A general theory of the spectroscopic properties of partially ordered ensembles. II. Two-vector problems

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We have expanded on the results of an earlier paper [J. Chem. Phys. **72**, 221 (1980)] which deals with a method for determining the response of a static, partially ordered ensemble of molecules to various types of electromagnetic probes. In this paper we consider types of spectroscopy whose response depends on the location of two vectors in an axis system fixed with respect to the molecule. Examples of such spectroscopies discussed in detail include fluorescence polarization, photoselection linear dichroism, Raman spectroscopy, and two-photon absorption. We outline the kinds of structural information available from polarization experiments on partially ordered ensembles.

I. INTRODUCTION

Spectroscopic studies on oriented systems provide important sources of structural information in chemical and biological systems. The problem that we undertake is how to extract structural information from an observed response in a partially ordered ensemble. In many cases, the molecules that comprise the ensemble are spectroscopically identical and noninteracting. The observed response is, therefore, a superposition of the responses for the individual molecules. The superposition can be calculated by averaging a response function over an orientational distribution function. In this paper, we will be concerned with only the static regions in which the molecular motion is negligible. The orientational averaging will then be done using a distribution function that is independent of time.

In an earlier paper[1] (hereafter referred to as paper I) we developed much of the theory involved in calculating spectroscopic properties of partially ordered ensembles, and we applied the theory to one-vector problems. One-vector problems are spectroscopic calculations in which the response function depends on the orientation of only one vector in the molecular axis system—i.e., one that is fixed with respect to the molecule. An example of a one-vector problem is electron paramagnetic resonance (EPR), where the signal depends only on the orientation of the Zeeman field in the molecular axis system. In one-vector problems, the observed response can be written as

$$\bar{I} = \int_0^\pi d\theta \int_0^{2\pi} d\phi\, D(\theta, \phi, \Delta) I(\theta, \phi) d\theta\, d\phi , \qquad (1)$$

where $I(\theta, \phi)$ is the response when the vector of interest has spherical angles θ and ϕ in the molecular axis system, $D(\theta, \phi, \Delta)$ is the one-vector density of states function which gives the probability that the vector of interest has spherical angles θ and ϕ in the molecular axis system, and Δ is a set of parameters that describe the partial ordering. The chief advantage afforded by the use of Eq. (1) in paper I lies in a formalism, developed

earlier,[2] for calculating one-vector density of states functions from arbitrary models of partially ordered ensembles. Paper I and Ref. 2 describe the details of how to calculate one-vector density of states functions. Frank et al.[3] and Nairn et al.[4] have applied the one-vector density of states formalism to obtain structural information in photosynthetic systems from EPR[3] and linear dichroism[4] experiments.

The response functions for many spectroscopic properties are not adequately described by the location of one vector in the molecular axis system, but depend on the location of two vectors in the molecular axis system. Examples of such spectroscopies are fluorescence polarization, photoselection linear dichroism, Raman spectroscopy, and two-photon absorption. Although the density of states approach was first used for one-vector problems, it can be extended to include two-vector problems; this extension is advantageous because it retains many favorable aspects of the one-vector density of states techniques.[1-4]

We begin with two unit vectors $\hat{v}_1$ and $\hat{v}_2$ in the laboratory axis system which are perpendicular to each other and which define directions of interest. For example, in a fluorescence polarization experiment, $\hat{v}_1$ could be the polarization direction of the exciting light and $\hat{v}_2$ could be the polarization direction of the detected fluorescence. We now introduce the two-vector density of states function $P(\theta, \phi, \omega, \Delta)$ which gives the probability that the location of $\hat{v}_2$ in the molecular axis system (Note: The molecular axis system is equivalent to the intermediate axis system of Paper I) is defined by ω when the spherical angles of $\hat{v}_1$ in the molecular axis system are θ and ϕ (see Fig. 1.) The observed response will then be

$$\bar{I} = \int_0^{2\pi} d\omega \int_0^{2\pi} d\phi \int_0^\pi d\theta\, I(\theta, \phi, \omega) P(\theta, \phi, \omega, \Delta) , \qquad (2)$$

where $I(\theta, \phi, \omega)$ is the response when $\hat{v}_1$ and $\hat{v}_2$ are defined by θ, ϕ, and ω in the molecular axis system. As will be shown in Sec. II, $P(\theta, \phi, \omega, \Delta)$ can be derived in a manner that is analogous to the derivation of $D(\theta, \phi, \Delta)$ in Ref. 2.

Evaluation of $P(\theta, \phi, \omega, \Delta)$ and use of Eq. (2) is suf-
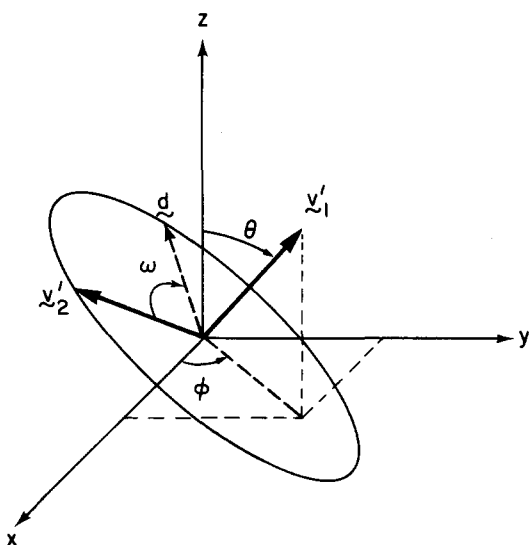
FIG. 1. Definition of the angles θ, ϕ, and ω in the molecular axis system. θ and ϕ are the tradiational spherical angles for the vector $\hat{v}_1'$; θ is the polar angle and ϕ is the azimuthal angle. ω is the angle between $\hat{v}_2'$ and an arbitrary (but fixed) vector d in the plane perpendicular to $\hat{v}_1'$.

ficient for analyzing any two-vector problems We will consider several examples having the same type of response function,

$$I(\theta, \phi, \omega) = (\hat{v}_2 \cdot \mathbf{T} \cdot \hat{v}_1)^2 . \tag{3}$$

where $\mathbf{T}$ is a constant tensor in the molecular axis system. We define $\overline{I}_\perp$ as the average of a response function such as given in Eq. (3). Structural information is obtained by comparing $\overline{I}_\perp$ to $\overline{I}_\parallel$, where $\overline{I}_\parallel$ is the average of the response function

$$I(\theta, \phi) = (\hat{v}_1 \cdot \mathbf{T} \cdot \hat{v}_1)^2 . \tag{4}$$

Because Eq. (4) is independent of ω, calculation of $\overline{I}_\parallel$ is a one-vector problem, and it is evaluated using Eq. (1). Spectroscopies having these response functions include fluorescence polarization, photoselection linear dichroism, Raman spectroscopy, and two-photon absorption

II. EVALUATION OF $P(\omega, \theta, \phi, \Delta)$

We follow the same procedure used in Ref. 2, where we began with a set of n rotations $R_1(\alpha_1) \cdots R_n(\alpha_n)$ and n weighting functions $g_1(\alpha_1) \cdots g_n(\alpha_n)$ that generate the partially ordered ensemble. The partially ordered ensemble can be thought of as a set of cubes in which the unit vectors in the molecular axis system $(\hat{x}', \hat{y}', \hat{z}')$ lie along the joined edges of the cube. To generate an ensemble by a set of rotations, we begin by placing a cube at the origin of the laboratory axis system (with $\hat{x}', \hat{y}'$, and $\hat{z}'$ coincident with the laboratory axis system unit vectors $\hat{x}$, $\hat{y}$, and $\hat{z}$). When this cube is rotated by

n rotations $[R_1(\alpha_1) \cdots R_n(\alpha_n)]$ in the laboratory frame, it will become a member of the ensemble. Furthermore, the probability that the angular variables are α_1, α_2, ..., α_n is proportional to the product of the weighting functions.

