orientational distribution function, which is represented as a volume integral over a set of weighting functions. Procedures are given for obtaining geometrical and statistical parameters from analysis of the oriented line shapes and intensities. Explicit treatments of linear dichroism, circular dichroism, and magnetic resonance are developed as well as detailed mathematical techniques for calculation of the distribution function.

I. INTRODUCTION

Spectroscopic experiments are ordinarily performed on a macroscopic assemblage of molecules. In many cases the species of interest are present in sufficiently low density that they can be treated as noninteracting. An idealized representation of such a sample is an ensemble of isolated, chemically identical systems. We further partition this ensemble into many smaller ensembles, each of which is homogeneous with respect to the magnetic and electronic state of the individual constituent systems; the observed response of the sample will be a weighted superposition of the response of every relevant subensemble.

In this paper we develop a general method for determining the response of any homogeneous ensemble to various types of electromagnetic probes. We can define a laboratory coordinate system which is fixed with respect to the radiation source; every member of the ensemble will have a particular orientation in this reference frame. If the interaction of an individual system to the electromagnetic field is anisotropic, the net response of the ensemble will be a sum over all possible orientations, with each term in the sum weighted by the probability that a member of the ensemble has that specific orientation.

The usual way of describing the orientation of an anisotropic system in the laboratory frame is by means of the Euler angles Θ , Φ , and Ψ , i. e., $P(\Theta\Phi\Psi)$ is the probability that a system-fixed coordinate system will be related to the laboratory axis system (LAS) by the Euler rotation matrix $M(\Theta\Phi\Psi)$ (see Appendix A). Let us represent the response of a system at orientation $(\Theta\Phi\Psi)$ by an intensity function $I(\Theta\Phi\Psi)$; then, the ensemble averaged response, \bar{I} , is given by

$$\bar{I} = \iiint I(\Theta\Phi\Psi) P(\Theta\Phi\Psi) d\Theta d\Phi d\Psi. \quad (1)$$

This formula is quite general and can be utilized with any intensity function I and any $P(\Theta\Phi\Psi)$. However, orientational averaging in the LAS is not always the most

convenient or efficient method in practice. It is possible to view the problem in a different manner which leads to an alternate formulation of Eq. (1). A great many intensity functions depend upon the coordinates of a laboratory-fixed vector \mathbf{V} in a system-fixed coordinate system. We shall designate the coordinate framework of choice the principal axis system (PAS). For linearly polarized radiation, this vector will be the direction of polarization \mathbf{P} , while for a circularly polarized field it will be the direction of propagation \mathbf{k} ; two photon problems will in general require two vectors, one for incident radiation and one for emitted radiation. The last situation will be treated in a separate publication, and requires a modification of the formalism presented here. For dependence on a single vector in the PAS, we can write

$$\bar{I} = \iint I(\theta, \phi) D(\theta, \phi) d\theta d\phi, \quad (2)$$

where $I(\theta, \phi)$ is the response of a system in which \mathbf{V} has coordinates $|\mathbf{V}|(\sin\theta \cos\phi, \sin\theta \sin\phi, \cos\theta)$ in the PAS and $D(\theta, \phi)$ is a density of states function, the probability that \mathbf{V} will be specified by (θ, ϕ) for a randomly chosen member of the ensemble.

In the above method we perform the orientational averaging in the PAS rather than the LAS. An obvious advantage is the reduction of Eq. (1) from a triple to a double integral and a corresponding simplification of the intensity and probability functions. The major difference in our approach, however, arises in the calculation of the density of states $D(\theta, \phi)$. In a previous paper¹ (Paper I), we derived a procedure for construction of $D(\theta, \phi)$ from a physical model by considering the symmetry operations needed to generate the ensemble in the LAS. The density of states function obtained in this analysis is of the form $D(\theta, \phi, \Delta)$, where $\Delta = (\Delta_1 \cdots \Delta_n)$ are parameters which determine the weighting of the various symmetry angles.

Specification of $D(\theta, \phi)$ then requires evaluation of Δ ; this is accomplished by a curve-fitting procedure. In this respect our method is similar to a moment analysis; however, the fitting parameters have a physically intuitive meaning and are likely to be fewer in number than those required by an expansion in an arbitrary set of functions. This is particularly true when some of the

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disorder in the system is due to random fluctuations or heterogeneity, e.g., a Gaussian distribution. In such cases the moment expansion will be slowly convergent and a large number of fitting parameters needed; the density of states method may be able to represent this distribution with a single parameter. For cases where only a few moments survive because of the symmetry of the intensity function, the density of states parameters provide a means of relating the nonzero moments of the distribution to structural features and/or potential energy surfaces of the ensemble.

We present here a comprehensive treatment of the density of states approach to the analysis of spectral line shapes due to partially ordered ensembles. We will consider only ensembles in the static limit in which effects of molecular motion are negligible. In Sec. II the general theory is developed without reference to a specific intensity function. Section III develops the mathematical formalism and derives a number of compact algorithms for use in actual computations. In Sec. IV, several types of spectroscopy are discussed in detail; explicit intensity formulas are determined, and summaries of the information which can be obtained from each experiment are given. In the conclusion, we compare our method with other formulations and suggest further applications.

II. GENERAL THEORY

A. Calculation of \bar{I} for a homogeneous, static ensemble

We consider an ensemble of noninteracting systems which differ only in their fixed orientations with respect to the LAS. As in Paper I, we define an intermediate axis system (IAS) which is related to the PAS by an Euler transformation $A(\beta\gamma\delta)$ (this should not be confused with the Euler rotation described in the introduction, which differs for each member of the ensemble and relates the PAS to the LAS). The IAS is constructed so that its axes lie along the symmetry axes of the ensemble elements, which are subject to alignment forces; the PAS is the coordinate system in which calculations are carried out and is related directly to the quantum mechanical parameters of the interacting species. In certain cases the intensity calculations are equally convenient in any molecule-fixed coordinate system; then, the PAS and IAS are chosen to be identical, and β , γ , and δ directly fix the molecular moments in the IAS.

The parameters β , γ , and δ therefore relate the tensor elements of the response functions to the macroscopic structural features which are responsible for the ordering. For example, a molecule may be embedded in an ensemble of aligned, anisotropic particles; analysis of the linear dichroism allows determination of the orientation of the molecular transition moment with respect to the particle symmetry axes.

Once the relevant axis systems have been defined, the spectral intensity \bar{I} is computed in the following manner:

(1) $D'(\theta', \phi')$, the density of states of \mathbf{V} in the IAS, is determined;

(2) If necessary, $D'(\theta', \phi')$ is converted to $D(\theta, \phi)$,

the density of states in the PAS. This procedure requires knowledge of the parameters β , γ , and δ ; if unknown, these quantities may be treated as fitting parameters and evaluated in the line shape analysis. Symmetry considerations may reduce the number of angles to one or two, i.e., if the IAS is axially symmetric, only two parameters are needed;

(3) $I(\theta, \phi)$, the intensity when \mathbf{V} has orientation (θ, ϕ) in the PAS, is computed. If only one molecule-fixed coordinate system is used, the intensity $I(\theta', \phi')$ is evaluated in the IAS; the parameters β , γ , and δ now enter directly into the intensity expression and may be determined as before by simulations of \bar{I} ;

(4) \bar{I} is calculated from Eq. (2).

