Using Rotational Averaging To Calculate the Bulk Response of Isotropic and Anisotropic Samples from Molecular Parameters

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Despite recent advances in single-molecule measurements, nearly all of our knowledge of the microscopic structure of molecules arises from measurements of bulk samples. As a result, part of the art of experimental chemistry is in figuring out properties of individual molecules, which are on the scale of nanometers, based on measurements with characteristic size scales that are many orders of magnitude larger. Conversely, chemical engineers may need to predict the behavior of bulk samples from known parameters for individual molecules. In some cases, there is a simple correspondence between bulk and microscopic properties. For example, if we experimentally determine that a sample of pure carbon dioxide has two moles of atomic oxygen for each mole of carbon, we can immediately deduce that each individual carbon dioxide molecule has two atoms of oxygen for each atom of carbon. In contrast, absorption spectroscopy does not scale so easily.

Suppose we are interested in the electronic properties of alkenes. On recording the ultraviolet spectrum of 1-octene dissolved in *n*-heptane, we see a peak at 177 nm with an absorption coefficient of 13,000 M^{-1} cm^{-1} *(1)*. Dividing by Avogadro's number and changing units seems to imply that the absorption cross-section of each 1-octene molecule is 2.2×10^{-3} nm^2. However, this is wrong. Using a classical picture, absorption of light occurs by the excitation of electron cloud fluctuations along the direction of the molecular transition dipole moment by the oscillating electric field of the light wave *(2)*. Absorption is maximal when the transition dipole moment is parallel to the light polarization and is equal to zero when the vectors are perpendicular. While it is correct that the absorption cross section of 1-octene is 2.2×10^{-3} nm^2 per molecule *on average*, the actual value for an individual molecule varies from 0 to 6.6×10^{-3} nm^2, depending on the orientation of the molecule relative to the light polarization. The average absorption cross-section is exactly one third of the maximum value, a correction factor that is well known, but whose quantitative derivation is neither obvious nor typically presented in textbooks. This article presents the mathematics behind this and other rotational averages to satisfy the curiosity of mathematically-inclined students and because new experiments may require rotational averages that are not readily available, making additional derivations necessary.

Rotational-averaging methods are used routinely for quantitative single- or multiphoton spectroscopy *(3)*. The former includes simple absorption and emission spectroscopy and the latter includes fluorescence *(4)*, Raman *(5)*, photoselection *(6)*, dichroism *(7)*, pump-probe, and several other conventional and laser spectroscopy methods. Rotational averaging has also been useful for Stark effect *(8–10)* and Zeeman effect spectroscopy. While rotational averaging is rare outside the field of spectroscopy, the method is general and could be used in other branches of physical chemistry. For example, it could be used to quantify molecular alignment in a rheology or surface science experiment.

Before starting to write equations, it is helpful to define the problem more carefully. The goal is to calculate experimental observables, or other properties of a bulk sample, in terms of microscopic molecular parameters. This requires a summation of experimental responses over all molecules in the sample, followed by division by the number of molecules to yield results on a per molecule basis. Alternatively, it is equivalent and easier to calculate a statistical average over all orientations of a single molecule. While it is typically valid, an assumption is being made here, which is that enough molecules are detected, or the measurement timescale is sufficiently long, that random molecular fluctuations do not appear in the experimental result. At the end, the calculated equation can be inverted to yield molecular parameters in terms of experimental results.

Isotropic Averages

Some axes are required to express a molecule's orientation, as shown in Figure 1. Following the standard convention *(4)*, *X*, *Y*, and *Z* are the Cartesian axes in the laboratory
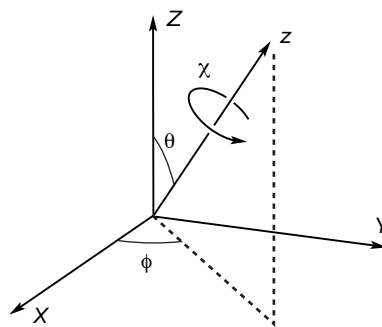

Figure 1. Laboratory and molecular coordinate systems: *X*, *Y*, and *Z* are the laboratory reference frame axes, and *x*, *y*, and *z* are the molecule reference frame axes. For clarity, only *z* is shown; *x* and *y* are perpendicular to each other and to *z*, although their exact positions are not important. θ, ϕ, and χ are the Euler angles that relate the coordinate systems. A rotational average integrates over the full ranges of θ, ϕ, and χ to account for the range of molecule orientations in a bulk sample.

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reference frame (also called the space-fixed reference frame) used for specifying orientations of polarizers, detectors, molecular beams, and other laboratory apparatus. For a molecule (sometimes called the body-fixed reference frame), the Cartesian axes are x, y, and z, which are used for dipole moments, polarizabilities, transition dipoles, symmetry axes, and other molecular properties. The molecule's orientation in the laboratory is given by the Euler angles θ, ϕ, and χ, where these angles express the rotation of the molecular axes with respect to the laboratory coordinate system (4,11,12). θ and ϕ are the familiar angles from spherical coordinates that give the direction of the molecule's z axis in the laboratory frame: θ is the angle between Z and z, and ϕ is the angle between X and the projection of z on the XY plane. The third Euler angle, χ, expresses the rotation of the molecule about its z axis.

When a molecule interacts with the experimental system, the result (e.g., an absorption intensity) typically depends upon the molecule's orientation and may be given generally by $f(\theta, \phi, \chi)$. The bulk response, scaled to a per molecule basis, is the value of $f(\theta, \phi, \chi)$ averaged uniformly over all orientations:

$$\langle f \rangle = \frac{1}{8\pi^2} \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} f(\theta, \phi, \chi) \sin\theta \, d\theta \, d\phi \, d\chi \tag{1}$$

This equation is taken as the definition of a rotational average for an isotropic sample, as well as the definition of the brackets notation. To demonstrate a rotational average using a trivial example, suppose $f(\theta, \phi, \chi)$ is a measurement of the mass of a molecule, given as m, and we want to calculate the rotationally averaged mass. As $f(\theta, \phi, \chi)$ is independent of the molecule's orientation in this case, it factors out of the integral and it is found that the average is just equal to the mass (i.e., $\langle m \rangle = m$). The interpretation is that the average mass of a molecule in an isotropically oriented sample is the same as the mass of a molecule in some specific orientation, which is obviously true. Much more generally, all rotational averaging for isotropic samples can be carried out with a suitable choice of $f(\theta, \phi, \chi)$ and eq 1.

