

Selection Rules and Symmetry Relations for Four-Wave Mixing Measurements of Uniaxial Assemblies

Ryan P. Davis,^{†,‡} Andrew J. Moad,^{†,‡,§} G. Scott Goeken,[†] Ronald D. Wampler,[†] and Garth J. Simpson^{*,†}

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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Uniaxial systems represent the next lowest symmetry below isotropic and are ubiquitous. The objective of the present work is to present a systematic foundation for interpreting polarization-dependent four-wave mixing measurements of oriented and aligned assemblies. Orientational averages connecting the molecular frame to the macroscopic frame in uniaxial assemblies were derived for several common molecular symmetry groups for coherent anti-Stokes Raman spectroscopy (CARS) measurements, coherent anti-Stokes two-photon spectroscopy (CATS) probing electronic transitions, resonant two-photon absorption (2PA), and traditional Raman measurements. First, the complete set of orientational averages connecting the molecular and macroscopic frames was compiled for the most general case of C_1 molecular symmetry. Then, the orientational averages of a select few commonly occurring molecular symmetry groups (C_s , C_2 , C_{2v} , and C_{3v}) were explored in greater detail to illustrate the approach and to facilitate the interpretation of routine experimental measurements. One outcome of this analysis is the prediction of efficient electric dipole-allowed chiral-specific four-wave mixing in uniaxially oriented media.

Introduction

Raman, coherent anti-Stokes Raman (CARS), degenerate and nondegenerate four-wave mixing (FWM), and two-photon absorption have all found broad applicability in spectroscopic analyses of isotropic and oriented media. In isotropic media, the relationships between the molecular tensor and the macroscopic observables are reasonably well-established.^{1–6} However, these methods are finding increasing use in the measurement of ordered assemblies, for which comparatively few systematic bodies of literature are currently present to assist in bridging the molecular and macroscopic nonlinear optical (NLO) properties. The next lowest orientation below isotropic is uniaxial, in which molecular assemblies exhibit some degree of preferred alignment either along or perpendicular to a particular Cartesian axis. Uniaxial systems are ubiquitous in nature, including thin films, stretched polymers, lipid bilayers, many biopolymers, and so forth.

The growing interest in third-order NLO measurements has led to significant efforts toward development of conceptual frameworks for interpreting polarization-dependent $\chi^{(3)}$ measurements of uniaxial systems. Excellent general descriptions of Raman and two-photon absorption (2PA) in oriented and aligned media have been presented previously by Long⁵ and by Michl and Thulstrup,⁶ among others.^{7,8} These processes can be described by the imaginary components of rank four $\chi^{(3)}$ tensors (Figure 1), closely related to those describing FWM.³ However, the coherent nature of the four-wave mixing process affords greater polarization manipulation than with these related incoherent analogs, warranting the compilation of relationships

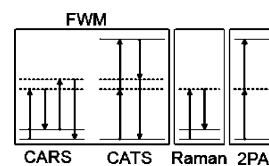


Figure 1. Energy level diagrams describing two of the most common four-wave mixing measurements (left) and their incoherent analogs (right).

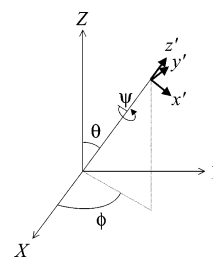


Figure 2. Definition of the Euler angles, with the Z axis being the unique axis. Orientational averaging is performed by assuming a uniform probability distribution in the azimuthal angle ϕ .

focusing primarily on interpreting $\chi^{(3)}$ measurements in uniaxially ordered systems for both coherent and incoherent processes. More recent work by Wang and co-workers summarizes several relationships connecting molecular and macroscopic frames in four- and five-wave mixing processes of uniaxial systems for rod-like molecules (i.e., molecules exhibiting uniform distributions in the Euler twist angle ψ about the molecular z axis in Figure 2).⁹

The objectives of the present work are to help connect and expand upon these previous efforts for describing uniaxial systems by (1) explicit derivation of the complete set of orientational averages connecting the molecular and macroscopic frames in all four-wave mixing processes with arbitrary

* Author to whom correspondence should be addressed. E-mail: gsimpson@purdue.edu.

[†] Purdue University.

[‡] Contributed equally.

[§] Current address: National Institute of Standards and Technology, Gaithersburg, MD 20899-8372.

TABLE 1: Nonzero $\chi^{(3)}$ Tensor Elements for Macroscopic D_∞ , $D_{\infty h}$, and $C_{\infty v}$ Symmetries

First two indices	Last two indices								
	XX	YY	ZZ	XY	YX	XZ	ZX	YZ	ZY
XX	f_{11}	f_{12}	f_{13}	0	0				
YY	f_{12}	f_{11}	f_{13}	0	0				
ZZ	f_{31}	f_{31}	f_{33}	0	0			0	
XY	0	0	0	f_{44}	f_{45}				
YX	0	0	0	f_{45}	f_{44}				
XZ						f_{66}	f_{67}	0	0
ZX						f_{76}	f_{77}	0	0
YZ			0			0	0	f_{66}	f_{67}
ZY						0	0	f_{76}	f_{77}

molecular symmetry and (2) preparation of character tables for the treatment of a few select common molecular symmetries, focusing on singly degenerate FWM, which includes both vibrational CARS and electronic coherent anti-Stokes two-photon spectroscopy (CATS), which often dominates the nonresonant background in CARS measurements. These systems illustrate the analytical procedure, serving as examples for other FWM measurements and higher molecular symmetries.

Theory

Macroscopic $\chi^{(3)}$ Tensor for FWM in Uniaxial Films. In a uniaxial system using the coordinates defined in Figure 2, the system is assumed to be invariant to azimuthal rotation by the angle ϕ about the unique macroscopic Z axis. Any number of forces may be responsible for breaking the isotropic symmetry and producing a unique axis, including surface-induced directions, mechanical perturbations from stretching, interactions driving polymer microfiber formation, and so forth. The symmetry-allowed elements of the $\chi^{(3)}$ tensor of material classes have been extensively documented,^{3,4,10} including uniaxial systems of macroscopic C_∞ (oriented and exhibiting polar order) and D_∞ (aligned but not oriented) symmetries.¹⁰ Recent studies by Wang and co-workers have reported simplified orientational averages assuming a uniform distribution in the twist angle ψ .⁹ However, the assumption of a uniform distribution in the twist angle limits the applicability of the analysis to structurally rod-like moieties. This approximation will generally not hold for planar molecular structures or complex molecular architectures, in which such an axis may not be present. Additionally, these previous expressions are only valid for a particular definition of the molecular coordinates and are no longer valid for different definitions of the molecular coordinates.

In the present more general treatment, the nonzero macroscopic $\chi_{ijkl}(-\omega_{\text{sum}}; \omega_a, \omega_b, \omega_c)$ tensor elements can be represented in matrix form by a “uniaxial contraction”, in which the 81 elements are presented in a 9×9 matrix, with the first two indices corresponding to the row and the last two indices corresponding to the column (Table 1). This notation is modeled loosely after the well-known “piezoelectric contraction” in second order nonlinear optics. For the most common systems of D_∞ (aligned but not oriented), $D_{\infty h}$ (achiral and aligned, but not oriented) and $C_{\infty v}$ (achiral and oriented) symmetry, 11 unique tensor elements remain, 10 of which are independent; $f_{12} = \chi_{XXYY} = \chi_{YYXX}$, $f_{13} = \chi_{XXZZ} = \chi_{YYZZ}$, $f_{31} = \chi_{ZZXX} = \chi_{ZZYY}$, $f_{33} = \chi_{ZZZZ}$, $f_{44} = \chi_{XXYY} = \chi_{YYXX}$, $f_{45} = \chi_{XXYY} = \chi_{YYXX}$, $f_{66} = \chi_{XZZX} = \chi_{YZYZ}$, $f_{67} = \chi_{XZZX} = \chi_{YZYZ}$, $f_{76} = \chi_{XZZX} = \chi_{YZYZ}$, and $f_{77} = \chi_{XZZX} = \chi_{YZYZ}$, with $f_{11} = \chi_{XXXX} = \chi_{YYYY} = \chi_{XXYY} + \chi_{YYXX} + \chi_{XXYY}$. From this matrix representation, the nonlinear polarization vector \mathbf{P}^{NL} is generated first by multiplication by a vector representing the

TABLE 2: Additional Chiral-Specific Nonzero $\chi^{(3)}$ Tensor Elements Introduced for C_∞ Symmetry

First two indices	Last two indices								
	XX	YY	ZZ	XY	YX	XZ	ZX	YZ	ZY
XX	0	0	0	f_{14}	f_{15}				
YY	0	0	0	$-f_{15}$	$-f_{14}$				
ZZ	0	0	0	f_{34}	$-f_{34}$			0	
XY	f_{41}	f_{51}	f_{43}	0	0				
YX	$-f_{51}$	$-f_{41}$	$-f_{43}$	0	0				
XZ						0	0	f_{68}	f_{69}
ZX						0	0	$-f_{96}$	f_{79}
YZ			0			$-f_{68}$	$-f_{69}$	0	0
ZY						f_{96}	f_{79}	0	0

combined polarization components of the electric fields corresponding to the last two indices in the $\chi^{(3)}$ tensor, \mathbf{E}_b and \mathbf{E}_c . The products of this multiplication form a 3×3 matrix \mathbf{A} , with the positions in the matrix given by the row headings to the left. Multiplication of this new matrix by the electric field vector for the next highest frequency \mathbf{E}_a yields a vector describing the nonlinear source polarization \mathbf{P}^{NL} (eq 1).

$$\mathbf{P}^{\text{NL}} = \begin{bmatrix} A_{XX} & A_{XY} & A_{XZ} \\ A_{YX} & A_{YY} & A_{YZ} \\ A_{ZX} & A_{ZY} & A_{ZZ} \end{bmatrix} \cdot \begin{bmatrix} E_a^X \\ E_a^Y \\ E_a^Z \end{bmatrix} \quad (1)$$

For a system with macroscopic C_∞ symmetry (i.e., exhibiting polar order), no additional tensor elements beyond those already present for D_∞ symmetry are introduced unless the system is also chiral. In systems that both are chiral and exhibit polar order, 10 new unique tensor elements emerge, 9 of which are independent (Table 2); $f_{14} = \chi_{XXXY} = -\chi_{YYXX}$, $f_{41} = \chi_{XXYY} = -\chi_{YYXX}$, $f_{15} = \chi_{XXYY} = -\chi_{YYXX}$, $f_{34} = \chi_{ZZXY} = -\chi_{ZZYX}$, $f_{43} = \chi_{XXYZ} = -\chi_{YYZX}$, $f_{68} = \chi_{XZZX} = -\chi_{YZYZ}$, $f_{79} = \chi_{XZZX} = -\chi_{YZYZ}$, $f_{69} = \chi_{XZZX} = -\chi_{YZYZ}$, $f_{96} = \chi_{XZZX} = -\chi_{YZYZ}$, with $f_{51} = \chi_{XXYY} = -\chi_{YYXX} - \chi_{XXYY} - \chi_{XXYY}$. The requirement of chirality is made clear by inspection of the nonzero elements introduced upon relaxation of the symmetry from D_∞ to C_∞ . The presence of a mirror plane to raise the symmetry to $C_{\infty v}$ results in the removal of all elements with an odd number of X or Y indices from the $\sigma(YZ)$ and $\sigma(XZ)$ operations, respectively. Since all of the new elements fall within this set, polar order alone or chirality alone is insufficient to generate additional electric-dipole-allowed nonzero values for these tensor elements. The net nonlinear source polarization \mathbf{P}^{NL} is given by the summation of the achiral and chiral contributions from \mathbf{A} and \mathbf{B} , respectively (eq 2).

$$\mathbf{P}^{\text{NL}} = \left\{ \begin{bmatrix} A_{XX} & A_{XY} & A_{XZ} \\ A_{YX} & A_{YY} & A_{YZ} \\ A_{ZX} & A_{ZY} & A_{ZZ} \end{bmatrix}_{\text{achiral}} + \begin{bmatrix} B_{XX} & B_{XY} & B_{XZ} \\ B_{YX} & B_{YY} & B_{YZ} \\ B_{ZX} & B_{ZY} & B_{ZZ} \end{bmatrix}_{\text{chiral}} \right\} \cdot \begin{bmatrix} E_a^X \\ E_a^Y \\ E_a^Z \end{bmatrix} \quad (2)$$

