Phased and Boltzmann-weighted rotational averages

David L. Andrews and Michael J. Harlow
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England
(Received 26 September 1983)

This paper deals with two types of rotational average which arise in a number of physical processes in fluids. The first are termed "phased averages," and occur in the theory of bimolecular interactions with radiation; the second are "Boltzmann-weighted" averages, which occur in the theory of anisotropic media. A general method for obtaining these results is presented, and analytic results are given for tensorial interactions up to and including the fourth rank. Several applications are discussed including laser-induced forces, cooperative two-photon absorption, and electric-field-induced harmonic generation. The proof of a relation involving conventional rotational averages is also given.

I. INTRODUCTION

Three-dimensional rotational averages are involved in the theory of a great many physical phenomena which take place in isotropic media. Typically, the response of the component molecules to external conditions represented by a rank-n tensor $T_{i_1,\ldots,i_n}$ is given by the inner product of this tensor with a molecular response tensor $V_{i_1,\ldots,i_n}$, and the result is generally dependent on molecular orientation. Observations on the bulk system, however, provide measurements of the ensemble-average response A; by virtue of the ergodic hypothesis, the result is thus written as the rotational average of the molecular response, i.e.,

$$A=\langle T_{i_1,\ldots,i_n}V_{i_1,\ldots,i_n}\rangle\ , \tag{1.1}$$

where we use the implied summation convention for repeated tensor indices. The procedure for the evaluation of this type of rotational average using isotropic tensors is now well established.[1,2] An alternative method appropriate for the special case where $T_{i_1,\ldots,i_n}$ and $V_{i_1,\ldots,i_n}$ are expressible as products of vector components has also recently been discussed.[3]

Other types of rotational average may arise, however. In this paper we deal specifically with two different cases, and the procedure we adopt may readily be adapted for others.

The first type of average we consider is of the form

$$A^{(n)\phi}=\langle T_{i_1,\ldots,i_n}V_{i_1,\ldots,i_n}e^{i\vec{u}\cdot\vec{w}}\rangle\ . \tag{1.2}$$

Here $T_{i_1,\ldots,i_n}$ and $\vec{u}$ are tensors and vectors which are fixed in a laboratory frame of reference; $V_{i_1,\ldots,i_n}$ and $\vec{w}$ are tensors and vectors fixed in a molecular frame. The superscript n on the left-hand side of the equation refers to the rank of the tensorial interaction; the label ϕ denotes the fact that the result is a *phased* rotational average, i.e., the quantity to be averaged involves a phase factor $\exp(i\vec{u}\cdot\vec{w})$. Averages of this kind frequently arise in the study of pairwise interactions of molecules with radiation. For example, if a traveling wave of phase $\exp[i(\vec{k}\cdot\vec{r}-\omega t)]$ is incident upon two molecules with vector displacement $\vec{R}$, then any process which results in interference of probability amplitudes associated with the two centers yields a phase factor $\exp(i\vec{k}\cdot\vec{R})$, leading to rotational averages of the kind (1.2). Specific examples, which we discuss in detail later, include calculation of laser-induced intermolecular forces, and rates of cooperative two-photon absorption due to short-range energy transfer.

The second kind of rotational average we consider has a real rather than imaginary argument to the exponential:

$$A^{(n)\theta}=\langle T_{i_1,\ldots,i_n}V_{i_1,\ldots,i_n}e^{-\vec{u}\cdot\vec{w}}\rangle\ . \tag{1.3}$$

This type of average frequently arises in dealing with anisotropic fluids. For example, if any polar liquid is subjected to an applied static electric field $\vec{E}$, then a Boltzmann-weighting factor $\exp(\vec{\mu}\cdot\vec{E}/kT)$ has to be included in the evaluation of any ensemble-average property in order to account for the field-induced anisotropy. A specific example discussed later is the derivation of the well-known Langevin function. The label θ is used in (1.3) to denote the temperature dependence of the average in such a case. Since the results of averages of this type are readily obtained from the phased averages, however, calculations and results are only presented explicitly for the latter.

The format of the paper is as follows. In Sec. II, the procedure used for the evaluation of phased rotational averages is discussed in detail, and in Sec. III the results are given for tensorial interactions up to and including the fourth rank. Various applications of the results are given in Sec. IV and, finally, in an appendix, a hitherto unproved identity involving conventional rotational averages is proved using the results for the phases averages.

II. CALCULATION PROCEDURE

In this section we demonstrate the method for calculating the phased average defined by Eq. (1.2); defining

$$\alpha = |\vec{u}||\vec{w}| \;, \tag{2.1}$$

we have

$$A^{(n)\phi} = \langle T_{i_1,\ldots,i_n} V_{i_1,\ldots,i_n} e^{i\alpha\hat{u}\cdot\hat{w}} \rangle \;. \tag{2.2}$$

The first step in the calculation is to express the exponential function as an expansion in terms of Legendre polynomials $P_j(\hat{u}\cdot\hat{w})$;

$$e^{i\alpha\hat{u}\cdot\hat{w}} = \sum_{j=0}^{\infty} (2j+1) i^j j_j(\alpha) P_j(\hat{u}\cdot\hat{w}) \;, \tag{2.3}$$

where $j_j(\alpha)$ is a spherical Bessel function of the first kind.

To proceed further, we introduce the decomposable tensors $u_{j_1,\ldots,j_m}$ and $w_{j_1,\ldots,j_m}$, defined by

$$u_{j_1,\ldots,j_m} = \prod_{r=1}^{m} u_{j_r} \;, \tag{2.4}$$

$$w_{j_1,\ldots,j_m} = \prod_{r=1}^{m} w_{j_r} \;. \tag{2.5}$$

In general, any Cartesian tensor of rank m may be written as a sum of irreducible Cartesian tensors,[4] for example,

$$u_{j_1,\ldots,j_m} = \sum_{s=1}^{m} u^{(s)}_{j_1,\ldots,j_m} \;. \tag{2.6}$$

Here $u^{(s)}_{j_1,\ldots,j_m}$ is an irreducible tensor of rank m and weight s, i.e., its elements provide a basis for an irreducible representation of dimension $(2s+1)$ under the symmetry operations of the rotation-inversion group $O(3)$. Irreducible tensors with equal rank and weight such as $u^{(m)}_{j_1,\ldots,j_m}$ are refered to as *nature tensors*.[5] Zemach[6] has shown that Legendre polynomials of the type appearing in Eq. (2.3) may be expressed in terms of natural tensors as follows:

$$P_j(\vec{u}\cdot\vec{w}) = \frac{(2j)!}{2^j (j!)^2} u^{(j)}_{j_1,\ldots,j_j} w^{(j)}_{j_1,\ldots,j_j} \;. \tag{2.7}$$

From Eqs. (2.2), (2.3), and (2.7) we thus have the following:

$$A^{(n)\phi} = \sum_{j=0}^{\infty} \frac{(2j+1)!}{2^j (j!)^2} i^j j_j(\alpha) \langle T_{i_1,\ldots,i_n} u^{(j)}_{j_1,\ldots,j_j} V_{i_1,\ldots,i_n} \times w^{(j)}_{j_1,\ldots,j_j} \rangle \;, \tag{2.8}$$

where $T_{i_1,\ldots,i_n} u^{(j)}_{j_1,\ldots,j_j}$ is fixed in a laboratory reference frame, and $V_{i_1,\ldots,i_n} w^{(j)}_{j_1,\ldots,j_j}$ is fixed in a molecular frame. According to a theorem of Weyl,[7] the result of the rotational average represented by angular brackets in Eq. (2.8) is a linear combination of products of scalars obtained by contacting both $T_{i_1,\ldots,i_n} u^{(j)}_{j_1,\ldots,j_j}$ and $V_{i_1,\ldots,i_n} w^{(j)}_{j_1,\ldots,j_j}$ with isotropic (weight-0) tensors of rank $(n+j)$. We now decompose $T_{i_1,\ldots,i_n}$ and $V_{i_1,\ldots,i_n}$ into a sum of irreducible parts $T^{(j')}_{i_1,\ldots,i_n}$ and $V^{(j'')}_{i_1,\ldots,i_n}$ with weights j' and j'', respectively, according to the formulas

$$T_{i_1,\ldots,i_n} = \sum_{j'=0}^{n} T^{(j')}_{i_1,\ldots,i_n} \;, \tag{2.9}$$

$$V_{i_1,\ldots,i_n} = \sum_{j''=0}^{n} V^{(j'')}_{i_1,\ldots,i_n} \;. \tag{2.10}$$

Thus, $T^{(j')}_{i_1,\ldots,i_n} u^{(j)}_{j_1,\ldots,j_j}$ is a tensor of rank $(n+j)$ and weight j''' in the range $|j'-j| \le j''' \le j'+j$, and in order to contract with an isotropic tensor of weight 0 to give a scalar, only the weight-0 term ($j'''=0$) resulting from $j'=j$ can contribute. Similar reasoning shows that only the term with $j''=j$ in (2.10) can contribute to Eq. (2.8). It also follows from Eqs. (2.9) and (2.10) that terms with $j>n$ provide vanishing contributions; hence, Eq. (2.8) may be rewritten as

$$A^{(n)\phi} = \sum_{j=0}^{n} \frac{(2j+1)!}{2^j (j!)^2} i^j j_j(\alpha) \times \langle T^{(j)}_{i_1,\ldots,i_n} u^{(j)}_{j_1,\ldots,j_j} V^{(j)}_{i_1,\ldots,i_n} w^{(j)}_{j_1,\ldots,j_j} \rangle \;. \tag{2.11}$$