It is worth noting some basic properties of eq 1. In a manner similar to the calculation of an average mass, it can be seen that this definition of rotational averaging is normalized so that $\langle 1 \rangle = 1$. Secondly, rotational averaging is a linear operation, for example:

$$\langle k_1 f_1 + k_2 f_2 \rangle = k_1 \langle f_1 \rangle + k_2 \langle f_2 \rangle \tag{2}$$

Finally, the only angles that appear in eq 1 are relative angles between the laboratory and molecular coordinate systems. This gives us the freedom to define both sets of axes as desired, often allowing for a relatively simple analysis.

Energy of Immobilized Dipoles in a Uniform Field

Suppose we want to calculate the potential energy of a sample of molecules in an externally applied uniform electric field. Each molecule has a dipole moment vector $\mathbf{p}$ and is immobilized so it cannot rotate, as one might find for molecules suspended in a polymer matrix. Considering a specific molecule, $\mathbf{p}$ is its dipole moment expressed in the molecule coordinate system; the same vector, for the same molecule, is called $\mathbf{p}_L$ when coordinates for the laboratory reference

frame are used. The two representations are related by the equation $\mathbf{p}_L = \mathbf{p}\boldsymbol{\Phi}$, where $\boldsymbol{\Phi}$, called the direction cosine matrix, contains information about the molecule's orientation in the laboratory. (To be rigorous, $\mathbf{p}$ and $\mathbf{p}_L$ are being used as row vectors because this will turn out to be more convenient than column vectors). In terms of the Euler angles that define the relative rotation of the two coordinate systems, the direction cosine matrix is (4, 11):

$$\boldsymbol{\Phi} = \begin{bmatrix} c\phi\, c\theta\, c\chi - s\phi\, s\chi & s\phi\, c\theta\, c\chi + c\phi\, s\chi & -s\theta\, c\chi \\ -c\phi\, c\theta\, s\chi - s\phi\, c\chi & -s\phi\, c\theta\, s\chi + c\phi\, c\chi & s\theta\, s\chi \\ c\phi\, s\theta & s\phi\, s\theta & c\theta \end{bmatrix}$$

$$= \begin{bmatrix} \Phi_{Xx} & \Phi_{Yx} & \Phi_{Zx} \\ \Phi_{Xy} & \Phi_{Yy} & \Phi_{Zy} \\ \Phi_{Xz} & \Phi_{Yz} & \Phi_{Zz} \end{bmatrix} \tag{3}$$

In the former matrix, "c" is used for cosine and "s" is used for sine. The Φ_{Fi} coefficients in the latter matrix, using F as an index for X, Y, and Z and i as an index for x, y, and z, are nothing more than a convenient notation for elements of the $\boldsymbol{\Phi}$ matrix. Thus, each Φ_{Fi} term is a function of θ, ϕ, and χ. A general property of rotation matrices, such as this one, is that they are unitary (all eigenvalues are equal to 1). As all the coefficients in $\boldsymbol{\Phi}$ are also real, a useful identity is that $\boldsymbol{\Phi}^T \boldsymbol{\Phi}$ is the identity matrix, where the symbol ^{T} denotes the matrix transpose.

For a single molecule, the potential energy from electric field interactions is $U = -\mathbf{p}_L \cdot \mathbf{E}$, where $\mathbf{E}$ is the electric field (13). The desired equation is the rotational average of this, to yield the average potential energy per molecule in a bulk sample. For convenience, the laboratory coordinate system is defined so that the Z axis is parallel to the electric field, allowing the field to be written as the scalar E times $\hat{\mathbf{Z}}$, where $\hat{\mathbf{Z}}$ is a unit vector on the Z axis. The average is:

$$U_{av} = \langle -\mathbf{p}_L \cdot \mathbf{E} \rangle = -E \langle \mathbf{p}_L \cdot \hat{\mathbf{Z}} \rangle \tag{4}$$

The term within brackets, including the brackets, is called the sample polarization and denoted P. It is converted to the laboratory coordinate system and then solved using eq 3:

$$P = \langle \mathbf{p}_L \cdot \hat{\mathbf{Z}} \rangle = \langle \mathbf{p}\boldsymbol{\Phi}\hat{\mathbf{Z}} \rangle$$

$$= \langle p_x \Phi_{Zx} + p_y \Phi_{Zy} + p_z \Phi_{Zz} \rangle = \sum_i p_i \langle \Phi_{Zi} \rangle = 0 \tag{5}$$

The final equality follows by direct integration of the relevant $\boldsymbol{\Phi}$ coefficients using eqs 1 and 3, by an analysis of the symmetry of the underlying sines and cosines, or by looking up the result in List 1. Because the polarization is zero, the answer to our problem is that the average potential energy of randomly oriented dipoles in a uniform field is also zero. While this result could have been deduced from symmetry, the derivation process and the intermediate equations are central aspects of rotational averaging. They are repeated many times in subsequent examples, although with decreasing detail.

Absorption of Light

As mentioned in the introduction, the classical picture of the absorption of light is that electronic fluctuations in

List 1. Rotational Averages of Direction Cosines

1 $\langle 1 \rangle = 1$

2 $\langle \Phi_{Fi} \rangle = \langle \Phi_{Fi}\Phi_{Fj}\Phi_{Fk} \rangle = \langle \Phi_{Fi}\Phi_{Fj}\Phi_{Fk}\Phi_{Fl}\Phi_{Fm} \rangle = \ldots = 0$

3 $\langle \Phi_{Fi}\Phi_{Fj} \rangle = \dfrac{\delta_{ij}}{3}$

4 $\langle \Phi_{Fi}\Phi_{Fj}\Phi_{Fk}\Phi_{Fl} \rangle = \dfrac{\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}}{3 \times 5}$

5 $\langle \Phi_{Fi}\Phi_{Fj}\Phi_{Fk}\Phi_{Fl}\Phi_{Fm}\Phi_{Fn} \rangle = \dfrac{\delta_{ij}\delta_{kl}\delta_{mn} + \delta_{ij}\delta_{km}\delta_{ln} + \ldots}{3 \times 5 \times 7}$ 15 terms

6 $\langle \Phi_{Fi_1}\Phi_{Fi_2}\ldots\Phi_{Fi_n} \rangle = \begin{cases} 0 & n \text{ odd} \\ \dfrac{\delta_{i_1 i_2}\delta_{i_3 i_4}\ldots\delta_{i_{n-1} i_n} + \ldots}{(n+1)!!} & n \text{ even} \end{cases}$ $(n-1)!!$ terms

7 $\langle \Phi_{Fi}\Phi_{Gj} \rangle = \langle \Phi_{Fi}\Phi_{Gj}\Phi_{Gk} \rangle = \langle \Phi_{Fi}\Phi_{Gj}\Phi_{Gk}\Phi_{Gl} \rangle = \ldots = 0$ $G \neq F$ here and in the following terms