B. Determination of $D'(\theta', \phi')$

The derivation of $D'(\theta', \phi')$ has been carried through in detail in Paper I, and explicit prescriptions for particular cases are given in Sec. III. (Note that the first sentence of Sec. B in Paper I is misprinted and it should state that we set out "to calculate a distribution function in the IAS, $D'(\theta', \phi')$, where θ' and ϕ' specify the orientation of \mathbf{H}_0 in the IAS, and then construct $D(\theta, \phi)$ for the PAS...") In this section we present a brief review of the formalism in Paper I.

The averaged intensity is originally written as

$$\bar{I} = \int_{\alpha_1} \cdots \int_{\alpha_n} I(\alpha) W(\alpha, \Delta) d\alpha, \quad (3)$$

where $\alpha = (\alpha_1 \cdots \alpha_n)$ are the n symmetry variables used in the n rotations $[R_1(\alpha_1) \cdots R_n(\alpha_n)]$ of the IAS about laboratory axes to generate the ensemble, $W(\alpha, \Delta)$ is a weighting function which gives the probability that an IAS will be characterized by a set of symmetry variables α , and the Δ_i 's are parameters of the weighting function. A coordinate transformation $(\alpha_1 \cdots \alpha_n) \rightarrow (\theta', \phi', v_1 \cdots v_{n-2})$ is performed under the constraint

$$|\mathbf{V}|(\sin\theta' \cos\phi', \sin\theta' \sin\phi', \cos\theta') \\ = \mathbf{V}'(\alpha) = \left(\prod_{i=1}^n R_i(\alpha_i) \right) \mathbf{V}, \quad (4)$$

where \mathbf{V} is the relevant electromagnetic vector in the LAS, and \mathbf{V}' is the vector \mathbf{V} in the IAS. From the n -dimensional change of variable theorem

$$\bar{I} = \int_{\theta'} \int_{\phi'} I(\theta', \phi') d\theta' d\phi' \int_{v_1} \cdots \int_{v_{n-2}} W(\theta', \phi', v_1 \cdots v_{n-2}, \Delta) \\ \times \mathcal{J}(\theta', \phi', v_1 \cdots v_{n-2}) d\mathbf{v}, \quad (5)$$

where \mathcal{J} is the Jacobian of the coordinate transformation. By inspection we can set

$$D'(\theta', \phi') = \int_{v_1} \cdots \int_{v_{n-2}} W(\theta', \phi', v_1 \cdots v_{n-2}, \Delta) \\ \times \mathcal{J}(\theta', \phi', v_1 \cdots v_{n-2}) d\mathbf{v}. \quad (6)$$

C. Conversion to the PAS

The PAS can always be related to the IAS by an Euler rotation matrix $A(\beta\gamma\delta)$. If we work directly in the IAS, the matrix A is the identity, and the geometrical pa-

rameters are incorporated directly into the intensity function. For the case when the PAS is distinct, we need to transform $D'(\theta', \phi')$ to $D(\theta, \phi)$.

In actual numerical calculations it is most convenient to perform the integration over the PAS variables θ and ϕ . The following sequence of operations is required:

- (1) Generate an orientation (θ, ϕ) of \mathbf{V} in the PAS;
- (2) Determine θ' and ϕ' from θ and ϕ via the Euler transformation, i. e., obtain $\theta'(\theta, \phi)$ and $\phi'(\theta, \phi)$;
- (3) Compute $I(\theta, \phi)$;
- (4) $D(\theta, \phi)$ is obtained from $D'(\theta', \phi')$ as explained below.
- (5) The contribution of this orientation to the integral is $I(\theta, \phi) \times D(\theta, \phi)$.

We first note that $D'(\theta', \phi')$ can always be written as (see Paper I)

$$D'(\theta', \phi') = \sin\theta' \times h'(\theta', \phi'). \quad (7)$$

The Jacobian of the transformation IAS-PAS is $\sin\theta'/\sin\theta$; thus,

$$\begin{aligned} D(\theta, \phi) &= (\sin\theta/\sin\theta') \sin\theta' h'[\theta'(\theta, \phi), \phi'(\theta, \phi)] \\ &= \sin\theta \times h'(\theta', \phi'). \end{aligned} \quad (8)$$

The angles θ' and ϕ' are obtained from the equation

$$\mathbf{V}' = A^{-1}(\beta\gamma\delta)\mathbf{V}'' \quad (9)$$

Solving for θ' , ϕ' yields

$$\theta' = \cos^{-1} \left(\frac{\sum_{i=x,y,z} A_{ix} V_i'' / |V|}{|V|} \right), \quad (10)$$

$$\phi' = \tan^{-1} \left(\frac{\sum_{i=x,y,z} A_{iy} V_i''}{\sum_{i=x,y,z} A_{ix} V_i''} \right). \quad (11)$$

When $D'(\theta')$ is axially symmetric [i. e., $D'(\theta')$ is a function only of θ'] the transformation simplifies considerably. All geometrical information is now determined by specifying the projections P_x , P_y , and P_z of the z' axis of the IAS on the three PAS axes; θ' is given by

$$\theta' = \cos^{-1}(P_x \sin\theta \cos\phi + P_y \sin\theta \sin\phi + P_z \cos\theta), \quad (12)$$

where $P_x^2 + P_y^2 + P_z^2 = 1$.

III. EVALUATION OF $D'(\theta', \phi')$ FROM A MODEL

A. Introduction

The spectroscopic simulation technique discussed in this paper is based on a distribution function $D'(\theta', \phi')$ in the IAS which we call the density of states function. Paper I outlined the theory of how $D'(\theta', \phi')$ is obtained from an arbitrary model; we present here more details of how it is obtained in practice. The key step is to determine a set of n rotations $R_1(\alpha_1) \cdots R_n(\alpha_n)$ that will generate the partially ordered ensemble of IAS's. The orientation of a given member of the ensemble is specified by $\alpha = (\alpha_1 \cdots \alpha_n)$. The density of states function is determined by the weighting function $W(\alpha, \Delta)$ which gives the probability that a member of the ensemble has orientation α . Because it takes only three angles to specify the orientation of the IAS with respect to the

LAS, one might ask why n would ever be greater than three. The answer is that the n rotations are chosen to utilize the symmetry properties of the system and allow one to write down $W(\alpha, \Delta)$. In contrast, if three rotations, such as the Euler rotations, are used, it is not possible in general to construct $W(\alpha, \Delta)$ in a straightforward fashion.

B. Density of states for a thin film

As an example, consider an ensemble of cylindrical particles that are oriented by drying in a thin film. The LAS (xyz) is defined such that the xz plane is the plane of the film with its normal along the y axis. The IAS ($x'y'z'$) will be taken with the z' axis along the long axis of the cylinder. A reasonable model for this system is that the particles tend to align such that the angle between the long axis of the cylinder and the plane of the film, α_2 , is zero. That is, the probability distribution in α_2 is

$$w_{DF}(\alpha_2, \Delta) = \exp[-E(\alpha_2, \Delta)/kT], \quad (13)$$

where $E(\alpha_2, \Delta)$ is a potential energy function with a minimum at $\alpha_2 = 0$. The ensemble of IAS's can be generated by beginning with the IAS aligned with the LAS and applying the following three rotations: a free rotation of α_1 about the z axis, a rotation of α_2 weighted by Eq. (13) about the x axis, and a free rotation of α_3 about the y axis. The probability that a particular member of the ensemble has orientation $\alpha = (\alpha_1, \alpha_2, \alpha_3)$ is given by Eq. (13).