The average intensity for a two-vector problem can be written directly as an integral of the variables α_1, ..., α_n

$$\overline{I} = \frac{1}{N} \int_{\alpha_1} \cdots \int_{\alpha_n} I[\hat{v}_1'(\alpha_1, \ldots, \alpha_n), \hat{v}_2'(\alpha_1, \ldots, \alpha_n)]$$
$$\times g_1(\alpha_1) \cdots g_n(\alpha_n) d\alpha_1 \cdots d\alpha_n , \tag{5}$$

where N is a normalization constant, $I[\hat{v}_1'(\alpha_1, \ldots, \alpha_n), \hat{v}_2'(\alpha_1, \ldots, \alpha_n)]$ is the two-vector response function, and $\hat{v}_1'$ and $\hat{v}_2'$ are the two vectors of interest in the molecular axis system. From Ref. 2, the two vectors are

$$\hat{v}_1' = R_1(\alpha_1) \cdots R_n(\alpha_n)\hat{v}_1 , \tag{6}$$

$$\hat{v}_2' = R_1(\alpha_1) \cdots R_n(\alpha_n)\hat{v}_2 , \tag{7}$$

where $\hat{v}_1$ and $\hat{v}_2$ are the two vectors in the laboratory axis system.

The two-vector density of states function $P(\theta, \phi, \omega, \Delta)$ describes the probability as a function of Δ that $\hat{v}_1'$ has spherical angles θ and ϕ, and $\hat{v}_2'$ is described by the angle ω defined in Fig. 1; in other words, the probability that

$$\hat{v}_1' = \begin{pmatrix} \cos\phi \sin\theta \\ \sin\phi \sin\theta \\ \cos\theta \end{pmatrix} \tag{8}$$

and

$$\hat{v}_2' = \begin{pmatrix} \cos\phi \cos\theta \cos\omega + \sin\phi \sin\omega \\ \sin\phi \cos\theta \cos\omega - \cos\phi \sin\omega \\ - \sin\theta \cos\omega \end{pmatrix} . \tag{9}$$

To evaluate $P(\theta, \phi, \omega, \Delta)$, we perform the transformation

$$(\alpha_1, \ldots, \alpha_n) \rightarrow (\phi, \nu_1, \nu_{n-3}, \theta, \omega) \tag{10}$$

under the constraints

$$v_{1x}' = \sin\theta \cos\phi , \quad v_{1y}' = \sin\theta \sin\phi , \quad v_{1z}' = \cos\theta ,$$
$$v_{2x}' = \cos\phi \cos\theta \cos\omega + \sin\phi \sin\omega, \tag{11}$$
$$v_{2y}' = \sin\phi \cos\theta \cos\omega - \cos\phi \sin\omega, \quad v_{2z}' = - \sin\theta \cos\omega ,$$

where ν_1, ..., ν_{n-3} are dummy variables that will be integrated out in the final result.

The n-dimensional coordinate transformation is done following the approach of Ref. 2. The details are presented in the Appendix and the result for the two-vector density of states function is

$$P(\theta, \phi, \omega, \Delta) = \frac{\sin^2\theta \sin\omega}{N} \int_{\nu_1} \cdots \int_{\nu_{n-3}} g_1[-\phi + f_4(\nu_1, \ldots, \nu_{n-3}, \theta, \omega)] g_{n-1}[f_2(\nu_1, \ldots, \nu_{n-3}, \theta, \omega)]$$

$$\times g_n[f_3(\nu_1, \ldots, \nu_{n-3}, \theta, \omega)] \frac{\Pi_{i=2}^{n-2} g_i(\nu_{i-1}) d\nu_{i-1}}{\left| \dfrac{\partial v_{1z}'}{\partial \alpha_{n-1}} \dfrac{\partial v_{2z}'}{\partial \alpha_n} - \dfrac{\partial v_{1z}'}{\partial \alpha_n} \dfrac{\partial v_{2z}'}{\partial \alpha_{n-1}} \right|} , \tag{12}$$

where f_2, f_3, and f_4 are defined in the Appendix. This equation is an extension of Eq. (31) in Ref. 2 for the one vector density of states function. We note that if $g_1(\alpha_1) = 1$, we have an axially symmetric distribution; i.e., $P(\theta, \phi, \omega, \Delta)$ is independent of ϕ. If we have a randomly oriented system, it can be shown that $P(\theta, \phi, \omega, \Delta) = \text{const} \times \sin\theta$.

When the partially ordered ensemble can be generated with three rotations, there is no need for the dummy variables $\nu_1, \ldots, \nu_{n-3}$ in Eq. (A3) of the Appendix, and hence Eq. (12) will not involve any integration. In such a case, Eq. (12) can be shown to simplify to

$$P(\theta, \phi, \omega, \Delta) = \sin\theta\, G[\alpha_1(\theta, \phi, \omega), \alpha_2(\theta, \omega), \alpha_3(\theta, \omega)], \quad (13)$$

where $G(\alpha_1, \alpha_2, \alpha_3)$ is the product of the weighting functions for the three rotations. The two-vector density of states is thus determined by finding the functional form of $\alpha_1(\theta, \phi, \omega)$, $\alpha_2(\theta, \omega)$, and $\alpha_3(\theta, \omega)$. These functional forms for all possible three-rotation schemes and combinations of v_1 and v_2 are listed in Table I. We do not include $\alpha_1(\theta, \phi, \omega)$, and therefore Table I is restricted to axially symmetric two-vector densities of states.

III. AN EXAMPLE—FLUORESCENCE POLARIZATION

To illustrate the density of states approach to analysis of two-vector problems, we will work through a hypothetical example. The example is a fluorescence polarization study of a fluorophore attached to a macromolecular structure which can be oriented in a stretched film. This example is shown in Fig. 2 with the laboratory z axis as the stretch direction.
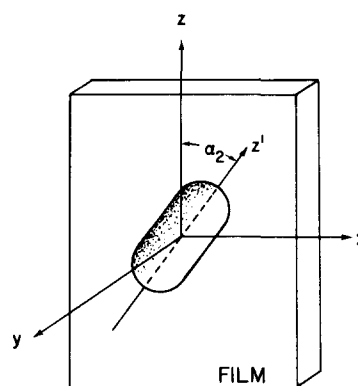

FIG. 2. Orientation of macromolecular structure in a stretched film. xyz define the laboratory axis system, z' defines the symmetry axis of the macromolecular structure, and α_2 is the angle between z' and the stretch direction, z.