8 $\langle \Phi_{Fi}\Phi_{Fj}\Phi_{Gk}\Phi_{Gl} \rangle = \dfrac{4\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}}{2 \times 3 \times 5}$

9 $\langle \Phi_{Fi}\Phi_{Fj}\Phi_{Gk}\Phi_{Gl}\Phi_{Gm}\Phi_{Gn} \rangle = \dfrac{6\delta_{ij}\delta_{kl}\delta_{mn} + 6\delta_{ij}\delta_{km}\delta_{ln} + 6\delta_{ij}\delta_{kn}\delta_{lm} - \delta_{ik}\delta_{jl}\delta_{mn} - \ldots}{2 \times 3 \times 5 \times 7}$ 18 terms

10 $\langle \Phi_{Fi_1}\Phi_{Fi_2}\Phi_{Gi_3}\Phi_{Gi_4}\ldots\Phi_{Gi_n} \rangle = \begin{cases} 0 & n \text{ odd} \\ \dfrac{\delta_{i_1 i_2}\langle \Phi_{Gi_3}\Phi_{Gi_4}\ldots\Phi_{Gi_n} \rangle - \langle \Phi_{Gi_1}\Phi_{Gi_2}\ldots\Phi_{Gi_n} \rangle}{2} & n \text{ even} \end{cases}$

11 $\left\langle \dfrac{\Phi_{Fi_1}\Phi_{Fi_2} + 2\Phi_{Gi_1}\Phi_{Gi_2}}{3}\Phi_{Fi_3}\Phi_{Fi_4}\ldots\Phi_{Fi_n} \right\rangle = \dfrac{\delta_{i_1 i_2}\langle \Phi_{Fi_3}\Phi_{Fi_4}\ldots\Phi_{Fi_n} \rangle}{3}$

12 $\left\langle \dfrac{\Phi_{Fi_1}\Phi_{Fi_2} - \Phi_{Gi_1}\Phi_{Gi_2}}{3}\Phi_{Fi_3}\Phi_{Fi_4}\ldots\Phi_{Fi_n} \right\rangle = \dfrac{\langle \Phi_{Fi_1}\Phi_{Fi_2}\ldots\Phi_{Fi_n} \rangle}{2} - \dfrac{\delta_{i_1 i_2}\langle \Phi_{Fi_3}\Phi_{Fi_4}\ldots\Phi_{Fi_n} \rangle}{6}$

NOTE: Φ_{Fi} terms are direction cosine matrix elements where the former index represents a laboratory frame axis, equal to *X*, *Y*, or *Z*, and the latter represents a molecule frame axis, equal to *x*, *y*, or *z*. Where an equation includes two laboratory frame axes, *F* and *G*, it is assumed that they are not the same axis. The brackets represent a rotational average as defined by eq 1. In several equations, ellipses indicate that a series includes all products of Kronecker delta functions with distinct permutations of the indices; the total number of terms in the expression is listed. See the Appendix for the derivation methods of the equations shown here. Note that $n!! = n(n-2)(n-4)\ldots(2 \text{ or } 1)$.

the molecule along the transition dipole moment, **m**, are excited by the oscillating electric field of a light wave *(2)*, whose direction is now given as **ê**. The transition dipole moment can be calculated from first principles using quantum mechanics. However, it is not directly measurable; instead one measures the absorption coefficient of the transition as a function of frequency over the entire absorption band, which is then linked to theory through its integral. For a single molecule, the integral is *(12, 14)*,

$$\int \varepsilon(\nu)\,d\nu = \frac{2\pi^2 N_A \nu}{\varepsilon_0 h c \ln 10}(\mathbf{m}_L \cdot \hat{\mathbf{e}})^2 \qquad (6)$$

where $\varepsilon(\nu)$ is the absorption coefficient as a function of the frequency, N_A is Avogadro's number, ε_0 is the vacuum permittivity, *h* is Planck's constant, and *c* is the speed of light in vacuum. As before, the 'L' subscript on $\mathbf{m}_L$ indicates that this equation uses the laboratory reference frame expression of the transition dipole moment vector. From the dot product in the equation, it can be seen that absorption is maximal for molecules oriented so that $\mathbf{m}_L$ is parallel or antiparallel to **ê** and is zero for those with $\mathbf{m}_L$ perpendicular to **ê**. For convenience, the *Z* axis is oriented parallel to the light polarization. The rotationally averaged integrated absorption coefficient, which is the experimental observable, is expressed by putting brackets around both sides of eq 6. On the right

side of the equation, the constants factor out, leaving a result that is simplified:

$$\left\langle \left(\mathbf{m}_L \cdot \hat{\mathbf{Z}} \right)^2 \right\rangle = \left\langle \left(\mathbf{m}\boldsymbol{\Phi}\hat{\mathbf{Z}} \right)^2 \right\rangle$$

$$= \left\langle \left(m_x \Phi_{Zx} + m_y \Phi_{Zy} + m_z \Phi_{Zz} \right)^2 \right\rangle$$

$$= \left\langle \left(\sum_i m_i \Phi_{Zi} \right)^2 \right\rangle = \left\langle \left(\sum_i m_i \Phi_{Zi} \right) \left(\sum_j m_j \Phi_{Zj} \right) \right\rangle \qquad (7)$$

$$= \sum_{i,j} m_i m_j \left\langle \Phi_{Zi} \Phi_{Zj} \right\rangle = \sum_{i,j} m_i m_j \frac{\delta_{ij}}{3} = \sum_i \frac{m_i m_j}{3} = \frac{|\mathbf{m}|^2}{3}$$

The $\langle \Phi_{Zi} \Phi_{Zj} \rangle$ factor can be solved by integration of the sines and cosines in eq 3 or the solution can be found in List 1. The δ_{ij} factor is a Kronecker delta function that, by definition, is equal to 1 if $i = j$ or 0 if $i \neq j$. In the final equality, it is recognized that the sum of the squared components of $\mathbf{m}$ is equal to the vector magnitude squared, leading to a notationally clean result. This tidiness is a consequence of the fact that the molecular axes were chosen by us rather than being an intrinsic property of the molecule, so they must become irrelevant at the end of the calculation. Comparison of the result in eq 7 with the last term of eq 6 shows that an isotropic bulk sample absorbs one third as much light as a sample of molecules that are aligned parallel to the light polarization, as mentioned in the introduction. This indicates that most molecules in an isotropic sample are in orientations that have poor overlap between their transition dipole moments and an external axis.