Let \mathbf{V}' be the field direction in the IAS; then the probability that the \mathbf{V}' has spherical angles θ' and ϕ' in the IAS is given by the density of states function $D'(\theta', \phi')$. In Paper I, we showed that the Jacobian in Eq. (6) is $\sin\theta' / [|\partial V_z(\alpha)/\partial \alpha_n|_{v_1, v_2, \dots, v_{n-2}, \theta'}]$. Therefore, Eq. (6) reduces to

$$\begin{aligned} D'(\theta', \phi') &= \frac{\sin\theta'}{N} \\ &\times \int_{v_1} \cdots \int_{v_{n-2}} \frac{W[\alpha(\phi', v_1, \dots, v_{n-2}, \theta')]}{|\partial V_z(\alpha)/\partial \alpha_n|_{v_1, v_2, \dots, v_{n-2}, \theta'}} dv, \end{aligned} \quad (14)$$

where N is a normalization constant,

$$\alpha_1 = -\phi' + f_1(v_1, v_2, \dots, v_{n-2}, \theta'), \quad (15)$$

$$\alpha_2 = v_1, \quad (16)$$

⋮

$$\alpha_{n-1} = v_{n-2}, \quad (17)$$

$$\alpha_n = f_2(v_1, \dots, v_{n-2}, \theta'), \quad (18)$$

$|\partial V_z(\alpha)/\partial \alpha_n|_{v_1, \dots, v_{n-2}, \theta'}$ is the indicated partial derivative with $\alpha_2 \cdots \alpha_n$ replaced by the transformed variables in Eqs. (16)–(18), $f_1(v_1, \dots, v_{n-2}, \theta')$ and $f_2(v_1, \dots, v_{n-2}, \theta')$ are determined from the constraints in Eq. (4), and dv includes all of the necessary volume elements. To illustrate, we will consider a polarized absorption experiment on dried films done with \mathbf{V} in the LAS equal to $(\cos\psi, \sin\psi, 0)$. Application of Eq. (14) yields (see Appendix B)

TABLE I. The functional forms of $\alpha_1(\theta', \phi', x_i)$, $\alpha_2(\theta', x_i)$, and $\alpha_3(\theta', x_i)$ in Eq. (26). The normalization constant in Eq. (26) is chosen such that $\int_0^{\pi/2} d\phi' \int_0^{\pi/2} d\theta' D_{v,\psi}^{\text{RS}}[\theta', \phi', W] = 1$; Q is chosen to insure convergence of the numerical integration formula ($Q = 25$ is usually sufficient).

RS	v	$\alpha_2(\theta', x)$	$\alpha_3(\theta', x)$	$\alpha_1(\theta', \phi', x)$
zyz	1	$\cos^{-1} [\sin\theta' \sqrt{(1-x)/2}]$	$\psi \pm \cos^{-1} \left(\frac{\cos\theta'}{\sin\alpha_2} \right)^a$	$-\phi' + \cos^{-1} (\cot\alpha_2 \cot\theta')$
zyz	2	$\cos^{-1} (x \cos\psi \sin\theta' + \sin\psi \cos\theta')$	$\cos^{-1} \left(\frac{\cos\theta' - \sin\psi \cos\alpha_2}{\cos\psi \sin\alpha_2} \right)^b$	$-\phi' + \sin^{-1} \left(\left \frac{\cos\psi \sin\alpha_3}{\sin\theta'} \right \right)$
zyz	3	$\cos^{-1} (x \cos\psi \sin\theta' + \sin\psi \cos\theta')$	$\sin^{-1} \left(\frac{\cos\theta' - \sin\psi \cos\alpha_2}{\cos\psi \sin\alpha_2} \right)^b$	$-\phi' + \sin^{-1} \left(\left \frac{\cos\psi \cos\alpha_3}{\sin\theta'} \right \right)$
zxy	1	$\sin^{-1} (x \cos\psi \sin\theta' - \sin\psi \cos\theta')$	$\sin^{-1} \left(\frac{\cos\theta' + \sin\psi \sin\alpha_2}{\cos\psi \cos\alpha_2} \right)^c$	$-\phi' + \sin^{-1} \left(\left \frac{\cos\psi \cos\alpha_3}{\sin\theta'} \right \right)$
zxy	2	$\sin^{-1} [\sin\theta' \sqrt{(1+x)/2}]$	$\pm \psi + \sin^{-1} \left(\frac{\cos\theta'}{\cos\alpha_2} \right)^a$	$-\phi' + \sin^{-1} (\tan\alpha_2 \cot\theta')$
zxy	3	$\sin^{-1} (x \sin\theta' \sin\psi - \cos\psi \cos\theta')$	$\cos^{-1} \left(\frac{\cos\theta' + \cos\psi \sin\alpha_2}{\sin\psi \cos\alpha_2} \right)^c$	$-\phi' + \sin^{-1} \left(\left \frac{\sin\psi \sin\alpha_3}{\sin\theta'} \right \right)$

^aBoth the + and - forms of $\alpha_3(\theta', x)$ must be included in the sum in Eq. (26).

^bThese formulas are inconvenient when the denominators are zero; instead use $D_{2,\pi/2}^{\text{RS}}[\theta', \phi', w] = D_{3,\pi/2}^{\text{RS}}[\theta', \phi', w] = (\sin\theta'/N) \int_0^{\pi/2} w(\alpha_1, \alpha_2, \alpha_3) d\alpha_3$, where $\alpha_1 = \phi'$ and $\alpha_2 = \theta'$.

^cThese formulas are inconvenient when the denominators are zero; instead use $D_{1,\pi/2}^{\text{RS}}[\theta', \phi', w] = D_{3,0}^{\text{RS}}[\theta', \phi', w] = (\sin\theta'/N) \int_0^{\pi/2} w(\alpha_1, \alpha_2, \alpha_3) d\alpha_3$, where $\alpha_1 = \pi/2 - \phi'$, and $\alpha_2 = \theta' - \pi/2$.

$$D'(\theta') = \frac{\sin\theta'}{N} \int_{-\theta-\psi}^{\theta-\psi} \cos v_1 w_{DF}(v_1, \Delta) \{[\sin v_1 + \sin(\theta + \psi)] \times [\sin(\theta - \psi) - \sin v_1]\}^{-1/2} dv_1. \quad (19)$$

Note that $D'(\theta')$ is axially symmetric. In fact, any density of states derived from a rotation scheme where the first rotation is unrestricted will be axially symmetric. The reason is that the only occurrence of ϕ' in Eqs. (14)–(18) is in the equation for α_1 , and if the first rotation is unrestricted [i.e., $W(\alpha, \Delta)$ independent of α_1], $D'(\theta')$ will be independent of ϕ' .