The first step for analysis is to construct a model for the partially ordered ensemble. That is, we seek a set of n rotations $[R_1(\alpha_1) \cdots R_n(\alpha_n)]$ and weighting function $G(\alpha_1, \alpha_2, \ldots, \alpha_n)$ that will generate the ensemble (see Sec. II). If we take the z axis of the molecular axis system to be the axis of symmetry for the macromolecular structure, the partially ordered ensemble can be generated by the following three rotations: (1) A free rotation of α_1 about the laboratory z axis; (2) a weighted rotation of α_2 about the laboratory y axis (this rotation is weighted by the probability that the symmetry axis tilts by α_2 from the stretch direction); and (3) a free rotation of α_3 about the laboratory z axis.

TABLE I. The functional forms of $\alpha_2(\theta, \omega)$ and $\alpha_3(\theta, \omega)$ in Eq. (13). When $\delta \pm$ appears in an equation for $\alpha_2(\theta, \omega)$ or $\alpha_3(\theta, \omega)$, both terms must be included; i.e., $P(\theta, \omega) = \sin\theta\,\{G[\alpha_2^+(\theta, \omega),\ \alpha_3^+(\theta, \omega)] + G[\alpha_2^-(\theta, \omega),\ \alpha_3^-(\theta, \omega)]\}$.

RS^a	$\hat{v}_1$	$\hat{v}_2$	$\alpha_2(\theta, \omega)$	$\alpha_3(\theta, \omega)^b$	$\alpha_3(\theta, \omega)^c$
ZYZ	$(\cos\psi,\ \sin\psi,\ 0)$	$(0,\ 0,\ 1)$	$\cos^{-1}(\sin\theta\cos\omega)$	$\psi - \cos^{-1}(\pm\cos\theta/\sin\alpha_2)$	0^d
ZYZ	$(\cos\psi,\ 0,\ \sin\psi)$	$(0,\ 1,\ 0)$	$\cos^{-1}(\cos\theta\sin\psi \pm \cos\psi\sin\theta\sin\omega)$	$\sin^{-1}(\sin\theta\cos\omega/\sin\alpha_2)$	$\dfrac{\pi}{2} - \omega$
ZYZ	$(0,\ \cos\psi,\ \sin\psi)$	$(1,\ 0,\ 0)$	$\cos^{-1}(\cos\theta\sin\psi \pm \cos\psi\sin\theta\sin\omega)$	$\cos^{-1}(\sin\theta\cos\omega/\sin\alpha_2)$	ω
ZYZ	$(0,\ 0,\ 1)$	$(\cos\psi,\ \sin\psi,\ 0)$	θ	$\psi \pm \omega$	$\psi \pm \omega$
ZYZ	$(0,\ 1,\ 0)$	$(\cos\psi,\ 0,\ \sin\psi)$	$\cos^{-1}[\sin\theta\sin(\psi \pm \omega)]$	$\sin^{-1}(\cos\theta/\sin\alpha_2)$	0^d
ZYZ	$(1,\ 0,\ 0)$	$(0,\ \cos\psi,\ \sin\psi)$	$\cos^{-1}[\sin\theta\sin(\psi \pm \omega)]$	$\cos^{-1}(\cos\theta/\sin\alpha_2)$	0^d
ZXY	$(\cos\psi,\ \sin\psi,\ 0)$	$(0,\ 0,\ 1)$	$\sin^{-1}(\cos\theta\sin\psi \pm \cos\psi\sin\theta\sin\omega)$	$\cos^{-1}(\sin\theta\cos\omega/\cos\alpha_2)$	ω
ZXY	$(\cos\psi,\ 0,\ \sin\psi)$	$(0,\ 1,\ 0)$	$\sin^{-1}(\sin\theta\cos\omega)$	$\psi - \sin^{-1}(\pm\cos\theta/\cos\alpha_2)$	0^d
ZXY	$(0,\ \cos\psi,\ \sin\psi)$	$(1,\ 0,\ 0)$	$\sin^{-1}(\cos\theta\cos\psi \pm \sin\psi\sin\theta\sin\omega)$	$\sin^{-1}(\sin\theta\cos\omega/\cos\alpha_2)$	$\dfrac{\pi}{2} - \omega$
ZXY	$(0,\ 0,\ 1)$	$(\cos\psi,\ \sin\psi,\ 0)$	$\sin^{-1}[\sin\theta\sin(\psi \pm \omega)]$	$\cos^{-1}(\cos\theta/\cos\alpha_2)$	0^d
ZXY	$(0,\ 1,\ 0)$	$(\cos\psi,\ 0,\ \sin\psi)$	$\dfrac{\pi}{2} - \theta$	$\dfrac{\pi}{2} - \psi \pm \omega$	$\dfrac{\pi}{2} - \psi \pm \omega$
ZXY	$(1,\ 0,\ 0)$	$(0,\ \cos\psi,\ \sin\psi)$	$\sin^{-1}[\sin\theta\cos(\psi \pm \omega)]$	$\sin^{-1}(\cos\theta/\cos\beta)$	0^d

aRotation scheme or the order and axes of three rotations required to generate the ensemble.
bUse these formulas if the denominators are not equal to zero.
cUse these formulas if the denominators in the previous column equal zero.
dIn these cases, any value of α_3 can be used because for any physically realizable model $G(\alpha_2, \alpha_3)$ will be independent of α_3 when the denominators in the previous column equal zero.

For the weighting function of the second rotation, we choose a Gaussian distribution

$$g(\alpha_2) = \exp(-\alpha_2^2/\Delta^2) \,, \tag{14}$$

where Δ is related to the width of the Gaussian. We note that because the first rotation is a free rotation, the density of states functions will all be axially symmetric. We will restrict our consideration in the rest of this paper to the axially symmetric case. This restriction is not so limiting as it might seem, because the density of states is axially symmetric in some systems even when the distribution function in the laboratory reference frame is not axially symmetric.[4]

To calculate the density of states function, we need to know the two vectors $\hat{v}_1$ and $\hat{v}_2$ in the laboratory axis system. Fluorescence polarization experiments are typically done with the configuration shown in Fig. 3. A sample is excited with light polarized in the z direction and propagating along the y axis and fluorescence is detected along the x axis; the fluorescence intensities F_{zz} and F_{zy} are measured with an analyzing polarizer oriented either along the z axis or the y axis, respectively. We take $\hat{v}_1$ to be the polarization direction of the exciting light and $\hat{v}_2$ to be the polarization direction of the detected fluorescence. Thus for F_{zz} and F_{zy}, $\hat{v}_1$ is along the laboratory z axis while $\hat{v}_2$ is along either the laboratory z or y axis. It is also possible to excite with a different polarization, such as along the laboratory x axis (see Fig. 4), and correspondingly measure F_{xz} and F_{xy}. (Here $\hat{v}_1 = \hat{x}$ and $\hat{v}_2 = \hat{z}$ or $\hat{y}$.) In a randomly distributed sample, F_{xz} and F_{xy} do not provide any new information because $F_{zy} = F_{xy} = F_{xz}$. In an ordered sample, however, the $\hat{z}$ direction and the $\hat{x}$ direction will not be equivalent (unless the y axis is an axis of symmetry in the laboratory axis system); F_{zy}, F_{xz}, and F_{xy} will all be different and, in principle, will provide new information.