Fluorescence

Fluorescence is a two photon process in which a molecule absorbs incident light with its absorption transition dipole moment, $\mathbf{m}_a$, and subsequently emits a photon from its emission transition dipole moment, $\mathbf{m}_e$. These transition dipoles, including their magnitudes and relative orientations, form another important link between experiment and quantum mechanics, such as for studying intra- and intermolecular energy transfer. In the experiment, shown in Figure 2, a fluorimeter excites an isotropic sample with light polarized along the Z axis and detects emitted light using a polarizer that transmits light polarized parallel to $\hat{\mathbf{e}}$. The laboratory reference frame is defined so $\hat{\mathbf{e}}$ is in the XZ plane at angle α away from Z. The absolute fluorescence intensity, integrated over both the absorption and emission peaks, is essentially just eq 6 written twice, once for absorption and once for emission, but with the product multiplied by the fluorescence quantum yield (the fraction of excited molecules that emit a photon). Brackets are placed around the whole works, leading to the rotationally averaged integrated fluorescence intensity,

$$I = A \left\langle \left(\mathbf{m}_{e,L} \cdot \hat{\mathbf{e}} \right)^2 \left(\mathbf{m}_{a,L} \cdot \hat{\mathbf{Z}} \right)^2 \right\rangle \qquad (8)$$

where A is a proportionality constant equal to the products of the prefactors from eq 6 and the quantum yield. The detector polarization direction, $\hat{\mathbf{e}}$, is expanded into its X axis and Z axis components:

$$I = A \left\langle \left[\mathbf{m}_{e,L} \cdot \left(\hat{\mathbf{Z}} \cos\alpha + \hat{\mathbf{X}} \sin\alpha \right) \right]^2 \left(\mathbf{m}_{a,L} \cdot \hat{\mathbf{Z}} \right)^2 \right\rangle$$

$$= A \left\langle \left(\mathbf{m}_{e,L} \cdot \hat{\mathbf{Z}} \right)^2 \left(\mathbf{m}_{a,L} \cdot \hat{\mathbf{Z}} \right)^2 \right\rangle \cos^2\alpha$$

$$+ A \left\langle \left(\mathbf{m}_{e,L} \cdot \hat{\mathbf{X}} \right) \left(\mathbf{m}_{e,L} \cdot \hat{\mathbf{Z}} \right) \left(\mathbf{m}_{a,L} \cdot \hat{\mathbf{Z}} \right)^2 \right\rangle \cos\alpha \, \sin\alpha \qquad (9)$$

$$+ A \left\langle \left(\mathbf{m}_{e,L} \cdot \hat{\mathbf{X}} \right)^2 \left(\mathbf{m}_{a,L} \cdot \hat{\mathbf{Z}} \right)^2 \right\rangle \sin^2\alpha$$

$$= I_{\parallel} \cos^2\alpha + I_{\times} \cos\alpha \, \sin\alpha + I_{\perp} \sin^2\alpha$$

In the last equality, $I_{\parallel}$, $I_{\times}$, and $I_{\perp}$ are defined as the constant A times the respective rotational averages given in the previous expression. It can also be seen that $I_{\parallel}$ is the fluorescence intensity measured if the fluorimeter polarizations are parallel ($\alpha = 0°$) and $I_{\perp}$ is the value if they are perpendicular ($\alpha = 90°$). The averages for these terms are solved independently, using more generic notation and the same overall method as in the previous examples:

$$\left\langle \left(\mathbf{r}_L \cdot \hat{\mathbf{Z}} \right)^2 \left(\mathbf{s}_L \cdot \hat{\mathbf{Z}} \right)^2 \right\rangle = \sum_{i,j,k,l} r_i r_j s_k s_l \left\langle \Phi_{Zi} \Phi_{Zj} \Phi_{Zk} \Phi_{Zl} \right\rangle$$

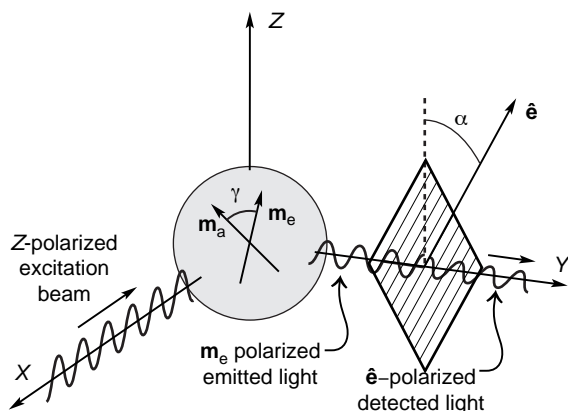$$= \frac{|\mathbf{r}|^2 |\mathbf{s}|^2 + 2(\mathbf{r} \cdot \mathbf{s})}{15} \qquad (10)$$

Figure 2. Vectors and angles in fluorescence spectroscopy. The sphere at the origin represents a sample molecule, including its absorption and emission transition dipole moments, $\mathbf{m}_a$ and $\mathbf{m}_e$, respectively. It is excited by Z-polarized light incident along the X axis and fluoresces with a polarization that is parallel to the emission transition dipole moment. The $\hat{\mathbf{e}}$ component of this emitted light is selected by a polarizer in the fluorimeter, shown with the grid on the right side of the figure, leading to $\hat{\mathbf{e}}$-polarized light that propagates outward along the Y axis. The intensity of this beam is measured with the fluorimeter detector; after integrating the result over excitation and emission frequencies, the detected intensities at multiple polarizer angles (α), can be used to quantify the molecular parameters $|\mathbf{m}_a|^2 |\mathbf{m}_e|^2$ and γ, as described in the text.

$$\left\langle \left(\mathbf{r}_L \cdot \hat{\mathbf{X}}\right)\left(\mathbf{r}_L \cdot \hat{\mathbf{Z}}\right)\left(\mathbf{s}_L \cdot \hat{\mathbf{Z}}\right)^2 \right\rangle =$$
$$\sum_{i,j,k,l} r_i\, r_j\, s_k\, s_l \left\langle \Phi_{Xi}\, \Phi_{Zj}\, \Phi_{Zk}\, \Phi_{Zl} \right\rangle = 0 \tag{11}$$

$$\left\langle \left(\mathbf{r}_L \cdot \hat{\mathbf{X}}\right)^2 \left(\mathbf{s}_L \cdot \hat{\mathbf{Z}}\right)^2 \right\rangle = \sum_{i,j,k,l} r_i\, r_j\, s_k\, s_l \left\langle \Phi_{Xi}\Phi_{Xj}\Phi_{Zk}\Phi_{Zl} \right\rangle$$
$$= \frac{2|\mathbf{r}|^2 |\mathbf{s}|^2 - (\mathbf{r} \cdot \mathbf{s})^2}{15} \tag{12}$$