The tensors $u_{j_1,\ldots,j_j}$ and $w_{j_1,\ldots,j_j}$ of rank j have only one representation of weight j; however, the representation of weight j in the rank-n tensors $T_{i_1,\ldots,i_n}$ and $V_{i_1,\ldots,i_n}$ is generally associated with a multiplicity $N_n^{(j)}$, given by[8]

$$N_n^{(j)} = \sum_k (-1)^k \begin{bmatrix} n \\ k \end{bmatrix} \begin{bmatrix} 2n-3k-j-2 \\ n-2 \end{bmatrix} \;, \tag{2.12}$$

where $0 \le k \le [(n-j)/3]$. Hence, we write

$$T^{(j)}_{i_1,\ldots,i_n} = \sum_{p=1}^{N_n^{(j)}} T^{(j;p)}_{i_1,\ldots,i_n} \;, \tag{2.13}$$

$$V^{(j)}_{i_1,\ldots,i_n} = \sum_{q=1}^{N_n^{(j)}} V^{(j;q)}_{i_1,\ldots,i_n} \;, \tag{2.14}$$

where $T^{(j;p)}_{i_1,\ldots,i_n}$ and $V^{(j;q)}_{i_1,\ldots,i_n}$ are expressible in terms of natural tensors $t^{(j;p)}_{k_1,\ldots,k_j}$ and $v^{(j;q)}_{l_1,\ldots,l_j}$ by use of the mapping formulas[9]

$$T^{(j;p)}_{i_1,\ldots,i_n} = G^{(0;p)}_{i_1,\ldots,i_n;k_1,\ldots,k_j} t^{(j;p)}_{k_1,\ldots,k_j} \;, \tag{2.15}$$

$$V^{(j;q)}_{i_1,\ldots,i_n} = G^{(0;q)}_{i_1,\ldots,i_n;l_1,\ldots,l_j} v^{(j;q)}_{l_1,\ldots,l_j} \;. \tag{2.16}$$

By substituting these results into Eq. (2.11), we now obtain

$$A^{(n)\phi} = \sum_{j=0}^{n} \frac{(2j+1)!}{2^j (j!)^2} i^j j_j(\alpha) \times \sum_{p,q=1}^{N_n^{(j)}} \langle G^{(0;p)}_{i_1,\ldots,i_n;k_1,\ldots,k_j} G^{(0;q)}_{i_1,\ldots,i_n;l_1,\ldots,l_j} \times t^{(j;p)}_{k_1,\ldots,k_j} u^{(j)}_{j_1,\ldots,j_j} \times v^{(j;q)}_{l_1,\ldots,l_j} w^{(j)}_{j_1,\ldots,j_j} \rangle \;. \tag{2.17}$$

However, the product of mappings in this equation is related to the natural projection $E^{(j)}_{k_1,\ldots,k_j;l_1,\ldots,l_j}$ through the relation[9]

$$G^{(0;p)}_{i_1,\ldots,i_n;k_1,\ldots,k_j}G^{(0;q)}_{i_1,\ldots,i_n;l_1,\ldots,l_j} = g^{(n;j)}_{pq}E^{(j)}_{k_1,\ldots,k_j;l_1,\ldots,l_j} , \quad (2.18)$$

and $v^{(j;q)}_{l_1,\ldots,l_j}$ satisfies the relation

$$E^{(j)}_{k_1,\ldots,k_j;l_1,\ldots,l_j}v^{(j;q)}_{l_1,\ldots,l_j} = v^{(j;q)}_{k_1,\ldots,k_j} . \quad (2.19)$$

Hence, (2.17) gives

$$A^{(n)\phi} = \sum_{j=0}^{n} \frac{(2j+1)!}{2^j(j!)^2} i^j j_j(\alpha) \times \sum_{p,q=1}^{N_n^{(j)}} g^{(n;j)}_{pq} \langle t^{(j;p)}_{k_1,\ldots,k_j} u^{(j)}_{j_1,\ldots,j_j} \times v^{(j;q)}_{k_1,\ldots,k_j} w^{(j)}_{j_1,\ldots,j_j} \rangle . \quad (2.20)$$

The rotational average represented by angular brackets in the above equation is now readily evaluated. Noting that the result is a product of scalars resulting from the contraction of $t^{(j;p)}_{k_1,\ldots,k_j}u^{(j)}_{j_1,\ldots,j_j}$ and $v^{(j;q)}_{k_1,\ldots,k_j}w^{(j)}_{j_1,\ldots,j_j}$ with isotropic tensors of rank $2j$, we make use of the result[10]

$$(t^{(j;p)}_{k_1,\ldots,k_j}u^{(j)}_{j_1,\ldots,j_j})^{(0)} = (2j+1)^{-1} t^{(j;p)}_{i_1,\ldots,i_j}u^{(j)}_{i_1,\ldots,i_j} \times E^{(j)}_{j_1,\ldots,j_j;k_1,\ldots,k_j} \quad (2.21)$$

together with the relation,

$$E^{(j)}_{j_1,\ldots,j_j;k_1,\ldots,k_j} v^{(j;q)}_{k_1,\ldots,k_j} w^{(j)}_{j_1,\ldots,j_j} = v^{(j;q)}_{l_1,\ldots,l_j} w^{(j)}_{l_1,\ldots,l_j} \quad (2.22)$$

to obtain

$$A^{(n)\phi} = \sum_{j=0}^{n} \frac{(2j)!}{2^j(j!)^2} i^j j_j(\alpha) \times \sum_{p,q=1}^{N_n^{(j)}} g^{(n;j)}_{pq} t^{(j;p)}_{j_1,\ldots,j_j} u^{(j)}_{j_1,\ldots,j_j} \times v^{(j;q)}_{\mu_1,\ldots,\mu_j} w^{(j)}_{\mu_1,\ldots,\mu_j} . \quad (2.23)$$

In writing Eq. (2.23), greek indices have been introduced for expression of the inner product $v^{(j;q)}_{\mu_1,\ldots,\mu_j}w^{(j)}_{\mu_1,\ldots,\mu_j}$, to denote reference to a molecule-fixed frame in which both $v^{(j;q)}_{\mu_1,\ldots,\mu_j}$ and $w^{(j)}_{\mu_1,\ldots,\mu_j}$ are rotation invariant. We now make use of the results

$$t^{(j;p)}_{j_1,\ldots,j_j} = \tilde{G}^{(0;p)}_{j_1,\ldots,j_j;i_1,\ldots,i_n} T_{i_1,\ldots,i_n} , \quad (2.24)$$

$$v^{(j;q)}_{\mu_1,\ldots,\mu_j} = \tilde{G}^{(0;q)}_{\mu_1,\ldots,\mu_j;\lambda_1,\ldots,\lambda_n} V_{\lambda_1,\ldots,\lambda_n} , \quad (2.25)$$

and

$$\sum_{p=1}^{N_n^{(j)}} g^{(n;j)}_{pq} \tilde{G}^{(0;p)}_{j_1,\ldots,j_j;i_1,\ldots,i_n} = G^{(0;q)}_{i_1,\ldots,i_n;j_1,\ldots,j_j} \quad (2.26)$$

to reexpress Eq. (2.23) in terms of the original tensors $T_{i_1,\ldots,i_n}$ and $V_{\lambda_1,\ldots,\lambda_n}$; the result is as follows:

$$A^{(n)\phi} = \sum_{j=0}^{n} \frac{(2j)!}{2^j(j!)^2} i^j j_j(\alpha) T_{i_1,\ldots,i_n} u^{(j)}_{i_1,\ldots,i_j} \times V_{\lambda_1,\ldots,\lambda_n} w^{(j)}_{\mu_1,\ldots,\mu_j} \times \sum_{q=1}^{N_n^{(j)}} G^{(0;q)}_{i_1,\ldots,i_n;j_1,\ldots,j_j} \times \tilde{G}^{(0;q)}_{\mu_1,\ldots,\mu_j;\lambda_1,\ldots,\lambda_n} . \quad (2.27)$$

It is useful to reexpress the result in a form in which $T_{i_1,\ldots,i_n}$ and $V_{\lambda_1,\ldots,\lambda_n}$ do not appear explicitly. Since the rotational average represented by Eq. (2.2) may be written as

$$A^{(n)\phi} = T_{i_1,\ldots,i_n} V_{\lambda_1,\ldots,\lambda_n} \langle l_{i_1\lambda_1} \cdots l_{i_n\lambda_n} e^{i\alpha\hat{u}\cdot\hat{w}} \rangle , \quad (2.28)$$

where $l_{i_p\lambda_p}$ is the direction cosine of the angle between the laboratory i_p axis and the molecular λ_p axis, then by comparing Eqs. (2.27) and (2.28) we find

$$I^{(n)\phi}_{i_1,\ldots,i_n;\lambda_1,\ldots,\lambda_n}(\alpha,\hat{u},\hat{w}) \equiv \langle l_{i_1\lambda_1} \cdots l_{i_n\lambda_n} e^{i\alpha\hat{u}\cdot\hat{w}} \rangle \quad (2.29)$$

$$= \sum_{j=0}^{n} \frac{(2j)!}{2^j(j!)^2} i^j j_j(\alpha) u^{(j)}_{j_1,\ldots,j_j} w^{(j)}_{\mu_1,\ldots,\mu_j} \times \sum_{q=1}^{N_n^{(j)}} G^{(0;q)}_{i_1,\ldots,i_n;j_1,\ldots,j_j} \tilde{G}^{(0;q)}_{\mu_1,\ldots,\mu_j;\lambda_1,\ldots,\lambda_n} . \quad (2.30)$$