Having established a rotation scheme and decided on $\hat{v}_1$ and $\hat{v}_2$, we can now calculate the density of states function. We will need one density of states function for each quantity; i.e., one density of states function for each of F_{zz}, F_{zy}, F_{xz}, F_{xy}. We begin with F_{zz}. Because
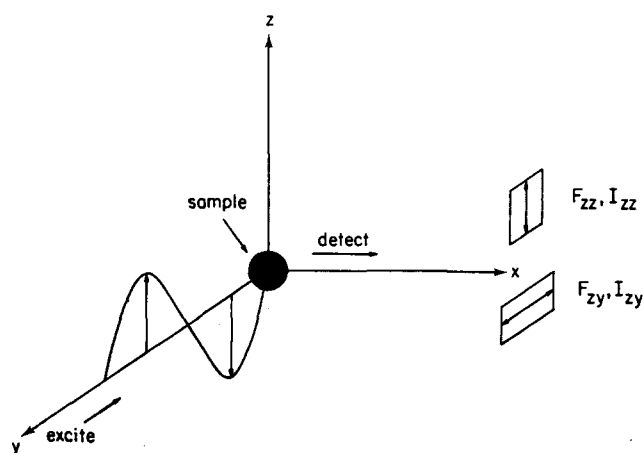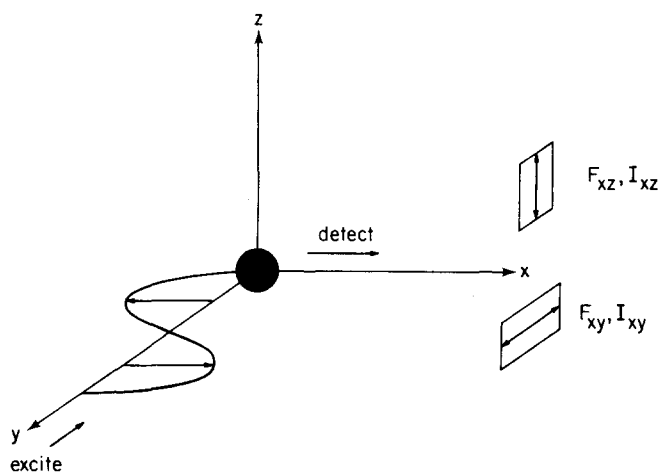

FIG. 4. Experimental set-up for a polarization experiment with exciting light polarized along the x axis. The axis system shown is the laboratory axis system.

$\hat{v}_1 = \hat{v}_2$, we need only a one-vector density of states function. The reader is referred to paper I for a detailed explanation of how to calculate one-vector density of states functions. We call this density of states function $D_{zz}(\theta, \Delta)$. F_{zy}, F_{xz}, and F_{xy} all need two-vector density of states functions. Because our hypothetical system can be generated with three rotations, the appropriate two-vector density of states functions are easily formed by proper use of Eq. (13) and Table I. We call these density of states functions $P_{zy}(\theta, \omega, \Delta)$, $P_{xz}(\theta, \omega, \Delta)$, and $P_{xy}(\theta, \omega, \Delta)$. A plot of $P_{xz}(\theta, \omega, \Delta)$ for $\Delta = 0.5$ is shown in Fig. 5.

The next step is to find the response function for fluorescence polarization. In the dipole approximation, the response function in a static noninteracting ensemble of molecules is

$$I(\theta, \phi, \omega) = K^2(\hat{\mu}_1 \cdot \hat{v}_1')^2(\hat{\mu}_2 \cdot \hat{v}_2')^2 \,, \tag{15}$$

where $\hat{\mu}_1 = (x_1, y_1, z_1)$ is a unit vector along the absorption dipole moment, $\hat{\mu}_2 = (x_2, y_2, z_2)$ is a unit vector along the

FIG. 3. Experimental set-up for a polarization experiment with exciting light polarized along the z axis. The axis system shown is the laboratory axis system.
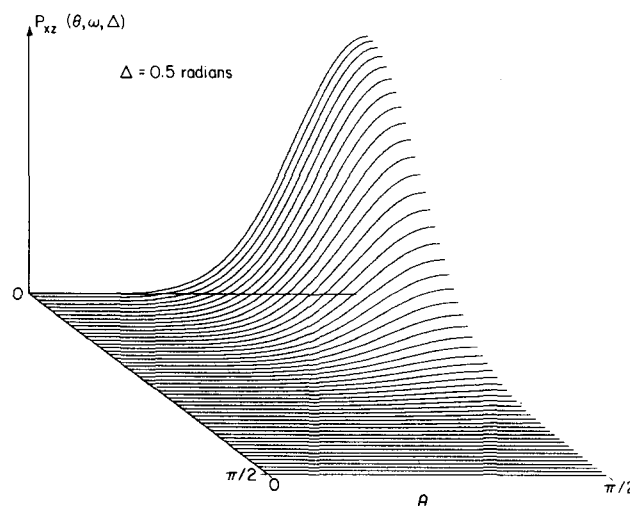

FIG. 5. Plot of two-vector density of states $P_{xz}(\theta, \omega, \Delta)$ for $\Delta = 0.5$ rad.

emission dipole moment, $\hat{v}_1'$ is the polarization direction of the exciting light, $\hat{v}_2'$ is the polarization direction of the detected fluorescence, and K^2 is a constant. Equation (15) is identical to Eq. (3) [or Eq. (4) when $\hat{v}_1 = \hat{v}_2$] when T is given by the dyad

$$T = K\hat{\mu}_2 : \hat{\mu}_1 = K \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} (x_1 y_1 z_1) = \begin{pmatrix} x_1 x_2 & y_1 x_2 & z_1 x_2 \\ x_1 y_2 & y_1 y_2 & z_1 y_2 \\ x_1 z_2 & y_1 z_2 & z_1 z_2 \end{pmatrix}.$$
(16)