Because eq 11 is equal to zero, the cross-term in eq 9 drops out, leaving only terms for the fluorescence intensity parallel and perpendicular to the excitation. Thus, the fluorescence intensity that is emitted at *any* polarization angle can be calculated from only the values for $I_\parallel$ and $I_\perp$. The corollary is that no additional information can be learned by measuring fluorescence at more than two polarization angles. Substituting the averages in eqs 10 and 12 into eq 9, the total fluorescence intensity is:

$$I = A \frac{|\mathbf{m}_e|^2 |\mathbf{m}_a|^2 + 2(\mathbf{m}_e \cdot \mathbf{m}_a)^2}{15} \cos^2\alpha$$
$$+ A \frac{2|\mathbf{m}_e|^2 |\mathbf{m}_a|^2 - (\mathbf{m}_a \cdot \mathbf{m}_e)^2}{15} \sin^2\alpha \tag{13}$$

Two trigonometric identities help simplify this result. The former replaces each of the two dot products in eq 13 with the product of the vector magnitudes and the cosine of the angle between them: $\mathbf{m}_a \cdot \mathbf{m}_e = |\mathbf{m}_a||\mathbf{m}_e|\cos\gamma$. This angle, γ, is a property of the molecules; it is the angle in a molecule between the absorption and emission transition dipole moments. The other identity confines the α dependence to only one of the terms:

$$I_\parallel \cos^2\alpha + I_\perp \sin^2\alpha = \frac{I_\parallel + 2I_\perp}{3} + \frac{I_\parallel - I_\perp}{3}\left(3\cos^2\alpha - 1\right) \tag{14}$$

While eq 14 is not obvious, it is fairly easy to verify. After some algebra, eq 13 simplifies to:

$$I = A \frac{|\mathbf{m}_a|^2 |\mathbf{m}_e|^2}{9}\left[1 + \frac{1}{5}\left(3\cos^2\gamma - 1\right)\left(3\cos^2\alpha - 1\right)\right] \tag{15}$$

This equation is a concise solution of the desired result, which is the rotationally averaged integrated fluorescence intensity in terms of molecular parameters and the polarizer angle. The process of absorbing a photon is the same for fluorescence as for a simple absorption experiment, so the fluorescence intensity is proportional to $|\mathbf{m}_a|^2$, as in eq 7 in the previous example. Although it is more subtle, the interactions between molecular electron cloud fluctuations and the radiation field during photon emission are equivalent, explaining the proportionality of eq 15 to $|\mathbf{m}_e|^2$. The product of these squared transition dipole moments can be found in a couple of ways, both of which serve to make eq 15 independent of γ. Experimentally, the polarizer angle can be set to $\alpha = 54.7°$, called the magic angle, which fixes the second term of eq 15 to zero and makes a fluorescence intensity measurement directly proportional to $|\mathbf{m}_a|^2 |\mathbf{m}_e|^2$. Alternatively, if

$I_\parallel$ and $I_\perp$ are available, eq 14 shows that $(I_\parallel + 2I_\perp)/3$ is equal to the initial term of eq 15. A different rearrangement of eqs 14 and 15 yields γ, the angle between the transition dipole moments, via a frequently used intermediate value called the fluorescence anisotropy (4):

$$\text{anisotropy} = \frac{I_\parallel - I_\perp}{2I_\parallel + I_\perp} = \frac{3\cos^2\gamma - 1}{5} \tag{16}$$

The value of the anisotropy ranges from $-1/5$ to $2/5$, for γ angles from $90°$ to $0°$, respectively, and is 0 if γ is the magic angle.

The situation is often not this simple, owing to yet another incidence of rotational averaging. In a gas or liquid phase sample, rotational diffusion often provides significant reorientation of a fluorescent molecule during the time between the absorption of a photon and the subsequent fluorescent emission. In these cases, if γ is known from other experiments, then $I_\parallel$ and $I_\perp$ can yield the rotational diffusion constant, a topic that is discussed at length in reference (15).

The algebraic manipulations between eqs 13 and 15 could have been simplified. Rather than rearranging the result after rotational averaging, it is generally more convenient to do so beforehand. If this were done, the identity in eq 14 would have been applied to eq 9 and the required rotational averages would have been:

$$\left\langle \frac{\Phi_{Zi}\Phi_{Zj} + 2\Phi_{Xi}\Phi_{Xj}}{3}\Phi_{Zk}\Phi_{Zl} \right\rangle$$
$$\left\langle \frac{\Phi_{Zi}\Phi_{Zj} - \Phi_{Xi}\Phi_{Xj}}{3}\Phi_{Zk}\Phi_{Zl} \right\rangle \tag{17}$$

While these averages appear more complicated than the ones used, they lead more directly to the simplified result. They are also equal to simpler sums of Kronecker delta functions, as seen in List 1.

Up to this point, we have been considering increasingly complicated products of vectors in the molecule reference frame with ones in the laboratory reference frame. In each case, the additional experimental complexity led to more mathematical complexity, but also to the ability to learn more about the microscopic structure of the sample molecules. This trend could be extended to higher-order multiphoton spectroscopy, using similar methods. Instead of continuing the trend, we address the issue of how to rotationally average with matrix properties.

Energy of Polarizable Molecules in a Field

The simplest electrostatic characterization of a molecule is its total charge, which is a scalar quantity; the next level of detail is its dipole moment, which is a vector; the next level is its polarizability, which is a matrix; and higher levels of detail are called hyperpolarizabilities, represented by higher rank tensors. Here, we consider rotational averaging with a matrix by calculating the average potential energy of a sample of immobilized polarizable molecules in an externally applied uniform electric field. $\boldsymbol{\alpha}$ is taken as a molecule's polarizability matrix and $\boldsymbol{\alpha}_L$ is the same matrix expressed in the labora-

tory coordinate system, terms that are related with the coordinate transformation $\alpha_L = \Phi^T \alpha \Phi$. The laboratory coordinates are defined so the electric field, E, is along the Z axis. From basic electrostatics (13), the potential energy of a single molecule is $U = -E\alpha_L E/2$, which is placed in brackets to yield the rotationally averaged energy:

$$U_{av} \;=\; -\frac{1}{2}\langle E\alpha_L E\rangle \;=\; -\frac{E^2}{2}\langle \hat{Z}\alpha_L \hat{Z}\rangle \qquad (18)$$

The rotational average is:

$$\langle \hat{Z}\alpha_L \hat{Z}\rangle \;=\; \langle \hat{Z}\Phi^T \alpha \Phi\hat{Z}\rangle$$
$$=\; \sum_{i,j}\alpha_{ij}\langle \Phi_{Zi}\Phi_{Zj}\rangle \;=\; \sum_{i,j}\frac{\alpha_{ij}\delta_{ij}}{3} \;=\; \frac{\mathrm{Tr}\,\alpha}{3} \qquad (19)$$

The notation "Tr" denotes the trace of a matrix (the sum of the matrix coefficients along the main diagonal). Because the trace of a matrix is also the sum of the matrix eigenvalues, the result is once again independent of the choice of axes, as it must be. Combining eq 19 with the terms that were left off from eq 18 shows that the energy becomes more negative with increasing polarizability and is proportional to the sum of the polarizability eigenvalues. On a practical level, it is difficult to experimentally determine individual polarizability eigenvalues, so a standard approximation is to assume that the polarizability is the same on all axes of the molecules of interest. In this approximation, the polarizability is reported as the scalar α, where $\alpha = \mathrm{Tr}\,\alpha/3$.