Further simplification of these 19 or 10 independent nonzero elements arises in the case of singly degenerate FWM (i.e., with two of the three incident frequencies equal),¹⁰ which includes the most common experimental configuration for CARS. In this case, the degeneracy in the incident frequencies introduces symmetry-driven equalities between several tensor elements. By using a convention in which the detected frequency is listed

TABLE 3: Nonzero $\chi^{(3)}$ Tensor Elements for Macroscopic D_{∞} , $D_{\infty h}$, and $C_{\infty v}$ Symmetries for Singly Degenerate Four-Wave Mixing with Interchangeability of the Middle Two Indices

	A	Last two indices								
		XX	YY	ZZ	XY	YX	XZ	ZX	YZ	ZY
First two indices	XX	f_{11}	f_{12}	f_{13}	0	0				
	YY	f_{12}	f_{11}	f_{13}	0	0				
	ZZ	f_{31}	f_{31}	f_{33}	0	0			0	
	XY	0	0	0	f_{12}	f_{45}				
	YX	0	0	0	f_{45}	f_{12}				
	XZ						f_{13}	f_{67}	0	0
	ZX						f_{76}	f_{31}	0	0
	YZ			0			0	0	f_{13}	f_{67}
	ZY						0	0	f_{76}	f_{31}

first as the sum frequency and the subsequent fields are listed in order of photon energy, the most common configuration for CARS measurements [i.e., using a red-shifted Stokes beam to generate a blue-shifted anti-Stokes beam corresponding to $\gamma_{ijkl}(-\omega_4; \omega_1, \omega_1, -\omega_3)$] introduces interchangeability of the center two indices of both the molecular $\gamma^{(3)}$ and macroscopic $\chi^{(3)}$ tensors. This degeneracy results in a significant simplification of the symmetry-allowed tensor elements. For D_{∞} , $D_{\infty h}$, and $C_{\infty v}$ symmetries (Table 3), $f_{13} = f_{66}$, $f_{31} = f_{77}$, and $f_{12} = f_{44}$ such that 8 unique elements remain, 7 of which are independent (since $f_{11} = 2f_{12} + f_{45}$).

In the case of C_{∞} symmetry (Table 4), interchangeability of the inner two indices demands that $f_{43} = f_{68}$, $f_{34} = f_{79}$, $f_{15} = f_{41}$, and $f_{96} = 0$, such that only 6 additional unique chiral-specific tensor elements appear (f_{14} , f_{15} , f_{51} , f_{34} , f_{43} , and f_{69}), 5 of which are independent since $f_{14} = -(2f_{15} + f_{51})$.¹⁰

In fully degenerate FWM [i.e., for $\gamma_{ijkl}(-\omega_1; \omega_1, \omega_1, -\omega_1)$], all four indices become interchangeable, further reducing the number of nonzero elements to just three for both C_{∞} and D_{∞} symmetry;¹⁰ $f_{11} = 3f_{12} = 3f_{44} = 3f_{45}$, $f_{13} = f_{31} = f_{66} = f_{67} = f_{76} = f_{77}$, and f_{33} , with $\mathbf{B} = 0$. Since all of the relationships for fully degenerate FWM can be derived from the more general cases of singly degenerate FWM, the bulk of the subsequent analysis will focus on the singly degenerate case.

Molecular $\gamma^{(3)}$ Tensor for FWM. The next step in relating the 19 and 10 independent symmetry allowed macroscopic $\chi^{(3)}$ tensor elements for singly degenerate FWM in systems of D_{∞} and C_{∞} symmetries, respectively, is formulation of the molecular

$\gamma^{(3)}$ tensor. The molecular tensor can be expressed in either the time domain or the frequency domain. The descriptions used in this section will focus on frequency-domain expressions, in which the simplifications imposed by molecular symmetry are arguably more intuitively applied. However, the same symmetry arguments also necessarily hold in analogous time-domain descriptions, as the two forms are Fourier transforms of each other.

In the frequency domain, the general form for the molecular tensor derived from time-dependent perturbation theory for a four-wave mixing process consists of a triple summation over all excited states with 48 quadruple products of transition moments.^{4,11} It has been shown that this general expression can be written identically in the equivalent contracted forms given in eq 3.¹²

The polarization indices $ijkl$ of the $\gamma^{(3)}$ tensor correspond in order to the frequencies within the parenthetical. The tensor for FWM can be expressed as a sum of four direct products of a transition moment $\mu^{(0)}$ and a rank three $\beta^{(2)}$ tensor, or as the sum of six direct products of two rank two $\alpha^{(1)}$ tensors. The subscripts 3PA, AHR, AR, 2PA, SHR refer to three photon absorption, anti-Stokes hyper-Raman, anti-Stokes Raman, two photon absorption, and Stokes hyper-Raman, respectively and are included only for convenience in interpretation. The frequencies corresponding to the $ijkl$ indices together with the initial and final states dictate the physical process described by the $\alpha^{(1)}$ or $\beta^{(2)}$ tensor. These three different contracted forms are all mathematically identical, although one or another representation may be significantly easier to use for describing a particular set of measurements. The damping term Γ_i is related to the line shape function of the i state through the lifetime. To illustrate the mathematical approach, the primary emphasis of the present work will be on just one representative and commonly encountered form, in which $\gamma^{(3)}$ is given by direct products of two $\alpha^{(1)}$ tensors (i.e., the middle set of relations in eq 3).

Molecular and Macroscopic Tensors for Singly Degenerate FWM (Including CARS). The contracted expression in eq 1 can be further reduced by considering the most common experimental conditions for $\chi^{(3)}$ measurements, in which two of the incident frequencies are degenerate and the third incident frequency is unique (typically, red-shifted), reducing the number of unique nonzero molecular tensor elements from 81 to 57. This condition includes both CARS and the nonresonant background in CARS. Setting $\omega_2 = \omega_1$ and defining a detec-

$$\begin{aligned}
 \gamma_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3) = & \\
 & \frac{-1}{4\hbar} \sum_p \left\{ \frac{(\beta_{0p}^{lkj})_{3PA} \mu_{p0}^i}{\omega_{pl}^* + \omega_4 + i\Gamma_p} + \frac{(\beta_{0p}^{ikl})_{AHR} \mu_{p0}^j}{\omega_{pl} - \omega_1 - i\Gamma_p} + \frac{(\beta_{0p}^{ijl})_{AHR} \mu_{p0}^k}{\omega_{pl} - \omega_2 - i\Gamma_p} + \frac{(\beta_{0p}^{ijk})_{AHR} \mu_{p0}^l}{\omega_{pl} - \omega_3 - i\Gamma_p} \right\} = \\
 & \frac{1}{4\hbar} \sum_q \left\{ \frac{(\alpha_{0q}^{il})_{AR} (\alpha_{q0}^{jk})_{2PA}}{\omega_{ql} - \omega_1 - \omega_2 - i\Gamma_q} + \frac{(\alpha_{0q}^{ik})_{AR} (\alpha_{q0}^{jl})_{2PA}}{\omega_{ql} - \omega_1 - \omega_3 - i\Gamma_q} + \frac{(\alpha_{0q}^{ij})_{AR} (\alpha_{q0}^{kl})_{2PA}}{\omega_{ql} - \omega_2 - \omega_3 - i\Gamma_q} \right. \\
 & \left. + \frac{(\alpha_{0q}^{kj})_{2PA} (\alpha_{q0}^{li})_{AR}}{\omega_{ql}^* + \omega_1 + \omega_2 + i\Gamma_q} + \frac{(\alpha_{0q}^{lj})_{2PA} (\alpha_{q0}^{ki})_{AR}}{\omega_{ql}^* + \omega_1 + \omega_3 + i\Gamma_q} + \frac{(\alpha_{0q}^{lk})_{2PA} (\alpha_{q0}^{ji})_{AR}}{\omega_{ql}^* + \omega_2 + \omega_3 + i\Gamma_q} \right\} = \\
 & \frac{-1}{4\hbar} \sum_r \left\{ \frac{\mu_{0r}^i (\beta_{r0}^{ikl})_{3PA}}{\omega_{rl} - \omega_4 - i\Gamma_r} + \frac{\mu_{0r}^j (\beta_{r0}^{lki})_{SHR}}{\omega_{rl}^* + \omega_1 + i\Gamma_r} + \frac{\mu_{0r}^k (\beta_{r0}^{lji})_{SHR}}{\omega_{rl}^* + \omega_2 + i\Gamma_r} + \frac{\mu_{0r}^l (\beta_{r0}^{kji})_{SHR}}{\omega_{rl}^* + \omega_3 + i\Gamma_r} \right\}
 \end{aligned} \quad (3)$$

TABLE 4: Additional Chiral-Specific Nonzero $\chi^{(3)}$ Tensor Elements for Macroscopic C_∞ Symmetry for Singly Degenerate Four-Wave Mixing with Interchangeability of the Middle Two Indices

		Last two indices									
First two indices	<i>B</i>	<i>XX</i>	<i>YY</i>	<i>ZZ</i>	<i>XY</i>	<i>YX</i>	<i>XZ</i>	<i>ZX</i>	<i>YZ</i>	<i>ZY</i>	
	<i>XX</i>	0	0	0	f_{14}	f_{15}					
	<i>YY</i>	0	0	0	$-f_{15}$	$-f_{14}$					
	<i>ZZ</i>	0	0	0	f_{34}	$-f_{34}$			0		
	<i>XY</i>	f_{15}	f_{51}	f_{43}	0	0					
	<i>YX</i>	$-f_{51}$	$-f_{15}$	$-f_{43}$	0	0					
	<i>XZ</i>						0	0	f_{43}	f_{69}	
	<i>ZX</i>						0	0	0	f_{34}	
	<i>YZ</i>			0			$-f_{43}$	$-f_{69}$	0	0	
	<i>ZY</i>						0	f_{34}	0	0	

tion energy at the sum of $\hbar\omega_4 = 2\hbar\omega_1 - \hbar\omega_3$ yields the following contracted expression for singly degenerate FWM in eq 4.

$$\gamma^{ijkl}(-\omega_4; \omega_1, \omega_1, -\omega_3) = \frac{1}{4\hbar} \sum_q \left\{ \frac{(\alpha_{0q}^{il})_{2PE}(\alpha_{q0}^{jk})_{2PA}}{\omega_{qI} - 2\omega_1 - i\Gamma_q} + \frac{1}{2!} \frac{(\alpha_{0q}^{ik})_{AR}(\alpha_{q0}^{jl})_{SR} + (\alpha_{0q}^{ij})_{AR}(\alpha_{q0}^{kl})_{SR}}{\omega_{qI} - \omega_1 + \omega_3 - i\Gamma_q} \right. \\ \left. + \frac{(\alpha_{0q}^{kj})_{2PA}(\alpha_{q0}^{li})_{2PE}}{\omega_{qI} + 2\omega_1 + i\Gamma_q} + \frac{1}{2!} \frac{(\alpha_{0q}^{lj})_{SR}(\alpha_{q0}^{ki})_{AR} + (\alpha_{0q}^{lk})_{SR}(\alpha_{q0}^{ji})_{AR}}{\omega_{qI}^* + \omega_1 - \omega_3 + i\Gamma_q} \right\} \quad (4)$$

The subscript SR indicates a Stokes Raman polarizability tensor. The additional factor of 2! corrects for the degeneracy introduced by the presence of the two identical frequencies. It is only required for the direct products of Raman tensors, as the 2! is implicitly included in the definition of the 2PA tensor for the CATS case.¹² If it is assumed that the molecules are all initially in the ground state, only the three terms with negative signs in the denominators exhibit obvious resonance enhancement.

By definition, CARS experiments are performed with vibrational resonance enhancement at ω_1 (i.e., ω_{pump}) $-\omega_3$ (i.e., ω_{SR}). Consequently, a comparatively small subset of the possible resonance-enhanced conditions contributes significantly in most experimental studies. To a very good approximation in the absence of one-photon resonance enhancement,^{3,13} the only remaining terms are those exhibiting resonance enhancement at the difference frequency between ω_1 and ω_3 and at or near the second harmonic of the pump frequency (i.e., $\omega_{q0} \cong \omega_1 - \omega_3$ and $\omega_{q0} \cong 2\omega_1$, respectively, for molecules initially in the ground state).^{1,12}

$$\gamma^{ijkl}(-\omega_4; \omega_1, \omega_1, -\omega_3) \cong \frac{1}{4\hbar} \sum_q \left\{ \frac{(\alpha_{0q}^{il})_{2PE}(\alpha_{q0}^{jk})_{2PA}}{\omega_{qI} - 2\omega_1 - i\Gamma_q} + \frac{1}{2!} \frac{(\alpha_{0q}^{ik})_{AR}(\alpha_{q0}^{jl})_{SR} + (\alpha_{0q}^{ij})_{AR}(\alpha_{q0}^{kl})_{SR}}{\omega_{qI} - \omega_1 + \omega_3 - i\Gamma_q} \right\} \quad (5)$$

In eq 5, the second term typically describes vibrational CARS, in which the energy of the vibrational transition matches the energy difference between the pump and Stokes beams, and the first term describes the nonresonant background to CARS arising primarily from electronic interactions with transitions of energies comparable to or greater than $2\omega_1$.¹² The relation-

ships in eq 5 impose symmetry conditions that introduce equalities between tensor elements, simplifying subsequent analysis.