To calculate F_{zz}, we substitute Eq. (4) with v_1' given by Eq. (8) into Eq. (1) using $D_{zz}(\theta, \Delta)$. For the moment we will retain the general tensor elements of T (i.e., T_{xx}, T_{xy}, etc.) rather than the specific tensor elements of Eq. (16). The partial ordering in our example is induced by exerting a mechanical stretch on the film. Because the sign of the direction of this force is arbitrary, $D_{zz}(\theta, \Delta)$ is symmetric about $\pi/2$; that is, $D_{zz}(\theta, \Delta) = D_{zz}(\pi - \theta, \Delta)$. Utilizing this symmetry property, expanding Eq. (1) and evaluating the integral over ϕ results in

$$I_{\parallel} = F_{zz} = \tfrac{1}{8}\{8T_{zz}^2 + \alpha[8T_{xx}T_{zz} + 4(T_{xz} + T_{zx})^2 + 8T_{yy}T_{zz} + 4(T_{yz} + T_{zy})^2 - 16T_{zz}^2]$$

$$+ \beta[3T_{xx}^2 + 3T_{yy}^2 + 2T_{xx}T_{yy} + (T_{xy} + T_{yx})^2 - 8T_{xx}T_{zz} - 4(T_{xz} + T_{zx})^2 - 8T_{yy}T_{zz} - 4(T_{yz} + T_{zy})^2 + 8T_{zz}^2]\} ,$$
(17)

where

$$\alpha = \int_0^{\pi/2} \sin^2\theta\, D_{zz}(\theta, \Delta)\, d\theta ,$$
(18)

$$\beta = \int_0^{\pi/2} \sin^4\theta\, D_{zz}(\theta, \Delta)\, d\theta ,$$
(19)

and $D(\theta, \Delta)$ is normalized such that

$$\int_0^{\pi/2} D_{zz}(\theta, \Delta)\, d\theta = 1 .$$
(20)

After incorporation of the elements of T from Eq. (16) into Eq. (17), we arrive at

$$F_{zz} = \frac{K}{8}[8z_1^2 z_2^2 + 4\alpha(z_1^2 + z_2^2 - 10z_1^2 z_2^2 + 4z_1 z_2 \cos\epsilon) + \beta(-5z_1^2 - 5z_2^2 + 35z_1^2 z_2^2 - 20z_1 z_2 \cos\epsilon + 2\cos^2\epsilon + 1)] ,$$
(21)

where ϵ is the angle between $\hat{\mu}_1$ and $\hat{\mu}_2$. F_{zy}, F_{xy}, and F_{xz} are calculated by inserting Eq. (3) with v_1' and v_2' given by Eqs. (8) and (9), respectively, into Eq. (2) using the appropriate density of states function. Expanding Eq. (2) and evaluating the integral over ϕ yields

$$I_{\perp} = F_{ij} = \tfrac{1}{8}\{4(T_{xz}^2 + T_{yz}^2) + \alpha_{ij}[4(T_{xy}^2 + T_{yx}^2 - T_{xz}^2 - T_{yz}^2) - (T_{xy} + T_{yx})^2 + (T_{xx} - T_{yy})^2] + \gamma_{ij}[4(T_{xx} - T_{zz})^2 + 4(T_{yy} - T_{zz})^2$$

$$- 2(T_{xx} - T_{yy})^2 + 2(T_{xy} + T_{yx})^2 - 4(2T_{xz}T_{zx} + 2T_{yz}T_{zy} + T_{xy}^2 + T_{yx}^2 + T_{xz}^2 + T_{yz}^2)] + \xi_{ij}[4(T_{xz} + T_{zx})^2$$

$$+ 4(T_{yz} + T_{zy})^2 - (T_{xy} + T_{yx}) + (T_{xx} - T_{yy})^2 - 4(T_{xx} - T_{zz})^2 - 4(T_{yy} - T_{zz})^2]\} ,$$
(22)

where

$$\gamma_{ij} = \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\omega\, \sin^2\theta \cos^2\omega\, P_{ij}(\theta, \omega, \Delta) ,$$
(23)

$$\xi_{ij} = \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\omega\, \sin^4\theta \cos^2\omega\, P_{ij}(\theta, \omega, \Delta) ,$$
(24)

$P_{ij}(\theta, \omega, \Delta)$ is normalized such that

$$\int_0^{\pi/2} d\theta \int_0^{\pi/2} d\omega\, P_{ij}(\theta, \omega, \Delta) = 1 ,$$
(25)

$i = x$ or z, and $j = y$ or z. Here α_{zy} is given by Eq. (18) but α_{xy} and α_{xz} are given by

$$\alpha_{xj} = \int_0^{\pi/2} \sin^2\theta\, D_{xx}(\theta, \Delta)\, d\theta ,$$
(26)

where $D_{xx}(\theta, \Delta)$ is the one-vector density of states function for a vector along the laboratory x axis. Inserting the tensor elements of Eq. (16) into Eq. (22) we obtain

$$F_{ij} = \frac{K}{8}[(4z_1^2 - 4z_1^2 z_2^2) + \alpha_{ij}(3 - 2\cos^2\epsilon - 7z_1^2 - 3z_2^2 + 5z_1^2 z_2^2 + 4z_1 z_2 \cos\epsilon) + \gamma_{ij}(4\cos^2\epsilon - 2z_1^2 + 2z_1^2 + 2z_2^2 - 2$$

$$+ 30z_1^2 z_2^2 - 24z_1 z_2 \cos\epsilon) + \xi_{ij}(5z_1^2 + 5z_2^2 - 35z_1^2 z_2^2 - 1 - 2\cos^2\epsilon + 20z_1 z_2 \cos\epsilon)] .$$
(27)

Fluorescence polarization data are generally in the form of ratios, to eliminate the experimental constant K. From the four quantities F_{zz}, F_{zy}, F_{xy} we can construct three ratios. For example,

$$P_1 = \frac{F_{zz} - F_{zy}}{F_{zz} + F_{zy}}$$

and P_2 and P_3 are derived from P_1 by replacing F_{zy} by F_{yz} and F_{xy}, respectively. In an ordered sample, one can measure P_1, P_2, and P_3. In a random sample $P_1 = P_2 = P_3 = P$, but it is worth measuring P, because it provides an independent measurement of the parameter ϵ (see below). We therefore find four measurable quantities P_1, P_2, and P_3 from an ordered sample and P from a random sample as data to determine the four parameters z_1, z_2, ϵ, and Δ in Eqs. (21) and (27). In our hypothetical example, we will use the following data: $P = 0.14 \pm 0.02$, $P_1 = 0.50 \pm 0.04$, $P_2 = -0.52 \pm 0.04$, and $P_3 = -0.26 \pm 0.04$.

In a random sample ($\alpha = \frac{2}{3}$, $\beta = \frac{8}{15}$, $\gamma = \frac{1}{3}$, $\xi = \frac{4}{15}$), Eqs. (21) and (27) reduce to

$$P = \frac{3 \cos^2 \epsilon - 1}{\cos^2 \epsilon + 3} . \tag{28}$$

From the data, we find $\epsilon = 45.0° \pm 1.5°$.

