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Connection of Jones and Mueller Tensors in Second Harmonic Generation and Multi-Photon Fluorescence Measurements

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Abstract

Despite the rapidly growing use of second harmonic generation (SHG) and two-photon excited fluorescence (TPEF) microscopy, opportunities for relating polarization-dependent measurements back to local structure and molecular orientation are often confounded by losses in polarization purity. In this work, connections linking Mueller tensor and Jones tensor descriptions of polarization-dependent SHG and TPEF are shown to substantially simplify partially depolarized microscopy measurements. These connections were facilitated by the derivation of several new tensor identity relations, based on generalization of established transformations of matrices and vectors. Methods are described for integrating local-frame symmetry and azimuthal rotation angle for simplifying the Mueller tensor. Through simple expressions bridging the Mueller and Jones formalisms, mathematical models for partial depolarization can greatly simplify interpretation of SHG and TPEF measurements to reconstruct the more general Mueller tensors using the much more concise Jones descriptions for the purely polarized components. Integrating the Mueller architecture allows polarization-dependent SHG and TPEF measurements to be connected back to a relatively small set of free parameters related to local structure and orientation.

Graphical abstract

$$M^{(2)} = A \cdot \left(\chi_J^{(2)*} \otimes \chi_J^{(2)} \right) : A^{-1} A^{-1}$$

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Notes

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I. INTRODUCTION

The polarization dependence of second harmonic generation (SHG) and two-photon excited fluorescence (TPEF) is highly sensitive to local structure and orientation. Consequently, polarization analysis is widely used to aid in the interpretation of SHG and TPEF microscopy measurements of biological tissues,^{1–13} microcrystals,^{10,14–26} macromolecular assemblies,^{27,28} and plasmonic assemblies.^{27,29–32} These nonlinear optical effects nicely complement linear polarization imaging methods, providing unique access to motifs and moments inaccessible with conventional linear optics. In the case of SHG, the unique symmetry properties of the process provide contrast that is sensitive to noncentrosymmetric ordering. Both TPEF and SHG have a key advantage in biological imaging, as they allow deep access in turbid media relative to their linear analogues.^{10,20,21} In brief, only the “ballistic” unscattered light generally contributes to the detected signals in a beam-scanning instrument; since both SHG and/or TPEF scale nonlinearly with the incident intensity, they arise almost exclusively from the surviving component of light reaching the focal plane.

The advantages of deep-tissue imaging in SHG and TPEF can significantly complicate polarization analysis, however. In anisotropic media including some tissues, birefringence can affect the incident and detected polarization, complicating polarization analysis.^{10,20,21,33,34} Even in uniform media, the traversal to the focal plane can induce phase shifts along different paths, resulting in partial scrambling of the incident polarization for the ballistic component contributing to signal.³⁵ Similarly, optical scattering of the detected SHG and/or TPEF can negatively impact the polarization purity ultimately reaching the detector.³⁵ Campagnola and co-workers have demonstrated a practical approach to reduce depolarization effects through optical clearing in *ex vivo* analyses.³⁶ Schanne-Klein and co-workers have proposed several strategies to address scattering, including the introduction of polarization “cross-talk” parameters from depolarization of the SHG signals in collagen from anisotropic scattering.^{33,37} In more recent studies,³⁸ conventional (linear) Mueller matrix imaging of collagenous tissues was found to provide information similar to that of SHG microscopy. Even with these advances, the degrees to which scattering and anisotropy play a significant role generally increase as the penetration depths of nonlinear optical imaging continue to be expanded.

In such cases, the extension of nonlinear optics to a framework based on Mueller tensors and Stokes vectors has several advantages. Unlike Jones vectors, Stokes vectors can describe both purely polarized and partially polarized optical signals. Similarly, Mueller matrices can describe optical elements that include some degree of depolarization, unlike Jones matrices. Several investigators have explored the extension of the Mueller/Stokes architecture to describe nonlinear optical interactions. Among the first studies was early work by Shi, McClain, and Harris,^{39,40} in which the concept of the Mueller tensor was first introduced, then simplified, and dubbed the double-Mueller matrix for the specific case of SHG and TPEF with a single incident beam. Barzda and co-workers have extended the Mueller tensor approach originally developed by Shi et al. to polarimetric measurements in SHG microscopy, both theoretically⁴¹ and experimentally,⁴² to great effect. Brasselet and co-workers have extensively considered the influence of depolarization and birefringence in nonlinear optical imaging,^{43,44} and more recently nicely demonstrated the use of four-wave