The next step is connecting the molecular $\gamma^{(3)}$ tensors and macroscopic $\chi^{(3)}$ tensors. In the limit of weak coupling between chromophores,^{14,15} the relationships bridging the two frames are given by simple orientational averages in eq 6, in which N_b is the bulk number density and ϵ_0 is the vacuum permittivity.^{11,16}

$$\chi_{IJKL} = \frac{N_b}{\epsilon_0} \sum_{i,j,k,l=x,y,z} \langle R_{iI} R_{jJ} R_{kK} R_{lL} \rangle \gamma_{ijkl} \quad (6)$$

In the most general case of C_1 molecular symmetry, each of the unique symmetry-allowed $\chi^{(3)}$ tensor elements present in uniaxial systems will contain contributions from as many as 81 unique molecular tensor elements through their associated orientational averages. All of these relationships for the general case of fully nondegenerate FWM are given explicitly in the Appendix for each of the nonzero $\chi^{(3)}$ tensor elements present in uniaxial films as references for discussions of the specific cases considered in subsequent sections.

Character Tables for Common $\chi^{(3)}$ Processes and Symmetry Classes

Although the set of general relations provided in the Appendix provides a starting point, significant reductions in complexity can arise when considering particular $\chi^{(3)}$ processes, particular resonance-enhanced conditions, particular molecular symmetries, and particular symmetries for individual transitions. The primary goal of the present work is to provide explicit expressions to assist in the interpretation of polarization-dependent $\chi^{(3)}$ processes for the most commonly encountered molecular symmetries, in order to serve as a reference for the interpretation of experimental measurements of such systems and as a template for extension to molecules of higher molecular symmetry. Consequently, two common model measurements will be considered in detail: vibrationally resonant CARS and electronically resonant singly degenerate FWM.

I. Vibrational CARS. From eq 3, the vibrationally resonant molecular $\gamma^{(3)}$ tensor for CARS is described by a direct product of two $\alpha^{(1)}$ Raman tensors multiplied by a line shape function. Under most experimental conditions (i.e., in the absence of one-photon resonance enhancement), the Raman tensors can be reasonably assumed to be real and symmetric.⁵ This approximation holds for vibrational transitions in the adiabatic limit, in which the electronic states contributing to the construction of the virtual state are all sufficiently high in energy that their contributions are equal for both the Stokes and the anti-Stokes virtual states (Figure 1).⁵ Within this limit for singly degenerate CARS measurements, only 21 nonzero independent elements of the $\gamma^{(3)}$ tensors remain, of six different forms: γ_{iiii} , $\gamma_{iiij} = \gamma_{ijii} = \gamma_{jiij} = \gamma_{jiii}$, $\gamma_{ijij} = \gamma_{jiij} = \gamma_{jiji} = \gamma_{jjii}$, $\gamma_{ijji} = \gamma_{jiij}$, $\gamma_{ijkj} = \gamma_{jikj} = \gamma_{kjij} = \gamma_{kiji} = \gamma_{kjji} = \gamma_{jkii} = \gamma_{kijj}$, and $\gamma_{ikji} = \gamma_{ikji} = \gamma_{jikk}$, where the indices can be x , y , or z with the condition $i \neq j \neq k$.

The simplification from 81 to 21 independent $\gamma^{(3)}$ tensor elements arising from the assumption of symmetric, real-valued $\alpha^{(1)}$ tensors combined with the relationship $\alpha_{n0}^{ij} = (\alpha_{0n}^{ji})^*$ results in 6 unique and 5 independent elements within the corresponding macroscopic $\chi^{(3)}$ tensor elements for both C_∞ and D_∞ macroscopic symmetry (Table 5); $f_{11}, f_{12} = f_{21} = f_{44}, f_{13} = f_{31} = f_{66} = f_{77}, f_{33}, f_{45}$, and $f_{67} = f_{76}$. All of the chiral tensor elements present in the general case of C_∞ symmetry disappear within the validity of a symmetric $\alpha^{(1)}$ tensor, such that $\mathbf{B} = 0$.

TABLE 5: Nonzero $\chi^{(3)}$ Tensor Elements for Singly Degenerate CARS and CATS of Uniaxial Assemblies in the Limit of Symmetric $\alpha^{(1)}$ Molecular Tensors; $B = 0$

First two indices	Last two indices								
	XX	YY	ZZ	XY	YX	XZ	ZX	YZ	ZY
XX	f_{11}	f_{12}	f_{13}	0	0				
YY	f_{12}	f_{11}	f_{13}	0	0				
ZZ	f_{13}	f_{13}	f_{33}	0	0			0	
XY	0	0	0	f_{12}	f_{45}				
YX	0	0	0	f_{45}	f_{12}				
XZ						f_{13}	f_{67}	0	0
ZX						f_{67}	f_{13}	0	0
YZ			0			0	0	f_{13}	f_{67}
ZY						0	0	f_{67}	f_{13}

TABLE 6: Vibrational CARS for C_s and C_2 Molecular Symmetries

A_1	γ_{xxxx} γ_{yyyy} γ_{zzzz} $\gamma_{xxyy} = \gamma_{yxxx} = \gamma_{xyyx} = \gamma_{xyxx}$ $\gamma_{xyxy} = \gamma_{xyxy} = \gamma_{yxyx} = \gamma_{yyxx}$ $\gamma_{xxzz} = \gamma_{xxzz} = \gamma_{zxzx} = \gamma_{zzxx}$ $\gamma_{yyzz} = \gamma_{yyzz} = \gamma_{zyzy} = \gamma_{zyzy}$ $\gamma_{xyyx} = \gamma_{xyyx}$ $\gamma_{xxzz} = \gamma_{xxzz}$ $\gamma_{yyzz} = \gamma_{yyzz}$
A_2	$2(\gamma_{xxzz} = \gamma_{xxzz} = \gamma_{zxzx} = \gamma_{zzxx}) = \gamma_{xxzz} = \gamma_{xxzz}$ $2(\gamma_{xyzz} = \gamma_{xyzz} = \gamma_{yxzz} = \gamma_{yzxz} = \gamma_{zyzx} = \gamma_{zyzx}) = \gamma_{xyzz} = \gamma_{xyzz}$ $2(\gamma_{yyzz} = \gamma_{yyzz} = \gamma_{zyzy} = \gamma_{zyzy}) = \gamma_{yyzz} = \gamma_{yyzz}$

The presence of molecular symmetry can further reduce the number of unique elements within the molecular tensor, simplifying the orientational averages connecting the molecular and macroscopic frames. Rather than generate an exhaustive list of all possible molecular symmetries and transitions for all possible FWM phenomena, a few common systems are described in detail to illustrate the approach (Tables 6–8). From this framework, extension to other FWM phenomena and different molecular symmetries for uniaxial systems is relatively straightforward using the explicit expressions for the full orientational averages compiled in the Appendix.

The simplifications arising from introduction of molecular symmetry are broken down into two elements. First, nonlinear optical “character tables” are presented, indicating additional molecular and macromolecular equalities arising based on molecular symmetry and the symmetry of the particular transition. The equalities presented in the tables are all in addition to those presented in the general discussion of vibrational CARS in Table 5.

The most general case of a molecule with no intrinsic symmetry (C_1) leaves only the symmetry imposed by the interchangeability of the two degenerate frequencies at ω_1 and the assumed interchangeability of the symmetric elements in the real-valued $\alpha^{(1)}$ tensors for Raman. In this case, no additional reductions or simplifications arise beyond the general relationships described in the preceding paragraphs for uniaxial macroscopic assemblies (Table 5).

While the character tables provide a simple means of assessing molecular symmetry from the macroscopic polarization dependence (or alternatively, predicting polarization dependence based on symmetry), they do not directly provide information that can be used to interpretation molecular orientation from polarization-dependent CARS measurement of uniax-

TABLE 7: Vibrational CARS for C_{2v} Molecular Symmetry

A_1	γ_{xxxx} γ_{yyyy} γ_{zzzz} $\gamma_{xxyy} = \gamma_{xyxy} = \gamma_{xyyx} = \gamma_{yyxx}$ $\gamma_{xxzz} = \gamma_{xxzz} = \gamma_{zxzx} = \gamma_{zzxx}$ $\gamma_{yyzz} = \gamma_{yyzz} = \gamma_{zyzy} = \gamma_{zyzy}$ $2\gamma_{xyyz} = 2\gamma_{xyyz} = 2\gamma_{yxyx} = 2\gamma_{yxyx} = \gamma_{xyxy} = \gamma_{xyxy}$ $\chi_{zzzz} = 8\chi_{xxyy} = 2\chi_{xxzz} - 4\chi_{xxzz}$ $f_{33} = 8f_{12} = 2f_{67} - 4f_{13}$
B_1	$2\gamma_{xxyy} = 2\gamma_{xyxy} = 2\gamma_{xyyx} = 2\gamma_{yyxx} = \gamma_{xyxy} = \gamma_{xyxy}$ $\chi_{zzzz} = 8\chi_{xxyy} = 2\chi_{xxzz} - 4\chi_{xxzz}$ $f_{33} = 8f_{12} = 2f_{67} - 4f_{13}$
B_2	$2\gamma_{yyzz} = 2\gamma_{yyzz} = 2\gamma_{zyzy} = 2\gamma_{zyzy} = \gamma_{yyzz} = \gamma_{yyzz}$ $\chi_{zzzz} = 8\chi_{xxyy} = 2\chi_{xxzz} - 4\chi_{xxzz}$ $f_{33} = 8f_{12} = 2f_{67} - 4f_{13}$

TABLE 8: Vibrational CARS for C_{3v} Molecular Symmetry

A_1	$\gamma_{xxxx} = \gamma_{yyyy} = 2(\gamma_{xxyy} = \gamma_{xyxy} = \gamma_{xyyx} = \gamma_{yyxx})$ $\gamma_{xxzz} = \gamma_{yyzz} = \gamma_{xxzz} = \gamma_{yyzz} = \gamma_{zxzx} = \gamma_{zyzy} = \gamma_{zzxx} = \gamma_{zzyy}$ γ_{zzzz}
A_2	0
E	$\gamma_{xxxx} = \gamma_{yyyy} = 2(\gamma_{xxyy} = \gamma_{xyxy} = \gamma_{xyyx} = \gamma_{yyxx}) + (\gamma_{xyxy} = \gamma_{xyxy})$ $\gamma_{xxzz} = \gamma_{yyzz} = \gamma_{xxzz} = \gamma_{yyzz} = \gamma_{zxzx} = \gamma_{zyzy} = \gamma_{zzxx} = \gamma_{zzyy}$ $-\gamma_{xxzz} = \gamma_{xyyz} = \gamma_{xyyz} = \gamma_{yxyz} = -\gamma_{zxzx} = \gamma_{zyzy} = \gamma_{zyzy} = \gamma_{zyzy}$ $-\gamma_{xxzz} = \gamma_{xyyz} = \gamma_{xyyz} = \gamma_{yxyz} = -\gamma_{xxzz} = \gamma_{xxzz} = \gamma_{zyzy} = \gamma_{zyzy}$ $\gamma_{xxzz} = \gamma_{yyzz} = \gamma_{xxzz} = \gamma_{yyzz}$

ial systems. Each macroscopic $\chi^{(3)}$ tensor element generally contains contributions from each of the nonzero elements within the molecular tensor through a set of orientational averages, using a notation defined in eq 7.

$$A = \langle \sin \theta \rangle \quad (7a)$$

$$B = \langle \cos \theta \rangle \quad (7b)$$

$$C = \langle \sin^2 \theta \rangle \quad (7c)$$

$$D = \langle \sin \theta \cos \theta \rangle \quad (7d)$$

$$E = \langle \cos^2 \theta \rangle \quad (7e)$$

$$F = \langle \sin^3 \theta \rangle \quad (7f)$$

$$G = \langle \sin^2 \theta \cos \theta \rangle \quad (7g)$$

$$H = \langle \sin \theta \cos^2 \theta \rangle \quad (7h)$$

$$I = \langle \cos^3 \theta \rangle \quad (7i)$$

$$J = \langle \sin^4 \theta \rangle \quad (7j)$$

$$K = \langle \sin^3 \theta \cos \theta \rangle \quad (7k)$$

$$L = \langle \sin^2 \theta \cos^2 \theta \rangle \quad (7l)$$

$$M = \langle \sin \theta \cos^3 \theta \rangle \quad (7m)$$

$$N = \langle \cos^4 \theta \rangle \quad (7n)$$

The corresponding averages for ψ are identical in form, with uppercase indicating an average over θ and lowercase an average over ψ . Although the expectation values in eq 7 are shown to indicate averaging over functions of θ alone, this representation is a little misleading. In general, the distributions in θ and ψ are not separable, such that the expectation values are implicitly taken over the combined distributions in both angles (e.g., $Jn = \langle \sin^4 \theta \cos^4 \psi \rangle$). By using this concise notation, the following expressions connect the molecular and macromolecular frames for singly degenerate FWM measurements of uniaxial assemblies.