Finally, using the relation

$$\tilde{G}^{(0;q)}_{\mu_1,\ldots,\mu_j;\lambda_1,\ldots,\lambda_n} = \sum_{p=1}^{N_n^{(j)}} g^{pq}_{(n;j)} G^{(0;p)}_{\lambda_1,\ldots,\lambda_n;\mu_1,\ldots,\mu_j} , \quad (2.31)$$

and by defining

$$U^{(n;j;q)}_{i_1,\ldots,i_n} = G^{(0;q)}_{i_1,\ldots,i_n;j_1,\ldots,j_j} u^{(j)}_{j_1,\ldots,j_j} , \quad (2.32)$$

$$W^{(n;j;p)}_{\lambda_1,\ldots,\lambda_n} = G^{(0;p)}_{\lambda_1,\ldots,\lambda_n;\mu_1,\ldots,\mu_j} w^{(j)}_{\mu_1,\ldots,\mu_j} , \quad (2.33)$$

we have

$$I^{(n)\phi}_{i_1,\ldots,i_n;\lambda_1,\ldots,\lambda_n}(\alpha,\hat{u},\hat{w}) = \sum_{j=0}^{n} \sum_{p,q=1}^{N_n^{(j)}} m^{(n;j)}_{pq}(\alpha) U^{(n;j;p)}_{i_1,\ldots,i_n} W^{(n;j;q)}_{\lambda_1,\ldots,\lambda_n} , \quad (2.34)$$

where

$$m^{(n;j)}_{pq}(\alpha) = \frac{(2j)!}{2^j(j!)^2} i^j j_j(\alpha) g^{pq}_{(n;j)} \quad (2.35)$$

are coefficients which are symmetric in the indices p and q. The results given in the following section have been derived by use of Eqs. (2.34) and (2.35) together with the expressions for $g^{pq}_{(n;j)}$ derived previously.[9,10] Before leaving this section, we note that the usual nonretarded rotational averages are readily obtained as limiting cases of the above results:

$$I^{(n)}_{i_1,\ldots,i_n;\lambda_1,\ldots,\lambda_n} \equiv \langle l_{i_1\lambda_1} \cdots l_{i_n\lambda_n} \rangle$$
$$= \lim_{\alpha\to 0} \langle l_{i_1\lambda_1} \cdots l_{i_n\lambda_n} e^{i\alpha\vec{u}\cdot\vec{w}} \rangle$$
$$= \sum_{p,q=1}^{N_n^{(0)}} m^{(n)}_{pq} f^{(0;p)}_{i_1,\ldots,i_n} f^{(0;q)}_{\lambda_1,\ldots,\lambda_n} , \quad (2.36)$$

where

$$m^{(n)}_{pq} = g^{pq}_{(n;0)} , \quad (2.37)$$

and $f^{(0;p)}_{i_1,\ldots,i_n}, f^{(0;q)}_{\lambda_1,\ldots,\lambda_n}$ are isotropic tensors of rank n. The result represented by Eq. (2.36) agrees exactly with that derived previously.[1]

TABLE I. Spherical Bessel functions $j_n(\alpha)$, $n \le 4$. Higher-order results can be determined from the relation $j_{n+1}(\alpha)=(2n+1)^{-1}j_n(\alpha)-j_{n-1}(\alpha)$.

n	$j_n(\alpha)$
0	$\frac{1}{\alpha}\sin\alpha$
1	$\frac{1}{\alpha^2}\sin\alpha-\frac{1}{\alpha}\cos\alpha$
2	$\left[\frac{-1}{\alpha}+\frac{3}{\alpha^3}\right]\sin\alpha-\frac{3}{\alpha^2}\cos\alpha$
3	$\left[\frac{-6}{\alpha^2}+\frac{15}{\alpha^4}\right]\sin\alpha+\left[\frac{1}{\alpha}-\frac{15}{\alpha^3}\right]\cos\alpha$
4	$\left[\frac{1}{\alpha}-\frac{45}{\alpha^3}+\frac{105}{\alpha^5}\right]\sin\alpha+\left[\frac{10}{\alpha^2}-\frac{105}{\alpha^4}\right]\cos\alpha$

III. RESULTS

In this section results are given for $I^{(n)\phi}_{i_1,\ldots,i_n;\lambda_1,\ldots,\lambda_n}(\alpha,\hat{u},\hat{w})$, defined by Eq. (2.29), for $n \le 4$. The results are expressed in terms of spherical Bessel functions $j_n(\alpha)$, the explicit forms of which are given in Table I:

A. $n=0$

$$I^{(0)\phi}(\alpha,\hat{u},\hat{w})=j_0(\alpha) . \quad (3.1)$$

B. $n=1$

$$I^{(1)\phi}_{i_1,\lambda_1}(\alpha,\hat{u},\hat{w})=ij_1(\alpha)\hat{u}_{i_1}\hat{w}_{\lambda_1} . \quad (3.2)$$

C. $n=2$

$$I^{(2)\phi}_{i_1i_2;\lambda_1\lambda_2}(\alpha,\hat{u},\hat{w})=\sum_{j=0}^{2} I^{(2;j)\phi}_{i_1i_2;\lambda_1\lambda_2} , \quad (3.3)$$

$$I^{(2;0)\phi}_{i_1i_2;\lambda_1\lambda_2}=\tfrac{1}{3}j_0(\alpha)\delta_{i_1i_2}\delta_{\lambda_1\lambda_2} , \quad (3.4)$$

$$I^{(2;1)\phi}_{i_1i_2;\lambda_1\lambda_2}=\frac{i}{2}j_1(\alpha)\epsilon_{i_1i_2i_\tau}\hat{u}_{i_\tau}\epsilon_{\lambda_1\lambda_2\lambda_\tau}\hat{w}_{\lambda_\tau} , \quad (3.5)$$

$$I^{(2;2)\phi}_{i_1,i_2;\lambda_1\lambda_2}=-\tfrac{3}{2}j_2(\alpha)(\hat{u}_{i_1}\hat{u}_{i_2}-\tfrac{1}{3}\delta_{i_1i_2})(\hat{w}_{\lambda_1}\hat{w}_{\lambda_2}-\tfrac{1}{3}\delta_{\lambda_1\lambda_2}) . \quad (3.6)$$

D. $n=3$

$$I^{(3)\phi}_{i_1i_2i_3;\lambda_1\lambda_2\lambda_3}(\alpha,\hat{u},\hat{w})=\sum_{j=0}^{3} I^{(3;j)\phi}_{i_1i_2i_3;\lambda_1\lambda_2\lambda_3} , \quad (3.7)$$

$$I^{(3;0)\phi}_{i_1i_2i_3;\lambda_1\lambda_2\lambda_3}=\tfrac{1}{6}j_0(\alpha)\epsilon_{i_1i_2i_3}\epsilon_{\lambda_1\lambda_2\lambda_3} , \quad (3.8)$$

$$I^{(3;1)\phi}_{i_1i_2i_3;\lambda_1\lambda_2\lambda_3}=\frac{i}{10}j_1(\alpha)\begin{bmatrix}\delta_{i_1i_2}\hat{u}_{i_3}\\ \delta_{i_1i_3}\hat{u}_{i_2}\\ \delta_{i_2i_3}\hat{u}_{i_1}\end{bmatrix}^T\begin{bmatrix}4 & -1 & -1\\ -1 & 4 & -1\\ -1 & -1 & 4\end{bmatrix}\begin{bmatrix}\delta_{\lambda_1\lambda_2}\hat{w}_{\lambda_3}\\ \delta_{\lambda_1\lambda_3}\hat{w}_{\lambda_2}\\ \delta_{\lambda_2\lambda_3}\hat{w}_{\lambda_1}\end{bmatrix} , \quad (3.9)$$

$$I^{(3;2)\phi}_{i_1i_2i_3;\lambda_1\lambda_2\lambda_3}=-\tfrac{1}{2}j_2(\alpha)\begin{bmatrix}\epsilon_{i_1i_2i_\tau}(\hat{u}_{i_3}\hat{u}_{i_\tau}-\tfrac{1}{3}\delta_{i_3i_\tau})\\ \epsilon_{i_1i_3i_\tau}(\hat{u}_{i_2}\hat{u}_{i_\tau}-\tfrac{1}{3}\delta_{i_2i_\tau})\end{bmatrix}^T\begin{bmatrix}2 & -1\\ -1 & 2\end{bmatrix}\begin{bmatrix}\epsilon_{\lambda_1\lambda_2\lambda_\tau}(\hat{w}_{\lambda_3}\hat{w}_{\lambda_\tau}-\tfrac{1}{3}\delta_{\lambda_3\lambda_\tau})\\ \epsilon_{\lambda_1\lambda_3\lambda_\tau}(\hat{w}_{\lambda_2}\hat{w}_{\lambda_\tau}-\tfrac{1}{3}\delta_{\lambda_2\lambda_\tau})\end{bmatrix} , \quad (3.10)$$

$$I^{(3;3)\phi}_{i_1i_2i_3;\lambda_1\lambda_2\lambda_3}=\frac{-5i}{2}j_3(\alpha)[\hat{u}_{i_1}\hat{u}_{i_2}\hat{u}_{i_3}-\tfrac{1}{5}(\delta_{i_1i_2}\hat{u}_{i_3}+\delta_{i_1i_3}\hat{u}_{i_2}+\delta_{i_2i_3}\hat{u}_{i_1})][\hat{w}_{\lambda_1}\hat{w}_{\lambda_2}\hat{w}_{\lambda_3}-\tfrac{1}{5}(\delta_{\lambda_1\lambda_2}\hat{w}_{\lambda_3}+\delta_{\lambda_1\lambda_3}\hat{w}_{\lambda_2}+\delta_{\lambda_2\lambda_3}\hat{w}_{\lambda_1})]\ . \tag{3.11}$$