Rotational Averages with Tensors

Higher rank tensors, such as hyperpolarizabilities, are averaged in a similar manner as shown above for vectors and matrices. However, one has to abandon the clean vector and matrix notation, shown in bold face type, and resort entirely to subscripts and indices. For example, the transformation of the first hyperpolarizability tensor β from the molecule reference frame to the laboratory reference frame is:

$$\beta_{L,lmn} \;=\; \sum_{i,j,k}\beta_{ijk}\Phi_{il}\Phi_{jm}\Phi_{kn} \qquad (20)$$

These equations become sufficiently cumbersome that the summation symbol is often implied rather than being written explicitly, a notational method called the Einstein summation convention (13).

Anisotropic Averages

There are many ways in which samples may become partially oriented, such as photoselection, external fields, flow gradients, or surface interactions. An example of photoselection was actually considered previously in the fluorescence example, although it was not interpreted that way. In this alternate view, fluorescence is a simple one photon emission process from an excited population of molecules, where the excited population is the collection of molecules that were selected by having a high overlap between their absorption transition dipole moments and the excitation beam polarization.

A general treatment of anisotropic samples requires a function that expresses the proportion of molecules in each orientation, using Euler angles. This density function, $\rho(\theta, \phi, \chi)$, is defined so that the fraction of molecules with orientations that are within $d\theta$, $d\phi$, and $d\chi$ of the exact orientation θ, ϕ, and χ is given by $(8\pi^2)^{-1}\rho(\theta, \phi, \chi)\sin\theta\,d\theta\,d\phi\,d\chi$. Because this is a fraction of the sample, it must integrate to 1. Referring back to eq 1, it can be seen that the integral needed to normalize $\rho(\theta, \phi, \chi)$ is identical to the one that defines the brackets notation, allowing this normalization constraint to be written as $\langle\rho\rangle = 1$. A second constraint on $\rho(\theta, \phi, \chi)$ is that it must be nonnegative for all θ, ϕ, and χ values, which also follows from the physical interpretation of the density function. Using the density function as a weighting factor, the rotational average of the generic molecular response function $f(\theta, \phi, \chi)$ now accounts for any sample anisotropy:

$$\langle f\rho\rangle \;=\; \frac{1}{8\pi^2}\int_0^\pi\int_0^{2\pi}\int_0^{2\pi} f(\theta, \phi, \chi)\rho(\theta, \phi, \chi)\sin\theta\,d\theta\,d\phi\,d\chi \qquad (21)$$

This anisotropic average uses the same definition of the brackets notation that was given before. If $\rho(\theta, \phi, \chi)$ is equal to the value 1 for all angles (which obeys the normalization constraint because $\langle 1\rangle = 1$), eq 21 simplifies to the isotropic average in eq 1. Thus, this equation should not be thought of as the anisotropic version of eq 1, but as the complete equation for a rotational average, for both isotropic and anisotropic samples.

Energy of Mobile Dipoles in an Electric Field: Approximate Solution

It was shown in the first example that a uniform electric field does not affect the potential energy of isotropically oriented immobilized dipoles. Here, the same experiment is considered but with mobile dipoles, as in a gas or liquid, so that they are able to become oriented in the field. As before, the laboratory frame axes are defined so the electric field, E, is parallel to the Z axis, the dipole moment of a molecule is p, and the potential energy of a dipole in a field is $U = -p_L\cdot E$. Because of thermal motion, the molecules are not all positioned in their lowest energy orientations, but have an equilibrium density function that is given by the Boltzmann distribution,

$$\rho(\theta, \phi, \chi) \;\propto\; e^{-\beta U} \;=\; e^{\beta p_L\cdot E} \;\approx\; 1 + \beta E p_L\cdot\hat{Z} \qquad (22)$$

where β is the Boltzmann factor, equal to $(k_B T)^{-1}$, k_B is Boltzmann's constant, T is the absolute temperature, and E is the magnitude of the electric field. The final equality is a valid approximation when the potential energy of a sample molecule in the electric field is small compared to its thermal energy, which is the situation for most experiments (10). Normalization with the constraint $\langle\rho\rangle = 1$ and the average in eq 5 shows that the normalization constant is simply equal to 1 in this case, yielding the approximate density function:

$$\rho(\theta, \phi, \chi) \;\approx\; 1 + \beta E p_L\cdot\hat{Z} \qquad (23)$$

As in the first example, the average energy is $U_{av} = -EP$. The polarization, P, is found using the linearity property of a ro-

tational average and some averages found previously in eqs 5 and 7:

$$P = \left\langle \left(\mathbf{p}_L \cdot \hat{\mathbf{Z}}\right) \rho \right\rangle = \left\langle \left(\mathbf{p}_L \cdot \hat{\mathbf{Z}}\right)\left(1 + \beta E \mathbf{p}_L \cdot \hat{\mathbf{Z}}\right) \right\rangle = \beta E \frac{|\mathbf{p}|^2}{3} \quad (24)$$

Thus, the average potential energy is $U_{av} = -\beta E^2 |\mathbf{p}|^2/3$. As a useful check on this result, it is worth considering the infinite temperature limit, in which β is decreased to 0. The density function in eq 23 approaches isotropy, while the polarization in eq 24 and the average potential energy approach zero, all of which are physically sensible and agree with the results of the first example. In the opposite limit of zero temperature, the large value of β makes the density function in eq 23 become negative for angles in which $\mathbf{p}_L$ is anti-parallel to Z. This is unrealistic and violates a restriction on $\rho(\theta, \phi, \chi)$; it arises, of course, from the approximation made in eq 22. Returning to typical temperatures, the negative value of the rotationally averaged energy and its proportionality with the square of the electric field are reminiscent of the result for immobilized polarizable molecules. This is not coincidental; whereas, in the previous case the field polarized the sample through the molecular polarizability, with a value of Tr $\boldsymbol{\alpha}/3$, in this case the field polarizes the sample through molecular reorientation. Combining these results shows that the orientational polarizability is $\beta|\mathbf{p}|^2/3$ for a sample of mobile polar molecules. The sum of the two polarizability contributions, multiplied by the constants $N_A/(3\varepsilon_0)$, is called the molar polarization; the sum is also a portion of the Debye equation, which relates electric properties of molecules to the electric field in matter *(14)*.