mixing as a polarization-dependent guide-star signal for characterizing birefringence and depolarization effects in nonlinear optical imaging of biological tissues, although not based on the Mueller formalism.^{43,45} Stokes ellipsometry^{46–49} and Stokes polarimetry⁵⁰ have both been developed for polarization analysis in SHG measurements but not explicitly incorporating a Mueller tensor formalism. By integrating >MHz polarization modulation, Dow et al., have demonstrated full nonlinear optical Stokes ellipsometric microscopy at each pixel in a 512×512 image at video rate,⁵¹ potentially enabling *in vivo* analysis.

Despite these previous advances both theoretically and experimentally, interpretation and modeling of Mueller tensors remain challenging within the existing mathematical framework. The studies by Shi et al. upon which subsequent studies are largely based drew no link connecting the Mueller tensor architecture to Jones tensors, which are well-established for describing second-order nonlinear optics in nondepolarized systems.^{46–48,52} The development of concise analytical models for describing depolarization effects in nonlinear optics is complicated by the absence of a mathematically compatible description in the absence of depolarization. In the limit of pure polarizations, the Mueller and Jones tensor formalisms must converge. Clear mathematical connections describing this convergence can enable simple analytical models for treating depolarization effects and recovering local structure and molecular orientation information.

In this work, the Jones and Mueller tensor frameworks are directly and intuitively connected, taking advantage of the derivations of several new tensor identity relations. The new toolkit available from these identities allows simple extension of the established Jones/Mueller connection in linear optics into the nonlinear optical regime. The presence of local-frame symmetry can be easily integrated into the Mueller tensor architecture, substantially reducing the number of unique nonzero Mueller tensor elements required to describe the accessible observables. Substantial additional simplification to the Mueller tensor can be achieved through development of analytical models for describing depolarization, which take advantage of the simplifying links connecting the Jones and Mueller descriptions. Targeting microscopy applications, this architecture allows for simple corrections for differences in orientation within the field of view, recovering the Mueller tensors expressed in the local sample frame. Mathematical expressions for both SHG and TPEF are provided for measurements acquired as a function of the incident polarization rotation angle as well as for phase-modulated incident light.

II. THEORETICAL FOUNDATION

In systems exhibiting optical scatter, the polarization states of both the incident and detected light can become partially depolarized. Polarization purity can be lost through refraction in turbid media while still retaining sufficient power to produce multiphoton fluorescence and SHG. However, perturbations due to both birefringence and depolarization generally affect the detected light to a greater extent than the incident light in the Mie scattering limit for two reasons: the shorter wavelength exhibits higher birefringence and more scattering, and both the scattered and ballistic signals are integrated for the detection wavelength while only the ballistic incident light contributes to the signal. As the central focus of the present work is development of connections bridging the nonlinear Jones and Mueller tensors, a relatively

simple model is introduced for describing depolarization contributions from optical scattering, although more elaborate approaches could be easily integrated to account for birefringence and anisotropic scattering.

II.A. Mueller Matrices and Stokes Vectors in Linear Optics

Stokes vectors can describe both purely and partially polarized light, providing capabilities complementary to those of Jones vectors, which are necessarily limited to purely polarized light. The Stokes vector $\vec{s}$ is defined in eq 1 below.⁵³

$$\vec{s} = \begin{bmatrix} I_H + I_V \\ I_H - I_V \\ I_{+45^\circ} + I_{-45^\circ} \\ I_R - I_L \end{bmatrix} \quad (1)$$

For purely polarized light, the Stokes vector can be related directly back to the Jones vector $\vec{e}$ through the transformation matrix A .

$$\vec{s} = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & i & -i & 0 \end{bmatrix} \cdot \begin{pmatrix} e_0^* e_0 \\ e_0^* e_1 \\ e_1^* e_0 \\ e_1^* e_1 \end{pmatrix} = A \cdot (\vec{e} * \otimes \vec{e}) \quad (2)$$

The symbol $\otimes$ denotes a Kronecker product.