E. $n=4$

$$I^{(4)\phi}_{i_1i_2i_3i_4;\lambda_1\lambda_2\lambda_3\lambda_4}(\alpha,\hat{u},\hat{w})=\sum_{j=0}^{4}I^{(4;j)\phi}_{i_1i_2i_3i_4;\lambda_1\lambda_2\lambda_3\lambda_4}\ , \tag{3.12}$$

$$I^{(4;0)\phi}_{i_1i_2i_3i_4;\lambda_1\lambda_2\lambda_3\lambda_4}=\tfrac{1}{30}j_0(\alpha)\begin{bmatrix}\delta_{i_1i_2}\delta_{i_3i_4}\\ \delta_{i_1i_3}\delta_{i_2i_4}\\ \delta_{i_1i_4}\delta_{i_2i_3}\end{bmatrix}^T\begin{bmatrix}4&-1&-1\\-1&4&-1\\-1&-1&4\end{bmatrix}\begin{bmatrix}\delta_{\lambda_1\lambda_2}\delta_{\lambda_3\lambda_4}\\ \delta_{\lambda_1\lambda_3}\delta_{\lambda_2\lambda_4}\\ \delta_{\lambda_1\lambda_4}\delta_{\lambda_2\lambda_3}\end{bmatrix}, \tag{3.13}$$

$$I^{(4;1)\phi}_{i_1i_2i_3i_4;\lambda_1\lambda_2\lambda_3\lambda_4}=\frac{i}{10}j_1(\alpha)\begin{bmatrix}\epsilon_{i_1i_2i_\tau}\hat{u}_{i_\tau}\delta_{i_3i_4}\\ \epsilon_{i_1i_3i_\tau}\hat{u}_{i_\tau}\delta_{i_2i_4}\\ \epsilon_{i_1i_4i_\tau}\hat{u}_{i_\tau}\delta_{i_2i_3}\\ \epsilon_{i_2i_3i_\tau}\hat{u}_{i_\tau}\delta_{i_1i_4}\\ \epsilon_{i_2i_4i_\tau}\hat{u}_{i_\tau}\delta_{i_1i_3}\\ \epsilon_{i_3i_4i_\tau}\hat{u}_{i_\tau}\delta_{i_1i_2}\end{bmatrix}^T\begin{bmatrix}3&-1&-1&1&1&0\\-1&3&-1&-1&0&1\\-1&-1&3&0&-1&-1\\1&-1&0&3&-1&1\\1&0&-1&-1&3&-1\\0&1&-1&1&-1&3\end{bmatrix}\begin{bmatrix}\epsilon_{\lambda_1\lambda_2\lambda_\tau}\hat{w}_{\lambda_\tau}\delta_{\lambda_3\lambda_4}\\ \epsilon_{\lambda_1\lambda_3\lambda_\tau}\hat{w}_{\lambda_\tau}\delta_{\lambda_2\lambda_4}\\ \epsilon_{\lambda_1\lambda_4\lambda_\tau}\hat{w}_{\lambda_\tau}\delta_{\lambda_2\lambda_3}\\ \epsilon_{\lambda_2\lambda_3\lambda_\tau}\hat{w}_{\lambda_\tau}\delta_{\lambda_1\lambda_4}\\ \epsilon_{\lambda_2\lambda_4\lambda_\tau}\hat{w}_{\lambda_\tau}\delta_{\lambda_1\lambda_3}\\ \epsilon_{\lambda_3\lambda_4\lambda_\tau}\hat{w}_{\lambda_\tau}\delta_{\lambda_1\lambda_2}\end{bmatrix}, \tag{3.14}$$

$$I^{(4;2)\phi}_{i_1i_2i_3i_4;\lambda_1\lambda_2\lambda_3\lambda_4}=-\tfrac{1}{14}j_2(\alpha)\begin{bmatrix}\delta_{i_1i_2}(\hat{u}_{i_3}\hat{u}_{i_4}-\frac{1}{3}\delta_{i_3i_4})\\ \delta_{i_1i_3}(\hat{u}_{i_2}\hat{u}_{i_4}-\frac{1}{3}\delta_{i_2i_4})\\ \delta_{i_1i_4}(\hat{u}_{i_2}\hat{u}_{i_3}-\frac{1}{3}\delta_{i_2i_3})\\ \delta_{i_2i_3}(\hat{u}_{i_1}\hat{u}_{i_4}-\frac{1}{3}\delta_{i_1i_4})\\ \delta_{i_2i_4}(\hat{u}_{i_1}\hat{u}_{i_3}-\frac{1}{3}\delta_{i_1i_3})\\ \delta_{i_3i_4}(\hat{u}_{i_1}\hat{u}_{i_2}-\frac{1}{3}\delta_{i_1i_2})\end{bmatrix}^T\begin{bmatrix}11&-3&-3&-3&-3&4\\-3&11&-3&-3&4&-3\\-3&-3&11&4&-3&-3\\-3&-3&4&11&-3&-3\\-3&4&-3&-3&11&-3\\4&-3&-3&-3&-3&11\end{bmatrix}\begin{bmatrix}\delta_{\lambda_1\lambda_2}(\hat{w}_{\lambda_3}\hat{w}_{\lambda_4}-\frac{1}{3}\delta_{\lambda_3\lambda_4})\\ \delta_{\lambda_1\lambda_3}(\hat{w}_{\lambda_2}\hat{w}_{\lambda_4}-\frac{1}{3}\delta_{\lambda_2\lambda_4})\\ \delta_{\lambda_1\lambda_4}(\hat{w}_{\lambda_2}\hat{w}_{\lambda_3}-\frac{1}{3}\delta_{\lambda_2\lambda_3})\\ \delta_{\lambda_2\lambda_3}(\hat{w}_{\lambda_1}\hat{w}_{\lambda_4}-\frac{1}{3}\delta_{\lambda_1\lambda_4})\\ \delta_{\lambda_2\lambda_4}(\hat{w}_{\lambda_1}\hat{w}_{\lambda_3}-\frac{1}{3}\delta_{\lambda_1\lambda_3})\\ \delta_{\lambda_3\lambda_4}(\hat{w}_{\lambda_1}\hat{w}_{\lambda_2}-\frac{1}{3}\delta_{\lambda_1\lambda_2})\end{bmatrix}, \tag{3.15}$$

$$\begin{aligned}I^{(4;3)\phi}_{i_1i_2i_3i_4;\lambda_1\lambda_2\lambda_3\lambda_4}=&-\frac{5i}{8}j_3(\alpha)\begin{bmatrix}\epsilon_{i_1i_3i_\tau}[\hat{u}_{i_2}\hat{u}_{i_4}\hat{u}_{i_\tau}-\frac{1}{5}(\delta_{i_2i_\tau}\hat{u}_{i_4}+\delta_{i_4i_\tau}\hat{u}_{i_2}+\delta_{i_2i_4}\hat{u}_{i_\tau})]\\ \epsilon_{i_2i_3i_\tau}[\hat{u}_{i_1}\hat{u}_{i_4}\hat{u}_{i_\tau}-\frac{1}{5}(\delta_{i_1i_\tau}\hat{u}_{i_4}+\delta_{i_4i_\tau}\hat{u}_{i_1}+\delta_{i_1i_4}\hat{u}_{i_\tau})]\\ \epsilon_{i_3i_4i_\tau}[\hat{u}_{i_1}\hat{u}_{i_2}\hat{u}_{i_\tau}-\frac{1}{5}(\delta_{i_1i_\tau}\hat{u}_{i_2}+\delta_{i_2i_\tau}\hat{u}_{i_1}+\delta_{i_1i_2}\hat{u}_{i_\tau})]\end{bmatrix}^T\\ &\times\begin{bmatrix}3&-1&1\\-1&3&1\\1&1&3\end{bmatrix}\begin{bmatrix}\epsilon_{\lambda_1\lambda_3\lambda_\tau}[\hat{w}_{\lambda_2}\hat{w}_{\lambda_4}\hat{w}_{\lambda_\tau}-\frac{1}{5}(\delta_{\lambda_2\lambda_\tau}\hat{w}_{\lambda_4}+\delta_{\lambda_4\lambda_\tau}\hat{w}_{\lambda_2}+\delta_{\lambda_2\lambda_4}\hat{w}_{\lambda_\tau})]\\ \epsilon_{\lambda_2\lambda_3\lambda_\tau}[\hat{w}_{\lambda_1}\hat{w}_{\lambda_4}\hat{w}_{\lambda_\tau}-\frac{1}{5}(\delta_{\lambda_1\lambda_\tau}\hat{w}_{\lambda_4}+\delta_{\lambda_4\lambda_\tau}\hat{w}_{\lambda_1}+\delta_{\lambda_1\lambda_4}\hat{w}_{\lambda_\tau})]\\ \epsilon_{\lambda_3\lambda_4\lambda_\tau}[\hat{w}_{\lambda_1}\hat{w}_{\lambda_2}\hat{w}_{\lambda_\tau}-\frac{1}{5}(\delta_{\lambda_1\lambda_\tau}\hat{w}_{\lambda_2}+\delta_{\lambda_2\lambda_\tau}\hat{w}_{\lambda_1}+\delta_{\lambda_1\lambda_2}\hat{w}_{\lambda_\tau})]\end{bmatrix},\end{aligned} \tag{3.16}$$

$$\begin{aligned}I^{(4;4)\phi}_{i_1i_2i_3i_4;\lambda_1\lambda_2\lambda_3\lambda_4}=&\tfrac{35}{8}j_4(\alpha)[\hat{u}_{i_1}\hat{u}_{i_2}\hat{u}_{i_3}\hat{u}_{i_4}-\tfrac{1}{7}(\delta_{i_1i_2}\hat{u}_{i_3}\hat{u}_{i_4}+\delta_{i_1i_3}\hat{u}_{i_2}\hat{u}_{i_4}+\delta_{i_1i_4}\hat{u}_{i_2}\hat{u}_{i_3}+\delta_{i_2i_3}\hat{u}_{i_1}\hat{u}_{i_4}\\ &+\delta_{i_2i_4}\hat{u}_{i_1}\hat{u}_{i_3}+\delta_{i_3i_4}\hat{u}_{i_1}\hat{u}_{i_2})+\tfrac{1}{35}(\delta_{i_1i_2}\delta_{i_3i_4}+\delta_{i_1i_3}\delta_{i_2i_4}+\delta_{i_1i_4}\delta_{i_2i_3})]\\ &\times[\hat{w}_{\lambda_1}\hat{w}_{\lambda_2}\hat{w}_{\lambda_3}\hat{w}_{\lambda_4}-\tfrac{1}{7}(\delta_{\lambda_1\lambda_2}\hat{w}_{\lambda_3}\hat{w}_{\lambda_4}+\delta_{\lambda_1\lambda_3}\hat{w}_{\lambda_2}\hat{w}_{\lambda_4}+\delta_{\lambda_1\lambda_4}\hat{w}_{\lambda_2}\hat{w}_{\lambda_3}+\delta_{\lambda_2\lambda_3}\hat{w}_{\lambda_1}\hat{w}_{\lambda_4}\\ &+\delta_{\lambda_2\lambda_4}\hat{w}_{\lambda_1}\hat{w}_{\lambda_3}+\delta_{\lambda_3\lambda_4}\hat{w}_{\lambda_1}\hat{w}_{\lambda_2})+\tfrac{1}{35}(\delta_{\lambda_1\lambda_2}\delta_{\lambda_3\lambda_4}+\delta_{\lambda_1\lambda_3}\delta_{\lambda_2\lambda_4}+\delta_{\lambda_1\lambda_4}\delta_{\lambda_2\lambda_3})]\ .\end{aligned} \tag{3.17}$$