1. Orientational Averages for C_1 , C_s , and C_2 . The large number of nonzero elements present within the molecular tensors for these three symmetry classes significantly complicates the use of analytical expressions for describing the orientational averages. In such cases, two strategies can be employed. The most common approach is to approximate the molecular tensor by invoking pseudo-symmetry relations, in which the symmetry of the $\gamma^{(3)}$ tensor is effectively reduced by assuming that many symmetry-allowed contributions are too small to be significant. Within the validity of these assumptions, the subsequent relationships derived for systems of higher symmetry can be employed for orientational analysis. The other route is to simply use computational approaches rather than analytical expressions to interpret the orientation distribution.¹⁷ This latter method has the benefit of minimizing the number of assumptions or approximations imposed on the molecular tensor but at the expense of the use of relatively simple analytical formulas.

2. Orientational Averages for C_{2v} . Explicit expressions for the orientational averages connecting the molecular tensor for a local oscillator with C_{2v} symmetry to the macroscopic tensor are summarized in eq 8–10 for CARS.

A_1 :

$$\chi_{zzzz} = \frac{N_b}{\epsilon_0} \left[Jn\gamma_{xxxx} + Jj\gamma_{yyyy} + N\gamma_{zzzz} + 4Jl\gamma_{xxyy} + 4Le\gamma_{xxzz} + 4Lc\gamma_{yyzz} \right] \quad (8a)$$

$$\chi_{xxxx} = \frac{N_b}{8\epsilon_0} \left[3(Nn + 2El + j)\gamma_{xxxx} + 3(Nj + 2El + n)\gamma_{yyyy} + 3J\gamma_{zzzz} + 4(E + 3Jl)\gamma_{xxyy} + 4(Cc + 3Le)\gamma_{xxzz} + 4(Ce + 3Lc)\gamma_{yyzz} \right] \quad (8b)$$

$$\chi_{xxyy} = \frac{N_b}{8\epsilon_0} \left[(Nn + 2El + j)\gamma_{xxxx} + (Nj + 2El + n)\gamma_{yyyy} + J\gamma_{zzzz} + 4(E + Jl)\gamma_{xxyy} + 4(Le + Cc)\gamma_{xxzz} + 4(Lc + Ce)\gamma_{yyzz} \right] \quad (8c)$$

$$\chi_{xyyx} = \frac{N_b}{8\epsilon_0} \left[(Nn + 2El + j)\gamma_{xxxx} + (Nj + 2El + n)\gamma_{yyyy} + J\gamma_{zzzz} + 4(Jl - E)\gamma_{xxyy} + 4(Le - Cc)\gamma_{xxzz} + 4(Lc - Ce)\gamma_{yyzz} \right] \quad (8d)$$

$$\chi_{xxzz} = \frac{N_b}{2\epsilon_0} \left[(Ln + Cl)\gamma_{xxxx} + (Lc + Jl)\gamma_{yyyy} + L\gamma_{zzzz} + (Cn - Jl + Ll + Cj)\gamma_{xxyy} + (e - 4Le + Ec)\gamma_{xxzz} + (c - 4Lc + Ee)\gamma_{yyzz} \right] \quad (8e)$$

$$\chi_{zzzz} = \frac{N_b}{2\epsilon_0} \left[(Jn + Cj)\gamma_{xxxx} + (Jl + Cj)\gamma_{yyyy} + L\gamma_{zzzz} - 4Jl\gamma_{xxyy} - 4Le\gamma_{xxzz} - 4Lc\gamma_{yyzz} \right] \quad (8f)$$

A_2 :

$$\chi_{zzzz} = \frac{N_b}{\epsilon_0} [8Jl]\gamma_{xxyy} = 8\chi_{xxyy} \quad (9a)$$

$$\chi_{xxyy} = \frac{N_b}{\epsilon_0} [Jl + E]\gamma_{xxyy} \quad (9b)$$

$$\chi_{xxzz} = \frac{N_b}{2\epsilon_0} [Le + Jn - 6Jl + Ll + Cj]\gamma_{xxyy} \quad (9c)$$

$$\chi_{xzzx} = \frac{N_b}{\epsilon_0} [Lc + Cn - 2Jl + Cj]\gamma_{xxyy} \quad (9d)$$

B_1 :

$$\chi_{zzzz} = \frac{N_b}{\epsilon_0} [8Le]\gamma_{xxzz} = 8\chi_{xxyy} \quad (10a)$$

$$\chi_{xxyy} = \frac{N_b}{\epsilon_0} [Le + Cc]\gamma_{xxzz} \quad (10b)$$

$$\chi_{xxzz} = \frac{N_b}{2\epsilon_0} [e - 8Le + Ec]\gamma_{xxzz} \quad (10c)$$

$$\chi_{xzzx} = \frac{N_b}{\epsilon_0} [e - 4Le + Ec]\gamma_{xxzz} \quad (10d)$$

B_2 : The orientational averages for B_2 symmetry are identical to those for B_1 , except with e and c inverted (i.e., every e in B_1 should be replaced by c in B_2 and vice versa).

Orientational Averages for C_{3v} . Explicit expressions for the orientational averages connecting the molecular tensor for a local oscillator with C_{3v} symmetry to the macroscopic tensor are summarized in eqs 11–13 for CARS.

A_1 :

$$\chi_{zzzz} = \frac{N_b}{\epsilon_0} [2L\gamma_{xzzx} + N\gamma_{zzzz}] \quad (11a)$$

$$\chi_{xxyy} = \frac{N_b}{8\epsilon_0} [J\gamma_{zzzz}] \quad (11b)$$

$$\chi_{xyyx} = \frac{N_b}{8\epsilon_0} [2(L + 3C)\gamma_{xzzx} + J\gamma_{zzzz}] \quad (11c)$$

$$\chi_{XXZZ} = \frac{N_b}{2\epsilon_0} [L\gamma_{zzzz} - 2L\gamma_{xzxx}] \quad (11d)$$

$$\chi_{XZZX} = \frac{N_b}{2\epsilon_0} [(J + E + N)\gamma_{xzxx} + L\gamma_{zzzz}] \quad (11e)$$

E:

$$\chi_{ZZZZ} = \frac{N_b}{\epsilon_0} \left[(J - 2I)\gamma_{xxxx} + 4J\gamma_{xxyy} + 2J\gamma_{xyyx} + 4L\gamma_{xzxx} \right] + (6Kg - 2Ki)(\gamma_{xxzz} + \gamma_{xxzx}) \quad (12a)$$

$$\chi_{XXYY} = \frac{N_b}{8\epsilon_0} \left[(N - 2I + 4E + 1 - 2I)\gamma_{xxxx} + 4(L + C)\gamma_{xzxx} + (I + N + E - 2E)(4\gamma_{xxyy} + 2\gamma_{xyyx}) + (6Kg - 2Ki)(\gamma_{xxzz} + \gamma_{xxzx}) \right] \quad (12b)$$

$$\chi_{XXYX} = \frac{N_b}{8\epsilon_0} \times \left[(N - 2I + 4E + 1 - 2I)\gamma_{xxxx} + 4(L - C)\gamma_{xzxx} + 4(I + N + E - 2E)\gamma_{xxyy} + 2(I + N + 3E - 2E)\gamma_{xyyx} + (6Kg - 2Ki)(\gamma_{xxzz} + \gamma_{xxzx}) \right] \quad (12c)$$

$$\chi_{XXZZ} = \frac{N_b}{2\epsilon_0} \times \left[(Ln + 2Cl + Lc - Ll)\gamma_{xxxx} + (J + E - 2L + N)\gamma_{xzxx} + (Le - Ln + C - 2Cl + Ll - 2Jl)\gamma_{xxyy} - 2Jl\gamma_{xyyx} + (2Ki - 6Kg)(\gamma_{xxzz} + \gamma_{xxzx}) \right] \quad (12d)$$

$$\chi_{XZZX} = \frac{N_b}{2\epsilon_0} \left[(Ln + 2Cl + Lc - Ll)\gamma_{xxxx} - 4Jl\gamma_{xxyy} + (Ll + C - 2Cl - Ln + Le)\gamma_{xyyx} + (2Ki - 6Kg)(\gamma_{xxzz} + \gamma_{xxzx}) - 4L\gamma_{xzxx} \right] \quad (12e)$$

II. CATS. C_1 Symmetry. The two-photon resonant singly degenerate 4WM (CATS) measurement is important for two reasons. First, it is partly responsible for the nonresonant background in CARS spectroscopy measurements. Second, it provides access to information on two-photon absorption while detecting light at an energy of roughly half that of the resonant state. Under the experimental conditions for which most CARS measurements are acquired, the two $\alpha^{(1)}$ tensors collectively contributing to CATS can also be assumed to be approximately symmetric and equal, provided that the energy difference between the two virtual states is much less than the energies of the excited electronic states used to construct the intermediate virtual states. In the case of two-photon excitation, the degeneracy in ω_1 requires that the 2PA tensor is symmetric by symmetry. Although this symmetry condition is relaxed in the two-photon emission case by the loss of degeneracy in the two frequencies, it can generally be safely assumed that the energy difference between $\hbar\omega_4$ and $\hbar\omega_3$ is sufficiently small that both $\alpha^{(1)}$ tensors can be reasonably approximated as symmetric and equal. In the absence of one-photon resonance enhancement with any of the incident or exigent frequencies, both of these approximations are expected to be quite good. Simplification of the molecular tensor yields the exact same 21 nonzero unique elements of the $\gamma^{(3)}$ tensors as for CARS, separated into the same six different forms: γ_{iiii} , $\gamma_{iiij} = \gamma_{ijii} = \gamma_{jiij} = \gamma_{jiii}$, $\gamma_{ijij} = \gamma_{jiij} = \gamma_{ijji} = \gamma_{jiji}$, $\gamma_{ijik} = \gamma_{jikj} = \gamma_{kiji} = \gamma_{kijj}$, $\gamma_{ijkj} = \gamma_{kjik} = \gamma_{kijj} = \gamma_{kiji}$, $\gamma_{ijik} = \gamma_{jikj} = \gamma_{kiji} = \gamma_{kijj}$, where the indices can be x, y, or z with the condition $i \neq j \neq k$. The corresponding character tables are summarized in Tables 9–11. The number of unique macroscopic tensor elements is similarly reduced using the same relationships as described for CARS; f_{11} , $f_{12} = f_{21} = f_{44}$, $f_{13} = f_{31} = f_{66} = f_{77}$, f_{33} , f_{45} , and $f_{67} = f_{76}$. Again, all of the chiral tensor elements present in the general case of C_∞ symmetry disappear within the validity of a symmetric $\alpha^{(1)}$ tensor, such that $\mathbf{B} = 0$ (Table 5).