In the ordered sample, we use Eqs. (18), (19), (23), (24), and (26) to calculate α, β, $\alpha_{xz} = \alpha_{xy}$, γ_{zy}, γ_{xy}, γ_{xz}, ξ_{xy}, ξ_{zy}, ξ_{xz} for several values of Δ; in our example, we calculated these values for Δ between 0 and 1 rad at increments of 0.05 rad. A simple computer program is then written to enumerate through all possible values of z_1 and z_2 (z_1 and z_2 are between 0 and 1). For each set of z_1 and z_2, the ratios P_1, P_2, P_3 are calculated for each value of Δ considered. Any set of z_1, z_2, and Δ where P_1, P_2, and P_3 all fall within experimental error of measured ratios is an acceptable solution. The set of all solutions for z_1, z_2, and Δ will define these values complete with uncertainties. Carrying out this procedure for our hypothetical data results in

$$z_1 = 0.22 \pm 0.08 , \tag{29}$$

$$z_2 = 0.70 \pm 0.03 , \tag{30}$$

$$\Delta = 0.35 \pm 0.10 . \tag{31}$$

It is important to emphasize that we have measured Δ in this example. That is, we did not need to know the distribution function to carry out the above analysis; we needed only a model which enabled us to parametrize the distribution function with Δ.

IV. OTHER TYPES OF TWO-VECTOR SPECTROSCOPIES

A. Photoselection linear dichroism

In a photoslection linear dichroism experiment, one excites a sample with polarized light and probes an induced absorption change with light polarized either parallel or perpendicular to the exciting light.[5] The response function is

$$I(\theta, \phi, \omega) = K^2 (\hat{\mu}_1 \cdot \hat{v}_1')^2 (\hat{\mu}_2 \cdot \hat{v}_2')^2 , \tag{32}$$

where $\hat{\mu}_1$ is the absorption dipole moment that is being

excited by light polarized along $\hat{v}_1'$ and $\hat{\mu}_2$ is the absorption dipole moment that is being probed by light polarized along $\hat{v}_2'$. Because Eq. (32) is identical with the response function for fluorescence polarization, the analysis of photoselection linear dichroism data is identical to that of fluorescence polarization data.

B. Raman spectroscopy

Polarization experiments in Raman spectroscopy are done by exciting along the y axis with light polarized along the z or x axes and detecting scattered intensity along the x axis with an analyzing polarizer oriented along the z or y axes. Analogously to fluorescence polarization experiments, one can measure four quantities I_{zz}, I_{zy}, I_{xz}, and I_{xy} (see Figs. 3 and 4). Depolarization ratios for a Raman band are derivable from these four quantities.

The intensity scattered in the x direction is given by[6]

$$I = \frac{(\omega - \omega_0)^4}{c^4} I_0 (\hat{v}_2' \cdot \mathbf{T} \cdot \hat{v}_1')^2 , \tag{33}$$

where ω and ω_0 are the scattered and incident frequencies, c is the speed of light, I_0 is the incident intensity, $\hat{v}_1'$ and $\hat{v}_2'$ are the polarization directions for the incident and scattered light, and $\mathbf{T}$ is the scattering tensor. The elements of the scattering tensor for a transition from vibronic state m to vibronic state n are

$$T_{ij} = (\alpha_{ij})_{mn} = \frac{1}{\hbar} \sum_r \left(\frac{(M_i)_m (M_j)_{mr}}{\omega_{rm} - \omega_0} + \frac{(M_i)_{mr} (M_j)_m}{\omega_m + \omega_0} \right) , \tag{34}$$

where i and j can be x, y, or z; $2\pi\hbar$ is Planck's constant and the sum is over vibronic states of the molecule. Here, $(M_i)_m$, $(M_j)_{mr}$, etc., refer to the components of the transition moments between vibronic levels and ω_{rm} and ω_m are frequencies obtained from the energy differences of the vibronic states.[7] The four quantities I_{zz}, I_{zy}, I_{xz}, and I_{xy} can be found (with T_{ij}'s as parameters) by use of Eqs. (17) or (22). For example, $I_{zz} = \overline{I}_\parallel$ when $D(\theta, \Delta)$ is the one-vector density of states for a unit vector along the z axis, $I_{xz} = \overline{I}_\perp$ when $D(\theta, \Delta)$ is the one-vector density of states for a unit vector along the x axis and $P(\theta, \omega, \Delta)$ is the two-vector density of states for a unit vector along the x axis and a unit vector along the z axis, and similarly for I_{zy} and I_{xy}. In this section, we will consider only symmetric scattering tensors; it is then possible to find an axis system, the principal axis system, where α_{mn} is diagonal with diagonal elements α_x, α_y, and α_z. Now, Eqs. (17) and (22) were derived by orientation averaging in a molecular axis system which in general is not the same as the principal axis system. This approach is necessary because, even though the density of states is axially symmetric in some molecular axis system, it may not be axially symmetric in the principal axis system.[2] We can find I in the molecular axis system by

$$\mathbf{T} = \mathbf{R}(\Theta, \Phi, \Psi) \begin{pmatrix} \alpha_x & 0 & 0 \\ 0 & \alpha_y & 0 \\ 0 & 0 & \alpha_z \end{pmatrix} \mathbf{R}^{-1}(\Theta, \Phi, \Psi) \tag{35}$$

or

$$T_{ij} = \sum_k R_{ik}(\Theta, \Phi, \Psi) R_{jk}(\Theta, \Phi, \Psi) \alpha_k , \qquad (36)$$

where $k = x$, y, and z, and $R(\Theta, \Phi, \Psi)$ is the Euler rotation matrix with Euler angles Θ, Φ, and Ψ.[8] Because both the principal axis system and the molecular axis system are fixed with respect to the molecule, Θ, Φ, and Ψ are constants that are the same for every member of the ensemble. We now see that there are six parameters inherent in a Raman experiment; those six are the three principal components of the scattering tensor and the three Euler angles that relate the principal axis system to the molecular axis system.

In a partially ordered sample, one can measure the four quantities I_{zz}, I_{zy}, I_{xz}, and I_{xy}, from which can be constructed three depolarization ratios. These three ratios are all that is available to extract the six structural parameters mentioned above. Although the ratio of parameters to data points is unfavorable, in some cases a few of the parameters may be known. For example, if the three Euler angles are known from other experiments, one would have three measured quantities to determine the three principal components of the scattering tensor and vice versa.

In a random sample $I_{zz} = \overline{I}_\parallel$ in Eq. (17) and $I_{zy} = I_{xz}$ $= I_{xy} = \overline{I}_\perp$ in Eq. (22), with $\alpha = \frac{2}{3}$, $\beta = \frac{8}{15}$, $\gamma = \frac{1}{3}$, and $\xi = \frac{4}{15}$. Because $I_{zy} = I_{xz} = I_{xy}$ there is only one possible depolarization ratio. The depolarization ratio is frequently reported as

$$P = \frac{I_{xz} + I_{xy}}{I_{zz} + I_{zy}} \qquad (37)$$

which, from Eqs. (17) and (22) for symmetric tensors is equal to

$$P = \frac{6[B^2 + 3(T_{xy}^2 + T_{xz}^2 + T_{yz}^2)]}{45A^2 + 7[B^2 + 3(T_{xy}^2 + T_{xz}^2 + T_{yz}^2)]} , \qquad (38)$$

where

$$A = \tfrac{1}{3}(T_{xx} + T_{yy} + T_{zz}) \qquad (39)$$

and

$$B = \tfrac{1}{2}[(T_{xx} - T_{yy})^2 + (T_{yy} - T_{zz})^2 + (T_{xx} - T_{zz})^2] . \qquad (40)$$