C. Three-rotation density of states: evaluation by Chebyshev quadratures

The integral in Eq. (19) must be evaluated numerically, a task which is complicated by the fact that the integrand has singularities at the endpoints. All density of states calculations that we have attempted have similar singularities, but the problem can be circumvented. By making the substitution

$$v_1(x) = \sin^{-1}(x \sin\theta \cos\psi - \sin\psi \cos\theta), \quad (20)$$

Eq. (19) can be transformed to

$$D'(\theta') = \frac{\sin\theta'}{N} \int_{-1}^1 w_{DF}[v_1(x), \Delta] (1-x^2)^{-1/2} dx. \quad (21)$$

The function $(1-x^2)^{-1/2}$ is the kernel for Chebyshev quadrature, and therefore Eq. (21) is trivial to evaluate by numerical techniques. The result to Q th order quadrature is

$$D'(\theta') = \frac{\pi \sin\theta'}{QN} \sum_{i=1}^Q w_{DF}[v_1(x_i), \Delta], \quad (22)$$

where

$$x_i = \cos\left(\frac{2i-1}{Q} \frac{\pi}{2}\right). \quad (23)$$

The dried film model is an example of a zxy rotation scheme. If one picks the z axis as the axis of the first rotation, the only possible three-rotation schemes are zxy , zyx , zyz , zxx . Furthermore, zxy and zyz are related to zyx and zxx by a simple exchange of x and y , which means that the only two unique three-rotation schemes are zxy and zyz . We will now consider all possible three-rotation density of states, but first it is convenient to introduce a general notation for density of states functions. The notation is

$$D_{v,\psi}^{\text{RS}}[\theta', \phi', w], \quad (24)$$

where RS is the rotation scheme (e.g., zyz , zxy , $zxyz$, etc.), v is the type of \mathbf{V} field vector [$v=1$ for $\mathbf{V}=(\cos\psi, \sin\psi, 0)$, $v=2$ for $\mathbf{V}=(\cos\psi, 0, \sin\psi)$, and $v=3$ for $\mathbf{V}=(0, \cos\psi, \sin\psi)$], ψ is the angle of the \mathbf{V} field vector, and w is the weighting function. Note that $D_{v,\psi}^{\text{RS}}[\theta', \phi', w]$ is a function of the weighting function w and is therefore a functional. We denote this functional quality with square brackets. As an example, the density of states for dried films in Eq. (22) is denoted by

$$D'(\theta') = D_{1,\psi}^{\text{RS}}[\theta', w_{DF}]. \quad (25)$$

We find that all three rotation density of states can be reduced to Chebyshev quadrature integrals. Analogous to Eq. (22), we write in the new notation

$$D_{v,\psi}^{\text{RS}}[\theta', \phi', w_{DF}] = \frac{1}{N} \sum_{i=1}^Q w\{\alpha_1(\theta', \phi', x_i), \alpha_2(\theta', x_i), \alpha_3(\theta', x_i)\}, \quad (26)$$

where x_i is given by Eq. (23) and N is a normalization constant. In Table I we quote the functional form of $\alpha_1(\theta', \phi', x_i)$, $\alpha_2(\theta', x_i)$, and $\alpha_3(\theta', x_i)$ for RS equal to zyz and zxy , and v equal to 1, 2, and 3.

D. Four-rotation density of states

Next we proceed to the density of states for models that require four rotations. In general, these are much

more difficult, and we will treat only axially symmetric $D'(\theta', \Delta)$; i.e., the cases when $W(\alpha, \Delta)$ is independent of α_1 . As will be explained later, it is straightforward to extend our results to cases that lack axial symmetry. We also make the simplifying assumption that the weighting function can be factored to

$$W(\alpha) = w_1(\alpha_4)w_2(\alpha_2\alpha_3). \tag{27}$$

This assumption is not crucial, but it is adequate for the density of states that we have been concerned with; furthermore, it leads to a simplification of the formulas.

Let us consider an example: we will calculate $D_{1,\phi}^{xy\epsilon}[\theta', \phi', w_1w_2]$. Application of Eq. (14) yields (see Appendix C)

$$D_{1,\phi}^{xy\epsilon}[\theta', w_1w_2] = \frac{\sin\theta'}{N'} \int_0^{2\pi} dv_2 w_1(v_2) \int_{-\theta'-\psi+v_2}^{\theta'-\psi+v_2} \cos v_1 w_2\{v_1, \alpha_3(v_1, v_2, \theta')\} \times \{[\sin v_1 + \sin(\theta' + \psi - v_2)][\sin(\theta' - \psi + v_2) - \sin v_1]\}^{-1/2} dv_1. \tag{28}$$

The v_1 integral together with the $\sin\theta'$ is identical to Eq. (19), except that ψ in Eq. (19) is replaced by $\psi - v_2$, there is no normalization constant, and w_{DF} is replaced by w_2 . Because the normalization constant in Eq. (19) is independent of ψ , we can write

$$D_{1,\phi}^{xy\epsilon}[\theta', w_1w_2] = \frac{1}{N'^{1/2}} \int_0^{2\pi} dv_2 w_1(v_2) D_{1,\psi-v_2}^{xy}[\theta', w_2]. \tag{29}$$

We now utilize the symmetry properties of $w_1(v_2)$ and $D_{1,\psi}^{xy}[\theta', w_2]$ to simplify Eq. (29). Because partial order is induced by some force the sign of whose direction is

arbitrary, $w_1(v_2)$ is periodic with period π and symmetric about $\pi/2$; i.e.,

$$w_1(v_2) = w_1(v_2 + \pi), \tag{30}$$

$$w_1(v_2) = w_1(\pi - v_2).$$

For weighting functions possessing these symmetry properties, the density of states has similar symmetry properties with respect to ψ ; i.e.,

$$D_{1,\psi}^{xy}[\theta', w_2] = D_{1,\psi+\pi}^{xy}[\theta', w_2], \tag{31}$$

$$D_{1,\psi}^{xy}[\theta', w_2] = D_{1,\pi-\psi}^{xy}[\theta', w_2].$$

Finally, using Eqs. (31) and (30), Eq. (29) reduces to

$$D_{1,\phi}^{xy\epsilon}[\theta', w_1w_2] = \frac{2}{N'^{1/2}} \int_0^{\pi/2} d\mu D_{1,\mu}^{xy}[\theta', w_2] \times \{w_1(\psi - \mu) + w_1(\psi + \mu)\}. \tag{32}$$

Equation (32) may not appear simpler than Eq. (29), but the extent of integration is decreased from the interval 0 to 2π to the interval 0 to $\pi/2$. When numerical integration techniques are used this reduction will save computer time.

In Table II, we present many four-rotation density of states functions. Five characteristics of these functions are as follows: (1) If the field has no component along the axis of the last rotation, the density of states can always be written as an integral over a three-rotation density of states analogous to Eq. (32); (2) If the field is along the axis of the last rotation, the last rotation is superfluous and the density of states is identical to the density of states function for the first three rotations; (3) If the field has a nonzero component along the axis of the last rotation and a nonzero component along another axis, evaluation of the density of states becomes very complicated. We do not consider this case; (4) These formulas are formally valid for non-axially-symmetric systems, except that new functional forms for α_1 in Table I must be used. These functional forms (which we have not evaluated) can be found from the constraints in Eq. (4); (5) When only the second rotation is weighted, the v_2 integral can be rewritten as a complete elliptical integral. When computer time is limited, this approach can save computer time.