TABLE 9: Electronic CATS for C_s and C_2 Molecular Symmetries

A_1	γ_{xxxx} γ_{yyyy} γ_{zzzz} $\gamma_{xyyx} = \gamma_{yxyx}$ $\gamma_{xzxx} = \gamma_{zxzx}$ $\gamma_{yzzy} = \gamma_{zyzy}$
A_2	$\gamma_{xxyy} = \gamma_{xyxy} = \gamma_{yyxx} = \gamma_{yyxx}$ $\chi_{zzzz} = -2\chi_{xzzx} = 4\chi_{xxyy} + 4\chi_{xyyx}$ $f_{33} = -2f_{67} = 4(f_{12} + f_{45})$

TABLE 10: Electronic CATS for C_{2v} Molecular Symmetry

A_1	γ_{xxxx} γ_{yyyy} γ_{zzzz} $\gamma_{xyyx} = \gamma_{yxyx}$ $\gamma_{xzxx} = \gamma_{zxzx}$ $\gamma_{yzzy} = \gamma_{zyzy}$
A_2	$\gamma_{xxyy} = \gamma_{xyxy} = \gamma_{yyxx} = \gamma_{yyxx}$ $\chi_{zzzz} = -2\chi_{xzzx} = 4\chi_{xxyy} + 4\chi_{xyyx}$ $f_{33} = -2f_{67} = 4(f_{12} + f_{45})$
B_1	$\gamma_{xxzz} = \gamma_{zxzx} = \gamma_{zzxx} = \gamma_{zzxx}$ $\chi_{zzzz} = -2\chi_{xzzx} = 4\chi_{xxyy} + 4\chi_{xyyx}$ $f_{33} = -2f_{67} = 4(f_{12} + f_{45})$
B_2	$\gamma_{yyzz} = \gamma_{zyzy} = \gamma_{zyzy} = \gamma_{zyzy}$ $\chi_{zzzz} = -2\chi_{xzzx} = 4\chi_{xxyy} + 4\chi_{xyyx}$ $f_{33} = -2f_{67} = 4(f_{12} + f_{45})$

$\gamma_{ijij} = \gamma_{jiij} = \gamma_{ijji} = \gamma_{jiji}$, and $\gamma_{ijik} = \gamma_{jikj} = \gamma_{kiji} = \gamma_{kijj} = \gamma_{ijkj} = \gamma_{kjik} = \gamma_{kijj} = \gamma_{kiji}$, where the indices can be x, y, or z with the condition $i \neq j \neq k$. The corresponding character tables are summarized in Tables 9–11. The number of unique macroscopic tensor elements is similarly reduced using the same relationships as described for CARS; f_{11} , $f_{12} = f_{21} = f_{44}$, $f_{13} = f_{31} = f_{66} = f_{77}$, f_{33} , f_{45} , and $f_{67} = f_{76}$. Again, all of the chiral tensor elements present in the general case of C_∞ symmetry disappear within the validity of a symmetric $\alpha^{(1)}$ tensor, such that $\mathbf{B} = 0$ (Table 5).

Orientalional Averages for C_{2v} Symmetry. Explicit expressions for the orientational averages connecting the molecular tensor for a local oscillator with C_{2v} symmetry to the macroscopic tensor are summarized in eq 13–15 for CATS.

A_1 :

$$\chi_{ZZZZ} = \frac{N_b}{\epsilon_0} \left[Jn\gamma_{xxxx} + Jj\gamma_{yyyy} + N\gamma_{zzzz} + 2Jl\gamma_{xxyy} + 2Le\gamma_{xzxx} + 2Lc\gamma_{yzzy} \right] \quad (13a)$$

$$\chi_{XXYY} = \frac{N_b}{8\epsilon_0} \left[(Nn + 2El + j)\gamma_{xxxx} + (Nj + 2El + n)\gamma_{yyyy} + J\gamma_{zzzz} + 2(I + Nl + 3E - 2El)\gamma_{xxyy} + 2(Le - Cc)\gamma_{xzxx} + 2(Lc - Ce)\gamma_{yzzy} \right] \quad (13b)$$

$$\chi_{XXYX} = \frac{N_b}{8\epsilon_0} \left[(Nn + 2El + j)\gamma_{xxxx} + (Nj + 2El + n)\gamma_{yyyy} + J\gamma_{zzzz} + 2(I + Nl + 3E - 2El)\gamma_{xxyy} + 2(Le + 3Cc)\gamma_{xzxx} + 2(Lc + 3Ce)\gamma_{yzzy} \right] \quad (13c)$$

$$\chi_{XXZZ} = \frac{N_b}{2\epsilon_0} \left[(Ln + Cl)\gamma_{xxxx} + (Lj + Cl)\gamma_{yyyy} + L\gamma_{zzzz} - 2Jl\gamma_{xxyy} - 2Le\gamma_{xzxx} - 2Lc\gamma_{yzzy} \right] \quad (13d)$$

$$\chi_{XZZX} = \frac{N_b}{2\epsilon_0} \left[\begin{aligned} &(Ln + Cl)\gamma_{xxxx} + (Lj + Cl)\gamma_{yyyy} \\ &+ L\gamma_{zzzz} + (Lc + Cj + Cn)\gamma_{xyyx} \\ &+ (e + 2Le + Ec)\gamma_{xxzx} + (c - 2Lc + Ec)\gamma_{yyzy} \end{aligned} \right] \quad (13e)$$

A_2 :

$$\chi_{ZZZZ} = \frac{N_b}{\epsilon_0} [4Jl]\gamma_{xyxy} = -2\chi_{XZZX} \quad (14a)$$

$$\chi_{XXYY} = \frac{N_b}{2\epsilon_0} [l + Nl + E - 2El]\gamma_{xyxy} \quad (14b)$$

$$\chi_{YYXX} = \frac{N_b}{2\epsilon_0} [l + Nl - E - 2El]\gamma_{xyxy} \quad (14c)$$

$$\chi_{XXZZ} = \frac{N_b}{2\epsilon_0} [C - 4Jl]\gamma_{xyxy} \quad (14d)$$

B_1 :

$$\chi_{ZZZZ} = \frac{N_b}{\epsilon_0} [4Le]\gamma_{xxzz} = -2\chi_{XZZX} \quad (15a)$$

$$\chi_{XXYY} = \frac{N_b}{2\epsilon_0} [Le + Cc]\gamma_{xxzz} \quad (15b)$$

$$\chi_{YYXX} = \frac{N_b}{2\epsilon_0} [Le - Cc]\gamma_{xxzz} \quad (15c)$$

$$\chi_{XXZZ} = \frac{N_b}{2\epsilon_0} [E - 2Le]\gamma_{xxzz} \quad (15d)$$

B_2 . The orientational averages for B_2 symmetry are identical to those for B_1 , except with e and c inverted (i.e., every e in B_1 should be replaced by c in B_2 and vice versa).

Orientational Averages for C_{3v} . Explicit expressions for the orientational averages connecting the molecular tensor for a local oscillator with C_{3v} symmetry to the macroscopic tensor are summarized in eq 16 for CARS.

A_1 . The orientational averages for CATS are identical to those for CARS for transitions of A_1 symmetry in eq 11 with one important exception; $\gamma_{xxz} = \gamma_{xxz}$ in the case of CATS. However, this equality does not result in significant additional simplifications in the orientational averages given in eq 11.

E :

$$\chi_{ZZZZ} = \frac{N_b}{\epsilon_0} \left[(J - 2Jl)\gamma_{xxxx} + 4Jl\gamma_{xyxy} + 2Jl\gamma_{xyyx} - 4(3Kg - Ki)\gamma_{xxzz} + 4L\gamma_{xxzz} \right] \quad (16a)$$

$$\chi_{XXYY} = \frac{N_b}{8\epsilon_0} \left[\begin{aligned} &(N - 2Nl + 4El + 1 - 2l)\gamma_{xxxx} \\ &+ 4(l + Nl + E - 2El)\gamma_{xyxy} \\ &+ 2(l - E - 2El + Nl)\gamma_{xyyx} \\ &+ 4(3Kg - Ki)\gamma_{xxzz} + 4(L + C)\gamma_{xxzz} \end{aligned} \right] \quad (16b)$$

$$\chi_{YYXX} = \frac{N_b}{8\epsilon_0} \left[\begin{aligned} &(N - 2Nl + 4El + 1 - 2l)\gamma_{xxxx} \\ &+ 4(l - E - 2El + Nl)\gamma_{xyxy} \\ &+ 2(l + 3E - 2El + Nl)\gamma_{xyyx} \\ &+ 4(3Kg - Ki)\gamma_{xxzz} + 4(L - C)\gamma_{xxzz} \end{aligned} \right] \quad (16c)$$

TABLE 11: Singly Degenerate Electronic FWM for C_{3v} Molecular Symmetry

A_1	$\gamma_{xxxx} = \gamma_{yyyy} = \gamma_{xyyx} = \gamma_{yxxy}$ $\gamma_{xxzz} = \gamma_{yyzz} = \gamma_{zzxx} = \gamma_{zzyy}$ γ_{zzzz}
A_2	0
E	$\gamma_{xxxx} = \gamma_{yyyy} = 2(\gamma_{xxxy} = \gamma_{xyxy} = \gamma_{yyxx} = \gamma_{yxyx}) + (\gamma_{xyyx} = \gamma_{yxxy})$ $\gamma_{xxzz} = \gamma_{yyzz} = \gamma_{xxzz} = \gamma_{yyzz} = \gamma_{zzxx} = \gamma_{zzyy} = \gamma_{zzxx} = \gamma_{zzyy}$ $-\gamma_{xxzz} = \gamma_{yyzz} = \gamma_{yyzz} = -\gamma_{zzxx} = \gamma_{zzxx} = \gamma_{zzxx} = \gamma_{zzxx}$ $= -\gamma_{xxzz} = \gamma_{yyzz} = \gamma_{yyzz} = \gamma_{yyzz} = -\gamma_{xxzz} = \gamma_{xxzz} = \gamma_{xxzz} = \gamma_{xxzz}$

$$\chi_{XXZZ} = \frac{N_b}{2\epsilon_0} \left[\begin{aligned} &(L - 2Ll + 2Cl)\gamma_{xxxx} \\ &+ (2Ll + C - 2Cl - 2Jl)\gamma_{xyxy} - 2Jl\gamma_{xyyx} \\ &+ 4(Ki - 3Kg)\gamma_{xxzz} \\ &+ (1 - 2L + E - 2Jl - 2Lc)\gamma_{xxzz} \end{aligned} \right] \quad (16d)$$

$$\chi_{XZZX} = \frac{N_b}{2\epsilon_0} \times \left[\begin{aligned} &(En - Lc)\gamma_{xxxx} - 4Jl\gamma_{xyxy} + (Lc + C - 2Cl)\gamma_{xyyx} \\ &+ 4(Ki - 3Kg)\gamma_{xxzz} - 4L\gamma_{xxzz} \end{aligned} \right] \quad (16e)$$

III. Electric Dipole-Allowed Chiral-Specific FWM. From the symmetry arguments described in the Introduction, it is theoretically possible to generate nonzero chiral-specific FWM responses in uniaxial assemblies that are fully electric dipole allowed through the tensor elements summarized in Tables 2 and 4. These elements disappear for systems of D_∞ symmetry (i.e., aligned by not oriented) and in isotropic media^{1-6,18} but remain in oriented chiral systems of C_∞ symmetry. Interestingly, the assumption of symmetric tensors both for CATS and for vibrational CARS also results in the loss of these chiral-specific tensor elements. However, relaxation of that assumption can allow for retention of chiral-specific contributions that are still fully electric dipole allowed, which is the focus of this section.