Energy of Mobile Dipoles in an Electric Field: Exact Solution

Because of the approximation in eq 22, the ensuing equations are necessarily approximate as well, becoming increasingly inaccurate at low temperatures. Exact solutions for the density function and polarization are derived in this example using a somewhat different method of rotational averaging. Using N as a normalization constant, the normalization condition on the density function is:

$$1 = \langle \rho \rangle = N \left\langle e^{\beta E \mathbf{p}_L \cdot \hat{\mathbf{Z}}} \right\rangle \quad (25)$$

In an exact version of the method used in eq 22, this would be expanded to an infinite series and averaged, term by term, using the appropriate general equation from List 1; at the end, the infinite series reverts to exponentials. An easier method is to temporarily abandon the method of averaging over direction cosines and instead express the rotational average as an integral, using the definition of the brackets in eq 1. To simplify the analysis, the molecular z axis is defined to be parallel to $\mathbf{p}$ and the product $\beta E \mathbf{p}$ is replaced by the generic vector $\mathbf{r}$, which has magnitude $r = |\mathbf{r}|$:

$$\frac{1}{N} = \left\langle e^{\mathbf{r}_L \cdot \mathbf{Z}} \right\rangle = \left\langle e^{\mathbf{r} \cdot \Phi \mathbf{Z}} \right\rangle = \left\langle e^{r\cos\theta} \right\rangle$$

$$= \frac{1}{8\pi^2} \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} e^{r\cos\theta} \sin\theta \, d\theta \, d\phi \, d\chi$$

$$= \frac{1}{2} \int_0^\pi e^{r\cos\theta} \sin\theta \, d\theta = \frac{e^r - e^{-r}}{2r} = \frac{\sinh r}{r} \quad (26)$$

The θ integral is solved using substitution, while the final simplification uses the definition of a hyperbolic sine function. Equation 26 yields the normalization constant, so the normalized density function is:

$$\rho = \frac{r}{\sinh r} e^{\mathbf{r}_L \cdot \hat{\mathbf{Z}}} \quad (27)$$

The sample polarization is set up as in eq 24. The exponential dependence of $\rho(\theta, \phi, \chi)$ makes this another rotational average over an exponential, which is simplified and then carried out like the one in eq 26:

$$\left\langle \left(\mathbf{r}_L \cdot \hat{\mathbf{Z}}\right) e^{\mathbf{r}_L \cdot \hat{\mathbf{Z}}} \right\rangle = \frac{1}{2}\left(e^r + e^{-r}\right) - \frac{1}{2r}\left(e^r - e^{-r}\right)$$

$$= \cosh r - \frac{\sinh r}{r} \quad (28)$$

Finally, the parts are assembled: eq 28 includes an extra factor of βE because the first term in the equation is $\mathbf{r}_L$ rather than $\mathbf{p}_L$; also, the prefactor of eq 27, which normalizes ρ, was not included in eq 28. The result is:

$$P = |\mathbf{p}|\left(\coth r - \frac{1}{r}\right) \quad (29)$$

This polarization is exact for all electric field strengths. More importantly, it expresses the degree of sample orientation for any system in which the potential energy of a molecule is the product of a vector in the molecule reference frame with a vector that represents an externally applied field. Because of its generality, the term in parentheses in eq 29 is well known and is called the Langevin function *(14)*.

Conclusions

Experiments that are used to investigate vector or matrix properties of molecules typically produce results that are averages from a wide range of molecular orientations. To link these experimental results to the underlying molecular properties, the rotational averaging has to be carried out mathematically as well. The averaging can be considered separately for each experiment using eqs 1 or 21 for isotropic or anisotropic samples, respectively. However, it is generally preferable to separate this portion of the mathematics from the rest of the analysis. The procedure for rotational averaging, repeated many times in this article, is straightforward. First, an expression is written for the observable for one molecule, with the molecular properties expressed as vectors or matrices in the laboratory reference frame. If the sample is anisotropic, the expression is multiplied by the density function, $\rho(\theta, \phi, \chi)$, which is normalized with the equation $\langle \rho \rangle = 1$. The total expression is enclosed in brackets to indicate rotational averaging, is simplified using the linearity property, and can often be solved immediately with substitutions from eqs 5, 7, 10, 11, 12, 19, 26, and 28. For a more detailed treatment or for other averages, the molecular properties are transformed to the molecule reference frame by multiplying by the direction cosine matrix, allowing the molecular properties to factor out of the average. The remaining average of direction cosine matrix elements simplifies to a series of Kronecker delta functions, listed in List 1, which select products of vector or matrix components of the molecular properties.

Because the result is independent of the axes chosen, it always simplifies to a collection of vector magnitudes, dot products, matrix traces, or similar reduced forms. The final result is an equation for the experimental response of a bulk sample in terms of the microscopic parameters of individual molecules. If desired, the result can be inverted to solve for the molecular parameters.

Acknowledgments

Literature Cited

1. Skoog, D. A.; West, D. M; Holler, F. J. *Fundamentals of Analytical Chemistry,* 7th ed.; Saunders College Publishing: Fort Worth, TX, 1996.
2. McMillin, D. R. *J. Chem. Educ.* **1978,** *55,* 7.
3. McClain, W. M. *J. Chem. Phys.* **1972,** *57,* 2264.
4. Zare, R. N. *Angular Momentum, Understanding Spatial Aspects in Chemistry and Physics;* John Wiley & Sons: New York, 1988.
5. Cyvin, S. J.; Rauch, J. E.; Decius, J. C. *J. Chem. Phys.* **1965,** *43,* 4083.
6. Cable, J. R.; Albrecht, A. C. *J. Chem. Phys.* **1986,** *85,* 3145.
7. Gårding, L.; Nordén, B. *Chem. Phys.* **1979,** *41,* 431.
8. Mathies, R. A. Experimental and Theoretical Studies on the Excited Electronic States of Some Aromatic Hydrocarbons through Electric Field Perturbation and through Chemical Substituents. Ph.D. Thesis, Cornell University, Ithaca, NY, 1974.
9. Bublitz, G. U.; Boxer, S. G. *Annu. Rev. Phys. Chem.* **1997,** *48,* 213.
10. Andrews, S. S.; Boxer, S. G. *J. Phys. Chem. A* **2000,** *104,* 11853.
11. Rose, M. E. *Elementary Theory of Angular Momentum;* Dover Publications: New York, 1995.
12. Sakurai, J. J. *Modern Quantum Mechanics,* revised ed.; Addison-Wesley: Reading, MA, 1995.
13. Griffiths, D. J. *Introduction to Electrodynamics,* 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1989.
14. Atkins, P. W. *Physical Chemistry,* 5th ed.; W.H. Freeman and Company: New York, 1994.
15. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy,* 2nd ed.; Plenum Publishers: New York, 1999.