IV. EXPLICIT CALCULATION OF SPECTROSCOPIC PROPERTIES

A. Linear dichroism

The simplest technique that we shall discuss is linear dichroism (LD). The probability that a molecular transition will be excited by a linearly polarized field \mathbf{E} is given by

$$P = |\boldsymbol{\mu} \cdot \mathbf{E}|^2 = |\boldsymbol{\mu}| |E| \cos^2\epsilon, \tag{33}$$

where $\boldsymbol{\mu}$ is the transition dipole moment and ϵ the angle between $\boldsymbol{\mu}$ and \mathbf{E} . We define an IAS for the absorbing species in accordance with the criteria of Secs. II and III. Here no PAS is needed because the response tensor of the system is diagonal in any coordinate system, i.e.,

TABLE II. Functional form of many density of states for ensembles generated by four rotations. The normalization constant is chosen such that $\int_0^{2\pi} d\theta' \int_0^{2\pi} d\phi' D_{v,\psi}^{RS}[\theta', \phi', W] = 1$: w_1 and w_2 are the weighting functions for the last rotation and the second and third rotations, respectively (see text); the three-rotation density of states can be evaluated by use of Eq. (26) and Table I.

RS	v	ψ^a	$D_{v,\psi}^{RS}[\theta', \phi', w]$
zyzy	1	$\pi/2$	$D_{1,\pi/2}^{xy\epsilon}[\theta', \phi', w_2]$
zyzy	2	All	$\frac{1}{N} \int_0^{\pi/2} D_{2,\mu}^{xy\epsilon}[\theta', \phi', w_2] [w_1(\mu - \psi) + w_1(\pi - \mu - \psi)] d\mu$
zyzy	3	0	$D_{1,\pi/2}^{xy\epsilon}[\theta', \phi', w_2]$
zyzx	1	0	$D_{1,\pi/2}^{xy\epsilon}[\theta', \phi', w_2]$
zyzx	2	0	$D_{1,\pi/2}^{xy\epsilon}[\theta', \phi', w_2]$
zyzx	3	All	$\frac{1}{N} \int_0^{\pi/2} D_{3,\mu}^{xy\epsilon}[\theta', \phi', w_2] [w_1(\mu - \psi) + w_1(\pi - \mu - \psi)] d\mu$
zxzx	1	0	$D_{1,\pi/2}^{xy\epsilon}[\theta', \phi', w_2]$
zxzx	2	0	$D_{1,\pi/2}^{xy\epsilon}[\theta', \phi', w_2]$
zxzx	3	All	$\frac{1}{N} \int_0^{\pi/2} D_{3,\mu}^{xy\epsilon}[\theta', \phi', w_2] [w_1(\mu - \psi) + w_1(\pi - \mu - \psi)] d\mu$
zxyz	1	All	$\frac{1}{N} \int_0^{\pi/2} D_{1,\mu}^{xy\epsilon}[\theta', \phi', w_2] [w_1(\mu - \psi) + w_1(\pi - \mu - \psi)] d\mu$
zxyz	2	$\pi/2$	$D_{2,\pi/2}^{xy\epsilon}[\theta', \phi', w_2]$
zxyz	3	$\pi/2$	$D_{2,\pi/2}^{xy\epsilon}[\theta', \phi', w_2]$

^aThese are the values of ψ for which the formula is valid.

$$P = \begin{bmatrix} \mu_x & & 0 \\ & \mu_y & \\ 0 & & \mu_z \end{bmatrix} \cdot \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}^2 \quad (34)$$

We therefore work directly in the IAS, dropping the prime on $D(\theta, \phi)$, θ , and ϕ . Writing

$$\mathbf{E}_{\text{IAS}} = (\sin\theta \cos\phi \sin\theta \sin\phi \cos\theta) \quad (35)$$

and

$$\boldsymbol{\mu}_{\text{IAS}} = (\mu_x \mu_y \mu_z),$$

we obtain

$$I_{\text{LD}}(\theta, \phi) = (\mu_x \sin\theta \cos\phi + \mu_y \sin\theta \sin\phi + \mu_z \cos\theta)^2. \quad (36)$$

The dichroic ratio R is defined as the ratio of absorbance when \mathbf{E} is perpendicular or parallel to a particular laboratory-fixed direction (usually the alignment direction); then, in the density of states formalism,

$$R = \frac{\iint I_{\text{LD}}(\theta, \phi) \times D_{\parallel}(\theta, \phi) d\theta d\phi}{\left(\iint I_{\text{LD}}(\theta, \phi) \times D_{\perp}(\theta, \phi) d\theta d\phi \right)^{-1}}, \quad (37)$$

where $D_{\parallel}(\theta, \phi)$ is the density of states function in the IAS with \mathbf{E} parallel to \hat{z}_{LAS} , and $D_{\perp}(\theta, \phi)$ is the density of states with \mathbf{E} perpendicular to \hat{z}_{LAS} . Both $D_{\perp}(\theta, \phi)$ and $D_{\parallel}(\theta, \phi)$ depend upon the same set of parameters which characterize the weighting function W .

One can simplify this formula considerably for cases where D has axial symmetry. A detailed analysis of this and other results along with a set of calculations on various experimental systems are presented in a separate paper.² We note here that the variables in a linear dichroism calculation are

- (1) the parameters Δ_i of the density of states;
- (2) the projections μ_x , μ_y , and μ_z of the transition dipole moment on the x , y , and z axes of the IAS.

Only two of these are independent, since $\mu_x^2 + \mu_y^2 + \mu_z^2 = |\boldsymbol{\mu}|^2$, the dipole strength. For an axially symmetric IAS, μ_x and μ_y are equivalent, and only μ_z can be determined unambiguously.

B. Circular dichroism

The circular dichroism (CD) of an ensemble is the difference in absorption of left and right circularly polarized light. To simplify the formalism we consider an ensemble of identical, noninteracting molecules with a single allowed electronic transition to excited state i ; the transition moment is $\boldsymbol{\mu}_{0i}$, and the wave functions of the ground and excited states are ψ_0 and ψ_i , respectively.

Circular dichroism is measured as a function of wavelength across the molecular absorption envelope. To first order, the CD line shape for a single transition will follow that of the absorption band; the response of the ensemble can therefore be characterized by a single parameter, the ensemble averaged rotational strength \bar{R} . Experimentally, we obtain \bar{R} from the equation

$$\bar{R} = [3(2303)\hbar c/16\pi^2 N] \int_0^\infty (\Delta\epsilon/\beta\lambda) d\lambda, \quad (38)$$

where $\Delta\epsilon$ is the differential extinction coefficient, $\epsilon_L - \epsilon_R$, for left and right circularly polarized light, respectively, and $\beta = [(3/\eta^2) + 2]$ is the refractive index correction.

The rotational strength due to an individual molecule will depend upon the orientation of the direction of propagation \mathbf{s} of the circularly polarized electromagnetic field in a molecule-fixed coordinate system. Tinoco has shown³ that for light propagating along the \hat{z} direction, the rotational strength is given by

$$R_z = (3e/2mc) \text{Im}[\mu_{y0i}(r_z p_x)_{i0} - \mu_{x0i}(r_z p_y)_{i0}], \quad (39)$$

where

$$\mu_{k0i} = \hat{k} \cdot \boldsymbol{\mu}_{0i}$$

and

$$(r_k p_j)_{0i} = \iiint \psi_0(r_k p_j) \psi_i d\tau.$$

r_k and p_j are the k th component of the position operator and j th component of the momentum operator, respectively, for the electron promoted in the $0 \rightarrow i$ transition.

x and y are directions normal to z and to each other; note that R_z is independent of the precise choices of x and y , because the circular polarization of \mathbf{E} renders directions normal to \hat{z} equivalent.