Although chiral molecules will generally possess relatively low symmetry, it is arguably easiest to explore the interactions leading to the possibility of chiral-specific singly degenerate FWM by considering a relatively simple molecular system of higher local symmetry first. Such an analysis can provide information on the molecular requirements and the potential magnitude of the chiral-specific signals. Subsequent extension to molecules of lower symmetry is straightforward through the use of the complete orientational averages summarized in the Appendix. For illustrative purposes, we will consider two-photon resonance enhanced measurements of an assembly of chromophores with C_{2v} symmetry, in which it is assumed that the molecular NLO response is dominated by an electronic transition with B_1 symmetry. In this case, only two nonzero elements remain within the $\alpha^{(1)}$ molecular tensor for 2PA; α_{xz} and α_{zx} . From these two $\alpha^{(1)}$ tensor elements, four nonzero $\gamma^{(3)}$ tensor elements emerge; γ_{xxzz} , γ_{xxzz} , γ_{zzxx} , and γ_{zzxx} (Table 10.). The orientational averages for the chiral $\chi^{(3)}$ tensor elements are straightforward in this example, given by the following relations.

$$\chi_{YZZX} = \frac{1}{2} \langle \sin^2 \theta \cos \theta \sin \psi \cos \psi \rangle (\gamma_{zzxx} - \gamma_{xxzz} + \gamma_{zzxx} - \gamma_{xxzz}) \quad (17a)$$

$$\chi_{YXZZ} = \frac{1}{2} \langle \sin^2 \theta \cos \theta \sin \psi \cos \psi \rangle (\gamma_{zzxx} - \gamma_{xxzz}) \quad (17b)$$

$$\chi_{ZYX} = \frac{1}{2} \langle \sin^2 \theta \cos \theta \sin \psi \cos \psi \rangle (\gamma_{zzx} - \gamma_{xxz}) \quad (17c)$$

For a singly degenerate CATS FWM measurement as described in Figure 1, the $\alpha^{(1)}$ tensor describing 2PA contains two identical frequencies [i.e., $\alpha_{n0}^{jk}(\omega_1, \omega_1)$] and is necessarily symmetric. However, the $\alpha^{(1)}$ tensor describing two-photon emission contains two unique frequency terms, $\alpha_{0n}^{il}(-\omega_4, -\omega_3)$, with the potential for significant asymmetry if these two frequencies are sufficiently different and/or if one of the two frequencies approaches one-photon resonance with a real state in the molecule. Substituting the relationship $\gamma_{ijkl} = S(2\omega_1) \alpha_{0n}^{il} \alpha_{n0}^{jk}$, where S is a line shape function (e.g., Lorentzian),¹⁷ into the orientational averages results in the following expressions for the anticipated chiral-specific FWM response in uniaxial media under such conditions.

$$\chi_{YZX} = S(2\omega_1) \langle \sin^2 \theta \cos \theta \sin \psi \cos \psi \rangle \alpha_{zx}^{ik} (\alpha_{zx}^{il} - \alpha_{xz}^{il}) \quad (18a)$$

$$\chi_{YXZ} = \chi_{ZYX} = \frac{1}{2} \chi_{YZX} \quad (18b)$$

Although chiral-specific FWM contributions can certainly also arise in molecules of lower symmetry, this example for C_{2v} molecular symmetry helps demonstrate that the molecular requirements necessary for the potential observation of electric dipole-allowed chiral FWM are actually not terribly restrictive. Indeed, the chromophore itself does not even need to be chiral or be coupled to another chromophore. Rather, it is solely the chiral orientation relative to the unique laboratory Z axis that is responsible for the predicted chiral-specific response in such instances.

The similarities between the predicted chiral response in FWM and the established chiral-specific response of three-wave mixing (TWM) are quite striking. A virtually identical mechanism is known to drive chiral effects in many TWM measurements of uniaxial assemblies, in which the resonant molecular tensor is described by the direct product of a transition moment μ and an $\alpha^{(1)}$ tensor,^{12,13} rather than by a direct product of two $\alpha^{(1)}$ tensors. Second harmonic generation (SHG) resonant at the second harmonic frequency with an excited state of B_1 symmetry yields the following expression for the chiral $\chi^{(2)}$ response, with the orientational averages differing only by a factor of $\cos \theta$.

$$\chi_{YZX} = -\frac{1}{2} S(2\omega) \langle \sin^2 \theta \sin \psi \cos \psi \rangle \mu_x^i \alpha_{xz}^{jk} \quad (19)$$

In light of these close similarities, it is interesting to compare and contrast the chiral-specific FWM response predicted here with the comparatively well-established chiral-specific activity of TWM.^{19–22} In TWM, chiral effects are electric-dipole allowed in both oriented and aligned media, but the achiral contributions are only nonzero in oriented media. The opposite is true in FWM, in which the achiral contributions are present in both aligned and oriented systems, but the chiral contributions disappear in the absence of preferred polar orientation. In TWM, chiral effects in uniaxial assemblies can arise even with a fully symmetric $\alpha^{(1)}$ tensor, but asymmetry in the $\alpha^{(1)}$ tensor is required for the observation of chiral-specific SFG in isotropic media. In contrast, electric dipole-allowed chiral effects disappear completely in isotropic media for FWM, and require asymmetry in the $\alpha^{(1)}$ tensor in order to be observed in uniaxially oriented systems. Finally, in both cases, chirality in the laboratory frame can arise even in the absence of chirality within

the chromophore, provided that chirality within the steric interactions driving uniaxial orientation produces asymmetry in the distribution in the twist angle ψ . Given that the chiral sensitivity of SHG and sum-frequency (SFG) has been firmly established through numerous measurements,^{19,21,22} it is tempting to suggest that the chiral-specific responses arising in FWM measurements of oriented systems may be similarly important.

Conclusions

A systematic framework has been developed to assist in the interpretation of FWM measurements of molecular assemblies exhibiting uniaxial order. The above relations provide a selective list of some of the most commonly encountered molecular point groups (i.e., those of relatively low symmetry). Consequently, many systems of higher symmetry can be described by subsequent simplifications of the relations considered explicitly in this work. More importantly, these point groups serve as ubiquitous examples to illustrate the general approach for relating molecular and macroscopic tensor elements in singly degenerate four-wave mixing for either electronic or vibrational spectroscopic characterization.

From this analysis, relatively large electric-dipole allowed chiral-specific FWM is predicted to be possible in uniaxial assemblies. The unique symmetry relationships in uniaxial systems between TWM and FWM with respect to both the chiral and achiral contributions has the potential to open up potentially exciting opportunities if these predictions can be subsequently confirmed experimentally.

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Appendix. Complete Orientational Averages for FWM of Uniaxially Oriented Assemblies

Explicitly writing out all of the electric dipole-allowed orientational averages would require a considerable amount of space. In the most general case considered here, each nonzero $\chi^{(3)}$ tensor element contains contributions from all 81 nonzero molecular tensor elements, each with its own orientational average. If the set of $\gamma^{(3)}$ tensor elements is expressed as a vector, the set of orientational averages can be expressed as another vector, with the dot product of the two recovering the full expression for a given $\chi^{(3)}$ tensor element. This is essentially the approach we have taken. However, writing out a vector with 81 elements is still not particularly concise, either. Consequently, the vectorized forms for the orientational averages are expressed as folded vector pseudo-matrices in order to conserve space. The dot product is given by summation over the dot products of the first row and the first column, the second row and the second column, the third row and the third column, and so forth. The orientational averages for χ_{zzzz} serve to illustrate this approach. Summation over all of nine of these dot products recovers the scalar χ_{zzzz} expressed through orientational averages to the full set of 81 possible elements within the molecular tensor. Using the substitutions for the individual orientational averages given in eq 7 further reduces the space required to represent the full set of orientational averages. Once the vectorized form for the $\gamma^{(3)}$ tensor has been established by eq A.1 (i.e., with the tensor elements listed in alphabetical order), the complete set of orientational averages can be concisely represented by a single folded-vector pseudo-matrix.

$$\chi_{zzzz} = \begin{bmatrix} +Jn & -Jm & -Ki & -Jm & +Jl & +Kh & -Ki & +Kh & +Le \\ -Jm & +Jl & +Kh & +Jl & -Jk & -Kg & +Kh & -Kg & -Ld \\ -Ki & +Kh & +Le & +Kh & -Kg & -Ld & +Le & -Ld & -Mb \\ -Jm & +Jl & +Kh & +Jl & -Jk & -Kg & +Kh & -Kg & -Ld \\ +Jl & -Jk & -Kg & -Jk & +Jj & -Kf & -Kg & -Kf & +Lc \\ +Kh & -Kg & -Ld & -Kg & -Kf & +Lc & -Ld & +Lc & -Ma \\ -Ki & +Kh & +Le & +Kh & -Kg & -Ld & +Le & -Ld & -Mb \\ +Kh & -Kg & -Ld & -Kg & -Kf & +Lc & -Ld & +Lc & -Ma \\ +Le & -Ld & -Mb & -Ld & +Lc & -Ma & -Mb & -Ma & +N \end{bmatrix} \bullet \begin{bmatrix} xxxx & xyxx & xzxx & yxxx & yyxx & yzxx & zxxx & zyxx & zzzx \\ xxxy & xyxy & xzxy & yxyx & yyyx & yzyx & zxyx & zyyx & zzzx \\ xxxz & xyxz & xzxz & yxxz & yyyz & yzzz & zxxz & zyyz & zzzz \\ xxyx & xyyx & xzyx & yxyx & yyyx & yzyx & zxyx & zyyx & zzzx \\ xxyy & xyyy & xzyy & yxyy & yyyy & yzyy & zxyy & zyyy & zzzz \\ xxyz & xyyz & xzyz & yxyz & yyyz & yzzz & zxyz & zyyz & zzzz \\ xxzx & xyzx & xzzx & yxxz & yyyz & yzzz & zxxz & zyyz & zzzz \\ xxzy & xyzy & xzzy & yxzy & yyyz & yzzz & zxzy & zyyz & zzzz \\ xxzz & xyzz & xzzz & yxzz & yyyz & yzzz & zxzz & zyzz & zzzz \end{bmatrix} \quad (\text{A.1})$$

$$\chi_{xxxy} = \frac{1}{8} \begin{bmatrix} (Ee + c)^2 & Cd(Ee + c) & Db(Ee + c) & Cd(Ee + c) & l(1 + 4E + N) + 3E(j + n) & -Da(Ee + 3c + 2e) & Db(Ee + c) & -Da(Ee + 3c + 2e) & C(Ee + 3c) \\ Cd(Ee + c) & l(1 - 4E + N) - E(j + n) & Da(c + 2e - Ee) & l(1 - 4E + N) - E(j + n) & Cd(Ec + e) & Db(Ec - e - 2c) & Da(c + 2e - Ee) & Db(Ec - e - 2c) & Cd(3 - E) \\ Db(Ee + c) & Da(c + 2e - Ee) & C(Ee - c) & Da(c + 2e - Ee) & Db(Ec + 2c + 3e) & -Cd(E + 1) & C(Ee - c) & -Cd(E + 1) & Kb \\ Cd(Ee + c) & l(1 - 4E + N) - E(j + n) & Da(c + 2e - Ee) & l(1 - 4E + N) - E(j + n) & Cd(Ec + e) & Db(Ec - e - 2c) & Da(c + 2e - Ee) & Db(Ec - e - 2c) & Cd(3 - E) \\ l(1 + 4E + N) + 3E(j + n) & Cd(Ec + e) & Db(Ec + 2c + 3e) & Cd(Ec + e) & (Ec + e)^2 & -Da(Ec + e) & Db(Ec + 2c + 3e) & -Da(Ec + e) & C(Ec + 3e) \\ -Da(Ee + 3c + 2e) & Db(Ec - e - 2c) & -Cd(E + 1) & Db(Ec - e - 2c) & -Da(Ec + e) & C(Ec - e) & -Cd(E + 1) & C(Ec - e) & -Ka \\ Db(Ee + c) & Da(c + 2e - Ee) & C(Ee - c) & Da(c + 2e - Ee) & Db(Ec + 2c + 3e) & -Cd(E + 1) & C(Ee - c) & -Cd(E + 1) & Kb \\ -Da(Ee + 3c + 2e) & Db(Ec - e - 2c) & -Cd(E + 1) & Db(Ec - e - 2c) & -Da(Ec + e) & C(Ec - e) & -Cd(E + 1) & C(Ec - e) & -Ka \\ C(Ee + 3c) & Cd(3 - E) & Kb & Cd(3 - E) & C(Ec + 3e) & -Ka & Kb & -Ka & J \end{bmatrix} \quad (\text{A.2})$$