Appendix

The equations shown in List 1 that include up to four direction cosine matrix elements are well known and are presented in several references *(1A, 2A)*. The others are likely to have been derived previously as well, although I have been unable to find references to them. There are no special tricks to the derivation of these equations; instead, each one is found by using eq 1 to integrate over the sines and cosines of the direction cosine matrix elements given in eq 3. However, some symmetry properties can be used to minimize the number of required integrals. One of these is that each average is independent of which laboratory frame axes are chosen to represent the indices F and G, so these are always taken to be Z and X, respectively. Similarly, it is possible to always assign the molecule reference frame index i to be equal to z, and j to be either x or z. For example, the average of $\langle \Phi_{Fi}\Phi_{Fj} \rangle$ requires only two integrals: $\langle \Phi^2_{Zz} \rangle$ and $\langle \Phi_{Zz}\Phi_{Zx} \rangle$, where all other index combinations are equal to the first case if $i = j$ and the second if $i \neq j$. Using these symmetry properties, this average can be simplified to:

$$\langle \Phi_{Fi}\, \Phi_{Fj} \rangle = \langle \Phi^2_{Zz} \rangle \delta_{ij} + \langle \Phi_{Zz}\Phi_{Zx} \rangle \left(1 - \delta_{ij}\right) \quad (30)$$

Other averages simplify in a similar manner, leading to the products of delta functions seen in List 1. Despite this simplification, the number of types of index combinations and the number of required integrals still increase rapidly as more direction cosine terms are included. It turns out that this is the limiting factor to these derivations, rather than the integrals themselves.

There are several methods of evaluating the integrals over direction cosines. For small numbers of integrations, it is easiest to evaluate the integrals directly with eq 1 and Mathematica software *(3A)*. A more traditional method is to change to a spherical basis *(1A)*, which has the advantage of making the integration trivial, although at the cost of tedious coordinate transformations between representations. The method chosen for the derivations in List 1 involved dividing the table into two halves: the first half involves averages that include only a single laboratory frame axis, while the second half involves two laboratory frame axes. In the former case, each direction cosine product can be reduced to the form $\langle \Phi^a_{Zx}\Phi^b_{Zy}\Phi^c_{Zz} \rangle$, where a, b, and c are constant integers. With substitutions from eq 3, the integral is:

$$\left\langle \Phi^a_{Zx}\Phi^b_{Zy}\Phi^c_{Zz} \right\rangle =$$

$$\frac{1}{8\pi^2}\int_0^\pi\int_0^{2\pi}\int_0^{2\pi} \left(-\sin\theta\,\cos\chi\right)^a \left(\sin\theta\,\sin\chi\right)^b \cos^c\theta\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}\chi \quad (31)$$

$$= \frac{(-1)^a}{4\pi}\int_0^\pi \sin^{a+b+1}\theta\,\cos^c\theta\,\mathrm{d}\theta\int_0^{2\pi}\sin^b\chi\,\cos^a\chi\,\mathrm{d}\chi$$

Consideration of the signs of the θ products in the two quadrants over which it is integrated, and the χ products in the four quadrants of that integral, shows that the result is always zero unless a, b, and c are all even values. Using a result from the *Handbook of Mathematical Sciences (4A)*, the nonzero integrals for eq 31 simplify to beta functions, and then to gamma functions:

$$\left\langle \Phi^a_{Zx}\Phi^b_{Zy}\Phi^c_{Zz} \right\rangle =$$

$$\frac{1}{2\pi}\mathrm{B}\!\left(\frac{a+b+2}{2},\frac{c+1}{2}\right)\mathrm{B}\!\left(\frac{b+1}{2},\frac{a+1}{2}\right)$$

$$= \frac{1}{2\pi}\frac{\Gamma\!\left(\dfrac{a+1}{2}\right)\Gamma\!\left(\dfrac{b+1}{2}\right)\Gamma\!\left(\dfrac{c+1}{2}\right)}{\Gamma\!\left(\dfrac{a+b+c+3}{2}\right)} \quad (32)$$

In this equation, it is assumed that a, b, and c are all even. These gamma functions with half-integer arguments evaluate to simple fractions *(4A)*, leading to the first set of required integrals. A similar analysis applies to integrals with two laboratory frame axes. However, with these it is impossible to avoid direction cosine matrix terms with sums or differences, with the result that the solution is a lengthy sum of beta functions,

$$\left\langle \Phi_{Xx}^{a'} \Phi_{Xy}^{b'} \Phi_{Xz}^{c'} \Phi_{Zx}^{a} \Phi_{Zy}^{b} \Phi_{Zz}^{c} \right\rangle = \frac{1}{2\pi^2} \sum_{i=0}^{a'} \sum_{j=0}^{b'} \binom{a'}{i} \binom{b'}{j} (-1)^{a'+b'+a-i}$$

$$\times B\left(\frac{a+b+c'+2}{2}, \frac{c+i+j+1}{2} \right)$$

$$\times B\left(\frac{a'+b'-i-j+1}{2}, \frac{c'+i+j+1}{2} \right) \qquad (33)$$

$$\times B\left(\frac{a'+b-i+j+1}{2}, \frac{a+b'+i-j+1}{2} \right)$$

The symmetry properties are that the integral is only equal to eq 33 if all of the following sums are even: $a + a'$, $b + b'$, $c + c'$, $a + b + c$, and $a' + b' + c'$; otherwise the result is zero.

The terms in parentheses following the summation symbols are binomial coefficients. A short computer program was written to evaluate eq 33 for arbitrary values of the exponents, which proved helpful for deriving several equations in List 1.

Averages in List 1 that include ellipses were not proved rigorously, but were generalized from trends that became obvious while calculating smaller averages. The two final equalities in the table were derived from previous equalities and the linearity property of rotational averages.

Literature Cited

1A. Zare, R. N. *Angular Momentum, Understanding Spatial Aspects in Chemistry and Physics;* John Wiley & Sons: New York, 1988.

2A. Mathies, R. A. Experimental and Theoretical Studies on the Excited Electronic States of Some Aromatic Hydrocarbons through Electric Field Perturbation and through Chemical Substituents. Ph.D. Thesis, Cornell University, Ithaca, NY, 1974.

3A. Mathematica; 2.2.2 ed.; Wolfram Research, Inc.: Champaign, IL, 1994.

4A. *CRC Handbook of Mathematical Sciences,* 6th ed.; Beyer, W. H., Ed.; CRC Press, Inc.: Boca Raton, FL, 1987.