We can write a general expression for R in tensor form, using dyadic notation, as

$$R_z = \hat{z} \cdot \mathbf{R} \cdot \hat{z} \quad (40)$$

where

$$\mathbf{R} = \frac{1}{2} [\boldsymbol{\mu}_{0i} \times (\mathbf{pr})_{i0} - (\mathbf{rp})_{i0} \times \boldsymbol{\mu}_{0i}].$$

We define j , k , and l as an arbitrary molecule-fixed coordinate system; \hat{z} is expressed in this coordinate system as

$$\hat{z} = (a_j \hat{j} + a_k \hat{k} + a_l \hat{l}). \quad (41)$$

Substituting Eq. (41) into Eq. (40) and evaluating the elements of \mathbf{R} in the j , k , l coordinate system, we obtain

$$R_z = \sum_{n=j,k,l} \sum_{m=j,k,l} R_{nm} a_n a_m. \quad (42)$$

We can eliminate the cross terms in Eq. (42) by finding a coordinate system in which \mathbf{R} is diagonal. Because \mathbf{R} is a symmetric tensor ($R_{ki} = R_{ik}$), this is always possible; then

$$\mathbf{R} = \begin{bmatrix} R_{xx} & & 0 \\ & R_{yy} & \\ 0 & & R_{zz} \end{bmatrix}. \quad (43)$$

The x , y , z coordinate system then becomes the PAS. Writing the unit propagation vector in the PAS as

$$\hat{s} = (\sin\theta \cos\phi \sin\theta \sin\phi \cos\theta), \quad (44)$$

we obtain

$$R_s = \hat{s} \cdot \mathbf{R} \cdot \hat{s} \\ = R_{xx} \sin^2 \theta \cos^2 \phi + R_{yy} \sin^2 \theta \sin^2 \phi + R_{zz} \cos^2 \theta, \quad (45)$$

and thus

$$\bar{R} = \iint D(\theta, \phi) \times R_s d\theta d\phi \\ = R_{xx} \iint \sin^2 \theta \cos^2 \phi D(\theta, \phi) d\theta d\phi + R_{yy} \iint \sin^2 \theta \\ \times \sin^2 \phi D(\theta, \phi) d\theta d\phi + R_{zz} \iint \cos^2 \theta D(\theta, \phi) d\theta d\phi. \quad (46)$$

In the general case $D(\theta, \phi)$ is determined from $D'(\theta', \phi')$ as in Sec. II; the angles β , γ , and δ relate the axes which diagonalize the rotational strength tensor to the symmetry axes of the macroscopic chromophore-containing system. When $D'(\theta')$ is axially symmetric, it is possible to eliminate the ϕ' integral by working directly in the IAS. In this coordinate system \mathbf{R}' is not diagonal, so all the terms in Eq. (42) must be retained. Setting

$$\hat{s}' = (\sin \theta' \cos \phi' \sin \theta' \sin \phi' \cos \theta') \quad (47)$$

in the IAS we obtain

$$R'_s = \hat{s}' \cdot \mathbf{R}' \cdot \hat{s}', \quad (48)$$

$$\bar{R} = \iint R'_s D'(\theta') d\theta' d\phi' \\ = \int D'(\theta') d\theta' \int d\phi' \sum_{n=x,y,z} \sum_{m=x,y,z} R'_{nm} a_n a_m, \quad (49)$$

where

$$a_x = \sin \theta' \cos \phi',$$

$$a_y = \sin \theta' \sin \phi',$$

$$a_z = \cos \theta',$$

and the R'_{nm} are the elements of \mathbf{R} in the IAS.

Evaluation of the ϕ' integral yields

$$\bar{R} = R'_{zz} \int_0^{\pi/2} D'(\theta') \cos^2 \theta' d\theta' \\ + \frac{1}{2} (R'_{xx} + R'_{yy}) \int_0^{\pi/2} D'(\theta') \sin^2 \theta' d\theta'. \quad (50)$$

Note that the diagonal elements here are not identical to those in the PAS. It is simply the case that, for an ensemble of axially symmetric IAS's, one can determine only a rotational strength perpendicular $[\frac{1}{2}(R'_{xx} + R'_{yy})]$ and parallel (R'_{zz}) to the symmetry axis. Relating these quantities to the molecular rotation tensor principal components requires knowledge of the transformation which links the PAS to the IAS.

We summarize below the complete set of parameters which characterize the partially ordered ensemble of optically active chromophores:

- (1) The Δ_i 's which determine $D'(\theta', \phi')$;
- (2) The angles β , γ , δ , which relate the IAS to the CD tensor;
- (3) The principal components R_{xx} , R_{yy} , and R_{zz} of the rotational strength tensor.

An interesting application of partially ordered CD

would be to investigate aggregated chromophores, such as dimers. Here the principal components can be related to the geometry of the aggregate in straightforward fashion if the rotational strength is due primarily to electric dipole interactions between the constituent molecules. A set of equations for the relative monomer orientations would be obtained which are different from those for isotropic CD.

C. Magnetic resonance

Paper I was explicitly concerned with analysis of magnetic resonance line shapes and presented a specific application of the theory to one such problem. Here we adopt a more general viewpoint, placing the magnetic resonance calculations in a wider context by contrasting them with those needed for other spectroscopic methods. We also extend the discussion to systems where the spin functions are not quantized along the direction of the Zeeman field \mathbf{H}_0 (i.e., where the high field approximation is not valid).

From a mathematical point of view the magnetic resonance experiment is unique because of the laboratory-fixed \mathbf{H}_0 field; the orientation dependence is introduced directly into the Hamiltonian via the Zeeman interaction. This is in contrast with the optical experiments (CD and LD) or scattering in which the oscillator strength and/or the direction of polarization is orientation independent.

One consequence of this is that it is impossible to choose a PAS in which the linear response tensor is diagonal for all orientations. The PAS is therefore selected to facilitate diagonalization of the Hamiltonian. Suppose we have a magnetic system characterized by a Hamiltonian (excluding the Zeeman interaction) \mathcal{H}_s . We choose a convenient coordinate system (PAS) and basis set defined in this coordinate system and write \mathcal{H}_s in matrix form;

$$\mathcal{H}_s = \begin{bmatrix} \mathcal{H}_{11} & & & \\ & \cdot & & \\ & & \cdot & \\ & & & \mathcal{H}_{kk} \end{bmatrix}, \quad (51)$$

where $\mathcal{H}_{ij} = \langle \phi_i | \mathcal{H}_s | \phi_j \rangle$ and $\{\phi_i\}_{i=1,k}$ is a set of k basis functions which span the spin space. The Zeeman field is now expressed in the PAS as

$$\mathbf{H}_0 = |H| (\sin \theta \cos \phi \sin \theta \sin \phi \cos \theta), \quad (52)$$

and an interaction matrix \hat{Z} is defined with elements

$$Z_{ij} = \langle \phi_i | \sum_{l=1,k} \beta \mathbf{S}_l \cdot \hat{g}_l \cdot \mathbf{H}_0 | \phi_j \rangle, \quad (53)$$

where \hat{g}_l is the g tensor for electron l in the PAS, \mathbf{S}_l the spin operator for electron l , and β the Bohr magneton. The total spin Hamiltonian is then found to be

$$\hat{\mathcal{H}}_m = \hat{\mathcal{H}}_s + \hat{Z}. \quad (54)$$

Then $\hat{\mathcal{H}}_m$ is diagonalized, energies $E_1 \cdots E_k$ and eigenfunctions $\psi_1 \cdots \psi_k$ are obtained and oscillator strengths O_{ij} for the $k(k-1)/2$ transitions of energy $U_{ij} = |E_i - E_j|$ are computed via the relation

$$O_{ij} = \left(\langle \psi_i | \frac{1}{2} \sum_x S_{ix} | \psi_j \rangle | H_1 | \right)^2, \quad (55)$$

where x is a direction normal to H_0 , and all directions in the plane are equivalent with respect to the rotating H_1 field.