Several identities involving direction cosine products may be utilized in order to obtain relationships between phased rotational averages of different ranks. By using the formulas

$$\epsilon_{i_a i_b i_c}\epsilon_{\lambda_a\lambda_b\lambda_c} l_{i_a\lambda_a} l_{i_b\lambda_b} l_{i_c\lambda_c}=6 ,$$

$$\delta_{i_a i_b}\delta_{\lambda_a\lambda_b} l_{i_a\lambda_a} l_{i_b\lambda_b}=3 ,$$

$$\epsilon_{i_a i_b i_c}\epsilon_{\lambda_a\lambda_b\lambda_c} l_{i_a\lambda_a} l_{i_b\lambda_b}=2 l_{i_c\lambda_c}$$

together with the defining relation (2.29) for the phased averages, we obtain the results

$$I^{(n-3)\phi}_{i_1,\ldots,i_{n-3};\lambda_1,\ldots,\lambda_{n-3}}(\alpha,\hat{u},\hat{w}) = \tfrac{1}{6} I^{(n)\phi}_{i_1,\ldots,i_n;\lambda_1,\ldots,\lambda_n}(\alpha,\hat{u},\hat{w})\epsilon_{i_{n-2}i_{n-1}i_n}\epsilon_{\lambda_{n-2}\lambda_{n-1}\lambda_n} ,$$

$$I^{(n-2)\phi}_{i_1,\ldots,i_{n-2};\lambda_1,\ldots,\lambda_{n-2}}(\alpha,\hat{u},\hat{w}) = \tfrac{1}{3} I^{(n)\phi}_{i_1,\ldots,i_n;\lambda_1,\ldots,\lambda_n}(\alpha,\hat{u},\hat{w})\delta_{i_{n-1}i_n}\delta_{\lambda_{n-1}\lambda_n} ,$$

$$I^{(n-1)\phi}_{i_1,\ldots,i_{n-1};\lambda_1,\ldots,\lambda_{n-1}}(\alpha,\hat{u},\hat{w}) = \tfrac{1}{2} I^{(n)\phi}_{i_1,\ldots,i_{n-2}i_n i_{n+1};\lambda_1,\ldots,\lambda_{n-2}\lambda_n\lambda_{n+1}}(\alpha,\hat{u},\hat{w}) \times \epsilon_{i_{n-1}i_n i_{n+1}}\epsilon_{\lambda_{n-1}\lambda_n\lambda_{n+1}} .$$

These equations can be used to obtain the phased average of any rank lower than n from the rank-n result. They do not permit the evaluation of higher-order results due to the index symmetry restrictions imposed by the tensor contractions on the right-hand sides.

IV. APPLICATIONS

In this section we consider examples of the kind of applications which may be made of the results provided in Sec. III.

A. Laser-induced intermolecular forces

In the presence of an intense source of radiation, intermolecular forces are modified by a dynamic Stark effect; as we have shown recently,[11] the shift in the intermolecular potential energy is given by the expression

$$\Delta U=(16\pi^2/c)I\alpha^A_{jl}(k)\alpha^B_{ik}(k)V_{kl}(k,\vec{R})e_i e_j\cos(\vec{k}\cdot\vec{R}) . \quad (4.1)$$

Here $\vec{k}$ is the wave vector and $\vec{e}$ is the polarization vector of the radiation with intensity I; $\alpha^A_{jl}(k)$ and $\alpha^B_{ik}(k)$ are the dynamic polarizability tensors of the two molecules labeled A and B; $V_{kl}(k,\vec{R})$ is the retarded resonance dipole-dipole interaction and $\vec{R}$ is the vector displacement of the molecule B from an origin located at A. The retardation factor $\cos(\vec{k}\cdot\vec{R})$ in (4.1) arises through the difference in phase of the radiation at the two molecular centers. In order to utilize the result for any fluid system, it is necessary to orientationally average Eq. (4.1) for each pair of molecules. This may be accomplished in two stages, the first of which involves averaging the orientation of each molecular pair with respect to the radiation. We thus have, by reference to Eq. (2.29),

$$\overline{\Delta U}=\frac{16\pi^2}{c}I\alpha^A_{\mu o}(k)\alpha^B_{\lambda\nu}(k)V_{\nu o}(k,\vec{R})e_i e_j \mathrm{Re} I^{(2)\phi}_{ij;\lambda\mu}(kR,\hat{k},\hat{R}) . \quad (4.2)$$

Using the result (3.3) and noting that the weight-1 contribution (3.5) vanishes by virtue of the i,j index symmetry, we obtain the following relation:

$$\overline{\Delta U}=(8\pi^2/c)I\alpha^A_{\mu o}(k)\alpha^B_{\lambda\nu}(k)V_{\nu o}(k,\vec{R})W_{\lambda\mu}(k,\vec{R}) , \quad (4.3)$$

where the explicit expressions for $V_{\nu o}(k,\vec{R})$ and $W_{\lambda\mu}(k,\vec{R})$ are as follows:

$$V_{\nu o}(k,\vec{R})=(4\pi)^{-1}R^{-3}[F(kR)\delta_{\nu o}+G(kR)\hat{R}_\nu\hat{R}_o] , \quad (4.4)$$

$$W_{\lambda\mu}(k,\vec{R})=(kR)^{-3}[M(kR)\delta_{\lambda\mu}+N(kR)\hat{R}_\lambda\hat{R}_\mu] , \quad (4.5)$$

$$F(kR)=\cos(kR)+kR\sin(kR)-k^2R^2\cos(kR) , \quad (4.6)$$

$$G(kR)=-3\cos(kR)-3kR\sin(kR)+k^2R^2\cos(kR) , \quad (4.7)$$

$$M(kR)=-\sin(kR)+kR\cos(kR)+k^2R^2\sin(kR) , \quad (4.8)$$

$$N(kR)=3\sin(kR)-3kR\cos(kR)-k^2R^2\sin(kR) . \quad (4.9)$$

Hence, we obtain the result

$$\overline{\Delta U}=\frac{\pi I}{ck^3R^6}\{\alpha^A_{\lambda\mu}(k)\alpha^B_{\lambda\mu}(k)[-\sin(2kR)+2kR\cos(2kR)+3k^2R^2\sin(2kR)-2k^3R^3\cos(2kR)-k^4R^4\sin(2kR)]$$
$$+2\alpha^A_{\lambda\nu}(k)\alpha^B_{\mu\nu}(k)\hat{R}_\lambda\hat{R}_\mu[3\sin(2kR)-6kR\cos(2kR)-7k^2R^2\sin(2kR)+4k^3R^3\cos(2kR)+k^4R^4\sin(2kR)]$$
$$+\alpha^A_{\lambda\nu}(k)\alpha^B_{\mu o}(k)\hat{R}_\lambda\hat{R}_\mu\hat{R}_\nu\hat{R}_o[-9\sin(2kR)+18kR\cos(2kR)+15k^2R^2\sin(2kR)$$
$$-6k^3R^3\cos(2kR)-k^4R^4\sin(2kR)]\} . \quad (4.10)$$

As it stands, the above result represents that Stark shift in the intermolecular potential energy of two molecules held in a fixed mutual orientation as, for example, in a van der Waals complex. In order to obtain an expression appropriate to the case of random mutual orientation, a second stage of calculation is required, involving two further rotational averages; the procedure is identical with that described by Schipper in the context of induced circular dichroism.[12] These secondary rotational averages involve only the simple unretarded rotational averages, and the final result is directly obtained as follows:

$$\overline{\overline{\Delta U}}=\frac{-2\pi I}{9ck^3R^6}\alpha^A_{\lambda\lambda}(k)\alpha^B_{\mu\mu}(k)\times[3\sin(2kR)-6kR\cos(2kR)-5k^2R^2\sin(2kR)+2k^3R^3\cos(2kR)+k^4R^4\sin(2kR)]\,. \tag{4.11}$$

This result is applicable to any pair of molecules, regardless of their symmetry properties; in the case of isotropic molecules, it reproduces the result previously obtained by Thirunamachandran.[13]

The laser-induced force associated with the Stark shift immediately follows from Eq. (4.11) and is given by the expression

$$\vec{F}(\vec{R})=\frac{4\pi I\hat{R}}{9ck^3R^7}\alpha^A_{\lambda\lambda}(k)\alpha^B_{\mu\mu}(k)\times[-9\sin(2kR)+18kR\cos(2kR)+16k^2R^2\sin(2kR)-8k^3R^3\cos(2kR)-3k^4R^4\sin(2kR)+k^5R^5\cos(2kR)]\,. \tag{4.12}$$

At large distances, the last term within brackets provides the dominant contribution, and effectively averages to zero over a range of more than half a wavelength. However, for small separations, where $2kR \ll 1$, it is readily shown that the forces assume a limiting R^{-2} dependence

$$\lim_{2kR\ll 1}\vec{F}(\vec{R})=\frac{-44\pi k^2 I}{135cR^2}\hat{R}\alpha^A_{\lambda\lambda}(k)\alpha^R_{\mu\mu}(k)\,, \tag{4.13}$$

which is always attractive.