A is equal to $\frac{1}{3}$ times the trace of $\mathbf{T}$; because the trace is invariant to rotation, A is also equal to $\frac{1}{3}(\alpha_x + \alpha_y + \alpha_z)$. This quantity is known as the spherical part of the polarizability.[6] In a similar fashion, the quantity $C^2 = B^2 + 3(T_{xy}^2 + T_{xz}^2 + T_{yz}^2)$ can be shown to be also invariant to rotations. In the principal axis system $C^2 = 1/2[(\alpha_y - \alpha_x)^2 + (\alpha_y - \alpha_z)^2 + (\alpha_z - \alpha_x)^2]$; this quantity is known as the anisotropy of the polarizability.[6] Equation (38) reduces to the classical result for the depolarization ratio

$$P = \frac{6C^2}{45A^2 + 7C^2} . \qquad (41)$$

Most Raman depolarization measurements have been done on random samples, but for two reasons it is worth undertaking depolarization measurements on ordered samples: (1) It is not possible to obtain structural information (e.g., the Euler angles in Eqs. (35) and (36)) through measurements on a random sample; (2) if the Euler angles in Eqs. (35) and (36) are known, depolar-

ization measurements on a random sample yield only one ratio involving α_x, α_y, and α_z, while depolarization measurements on an ordered sample yields three ratios.

C. Two-photon absorption

Simultaneous absorption of two different photons is governed by the formula[9]

$$I(\omega, \theta, \phi) = 8\pi^3 \alpha^2 \omega_1 \omega_2 \Gamma(\omega_1 + \omega_2)(\hat{v}_2 \cdot \mathbf{S}_{mn} \cdot \hat{v}_1)^2 , \qquad (42)$$

where α is the fine structure constant, ω_1 and ω_2 are the frequencies of the two photons whose polarizations are $\hat{v}_1$ and $\hat{v}_2$, $\Gamma(\omega)$ is the absorption line shape function for the molecule, and $\mathbf{S}_{mn}$ is the two-photon absorption tensor. The elements of $\mathbf{S}_{mn}$ are

$$(S_{ij})_{mn} = \sum_k \left(\frac{\langle m | r_i | k \rangle \langle k | r_j | n \rangle}{\omega_{km} - \omega_1} + \frac{\langle m | r_j | k \rangle \langle k | r_i | n \rangle}{\omega_{km} - \omega_2} \right) . \qquad (43)$$

Here, $\hbar\omega_{km}$ is the energy difference between the $|m\rangle$ and $|k\rangle$ states, and $\langle m | r_i | k \rangle$ is the ith coordinate of the transition moment.

McClain and Harris[9] have reviewed the theory of two-photon absorption in random systems. The parameters that enter are the elements of the absorption tensor. They used group theoretical arguments to list the irreducible tensor patterns of many types of molecules; these tensors contain from one to nine different elements. In a partially ordered sample, the elements of the irreducible absorption tensor will still be parameters, and three new parameters will be the three Euler angles that relate the molecular axis system to the principal axis system of the irreducible absorption tensor. Conceptually, the type of information available in a two-photon absorption experiment is similar to that available in a Raman experiment.

V. DISCUSSION

The chief result of this paper is the derivation of $P(\theta, \phi, \omega, \Delta)$ in Eq. (12). This result is an extension of the density of states theory introduced in Ref. 2. The two-vector density of states theory retains most of the advantages of the one-vector density of states theory, and these advantages are discussed at length in paper I. Here, we will outline the major benefits afforded by adopting our approach to analyzing the results of spectroscopies governed by the response functions in Eqs. (3) and (4).

Previous approaches to orientation averaging have introduced a distribution function $P'(\theta', \phi', \psi')$ which gives the probability that a member of the ensemble is related to the laboratory axis system by the Euler angles θ', ϕ', and ψ'. This distribution function is then expanded in terms of the Wigner rotation matrix elements[9,10]

$$P'(\theta', \phi', \psi') = \sum_{lmn} P_{lmn} \mathfrak{D}_{mn}^l(\theta', \phi', \psi') , \qquad (44)$$

where P_{lmn} are the lmnth moments of the distribution function defined by

$$P_{lmn} = \frac{2l+1}{8\pi^2} \int_0^{2\pi} \int_{-1}^1 \int_0^{2\pi} \mathfrak{D}_{mn}^l(\theta', \phi', \psi') P'(\theta', \phi', \psi')$$

$$\times d\phi' \, d\cos\theta' \, d\psi' . \qquad (45)$$

When Eq. (44) is substituted into orientational averaging . formulas with the response functions in Eqs. (3) and (4), the results are expressions that depend only on the $l=2$, and $l=4$ moments, and the structural parameters inherent in the type of spectroscopy analyzed (e.g., for fluorescence polarization, the expressions depend on the $l=2$ and $l=4$ moments, z_1, z_2, and ϵ).

There are two basic problems with the Wigner expansion approach.

(1) If one knows the spectroscopically inherent structural parameters, it is possible to probe the distribution function with an experiment on a partially ordered sample. In the Wigner expansion approach, this experiment can yield only the $l=2$ and $l=4$ moments, and these moments may be of little value in describing the distribution function, especially if the expansion in Eq. (44) is slowly convergent. The best one can do is to construct a model for the system, calculate $P'(\theta', \phi', \psi')$, and see if calculated moments from Eq. (45) agree with the measured moments. However, no general method for constructing $P'(\theta', \phi', \psi')$ from a model that involves a rotation scheme of four or more rotations has been described.

(2) If one wishes to measure the spectroscopically inherent structural parameters, it is necessary to know the $l=2$ and $l=4$ moments, or at least to be able to place limits on the moments. Because P_{lmn} are merely mathematical projections of the unknown distribution function on the Wigner rotation matrix elements, there is no justification for placing limits on the moments.

The density of states approach overcomes these problems. One way to think of the difference between our approach and the Wigner expansion approach is that we represent the distribution function in terms of the order parameter Δ instead of the P_{lmn} moments. The major benefits afforded by adopting our approach are as follows:

(1) If one uses known spectroscopically inherent structural parameters to probe the distribution function, one may obtain Δ. The Δ parameter in conjunction with the rotation scheme and weighting functions gives a complete definition of the distribution function. In fact, one could find all the P_{lmn} moments from Δ by an equation

$$P_{lmn} = \int \int \int \mathfrak{D}^l_{mn}(\theta', \phi', \psi') F(\theta', \phi', \psi', \Delta) d\theta' d\phi' d\psi', \quad (46)$$

where $F(\theta', \phi', \psi', \Delta)$ is a distribution function which could be derived from $P(\theta, \phi, \psi, \Delta)$ by converting from the molecular axis system to the laboratory axis system. Furthermore, each Δ_i is related to some physical property of the ensemble and, as such, is a quantity of interest.[1]

(2) If one wishes to measure the spectroscopically inherent structural parameters, it is necessary to know, the magnitude of Δ. It is easier to estimate the magnitude of Δ then to estimate the magnitude of the moments, because Δ may often be restricted from physical considerations.