The intensity $I(\theta, \phi)$ at H_0 is then

$$I(\theta, \phi, H_0) = \sum_i \sum_{j < i} O_{ij} f_{ij}(U_{ij} - H_0), \quad (56)$$

where f_{ij} is the broadening function for the individual ij th transition [e.g., $f_{ij} = \exp[-(U_{ij} - H_0)^2/\lambda^2]$ for a Gaussian line of half-width λ].

The averaged intensity $\bar{I}(H_0)$ is computed for each H_0 in the usual manner; $D(\theta, \phi)$ is determined as in Secs. II and III, and $A(\beta\gamma\delta)$ relates the IAS to the coordinate system in which \mathcal{H}_c is expressed (PAS).

The above procedure is valid for all field strengths and magnetic Hamiltonians and entails no serious approximations. The diagonalization of \mathcal{H}_m can be carried out numerically, although perturbative solutions can be sought if desired. In the high field limit the oscillator strengths O_{ij} assume a simple form with a suitable choice of basis (i.e., $\Delta m_s = \pm 1$), and this aspect of the calculation can be made trivial.

A major advantage of the magnetic resonance technique for analysis of partially ordered systems is that the entire line shape as a function of H_0 can be used as data to be fitted. Whereas a linear dichroism experiment yields only a single number, the dichroic ratio, the magnetic resonance experiment provides a set of amplitudes $\bar{I}_i(H_0^i)$, where i runs over all field positions necessary to characterize the spectrum. The exact number of independent points will depend upon the nature of the magnetic Hamiltonian. For a molecular triplet, for example, the intensities of the four canonical peaks Z , X , Y_1 , and Y_2 will specify the entire line shape.

V. CONCLUSION

There are three classes of parameters which can be determined from the study of partially ordered ensembles by spectroscopic methods:

(1) Parameters which describe the macroscopic ordering of the ensemble. In the density of states approach, this information is embodied in the form of the weighting functions w_i and the values of the components of Δ .

(2) Parameters relating the symmetry axes of the macroscopically ordered system to the quantum mechanically determined axes of the interacting molecular species. These are represented by the three Euler angles, $\beta\gamma\delta$, which transform the PAS to the IAS or, for the case of axial symmetry, by the projections P_x , P_y , and P_z (two of which are independent) of the z' axis of the IAS on the PAS x , y , and z axes.

(3) Fundamental molecular interaction parameters, e.g., elements of the polarizability tensor, matrix elements of the spin Hamiltonian, etc.

In any simulation procedure one begins with a set of

N experimental values $E_1 \cdots E_n$, and varies M parameters $P_1 \cdots P_m$ until an adequate fit is obtained. The accuracy to which the parameters can be specified is dependent in a complex way upon the ratio N/M and the details of the calculations. Examples can be found in Refs. 1 and 2, in which regions of solution are delineated for EPR and LD experiments.

If certain parameters can be determined independently, it will be possible to evaluate the remainder with more precision. For example, one might work with an ensemble of known geometry [i.e., parameters in classes (1) and (2) are well characterized] to evaluate elements of the optical rotation tensor. Conversely, the details of molecular quantum mechanics may be amenable to theoretical calculation, in which case geometrical information can be extracted more accurately.

One way of increasing the ratio of experimental data to unknown parameters is to perform more than one spectroscopic experiment on the same sample. Then, the Δ parameters will be identical for both experiments, and the overall N/M ratio will increase. A special case of this strategy is to determine Δ with one experiment in which N/M is favorable and then use these results in evaluating other parameters in a second experiment. This has been done in Ref. 2 (LD) using the Δ calculated in an EPR experiment.¹

We now turn to an assessment of the value of the density of states approach. It is clear that parameters of class (2) and (3) should enter into any calculation in the same manner. We have in this paper clarified the place of these quantities in the theory and avoided the necessity of approximations (e.g., direct diagonalization of the magnetic resonance Hamiltonian), but this could in principle be done for an approach like that of moment expansions. The significant difference between formulations must therefore lie in the description of the macroscopic ordering of the ensemble.

The construction of the density of states function requires formulation of a physical model for the ordering of the constituent systems of the ensemble. If such a model cannot be hypothesized because of lack of insight into the ordering process, our approach cannot be used. In this case an analysis of the distribution function via an expansion in Wigner rotation matrix elements $D_{mm}^l(\theta\phi\psi)^{4,5}$ is the best one can do, and provides all available information.

It is questionable, however, whether such an analysis would be worth pursuing. The information obtained is of limited value if the basic organization of the ensemble is not understood. If a model can be constructed, the density of states approach possesses formal mathematical advantages and facilitates greater physical insight.

We first consider the cases where only the second moment of the distribution function survives, i.e., the integral of the intensity function is nonzero only when convoluted with the $l=2$ terms in the Wigner expansion; both CD and LD fall into this category. It would seem that a moment expansion, focusing on the small number of contributing elements, would be preferable here.

A closer analysis, however, reveals the following benefits from adopting the density of states formalism:

(1) The Δ parameters have greater physical meaning than the coefficients of the Wigner expansion. In fact, one could interpret the moments P_{lmn} in terms of the Δ_i by an equation

$$P_{lmn} = \iiint D_{mn}^l(\Theta\Phi\Psi)F(\Theta\Phi\Psi, \Delta) d\Theta d\Phi d\Psi,$$

where $F(\Theta\Phi\Psi, \Delta)$ is a distribution function which could be derived from $D(\theta, \phi)$ by converting from the PAS to the LAS. Each Δ_i is related to some structural or energetic feature of the ensemble and, as such, is a quantity of interest; the moment P_{lmn} is a mathematical projection of the intensity function on the distribution function $P(\Theta\Phi\Psi)$ and has no intrinsic utility.

(2) It may be possible to place limits on Δ from physical considerations and so restrict the second moment. These limits could not be placed directly on the P_{lmn} because there would be no justification for this procedure. If parameters of class (2) or (3) need to be determined, restriction of the distribution function to a narrower range may be extremely helpful.

(3) In situations lacking axial symmetry, a number of moments (i. e., $l=2, m=0, \pm 1$) have nonzero projection on the intensity; in such cases there may be fewer Δ_i than moment fitting parameters. The density of states formalism is then able to eliminate nonphysical configurations of moments from considerations. If the reverse is true (more Δ_i than moments) only computer time is sacrificed, because the correct moments are projected out of $D(\theta, \phi)$ by the intensity function.