B. Cooperative two-photon absorption

We show in this section that phased averages are also important in the calculation of the rate of cooperative two-photon absorption, in which both molecules of an interacting pair (A,B) are excited when the system absorbs two photons from an intense laser beam:

$$|E_0^A\rangle|E_0^B\rangle\xrightarrow{2\hbar\omega}|E_\alpha^A\rangle|E_\beta^B\rangle\,. \tag{4.14}$$

There are two possible modes of cooperative two-photon absorption which are differentiated by the selection rules of the molecules involved. A common feature in both modes is that the interaction between the molecules is mediated by the exchange of a virtual photon. In the first case, which we have considered in detail in a recent paper,[11] both molecules have two-photon allowed transitions, resulting in the concerted absorption of a single incident laser photon and either the absorption or emission of a virtual photon at each center. In the second case, two-photon transitions are forbidden in both molecules and, as a result, only one- or three-photon interactions are allowed. In this mode one of the molecules absorbs both the incident photons, and virtual photon coupling excites the other.

A full and detailed discussion of this latter mode of cooperative two-photon absorption will be given in a forthcoming paper.[14] Here we outline the general results leading to the application of the fourth rank phased average. The matrix element connecting the initial and final states of the system is given by

$$M_{FI}=\frac{-8\pi^2 I}{c}e_ie_j[\chi^{\alpha 0}_{ijk}\mu^{\beta 0}_l V_{kl}(p,\vec{R})+\chi^{\beta 0}_{ijk}\mu^{\alpha 0}_l V_{kl}(q,\vec{R})e^{2i\vec{k}\cdot\vec{R}}]\,, \tag{4.15}$$

where the third rank transition tensor χ^{f0}_{ijk} is given by the expression

$$\chi^{f0}_{ijk}=\frac{1}{2}\sum_{r,s}\left[\frac{\mu_i^{r0}\mu_j^{sr}\mu_k^{fs}}{(E_{0s}+2\hbar\omega)(E_{0r}+\hbar\omega)}+\frac{\mu_i^{r0}\mu_j^{fs}\mu_k^{sr}}{(E_{fs}-\hbar\omega)(E_{0r}+\hbar\omega)}+\frac{\mu_i^{sr}\mu_j^{fs}\mu_k^{r0}}{(E_{fs}-\hbar\omega)(E_{fr}-2\hbar\omega)}+\frac{\mu_i^{sr}\mu_j^{r0}\mu_k^{fs}}{(E_{0s}+2\hbar\omega)(E_{0r}+\hbar\omega)}+\frac{\mu_i^{fs}\mu_j^{r0}\mu_k^{sr}}{(E_{fs}-\hbar\omega)(E_{0r}+\hbar\omega)}+\frac{\mu_i^{fs}\mu_j^{sr}\mu_k^{r0}}{(E_{fs}-\hbar\omega)(E_{fr}-2\hbar\omega)}\right] \tag{4.16}$$

and is seen to be the same form as the hyper-Raman transition tensor.[15] The parameters p and q which appear in Eq. (4.15) are defined by

$$\hbar cp=E_{\beta 0} \tag{4.17}$$

and

$$\hbar cq=E_{\alpha 0}\,. \tag{4.18}$$

The two terms in square brackets in Eq. (4.15) represent the probability amplitudes associated with the absorption of the two photons at centers A and B, respectively. Calculation of the rate equation using the Fermi rule[16] requires the square modulus of Eq. (4.15), resulting in interference of the probability amplitudes, and retention of phase-dependent terms in the final rate equation. The rate thus derived relates to a pair of molecules (A,B) fixed in space relative to each other and to the laser beam. In order to calculate the rate of cooperative absorption for a fluid sample, the rotational average of this initial expression is required. The result of such an average, in which the pair of molecules retain their fixed mutual orientation but where the (A,B) system is free to rotate in the space frame, is given by

$$\Gamma = K e_i e_j \bar{e}_m \bar{e}_n [\chi^{\alpha 0}_{\lambda\mu\nu}\mu^{\beta 0}_o \bar{\chi}^{\alpha 0}_{\pi\rho\sigma}\bar{\mu}^{\beta 0}_\tau V_{\nu o}(p,\vec{R})V_{\sigma\tau}(p,\vec{R})\langle l_{i\lambda}l_{j\mu}l_{m\pi}l_{n\rho}\rangle + \chi^{\beta 0}_{\lambda\mu\nu}\mu^{\alpha 0}_o \bar{\chi}^{\beta 0}_{\pi\rho\sigma}\bar{\mu}^{\alpha 0}_\tau V_{\nu o}(q,\vec{R})V_{\sigma\tau}(q,\vec{R})\langle l_{i\lambda}l_{j\mu}l_{m\pi}l_{n\rho}\rangle$$
$$+ \chi^{\beta 0}_{\lambda\mu\nu}\mu^{\alpha 0}_o \bar{\chi}^{\alpha 0}_{\pi\rho\sigma}\bar{\mu}^{\beta 0}_\tau V_{\nu o}(q,\vec{R})V_{\sigma\tau}(p,\vec{R})\langle l_{i\lambda}l_{j\mu}l_{m\pi}l_{n\rho}e^{2i\vec{k}\cdot\vec{R}}\rangle$$
$$+ \chi^{\alpha 0}_{\lambda\mu\nu}\mu^{\beta 0}_o \bar{\chi}^{\beta 0}_{\pi\rho\sigma}\bar{\mu}^{\alpha 0}_\tau V_{\nu o}(p,\vec{R})V_{\sigma\tau}(q,\vec{R})\langle l_{i\lambda}l_{j\mu}l_{m\pi}l_{n\rho}e^{-2i\vec{k}\cdot\vec{R}}\rangle] , \tag{4.19}$$

where

$$K = \frac{128\pi^5 I^2 g^{(2)}\rho_f}{\hbar c^2} . \tag{4.20}$$

It can be seen that the last two terms of Eq. (4.19) are of the same form as Eq. (2.2); in the case of cooperative two-photon absorption it is the fourth rank phased average [Eqs. (3.12)–(3.17)] that is required. Using the result for $I^{(4)}_{i_1,\ldots,i_4;\lambda_1,\ldots,\lambda_4}$ in the first two terms of (4.19) and those for $I^{(4)\phi}_{i_1,\ldots,i_4;\lambda_1,\ldots,\lambda_4}(\pm 2kR,\hat{k},\hat{R})$ in the last two terms gives the following final form of the rate equation:

$$\Gamma = \frac{K}{840}\{ 56[\chi^{\alpha 0}_{iik}\bar{\chi}^{\alpha 0}_{jjo}(2\eta-1)+\chi^{\alpha 0}_{ijk}\bar{\chi}^{\alpha 0}_{ijo}(3-\eta)]\mu^{\beta 0}_l\bar{\mu}^{\beta 0}_p V_{kl}(p,\vec{R})V_{op}(p,\vec{R})$$
$$+56 j_0(2kR)[\chi^{\beta 0}_{iik}\bar{\chi}^{\alpha 0}_{jjo}(2\eta-1)+\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{ijo}(3-\eta)]\mu^{\alpha 0}_l\bar{\mu}^{\beta 0}_p V_{kl}(q,\vec{R})V_{op}(p,\vec{R})$$
$$+336 i j_1(2kR)(\zeta)\epsilon_{im\tau}\hat{R}_\tau\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{jmo}\mu^{\alpha 0}_l\bar{\mu}^{\beta 0}_p V_{kl}(q,\vec{R})V_{op}(p,\vec{R})$$
$$-20 j_2(2kR)[\,2\chi^{\beta 0}_{iik}\bar{\chi}^{\alpha 0}_{mmo}(5\eta-4)+4\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{ijo}(3-2\eta)-3\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{mmo}\hat{R}_i\hat{R}_j(5\eta-4)$$
$$-3\chi^{\beta 0}_{iik}\bar{\chi}^{\alpha 0}_{mno}\hat{R}_m\hat{R}_n(5\eta-4)-12\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{jmo}\hat{R}_i\hat{R}_m(3-2\eta)]\mu^{\alpha 0}_l\bar{\mu}^{\beta 0}_p V_{kl}(q,\vec{R})V_{op}(p,\vec{R})$$
$$-84 i j_3(2kR)(\zeta)\epsilon_{im\tau}\hat{R}_\tau(\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{mjo}-5\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{mno}\hat{R}_j\hat{R}_n)\mu^{\alpha 0}_l\bar{\mu}^{\beta 0}_p V_{kl}(q,\vec{R})V_{op}(p,\vec{R})$$
$$+3 j_4(2kR)(2+\eta)(35\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{mno}\hat{R}_i\hat{R}_j\hat{R}_m\hat{R}_n-5\chi^{\beta 0}_{iik}\bar{\chi}^{\alpha 0}_{mno}\hat{R}_m\hat{R}_n-5\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{mmo}\hat{R}_i\hat{R}_j-20\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{ino}\hat{R}_j\hat{R}_n$$
$$+\chi^{\beta 0}_{iik}\bar{\chi}^{\alpha 0}_{mmo}+2\chi^{\beta 0}_{ijk}\bar{\chi}^{\alpha 0}_{ijo})\mu^{\alpha 0}_l\bar{\mu}^{\beta 0}_p V_{kl}(q,\vec{R})V_{op}(p,\vec{R})+(A,p\leftrightarrow B,q)\} , \tag{4.21}$$

where

$$\eta = (\vec{e}\cdot\vec{e})(\vec{\bar{e}}\cdot\vec{\bar{e}}) \tag{4.22}$$

and

$$\zeta = (\vec{e}\times\vec{\bar{e}})\cdot\hat{k} . \tag{4.23}$$

For plane polarized light, we have $\eta=1$ and $\zeta=0$. More interesting, however, is the case of circularly polarized light, where $\eta=0$ and $\zeta=\pm i$ depending on the handedness; $\zeta=i$ for right-handed radiation and $\zeta=-i$ for left-handed radiation. Because of the linear dependence of the j_1 and j_3 terms on ζ we find that the rate of cooperative two-photon absorption differs if the handedness of the radiation is reversed; in other words we have a manifestation of two-photon circular dichroism. The appearance of this feature directly results from the phased rotational average; a full discussion of the physical implications and a further development of the theory are given in our forthcoming paper.[14]