$$\chi_{xyyx} = \frac{1}{8} \begin{bmatrix} (Ee + c)^2 & Cd(Ee + c) & Db(Ee + c) & Cd(Ee + c) & l(1 - 4E + N) - E(j + n) & Da(c + 2e - Ee) & Db(Ee + c) & Da(c + 2e - Ee) & C(Ee - c) \\ Cd(Ee + c) & l(1 - 4E + N) - E(j + n) & Da(c + 2e - Ee) & l(1 + 4E + N) + 3E(j + n) & Cd(Ec + e) & Db(Ec + 2c + 3e) & -Da(Ee + 3c + 2e) & Db(Ec - e - 2c) & -Cd(E + 1) \\ Db(Ee + c) & Da(c + 2e - Ee) & C(Ee - c) & -Da(Ee + 3c + 2e) & Db(Ec - e - 2c) & -Cd(E + 1) & C(Ee + 3c) & Cd(3 - E) & Kb \\ Cd(Ee + c) & l(1 + 4E + N) + 3E(j + n) & -Da(Ee + 3c + 2e) & l(1 - 4E + N) - E(j + n) & Cd(Ec + e) & Db(Ec - e - 2c) & Da(c + 2e - Ee) & Db(Ec + 2c + 3e) & -Cd(E + 1) \\ l(1 - 4E + N) - E(j + n) & Cd(Ec + e) & Db(Ec - e - 2c) & Cd(Ec + e) & (Ec + e)^2 & -Da(Ec + e) & Db(Ec - e - 2c) & -Da(Ec + e) & C(Ec - e) \\ Da(c + 2e - Ee) & Db(Ec + 2c + 3e) & -Cd(E + 1) & Db(Ec - e - 2c) & -Da(Ec + e) & C(Ec - e) & Cd(3 - E) & C(Ec + 3e) & -Ka \\ Db(Ee + c) & -Da(Ee + 3c + 2e) & C(Ee + 3c) & Da(c + 2e - Ee) & Db(Ec - e - 2c) & Cd(3 - E) & C(Ee - c) & -Cd(E + 1) & Kb \\ Da(c + 2e - Ee) & Db(Ec - e - 2c) & Cd(3 - E) & Db(Ec + 2c + 3e) & -Da(Ec + e) & C(Ec + 3e) & -Cd(E + 1) & C(Ec - e) & -Ka \\ C(Ee - c) & -Cd(E + 1) & Kb & -Cd(E + 1) & C(Ec - e) & -Ka & Kb & -Ka & J \end{bmatrix} \quad (\text{A.3})$$

$$\chi_{xyxy} = \frac{1}{8} \begin{bmatrix} (Ee + c)^2 & Cd(Ee + c) & Db(Ee + c) & Cd(Ee + c) & l(1 - 4E + N) - E(j + n) & Da(c + 2e - Ee) & Db(Ee + c) & Da(c + 2e - Ee) & C(Ee - c) \\ Cd(Ee + c) & l(1 + 4E + N) + 3E(j + n) & -Da(Ee + 3c + 2e) & l(1 - 4E + N) - E(j + n) & Cd(Ec + e) & Db(Ec - e - 2c) & Da(c + 2e - Ee) & Db(Ec + 2c + 3e) & -Cd(E + 1) \\ Db(Ee + c) & -Da(Ee + 3c + 2e) & C(Ee + 3c) & Da(c + 2e - Ee) & Db(Ec - e - 2c) & Cd(3 - E) & C(Ee - c) & -Cd(E + 1) & Kb \\ Cd(Ee + c) & l(1 - 4E + N) - E(j + n) & Da(c + 2e - Ee) & l(1 + 4E + N) + 3E(j + n) & Cd(Ec + e) & Db(Ec + 2c + 3e) & -Da(Ee + 3c + 2e) & Db(Ec - e - 2c) & -Cd(E + 1) \\ l(1 - 4E + N) - E(j + n) & Cd(Ec + e) & Db(Ec - e - 2c) & Cd(Ec + e) & (Ec + e)^2 & -Da(Ec + e) & Db(Ec - e - 2c) & -Da(Ec + e) & C(Ec - e) \\ Da(c + 2e - Ee) & Db(Ec - e - 2c) & Cd(3 - E) & Db(Ec + 2c + 3e) & -Da(Ec + e) & C(Ec + 3e) & -Cd(E + 1) & C(Ec - e) & -Ka \\ Db(Ee + c) & Da(c + 2e - Ee) & C(Ee - c) & -Da(Ee + 3c + 2e) & Db(Ec - e - 2c) & -Cd(E + 1) & C(Ee + 3c) & -Cd(3 - E) & Kb \\ Da(c + 2e - Ee) & Db(Ec + 2c + 3e) & -Cd(E + 1) & Db(Ec - e - 2c) & -Da(Ec + e) & C(Ec - e) & Cd(3 - E) & C(Ec + 3e) & -Ka \\ C(Ee - c) & -Cd(E + 1) & Kb & -Cd(E + 1) & C(Ec - e) & -Ka & Kb & -Ka & J \end{bmatrix} \quad (\text{A.4})$$

$$\chi_{xxzz} = \frac{1}{2} \begin{bmatrix} Ce(Ee + c) & -Cd(Ee + c) & -Db(Ee + c) & -Cd(Ee + c) & Cc(Ee + c) & Da(Ee + c) & -Db(Ee + c) & Da(Ee + c) & E(Ee + c) \\ Jm & -Jl & -Kh & -Jl & Jk & Kg & -Kh & Kg & Ld \\ Ki & -Kh & -Le & -Kh & Kg & Ld & -Le & Ld & Mb \\ Jm & -Jl & -Kh & -Jl & Jk & Kg & -Kh & Kg & Ld \\ Ce(E - Ee + e) & -Cd(E - Ee + e) & -Db(E - Ee + e) & -Cd(E - Ee + e) & Cc(E - Ee + e) & Da(E - Ee + e) & -Db(E - Ee + e) & Da(E - Ee + e) & E(E - Ee + e) \\ -Kh & Kg & Ld & Kg & -Kf & -Lc & Ld & -Lc & -Ma \\ Ki & -Kh & -Le & -Kh & Kg & Ld & -Le & Ld & Mb \\ -Kh & Kg & Ld & Kg & -Kf & -Lc & Ld & -Lc & -Ma \\ Je & -Jd & -Kb & -Jd & Jc & Ka & -Kb & Ka & L \end{bmatrix} \quad (\text{A.5})$$

$$\chi_{zzxx} = \frac{1}{2} \begin{bmatrix} Ce(Ee + c) & Jm & Ki & Jm & Ce(E - Ee + e) & -Kh & Ki & -Kh & Je \\ -Cd(Ee + c) & -Jl & -Kh & -Jl & -Cd(E - Ee + e) & Kg & -Kh & Kg & -Jd \\ -Db(Ee + c) & -Kh & -Le & -Kh & -Db(E - Ee + e) & Ld & -Le & Ld & -Kb \\ -Cd(Ee + c) & -Jl & -Kh & -Jl & -Cd(E - Ee + e) & Kg & -Kh & Kg & -Jd \\ Cc(Ee + c) & Jk & Kg & Jk & Cc(E - Ee + e) & -Kf & Kg & -Kf & Jc \\ Da(Ee + c) & Kg & Ld & Kg & Da(E - Ee + e) & -Lc & Ld & -Lc & Ka \\ -Db(Ee + c) & -Kh & -Le & -Kh & -Db(E - Ee + e) & Ld & -Le & Ld & -Kb \\ Da(Ee + c) & Kg & Ld & Kg & Da(E - Ee + e) & -Lc & Ld & -Lc & Ka \\ E(Ee + e) & Ld & Mb & Ld & E(E - Ee + e) & -Ma & Mb & -Ma & L \end{bmatrix} \quad (\text{A.6})$$

$$\chi_{xzzx} = \frac{1}{2} \begin{bmatrix} Ce(Ee + c) & Jm & Ki & -Cd(Ee + c) & -Jl & -Kh & -Db(Ee + c) & -Kh & -Le \\ -Cd(Ee + c) & -Jl & -Kh & Cc(Ee + c) & Jk & Kg & Da(Ee + c) & Kg & Ld \\ -Db(Ee + c) & -Kh & -Le & Da(Ee + c) & Kg & Ld & E(Ee + c) & Ld & Mb \\ Jm & -Ce(Ee - E - e) & -Kh & -Jl & Cd(Ee - E - e) & Kg & -Kh & Db(Ee - E - e) & Ld \\ -Jl & Cd(Ee - E - e) & Kg & Jk & Cc(E - Ee + e) & -Kf & Kg & -Da(Ee - E - e) & -Lc \\ -Kh & Db(Ee - E - e) & Ld & Kg & -Da(Ee - E - e) & -Lc & Ld & E(E - Ee + e) & -Ma \\ Ki & -Kh & Je & -Kh & Kg & -Jd & -Le & Ld & -Kb \\ -Kh & Kg & -Jd & Kg & -Kf & Jc & Ld & -Lc & Ka \\ -Le & Ld & -Kb & Ld & -Lc & Ka & Mb & -Ma & L \end{bmatrix} \quad (\text{A.7})$$

$$\chi_{zxzx} = \frac{1}{2} \begin{bmatrix} Ce(Ee + c) & -Cd(Ee + c) & -Db(Ee + c) & Jm & -Jl & -Kh & Ki & -Kh & -Le \\ Jm & -Jl & -Kh & -Ce(Ee - E - e) & Cd(Ee - E - e) & Db(Ee - E - e) & -Kh & Kg & Ld \\ Ki & -Kh & -Le & -Kh & Kg & Ld & Je & -Jd & -Kb \\ -Cd(Ee + c) & Cc(Ee + c) & Da(Ee + c) & -Jl & Jk & Kg & -Kh & Kg & Ld \\ -Jl & Jk & Kg & Cd(Ee - E - e) & Cc(E - Ee + e) & -Da(Ee - E - e) & Kg & -Kf & -Lc \\ -Kh & Kg & Ld & Kg & -Kf & -Lc & -Jd & Jc & Ka \\ -Db(Ee + c) & Da(Ee + c) & E(Ee + c) & -Kh & Kg & Ld & -Le & Ld & Mb \\ -Kh & Kg & Ld & Db(Ee - E - e) & -Da(Ee - E - e) & E(E - Ee + e) & Ld & -Lc & -Ma \\ -Le & Ld & Mb & Ld & -Lc & -Ma & -Kb & Ka & L \end{bmatrix} \quad (A.8)$$

$$\chi_{zxzx} = \frac{1}{2} \begin{bmatrix} Ce(Ee + c) & -Cd(Ee + c) & -Db(Ee + c) & Jm & -Jl & -Kh & Ki & -Kh & -Le \\ -Cd(Ee + c) & Cc(Ee + c) & Da(Ee + c) & -Jl & Jk & Kg & -Kh & Kg & Ld \\ -Db(Ee + c) & Da(Ee + c) & E(Ee + c) & -Kh & Kg & Ld & -Le & Ld & Mb \\ Jm & -Jl & -Kh & -Ce(Ee - E - e) & Cd(Ee - E - e) & Db(Ee - E - e) & -Kh & Kg & Ld \\ -Jl & Jk & Kg & Cd(Ee - E - e) & Cc(E - Ee + e) & -Da(Ee - E - e) & Kg & -Kf & -Lc \\ -Kh & Kg & Ld & Db(Ee - E - e) & -Da(Ee - E - e) & E(E - Ee + e) & Ld & -Lc & -Ma \\ Ki & -Kh & -Le & -Kh & Kg & Ld & Je & -Jd & -Kb \\ -Kh & Kg & Ld & Kg & -Kf & -Lc & -Jd & Jc & Ka \\ -Le & Ld & Mb & Ld & -Lc & -Ma & -Kb & Ka & L \end{bmatrix} \quad (A.9)$$

$$\chi_{zxzx} = \frac{1}{2} \begin{bmatrix} Ce(Ee + c) & Jm & Ki & -Cd(Ee + c) & -Jl & -Kh & -Db(Ee + c) & -Kh & -Le \\ Jm & -Ce(Ee - E - e) & -Kh & -Jl & Cd(Ee - E - e) & Kg & -Kh & Db(Ee - E - e) & Ld \\ Ki & -Kh & Je & -Kh & Kg & -Jd & -Le & Ld & -Kb \\ -Cd(Ee + c) & -Jl & -Kh & Cc(Ee + c) & Jk & Kg & Da(Ee + c) & Kg & Ld \\ -Jl & Cd(Ee - E - e) & Kg & Jk & Cc(E - Ee + e) & -Kf & Kg & -Da(Ee - E - e) & -Lc \\ -Kh & Kg & -Jd & Kg & -Kf & Jc & Ld & -Lc & Ka \\ -Db(Ee + c) & -Kh & -Le & Da(Ee + c) & Kg & Ld & E(Ee + c) & Ld & Mb \\ -Kh & Db(Ee - E - e) & Ld & Kg & -Da(Ee - E - e) & -Lc & Ld & E(E - Ee + e) & -Ma \\ -Le & Ld & -Kb & Ld & -Lc & Ka & Mb & -Ma & L \end{bmatrix} \quad (A.10)$$