By analogy with a Jones transformation matrix χ_J , a Mueller matrix M serves as a polarization transfer matrix. Once the Mueller matrix has been established, the Stokes vector for the output is directly predictable from the input Stokes vector. Expressions for Jones and Mueller transformations are given in eqs 3 and 4, respectively.

$$\vec{e}^{\text{out}} = \chi_J \cdot \vec{e}^{\text{in}} = \chi_J \cdot \vec{e}^{\text{in}} \quad (3)$$

$$\vec{s}^{\text{out}} = M \cdot \vec{s}^{\text{in}} \quad (4)$$

In the absence of depolarization, the Mueller matrix M and Jones matrix χ_J can be connected by first taking the Kronecker product of $\vec{e}^{\text{out}}$ in eq 3 with its conjugate to produce a 4×1 vector of electric field combinations.

$$\begin{aligned} \vec{e}^{\text{out}*} \otimes \vec{e}^{\text{out}} &= (\chi_J \cdot \vec{e}^{\text{in}}) * \otimes (\chi_J \cdot \vec{e}^{\text{in}}) \\ &= (\chi_J^* \otimes \chi_J) \cdot (\vec{e}^{\text{in}*} \otimes \vec{e}^{\text{in}}) \end{aligned} \quad (5)$$

The identity relationship $(A \cdot B) \otimes (C \cdot D) = (A \otimes C) \cdot (B \otimes D)$ was used in the rearrangement of eq 5. The corresponding expression for the Stokes vector is given by the substitution in eq 2.

$$\begin{aligned}\vec{s}^{\text{out}} &= A \cdot (\vec{e}^{\text{out}*} \otimes \vec{e}^{\text{out}}) \\ &= A \cdot (\chi_J^* \otimes \chi_J) \cdot (\vec{e}^{\text{in}*} \otimes \vec{e}^{\text{in}}) \\ &= A \cdot (\chi_J^* \otimes \chi_J) \cdot A^{-1} \cdot \vec{s}^{\text{in}} \\ &= M \cdot \vec{s}^{\text{in}}\end{aligned}\quad (6)$$

The Mueller matrix from eq 6 is given by the Kronecker product of the Jones matrices and the matrix A .

$$M = A \cdot (\chi_J^* \otimes \chi_J) \cdot A^{-1} \quad (7)$$

Given that the matrix above in eq 7 describes the Mueller matrix in the absence of depolarization, the influence of partial depolarization can be introduced phenomenologically by a scaling factor α , in which the Mueller matrix is described by eq 7 when $\alpha = 0$ in the absence of any depolarization and is described by the Mueller matrix for complete depolarization in the limit of $\alpha = 1$. This latter matrix recovers s_0 as the only remaining nonzero element in the Stokes vector for the output polarization. This simple model for depolarization will not describe all systems with partial polarization^{54–56} but is a reasonable low-parameter starting point for describing propagation of a purely polarized source through a turbid medium. Consistent with this assertion, linear measurements of Mueller matrices from turbid suspensions of microspheres and cells have reported values for the M_{00} elements significantly larger (~ 10 -fold) than those of the other 15 elements in the matrix.^{54–56} From decomposition of Mueller matrices to independently account for depolarization,⁵⁷ the isotropic depolarization matrix contains only one nonzero element, $M_{00} = 1$.

$$M = (1 - \alpha)[A \cdot (\chi_J^* \otimes \chi_J) \cdot A^{-1}] + \alpha \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (8)$$

The expressions in eqs 7 and 8 provide a convenient connection bridging the Mueller and Jones formalisms in linear optics. If an optical element induces no depolarization, its Mueller matrix can be generated from the corresponding Jones matrix using eq 7. In this manner, the outgoing polarization state $\vec{s}^{\text{out}}$ can be predicted for either a purely or partially polarized input $\vec{s}^{\text{in}}$. Similarly, if the optical element itself introduces some partial depolarization, a modified version such as that given in eq 8 can be used, or alternatively the 16 elements of M can be experimentally determined directly rather than relying on an analytical model. The primary advantage of an analytical model such as that given in eq 8 is clearly the reduction in the number of parameters required to recover the Mueller matrix.