C. Electric field-induced polarization

As a simple example of a Boltzmann-weighted average we consider the polarization of a fluid induced by an applied static electric field. In the presence of an applied field $\vec{E}$, polar fluids become anisotropic, and the Boltzmann-weighting factor $e^{\vec{\mu}\cdot\vec{E}/kT}$ has to be introduced into any ensemble average. The mean electric dipole moment, per molecule, in the direction of the applied field is given by

$$\bar{\mu}=\langle \vec{\mu}\cdot\hat{E}\rangle =\langle (\vec{\mu}\cdot\hat{E})e^{\vec{\mu}\cdot\vec{E}/kT}\rangle/\langle e^{\vec{\mu}\cdot\vec{E}/kT}\rangle \tag{4.24}$$

$$=\hat{E}_i\mu_\lambda I_{i\lambda}^{(1)\phi}(-i\mu E/kT,\hat{E},\hat{\mu})/I^{(0)\phi}(-i\mu E/kT,\hat{E},\hat{\mu})$$

$$=i\mu j_1(-ix)/j_0(-ix)$$

$$=\mu(\coth x-1/x)\,, \tag{4.25}$$

where $x=\mu E/kT$. The result is the well-known Langevin function:[17] for $x\ll 1$ the Taylor-series expansion gives the well-known result

$$\bar{\mu}=\frac{\mu^2E}{3kT}\,. \tag{4.26}$$

D. Electric field-induced second harmonic generation

As a final example, we consider the generation of second harmonic radiation in a gas under the influence of an applied static electric field. We assume that the gas consists of polar molecules, and we restrict our attention to the temperature-dependent effect resulting from the field-induced anisotropy. (Our method of averaging enables results to be obtained without approximation of the dipolar Boltzmann-weighting exponential, in contrast to previous methods.[19–22]) The intensity of harmonic emission with polarization $\vec{e}\,'$ produced by an incident laser beam of frequency ω, polarization $\vec{e}$ and intensity I is given by[18]

$$\mathscr{I}=\frac{2\pi}{c}\left[\frac{2\omega}{c}\right]^4 I^2\,|\,\langle \beta_{ijk}\bar{e}_i'e_je_k\rangle\,|^2 \tag{4.27}$$

$$=\frac{32\pi\omega^4I^2}{c^5}\,|\,\bar{e}_i'e_je_k\beta_{\lambda\mu\nu}I_{ijk;\lambda\mu\nu}^{(3)\phi}(-i\mu E/kT,\hat{E},\hat{\mu})/I^{(0)\phi}(-i\mu E/kT,\hat{E},\hat{\mu})\,|^2\,, \tag{4.28}$$

where $\beta_{\lambda\mu\nu}$ is the molecular hyperpolarizability tensor, symmetric in its last two indices. Using the results in Sec. III, we obtain

$$\begin{aligned}\mathscr{I}=\frac{8\pi\omega^4I^2}{25c^5}\,|\,\{&2ij_1(-i\mu E/kT)[3(\vec{e}\,'\cdot\vec{e})(\vec{e}\cdot\hat{E})\beta_{\lambda\lambda\mu}\hat{\mu}_\mu-(\vec{e}\,'\cdot\vec{e})(\vec{e}\cdot\hat{E})\beta_{\lambda\mu\mu}\hat{\mu}_\lambda-(\vec{e}\cdot\vec{e})(\vec{e}\,'\cdot\hat{E})\beta_{\lambda\lambda\mu}\hat{\mu}_\mu\\&+2(\vec{e}\cdot\vec{e})(\vec{e}\,'\cdot\hat{E})\beta_{\lambda\mu\mu}\hat{\mu}_\lambda]-10j_2(-i\mu E/kT)(\vec{e}\cdot\hat{E})(\vec{e}\,'\times\vec{e})\cdot\hat{E}\epsilon_{\lambda\mu\tau}\beta_{\lambda\mu\nu}\hat{\mu}_\nu\hat{\mu}_\tau\\&-ij_3(-i\mu E/kT)[5(\vec{e}\,'\cdot\hat{E})(\vec{e}\cdot\hat{E})^2-2(\vec{e}\,'\cdot\vec{e})(\vec{e}\cdot\hat{E})-(\vec{e}\cdot\vec{e})(\vec{e}\,'\cdot\hat{E})]\\&\times(5\beta_{\lambda\mu\nu}\hat{\mu}_\lambda\hat{\mu}_\mu\hat{\mu}_\nu-2\beta_{\lambda\lambda\mu}\hat{\mu}_\mu-\beta_{\lambda\mu\mu}\hat{\mu}_\lambda)\}/j_0(-i\mu E/kT)\,|^2\,.\end{aligned} \tag{4.29}$$

It is clear from this equation that the harmonic intensity vanishes if the electric field $\vec{E}$ is parallel to the coherent scattering direction; hence, we shall assume that $\vec{E}$ lies perpendicular to the incident and harmonic beams. The j_2 term in (4.29) then disappears, and by using the explicit expressions for j_0, j_1, and j_3, we obtain

$$\begin{aligned}\mathscr{I}=\frac{8\pi\omega^4I^2}{25c^5}\,|\,&2(\coth x-1/x)[3(\vec{e}\,'\cdot\vec{e})(\vec{e}\cdot\hat{E})\beta_{\lambda\lambda\mu}\hat{\mu}_\mu-(\vec{e}\,'\cdot\vec{e})(\vec{e}\cdot\hat{E})\beta_{\lambda\mu\mu}\hat{\mu}_\lambda-(\vec{e}\cdot\vec{e})(\vec{e}\,'\cdot\hat{E})\beta_{\lambda\lambda\mu}\hat{\mu}_\mu+2(\vec{e}\cdot\vec{e})(\vec{e}\,'\cdot\hat{E})\beta_{\lambda\mu\mu}\hat{\mu}_\lambda]\\&+[(1+15/x^2)\coth x-(6/x+15/x^3)][5(\vec{e}\,'\cdot\hat{E})(\vec{e}\cdot\hat{E})^2-2(\vec{e}\,'\cdot\vec{e})(\vec{e}\cdot\hat{E})-(\vec{e}\cdot\vec{e})(\vec{e}\,'\cdot\hat{E})]\\&\times[5\beta_{\lambda\mu\nu}\hat{\mu}_\lambda\hat{\mu}_\mu\hat{\mu}_\nu-2\beta_{\lambda\lambda\mu}\hat{\mu}_\mu-\beta_{\lambda\mu\mu}\hat{\mu}_\lambda]\,|^2\,,\end{aligned} \tag{4.30}$$

where again we have set $x=\mu E/kT$. Finally, for the limiting case $\mu E\ll kT$, Eq. (4.30) reduces to

$$\begin{aligned}\mathscr{I}=\frac{8\pi\omega^4I^2}{225c^5}\,|\,&2(\mu E/kT)[3(\vec{e}\,'\cdot\vec{e})(\vec{e}\cdot\hat{E})\beta_{\lambda\lambda\mu}\hat{\mu}_\mu-(\vec{e}\,'\cdot\vec{e})(\vec{e}\cdot\hat{E})\beta_{\lambda\mu\mu}\hat{\mu}_\lambda-(\vec{e}\cdot\vec{e})(\vec{e}\,'\cdot\hat{E})\beta_{\lambda\lambda\mu}\hat{\mu}_\lambda+2(\vec{e}\cdot\vec{e})(\vec{e}\,'\cdot\hat{E})\beta_{\lambda\mu\mu}\hat{\mu}_\lambda]\\&+\tfrac{1}{35}(\mu E/kT)^3[5(\vec{e}\,'\cdot\hat{E})(\vec{e}\cdot\hat{E})^2-2(\vec{e}\,'\cdot\vec{e})(\vec{e}\cdot\hat{E})-(\vec{e}\cdot\vec{e})(\vec{e}\,'\cdot\hat{E})](5\beta_{\lambda\mu\nu}\hat{\mu}_\lambda\hat{\mu}_\mu\hat{\mu}_\nu-2\beta_{\lambda\lambda\mu}\hat{\mu}_\mu-\beta_{\lambda\mu\mu}\hat{\mu}_\lambda)\,|^2\,.\end{aligned} \tag{4.31}$$

Firstly, we note that in the absence of an applied field, i.e., where $E=0$, the system becomes isotropic and, as expected, $\mathscr{I}$ vanishes.[18] Secondly, in the presence of the field it is possible to produce harmonic emission from a circularly polarized source; the result from Eq. (4.31), in the case where the emission is analyzed for its polarization component parallel to $\vec{\mathrm{E}}$, is as follows:

$$\mathscr{I}=\frac{8\pi\omega^4 I^2}{225c^5}\,|\,(\mu E/kT)(3\beta_{\lambda\lambda\mu}\hat{\mu}_\mu-\beta_{\lambda\mu\mu}\hat{\mu}_\lambda)+\tfrac{3}{70}(\mu E/kT)^3(5\beta_{\lambda\mu\nu}\hat{\mu}_\lambda\hat{\mu}_\mu\hat{\mu}_\nu-2\beta_{\lambda\lambda\mu}\hat{\mu}_\mu-\beta_{\lambda\mu\mu}\hat{\mu}_\lambda)\,|^2 \ . \tag{4.32}$$

This contrasts with the well-known fact that harmonics cannot be generated with circularly polarized light in any isotropic medium.[23,24] Again a full discussion with these results will be given in a forthcoming paper.