$$\chi_{xxxy} = \frac{1}{8} \left[\begin{array}{ccccccccc} 0 & 3B(Ee + c) & -3Aa(Ee + c) & -B(Ee + c) & 2Gd & Ab(2Ec - Ee - 3c) & Aa(Ee + c) & Ab(2Ec + 3Ee + c) & -2Gd \\ -B(Ee + c) & 2Gd & Ab(2Ec - Ee - 3c) & -2Gd & B(Ec + e) & Aa(2Ee - Ec - 3e) & -Ab(Ee + 2Ec - c) & -Aa(2Ee + Ec - e) & G(a - b)(a + b) \\ Aa(Ee + c) & Ab(2Ec + 3Ee + c) & -2Gd & -Ab(Ee + 2Ec - c) & -Aa(2Ee + Ec - e) & G(a - b)(a + b) & 2Gd & G(c + 3e) & -Fa \\ -B(Ee + c) & 2Gd & Ab(2Ec - Ee - 3c) & -2Gd & B(Ec + e) & Aa(2Ee - Ec - 3e) & -Ab(Ee + 2Ec - c) & -Aa(2Ee + Ec - e) & G(a - b)(a + b) \\ -2Gd & B(Ec + e) & Aa(2Ee - Ec - 3e) & -3B(Ec + e) & 0 & -3Ab(Ec + e) & Aa(2Ee + 3Ec + e) & Ab(Ec + e) & 2Gd \\ -Ab(Ee + 2Ec - c) & -Aa(2Ee + Ec - e) & G(a - b)(a + b) & Aa(2Ee + 3Ec + e) & Ab(Ec + e) & 2Gd & -G(e + 3c) & -2Gd & -Fb \\ Aa(Ee + c) & Ab(2Ec + 3Ee + c) & -2Gd & -Ab(Ee + 2Ec - c) & -Aa(2Ee + Ec - e) & G(a - b)(a + b) & 2Gd & G(c + 3e) & -Fa \\ -Ab(Ee + 2Ec - c) & -Aa(2Ee + Ec - e) & G(a - b)(a + b) & Aa(2Ee + 3Ec + e) & Ab(Ec + e) & 2Gd & -G(e + 3c) & -2Gd & -Fb \\ 2Gd & G(c + 3e) & -Fa & -G(e + 3c) & -2Gd & -Fb & 3Fa & 3Fb & 0 \end{array} \right] \quad (\text{A.11})$$

$$\chi_{xyxx} = \frac{1}{8} \left[\begin{array}{ccccccccc} 0 & -B(Ee + c) & Aa(Ee + c) & 3B(Ee + c) & 2Gd & Ab(2Ec + 3Ee + c) & -3Aa(Ee + c) & Ab(2Ec - Ee - 3c) & -2Gd \\ -B(Ee + c) & -2Gd & -Ab(Ee + 2Ec - c) & 2Gd & B(Ec + e) & -Aa(2Ee + Ec - e) & Ab(2Ec - Ee - 3c) & Aa(2Ee - Ec - 3e) & G(a - b)(a + b) \\ Aa(Ee + c) & -Ab(Ee + 2Ec - c) & 2Gd & Ab(2Ec + 3Ee + c) & -Aa(2Ee + Ec - e) & G(c + 3e) & -2Gd & G(a - b)(a + b) & -Fa \\ -B(Ee + c) & -2Gd & -Ab(Ee + 2Ec - c) & 2Gd & B(Ec + e) & -Aa(2Ee + Ec - e) & Ab(2Ec - Ee - 3c) & Aa(2Ee - Ec - 3e) & G(a - b)(a + b) \\ -2Gd & -3B(Ec + e) & Aa(2Ee + 3Ec + e) & B(Ec + e) & 0 & Ab(Ec + e) & Aa(2Ee - Ec - 3e) & -3Ab(Ec + e) & 2Gd \\ -Ab(Ee + 2Ec - c) & Aa(2Ee + 3Ec + e) & -G(e + 3c) & -Aa(2Ee + Ec - e) & Ab(Ec + e) & -2Gd & G(a - b)(a + b) & 2Gd & -Fb \\ Aa(Ee + c) & -Ab(Ee + 2Ec - c) & 2Gd & Ab(2Ec + 3Ee + c) & -Aa(2Ee + Ec - e) & G(c + 3e) & -2Gd & G(a - b)(a + b) & -Fa \\ -Ab(Ee + 2Ec - c) & Aa(2Ee + 3Ec + e) & -G(e + 3c) & -Aa(2Ee + Ec - e) & Ab(Ec + e) & -2Gd & G(a - b)(a + b) & 2Gd & -Fb \\ 2Gd & -G(e + 3c) & 3Fa & G(c + 3e) & -2Gd & 3Fb & -Fa & -Fb & 0 \end{array} \right] \quad (\text{A.12})$$

$$\chi_{xyxx} = \frac{1}{8} \left[\begin{array}{ccccccccc} 0 & -B(Ee + c) & Aa(Ee + c) & -B(Ee + c) & -2Gd & -Ab(Ee + 2Ec - c) & Aa(Ee + c) & -Ab(Ee + 2Ec - c) & 2Gd \\ 3B(Ee + c) & 2Gd & Ab(2Ec + 3Ee + c) & 2Gd & B(Ec + e) & -Aa(2Ee + Ec - e) & Ab(2Ec + 3Ee + c) & -Aa(2Ee + Ec - e) & G(c + 3e) \\ -3Aa(Ee + c) & Ab(2Ec - Ee - 3c) & -2Gd & Ab(2Ec - Ee - 3c) & Aa(2Ee - Ec - 3e) & G(a - b)(a + b) & -2Gd & G(a - b)(a + b) & -Fa \\ -B(Ee + c) & -2Gd & -Ab(Ee + 2Ec - c) & -2Gd & -3B(Ec + e) & Aa(2Ee + 3Ec + e) & -Ab(Ee + 2Ec - c) & Aa(2Ee + 3Ec + e) & -G(e + 3c) \\ 2Gd & B(Ec + e) & -Aa(2Ee + Ec - e) & B(Ec + e) & 0 & Ab(Ec + e) & -Aa(2Ee + Ec - e) & Ab(Ec + e) & -2Gd \\ Ab(2Ec - Ee - 3c) & Aa(2Ee - Ec - 3e) & G(a - b)(a + b) & Aa(2Ee - Ec - 3e) & -3Ab(Ec + e) & 2Gd & G(a - b)(a + b) & 2Gd & -Fb \\ Aa(Ee + c) & -Ab(Ee + 2Ec - c) & 2Gd & -Ab(Ee + 2Ec - c) & Aa(2Ee + 3Ec + e) & -G(e + 3c) & 2Gd & -G(e + 3c) & 3Fa \\ Ab(2Ec + 3Ee + c) & -Aa(2Ee + Ec - e) & G(c + 3e) & -Aa(2Ee + Ec - e) & Ab(Ec + e) & -2Gd & G(c + 3e) & -2Gd & 3Fb \\ -2Gd & G(a - b)(a + b) & -Fa & G(a - b)(a + b) & 2Gd & -Fb & -Fa & -Fb & 0 \end{array} \right] \quad (\text{A.13})$$

$$\chi_{xyzz} = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ Ge & -Gd & -Hb & -Gd & Gc & Ha & -Hb & Ha & I \\ -Fh & Fg & Gd & Fg & -Ff & -Gc & Gd & -Gc & -Ha \\ -Ge & Gd & Hb & Gd & -Gc & -Ha & Hb & -Ha & -I \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -Fi & Fh & Ge & Fh & -Fg & -Gd & Ge & -Gd & -Hb \\ Fh & -Fg & -Gd & -Fg & Ff & Gc & -Gd & Gc & Ha \\ Fi & -Fh & -Ge & -Fh & Fg & Gd & -Ge & Gd & Hb \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (\text{A.14})$$

$$\chi_{xzyz} = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 & Ge & -Gd & -Hb & -Fh & Fg & Gd \\ 0 & 0 & 0 & -Gd & Gc & Ha & Fg & -Ff & -Gc \\ 0 & 0 & 0 & -Hb & Ha & I & Gd & -Gc & -Ha \\ -Ge & Gd & Hb & 0 & 0 & 0 & -Fi & Fh & Ge \\ Gd & -Gc & -Ha & 0 & 0 & 0 & Fh & -Fg & -Gd \\ Hb & -Ha & -I & 0 & 0 & 0 & Ge & -Gd & -Hb \\ Fh & -Fg & -Gd & Fi & -Fh & -Ge & 0 & 0 & 0 \\ -Fg & Ff & Gc & -Fh & Fg & Gd & 0 & 0 & 0 \\ -Gd & Gc & Ha & -Ge & Gd & Hb & 0 & 0 & 0 \end{bmatrix} \quad (\text{A.15})$$

$$\chi_{xzyz} = \frac{1}{2} \begin{bmatrix} 0 & Ge & -Fh & 0 & -Gd & Fg & 0 & -Hb & Gd \\ 0 & -Gd & Fg & 0 & Gc & -Ff & 0 & Ha & -Gc \\ 0 & -Hb & Gd & 0 & Ha & -Gc & 0 & I & -Ha \\ -Ge & 0 & -Fi & Gd & 0 & Fh & Hb & 0 & Ge \\ Gd & 0 & Fh & -Gc & 0 & -Fg & -Ha & 0 & -Gd \\ Hb & 0 & Ge & -Ha & 0 & -Gd & -I & 0 & -Hb \\ Fh & Fi & 0 & -Fg & -Fh & 0 & -Gd & -Ge & 0 \\ -Fg & -Fh & 0 & Ff & Fg & 0 & Gc & Gd & 0 \\ -Gd & -Ge & 0 & Gc & Gd & 0 & Ha & Hb & 0 \end{bmatrix} \quad (\text{A.16})$$

$$\chi_{zyxz} = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 & Ge & -Gd & -Hb & -Fh & Fg & Gd \\ -Ge & Gd & Hb & 0 & 0 & 0 & -Fi & Fh & Ge \\ Fh & -Fg & -Gd & Fi & -Fh & -Ge & 0 & 0 & 0 \\ 0 & 0 & 0 & -Gd & Gc & Ha & Fg & -Ff & -Gc \\ Gd & -Gc & -Ha & 0 & 0 & 0 & Fh & -Fg & -Gd \\ -Fg & Ff & Gc & -Fh & Fg & Gd & 0 & 0 & 0 \\ 0 & 0 & 0 & -Hb & Ha & I & Gd & -Gc & -Ha \\ Hb & -Ha & -I & 0 & 0 & 0 & Ge & -Gd & -Hb \\ -Gd & Gc & Ha & -Ge & Gd & Hb & 0 & 0 & 0 \end{bmatrix} \quad (\text{A.17})$$

$$\chi_{zyxz} = \frac{1}{2} \begin{bmatrix} 0 & -Ge & Fh & 0 & Gd & -Fg & 0 & Hb & -Gd \\ Ge & 0 & Fi & -Gd & 0 & -Fh & -Hb & 0 & -Ge \\ -Fh & -Fi & 0 & Fg & Fh & 0 & Gd & Ge & 0 \\ 0 & Gd & -Fg & 0 & -Gc & Ff & 0 & -Ha & Gc \\ -Gd & 0 & -Fh & Gc & 0 & Fg & Ha & 0 & Gd \\ Fg & Fh & 0 & -Ff & -Fg & 0 & -Gc & -Gd & 0 \\ 0 & Hb & -Gd & 0 & -Ha & Gc & 0 & -I & Ha \\ -Hb & 0 & -Ge & Ha & 0 & Gd & I & 0 & Hb \\ Gd & Ge & 0 & -Gc & -Gd & 0 & -Ha & -Hb & 0 \end{bmatrix} \quad (\text{A.18})$$

$$\chi_{zzxy} = \frac{1}{2} \begin{bmatrix} 0 & Ge & -Fh & -Ge & 0 & -Fi & Fh & Fi & 0 \\ 0 & -Gd & Fg & Gd & 0 & Fh & -Fg & -Fh & 0 \\ 0 & -Hb & Gd & Hb & 0 & Ge & -Gd & -Ge & 0 \\ 0 & -Gd & Fg & Gd & 0 & Fh & -Fg & -Fh & 0 \\ 0 & Gc & -Ff & -Gc & 0 & -Fg & Ff & Fg & 0 \\ 0 & Ha & -Gc & -Ha & 0 & -Gd & Gc & Gd & 0 \\ 0 & -Hb & Gd & Hb & 0 & Ge & -Gd & -Ge & 0 \\ 0 & Ha & -Gc & -Ha & 0 & -Gd & Gc & Gd & 0 \\ 0 & I & -Ha & -I & 0 & -Hb & Ha & Hb & 0 \end{bmatrix} \quad (\text{A.19})$$

References and Notes

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