Using eq 8, all 16 elements of M are dependent on just five parameters: the four elements of the Jones matrix for purely polarized light χ_J and the scaling parameter α .

We can relate this simple linear model to the degree of polarization, defined by the following expression.⁵³

$$\text{DoP} = \sqrt{s_1^2 + s_2^2 + s_3^2} / s_0 \quad (9)$$

The Stokes vector for the partially depolarized model described in eq 8 yields two contributions: the purely polarized component expressed with respect to the Jones matrix and the unpolarized component by the single-element matrix Mueller matrix to the right. Bearing in mind that the DoP approaches unity in the limit of purely polarized light, the contribution to the left of eq 8 will approach $(1 - \alpha)$ for coherent linear processes (e.g., scattering) when using a purely polarized incident beam. In this limit, the DoP reduced down to the following well-established link between the DoP and the degree of depolarization, given by α .

$$\text{DoP} = (1 - \alpha) \quad (10)$$

In the case of fluorescence, the DoP will not be related to α through the simple equality in eq 10, however. Even in the absence of depolarization from scattering, the fluorescence emitted at the source will not be purely polarized, as fluorescence is an incoherent process. Fortunately, the expression in eq 8 will still hold for TPEF, allowing additional depolarization effects to be included in the description of the net Mueller matrix.

II.B. The Mueller Tensor

The framework describing linear transformations serves as a foundation for extension to nonlinear optical interactions, introduced first for the general case of three-wave mixing (i.e., sum frequency generation, SFG), which includes SHG as a special case. For purely polarized light, the Jones tensor describing SFG is given by the following expression.

$$\vec{e}^{\text{sum}} = \chi_J^{(2)} : \vec{e}^a \vec{e}^b \quad (11)$$

In eq 11, the semicolon indicates a tensor product, consistent with the multiplication by $\vec{e}^a$ in one dimension and $\vec{e}^b$ in another. A notation is introduced, in which a superscripted parenthetical [e.g., (n)] is used to indicate a tensor of rank $(n + 1)$. The superscript is not used for individual scalar entries (e.g., χ_{HHH}). The corresponding Mueller tensor relationship is given by the analogous expression.

$$\vec{s}^{\text{sum}} = M^{(2)} : \vec{s}^a \vec{s}^b \quad (12)$$

By direct analogy with eq 6, the following expressions can be written to connect the Jones and Mueller tensors in the limit of pure polarizations.

$$\vec{e}^{\text{sum}*} \otimes \vec{e}^{\text{sum}} = (\chi_J^{(2)}; \vec{e} \vec{e})^* \otimes (\chi_J^{(2)}; \vec{e} \vec{e}) \quad (13)$$

From **Theorem 8** (see Appendix II), the Kronecker product can be propagated through.

$$\vec{e}^{\text{sum}*} \otimes \vec{e}^{\text{sum}} = (\chi_J^{(2)*} \otimes \chi_J^{(2)}); (\vec{e}^{a*} \otimes \vec{e}^a) (\vec{e}^{b*} \otimes \vec{e}^b) \quad (14)$$

The corresponding expression for the Stokes vector is given by multiplication by A .

$$\begin{aligned} \vec{s}^{\text{sum}} &= A \cdot (\vec{e}^{\text{sum}*} \otimes \vec{e}^{\text{sum}}) \\ &= A \cdot (\chi_J^{(2)*} \otimes \chi_J^{(2)}); (\vec{e}^{a*} \otimes \vec{e}^a) (\vec{e}^{b*} \otimes \vec{e}^b) \\ &= A \cdot (\chi_J^{(2)*} \otimes \chi_J^{(2)}); [A^{-1} \cdot \vec{s}^a] [A^{-1} \cdot \vec{s}^b] \end{aligned} \quad (15)$$

From **Theorem 4** (see Appendix II), the factors of A and A^{-1} can be folded in to generate the combined Mueller tensor of order two and rank three.