(3) $P(\theta, \phi, \omega, \Delta)$ is evaluated from a model for the system which is defined by the rotations $R_1(\alpha_1) \cdots R_n(\alpha_n)$ and the weighting functions $g_1(\alpha_1) \cdots g_n(\alpha_n)$. As such, it is straightforward to interpret data in light of a specific model.

(4) The fact that we average orientations in a molecular axis system, instead of a laboratory axis system, sometimes makes our approach more efficient. For example, Ref. 4 gives an example of a system where the distribution function is axially symmetric in the molecular axis system but not in the laboratory axis system.

Most experimental work involving two-vector problems has been done on random systems. Work on partially ordered systems has either resorted to the cumbersome expansion method[11-13] or been analyzed only qualitatively.[14] As a result, experimental studies of two-vector spectroscopies on partially ordered systems is probably an underexplored area. It can serve as a valuable probe to structural features such as the orientation of transition moments in the molecular axis system and the principal axis system. In closing, we note that two-vector spectroscopies having response functions other than Eqs. (3) and (4) can still be analyzed by our approach, with Eq. (2) serving as a starting point for such an analysis.

ACKNOWLEDGMENTS

APPENDIX

Application of the n-dimensional change of variable theorem to Eq. (5) yields

$$I = \frac{1}{N} \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^{2\pi} d\omega \, I[\hat{v}_1'(\theta, \phi), \hat{v}_2'(\theta, \phi, \omega)] \int_{\nu_1} \cdots \int_{\nu_{n-3}} \prod_{i=1}^n g_i[\alpha_i(\phi, \nu_1, \ldots, \nu_{n-3}, \theta, \omega)]$$

$$\times \left| \frac{\partial \alpha_1, \ldots, \alpha_n}{\partial \phi, \nu_1, \ldots, \nu_{n-3}, \theta, \omega} \right| d\nu_1, \ldots, d\nu_{n-3}, \quad (A1)$$

where $(\partial \alpha_1, \ldots, \alpha_n / \partial \phi, \nu_1, \ldots, \nu_{n-3}, \theta, \omega)$ is the Jacobian of the coordinate transformation. By inspection we set

$$P(\theta, \phi, \omega, \Delta) = \frac{1}{N} \int_{\nu_1} \cdots \int_{\nu_{n-3}} \prod_{i=1}^n g_i[\alpha_i(\phi, \nu_1, \ldots, \nu_{n-3}, \theta, \omega)] \left| \frac{\partial \alpha_1, \ldots, \alpha_n}{\partial \phi, \nu_1, \ldots, \nu_{n-3}, \theta, \omega} \right| d\nu_1, \ldots d\nu_{n-3}. \quad (A2)$$

Following the approach of Ref. 2, we pick the laboratory z axis to be the axis of the first rotation $[R_1(\alpha_1)]$, and we use the following transformation

$$\alpha_1 = f_1(\phi, \nu_1, \ldots, \nu_{n-3}, \theta, \omega) ,$$

$$\alpha_2 = \nu_1 ,$$

$$\vdots$$

$$\alpha_{n-2} = \nu_{n-3} ,$$

$$\alpha_{n-1} = f_2(\nu_1, \ldots, \nu_{n-3}, \theta, \omega) ,$$

$$\alpha_n = f_3(\nu_1, \ldots, \nu_{n-3}, \theta, \omega) ,$$

(A3)

where α_{n-1} and α_n are defined by solving the two equations

$$\cos\theta = v'_{1s}(\alpha_2, \ldots, \alpha_n) ,$$

(A4)

$$-\sin\theta\cos\omega = v'_{2s}(\alpha_2, \ldots, \alpha_n) ,$$

(A5)

for α_n and α_{n-1} and setting $\alpha_2, \ldots, \alpha_{n-2}$ equal to $\nu_1, \ldots, \nu_{n-3}$.

As shown in Ref. 2, under the above transformation,

$$\alpha_1 = -\phi + f_4(\nu_1, \ldots, \nu_{n-3}, \theta, \omega) ,$$

(A6)

$$\frac{\partial\alpha_1}{\partial\phi} = -1,$$

(A7)

and

$$\frac{\partial\alpha_i}{\partial\phi} = 0, \quad i \neq 1.$$

(A8)

From Eqs. (A6), (A7), and (A8), the Jacobian simplifies to

$$|\mathcal{J}| = \left| \frac{\partial\alpha_{n-1}}{\partial\theta} \frac{\partial\alpha_n}{\partial\omega} - \frac{\partial\alpha_{n-1}}{\partial\omega} \frac{\partial\alpha_n}{\partial\theta} \right| .$$

(A9)

By differentiating both sides of Eqs. (A4) and (A5) with respect to both θ and ω, we get four equations in the four unknowns $\partial\alpha_{n-1}/\partial\theta$, $\partial\alpha_n/\partial\omega$, $\partial\alpha_{n-1}/\partial\omega$, $\partial\alpha_n/\partial\theta$. Solving these equations for the Jacobian yields

$$|\mathcal{J}| = \frac{\sin^2\theta \sin\omega}{\left| \dfrac{\partial v'_{1s}(\alpha_2, \ldots, \alpha_n)}{\partial\alpha_{n-1}} \dfrac{\partial v'_{2s}(\alpha_2, \ldots, \alpha_n)}{\partial\alpha_n} - \dfrac{\partial v'_{1s}(\alpha_2, \ldots, \alpha_n)}{\partial\alpha_n} \dfrac{\partial v'_{2s}(\alpha_2, \ldots, \alpha_n)}{\partial\alpha_{n-1}} \right|} ,$$

(A10)

with $\alpha_2, \ldots, \alpha_n$ replaced by their transformed variables $\nu_1, \ldots, \nu_{n-3}, f_2(\nu_1, \ldots, \nu_{n-3}, \theta, \omega)$, and $f_3(\nu_1, \ldots, \nu_{n-3}, \theta, \omega)$. Substitution into Eq. (A2) yields

$$P(\theta, \phi, \omega, \Delta) = \frac{\sin^2\theta \sin\omega}{N} \int_{\nu_1} \cdots \int_{\nu_{n-3}} g_1[-\phi + f_4(\nu_1, \ldots, \nu_{n-3}, \theta, \omega)] g_{n-1}[f_2(\nu_1, \ldots, \nu_{n-3}, \theta, \omega)]$$

$$\times g_n[f_3(\nu_1, \ldots, \nu_{n-3}, \theta, \omega)] \frac{\Pi_{i=2}^{n-2} g_i(\nu_{i-1}) d\nu_{i-1}}{\left| \dfrac{\partial v'_{1s}}{\partial\alpha_{n-1}} \dfrac{\partial v'_{2s}}{\partial\alpha_n} - \dfrac{\partial v'_{1s}}{\partial\alpha_n} \dfrac{\partial v'_{2s}}{\partial\alpha_{n-1}} \right|} .$$

(A11)

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