In the magnetic resonance experiment, all moments may contribute to the observed line shape. Here the convergence problems of the moment expansion are serious and are usually treated by applying perturbation methods to diagonalization of the spin Hamiltonian to restrict the number of moments. Our approach obviates this difficulty directly and, if anything, is more efficient in computer time. No decisions need to be made vis-à-vis approximating solutions to the magnetic Hamiltonian or truncating the series expansion for the distribu-

tion function; confidence in the data analysis is correspondingly greater. Insofar as the original model for the ensemble is valid, the theory delineates the ranges of values of the parameters as accurately as is possible in principle; insofar as the model is deficient, the information obtained in any analysis would be of limited utility.

Finally, we believe that the general approach outlined here facilitates interpretation of subtle and complex changes in observed spectroscopic properties upon orientation. A systematic application of the suggested techniques will result in an extraction of all meaningful data and an appreciation of the range of parameter values consistent with experiment. Furthermore, because a working geometrical representation has been developed, the angles, distances, and matrix elements obtained can be placed in the appropriate context.

ACKNOWLEDGMENTS

This work was supported, in part, by the Biomedical and Environmental Research Division of the U. S. Department of Energy under contract No. 2-7405-ENG-48 and, in part, by National Science Foundation Grant PCM 76-5074.

APPENDIX A: EULER ROTATION MATRICES

We follow the convention used in Arfken,⁶ p. 179, and define an Euler rotation matrix M as

$$M(\Theta\Phi\Psi) = R_z(\Theta)R_y(\Phi)R_z(\Psi), \quad (\text{A1})$$

where

$$R_z(\Theta) = \begin{pmatrix} \cos\Theta & \sin\Theta & 0 \\ -\sin\Theta & \cos\Theta & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (\text{A2})$$

$$R_y(\Phi) = \begin{pmatrix} \cos\Phi & 0 & -\sin\Phi \\ 0 & 1 & 0 \\ \sin\Phi & 0 & \cos\Phi \end{pmatrix},$$

and $R_x(\Psi)$ is isomorphic to $R_z(\Theta)$.

When physically different Euler rotations are discussed, different matrices and angles are utilized.

APPENDIX B: DENSITY OF STATES FOR THIN FILMS

The three rotations that generate the ensemble of IAS's in a thin film are as follows: a free rotation of α_1 about the z axis, a rotation of α_2 weighted by Eq. (13) about the x axis, and a free rotation of α_3 about the y axis. In terms of $\alpha_1, \alpha_2,$ and $\alpha_3,$ the field direction in the IAS, $\mathbf{V}'(\alpha)$, is

$$\mathbf{V}'(\alpha) = R_z(\alpha_1)R_x(\alpha_2)R_y(\alpha_3) \begin{pmatrix} \cos\psi \\ \sin\psi \\ 0 \end{pmatrix}. \quad (\text{B1})$$

The z component of $\mathbf{V}'(\alpha)$ is

$$V'_z(\alpha) = |V| \cos\theta' = |V| (\cos\psi \cos\alpha_2 \sin\alpha_3 - \sin\psi \sin\alpha_2). \quad (\text{B2})$$

Following Eqs. (15)–(18), we choose the change of variables

$$\alpha_1 = -\phi' + f_1(v_1, \theta'), \quad \alpha_2 = v_1, \quad \alpha_3 = \sin^{-1} \left(\frac{\cos\theta' + \sin\psi \sin v_1}{\cos\psi \cos v_1} \right). \quad (\text{B3})$$

Evaluation of $\partial V'_z(\alpha)/\partial\alpha_3$ and substitution into Eq. (14) results in

$$D'(\theta') = \frac{\sin\theta'}{N} \int (\cos v_1) w_{DF}(v_1, \Delta) (\cos^2\psi \cos^2 v_1 - \cos^2\theta' - 2 \cos\theta' \sin\psi \sin v_1 - \sin^2\psi \sin^2 v_1)^{-1/2} dv_1, \quad (\text{B4})$$

where $\cos v_1 dv_1 = d\mathbf{v}$ is the necessary volume element for a zxy rotation scheme. Expansion of the denominator and integration where the integrand is real yields Eq. (19) in the text,

$$D'(\theta') = \frac{\sin\theta'}{N} \int_{-\theta'-\psi}^{\theta-\psi} \frac{(\cos v_1) w_{DF}(v_1, \Delta) dv_1}{\{[\sin v_1 + \sin(\theta' + \psi)][\sin(\theta' - \psi) - \sin v_1]\}^{1/2}}. \quad (\text{19})$$

APPENDIX C: A FOUR ROTATION DENSITY OF STATES

For an ensemble of IAS's generated by a $zxyz$ rotation scheme, the field direction in the IAS, $\mathbf{V}'(\alpha)$ is given by

$$\mathbf{V}'(\alpha) = R_z(\alpha_1)R_x(\alpha_2)R_y(\alpha_3)R_z(\alpha_4) \begin{pmatrix} \cos\psi \\ \sin\psi \\ 0 \end{pmatrix}, \quad (\text{C1})$$

The z component of $\mathbf{V}'(\alpha)$ is

$$V'_z(\alpha) = |V| \cos\theta' = |V| [\cos\psi(\cos\alpha_2 \sin\alpha_3 \cos\alpha_4 + \sin\alpha_2 \sin\alpha_4) + \sin\psi(\cos\alpha_2 \sin\alpha_3 \sin\alpha_4 - \sin\alpha_2 \cos\alpha_4)]. \quad (\text{C2})$$

Following Eqs. (15)–(18), we choose the change of variables

$$\alpha_1 = -\phi' + f_1(v_1, v_2, \theta'), \quad \alpha_2 = v_1, \quad \alpha_3 = \sin^{-1} \left(\frac{\cos\theta' + \sin v_1 \sin(\psi - v_2)}{\cos v_1 \cos(\psi - v_2)} \right), \quad \alpha_4 = v_2. \quad (\text{C3})$$

Now

$$\partial V'_z(\alpha)/\partial\alpha_3 = \cos v_1 \cos\alpha_3 \cos(\psi - v_2). \quad (\text{C4})$$

Using the α_3 equation in Eq. (C3) and substituting into Eq. (14) results in

$$D'(\theta') = \frac{\sin\theta'}{N} \int_{v_1} \int_{v_2} \cos v_1 w_1(v_2) w_2(v_1, \alpha_3) [\cos^2 v_1 \cos^2(\psi - v_2) - \cos^2\theta' - 2 \cos\theta' \sin v_1 \sin(\psi - v_2) - \sin^2 v_1 \sin^2(\psi - v_2)]^{-1/2} dv_1 dv_2, \quad (\text{C5})$$

where $\cos v_1 dv_1 dv_2 = d\mathbf{v}$ is the necessary volume element for a $zxyz$ rotation scheme. Expansion of the denominator and integration where the integrand is real yields Eq. (28),

$$D'(\theta') = \frac{\sin\theta'}{N} \int_0^{2\pi} dv_2 w_1(v_2) \int_{-\theta'-\psi+v_2}^{\theta'-\psi+v_2} \frac{(\cos v_1) w_2(v_1, \alpha_3) dv_1}{\{[\sin v_1 + \sin(\theta' + \psi - v_2)][\sin(\theta' - \psi + v_2) - \sin v_1]\}^{1/2}}. \quad (\text{28})$$

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