ACKNOWLEDGMENT

M. J. H. gratefully acknowledges financial support from the Science and Engineering Research Council, United Kingdom.

APPENDIX: PROOF OF A RELATION INVOLVING CONVENTIONAL ROTATIONAL AVERAGES

In the conventional expression for the rotational average of a product of n direction cosines,[1]

$$I^{(n)}_{i_1,\ldots,i_n;\lambda_1,\ldots,\lambda_n}=\langle l_{i_1\lambda_1}\cdots l_{i_n\lambda_n}\rangle \tag{A1}$$

$$=\sum_{r,s} m^{(n)}_{rs} f^{(0;r)}_{i_1,\ldots,i_n} f^{(0;q)}_{\lambda_1,\ldots,\lambda_n}\ , \tag{A2}$$

the coefficients $m^{(n)}_{rs}$ of the isotropic tensor products satisfy the relations

$$\sum_{r,s} m^{(n)}_{rs}=\begin{cases}(n+1)^{-1} & \text{for even } n \quad \text{(A3)}\\ (n-1)/12 & \text{for odd } n. \quad \text{(A4)}\end{cases}$$

The result (A3) for even n has been proved previously;[18] in this Appendix the result (A4) for odd n is proven, using averaging formulas derived in the main text.

Consider the rotational average

$$\langle(\hat{A}\cdot\hat{a})(\hat{B}\cdot\hat{b})e^{i\alpha\hat{C}\cdot\hat{c}}\rangle=\hat{a}_{i_1}\hat{b}_{i_2}\hat{A}_{\lambda_1}\hat{B}_{\lambda_2}I^{(2)\phi}_{i_1i_2;\lambda_1\lambda_2}(\alpha,\hat{c},\hat{C})\ , \tag{A5}$$

where $\hat{A}$, $\hat{B}$, and $\hat{C}$ are real molecule-fixed unit vectors which form a right-handed set, and $\hat{a}$, $\hat{b}$, and $\hat{c}$ are real space-fixed unit vectors which also form a right-handed orthogonal set. Using Eq. (3.3) to evaluate the right-hand side of (A5), it is readily seen that because of the orthogonality of the vectors in each frame, the only contribution comes from the term (3.5). Since $(\hat{a}\times\hat{b})\cdot\hat{c}=(\hat{A}\times\hat{B})\cdot\hat{C}=1$, this simply gives

$$(i/2)(\sin\alpha/\alpha^2-\cos\alpha/\alpha)\ . \tag{A6}$$

Taking Taylor-series expansions of both the left-hand side of (A5) and the result (A6) in terms of α we obtain

$$\sum_{p=0}^{\infty}\frac{(i\alpha)^p\langle(\hat{A}\cdot\hat{a})(\hat{B}\cdot\hat{b})(\hat{C}\cdot\hat{c})^p\rangle}{p!}=\sum_{q=0}^{\infty}\frac{(q+1)(i\alpha)^{2q+1}}{(2q+3)!}\ . \tag{A7}$$

The left-hand side of Eq. (A7) may be written as

$$\sum_{p=0}^{\infty}\frac{(i\alpha)^p}{p!}\hat{a}_{i_1}\hat{b}_{i_2}\hat{c}_{i_3}\cdots\hat{c}_{i_{p+2}}\hat{A}_{\lambda_1}\hat{B}_{\lambda_2}\hat{C}_{\lambda_3}\cdots\hat{C}_{\lambda_{p+2}}I^{(p+2)}_{i_1,\ldots,i_{p+2};\lambda_1,\ldots,\lambda_{p+2}}$$

$$=\sum_{p=0}^{\infty}\frac{(i\alpha)^p}{p!}\sum_{r,s} m^{(p+2)}_{rs}(\hat{a}_{i_1}\hat{b}_{i_2}\hat{c}_{i_3}\cdots\hat{c}_{i_{p+2}}f^{(0;r)}_{i_1,\ldots,i_{p+2}})(\hat{A}_{\lambda_1}\hat{B}_{\lambda_2}\hat{C}_{\lambda_3}\cdots\hat{C}_{\lambda_{p+2}}f^{(0;s)}_{\lambda_1,\ldots,\lambda_{p+2}})\ . \tag{A8}$$

The terms in parentheses on the right-hand side of (A8) vanish for *even* p because then the isotropic tensors of rank $p+2$ are products of $\frac{1}{2}(p+2)$ Kronecker delta tensors, which contract with the unit vector products to give zero. For *odd* p, the isotropic tensors are products of one Levi-Civita antisymmetric tensor with $\frac{1}{2}(p-1)$ Kronecker deltas and, taking the result for the rotational average in block diagonal form,[1] we note that only those isotropic tensors involving $\epsilon_{i_1i_2i_m},\epsilon_{\lambda_1\lambda_2\lambda_m}$ can yield a nonzero result. There are p such epsilon tensors, each of which contracts with the unit vector product to give unity. Since the full set of epsilon tensors obtained by index permutation contains $\frac{1}{6}p(p+1)(p+2)$ members, we thus have

$$\sum_{r,s} m^{(p+2)}_{rs}(\hat{a}_{i_1}\hat{b}_{i_2}\hat{c}_{i_3}\cdots\hat{c}_{i_{p+2}}f^{(0;r)}_{i_1,\ldots,i_{p+2}})(\hat{A}_{\lambda_1}\hat{B}_{\lambda_2}\hat{C}_{\lambda_3}\cdots\hat{C}_{\lambda_{p+2}}f^{(0;s)}_{\lambda_1,\ldots,\lambda_{p+2}})$$

$$=\begin{cases}0 \ \text{ for even } p & \text{(A9)}\\ 6(p+1)^{-1}(p+2)^{-1}\sum_{r,s} m^{(p+2)}_{rs} \ \text{ for odd } p. & \text{(A10)}\end{cases}$$

Taking Eqs. (A7), (A8), and (A9) and writing $p=2t+1$ we thus have

$$6\sum_{t=0}^{\infty}\frac{(i\alpha)^{2t+1}}{(2t+3)!}\sum_{r,s}m_{rs}^{(2t+3)}=\sum_{q=0}^{\infty}\frac{(q+1)(i\alpha)^{2q+1}}{(2q+3)!}\ . \tag{A11}$$

For odd n, comparison of the coefficients of $(i\alpha)^{n-2}$ on both sides of (A11) immediately gives the required result, Eq. (A4). Since the results for $I^{(n)}_{i_1,\ldots,i_n;\lambda_1,\ldots,\lambda_n}$ are only available for $n\leq 8$ at present,[1,2] the results (A3) and (A4) should provide a useful check on calculations of higher-order results.

[1]D. L. Andrews and T. Thirunamachandran, J. Chem. Phys. 67, 5026 (1977).
[2]D. L. Andrews and W. A. Ghoul, J. Phys. A 14, 1281 (1981).
[3]G. Wagnière, J. Chem. Phys. 76, 473 (1982).
[4]J. Jerphagnon, D. Chemla, and R. Bonneville, Adv. Phys. 27, 609 (1978).
[5]J. A. R. Coope, R. F. Snider, and F. R. McCourt, J. Chem. Phys. 43, 2269 (1965).
[6]C. Zemach, Phys. Rev. B 140, 97 (1965).
[7]H. Weyl, *The Classical Groups* (Princeton University Press, Princeton, N.J., 1946).
[8]V. V. Mikhailov, J. Phys. A 10, 147 (1977).
[9]D. L. Andrews and W. A. Ghoul, Phys. Rev. A 25, 2647 (1982).
[10]J. A. R. Coope and R. F. Snider, J. Math. Phys. 11, 1003 (1970).
[11]D. L. Andrews and M. J. Harlow, J. Chem. Phys. 78, 1088 (1983).
[12]P. E. Schipper, Chem. Phys. 57, 105 (1981).
[13]T. Thirunamachandran, Mol. Phys. 40, 393 (1980).
[14]D. L. Andrews and M. J. Harlow (unpublished).
[15]D. L. Andrews and T. Thirunamachandran, J. Chem. Phys. 68, 2941 (1978).
[16]E. Fermi, *Nuclear Physics* (University of Chicago Press, Chicago, 1950).
[17]C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973), Vol. 1.
[18]D. L. Andrews, J. Phys. B 13, 4091 (1980).
[19]G. Hauchecorne, F. Kerherne, and G. Mayer, J. Phys. (Paris) 32, 47 (1971).
[20]J. F. Ward and I. J. Bigio, Phys. Rev. A 11, 60 (1974).
[21]D. S. Chemla and R. Bonneville, J. Chem. Phys. 68, 2214 (1978).
[22]S. Kielich, *Nonlinear Behavior of Molecules, Atoms and Ions in Electric, Magnetic or Electromagnetic Fields* (Elsevier, Amsterdam, 1979), p. 111.
[23]N. Bloembergen, *Polarisation Matière et Rayonnement,* edited by Société Française de Physique (Presses Universitaires de France, Paris, 1969), p. 109.
[24]C. L. Tang and H. Rabin, Phys. Rev. B 13, 4025 (1971).