$$\begin{aligned} \vec{s}^{\text{sum}} &= [A \cdot (\chi_J^{(2)*} \otimes \chi_J^{(2)}); A^{-1} A^{-1}]; \vec{s}^a \vec{s}^b = M^{(2)}; \vec{s}^a \vec{s}^b \\ M^{(2)} &= A \cdot (\chi_J^{(2)*} \otimes \chi_J^{(2)}); A^{-1} A^{-1} \end{aligned} \quad (16)$$

Extension to n-Wave Mixing—Four-wave mixing using Jones tensor notation is given by the following expression for the general case of four-wave sum-frequency generation (which includes CARS, SRS, degenerate four-wave mixing, etc.).

$$\vec{e}^{\text{sum}} = \chi^{(3)}; \vec{e} \vec{e} \vec{e} \quad (17)$$

The corresponding Stokes vector is given below (which includes the effects above as well as partially polarized measurements such as fluorescence).

$$\vec{s}^{\text{sum}} = M^{(3)}; \vec{s} \vec{s} \vec{s} \quad (18)$$

The analogous operations connecting the Stokes and Jones formalisms in the limit of purely polarized inputs and outputs are given by the following equality.

$$M^{(3)} = A \cdot (\chi_J^{(3)*} \otimes \chi_J^{(3)}); A^{-1} A^{-1} A^{-1} \quad (19)$$

Obviously, the form of the expression in eq 19 is closely tied to that given in eq 16 for three-wave mixing. The primary differences are in the dimensionality of the tensors and lengths of the corresponding ascending vectorized forms. In the case of three-wave mixing, the length of $\vec{\chi}_J$ is $2 \cdot 2 \cdot 2 = 8$ elements long, while, for four-wave mixing, $\vec{\chi}_J$ has a length of $2 \cdot 2 \cdot 2 \cdot 2 = 16$. Similarly, $\vec{M}$ expands to $16^2 = 256$ elements in length in the case of four-wave mixing.

II.C. Models for Depolarization in SHG

In partially depolarizing systems, it would be a shame to not build on the connections bridging the Jones and Mueller tensors developed in the preceding sections. Indeed, it may well be necessary to do so, as the number of free parameters within the most general form for the Mueller tensor far outstrips the number of independent accessible observables in the most common measurement designs. Developing analytical models for treating depolarizing effects allows the number of unique parameters required to describe Mueller tensors to be kept manageable.

In a fairly general way, the process of SHG from a point source in a partially depolarizing sample can be broken down into three stages: (i) propagation of the fundamental light to the SHG-active source, (ii) production of SHG, and (iii) propagation of the doubled light to the detector. In this case, the Stokes vector for the fundamental light at the SHG-active source is related to the incident Stokes vector by a conventional Mueller matrix describing

polarization changes upon propagation to the source; $\vec{s}_{\text{source}}^{\omega} = M^{\omega} \cdot \vec{s}^{\omega}$. Similarly, the detected far-field Stokes vector is also related to the SHG produced at the source by a

Mueller matrix; $\vec{s}^{2\omega} = M^{2\omega} \cdot \vec{s}_{\text{source}}^{2\omega}$. Combining these two relationships into eq 16 yields the following general expression for the detected Stokes vector.

$$\vec{s}^{2\omega} = M^{2\omega} \cdot M^{(2)} : (M^{\omega} \cdot \vec{s}^{\omega}) (M^{\omega} \cdot \vec{s}^{\omega}) \quad (20)$$

Because the frequency conversion from the point source is general not in itself depolarizing, the Mueller tensor at the source can be reasonably described using the Jones matrix combinations from eq 16. From the theorem $B^{(2)} : (C \cdot D)(E \cdot F) = (B^{(2)} : CE)^{(2)} : DF$ in Appendix II, the linear Mueller matrices can be integrated into the definition of a net effective nonlinear Mueller tensor.

$$\begin{aligned} \vec{s}^{2\omega} &= [M^{2\omega} \cdot M^{(2)} : M^{\omega} M^{\omega}]^{(2)} : \vec{s}^{\omega} \vec{s}^{\omega} \\ M_{\text{net}}^{(2)} &= M^{2\omega} \cdot M^{(2)} : M^{\omega} M^{\omega} \end{aligned} \quad (21)$$

At this point, the Mueller tensor at the sample $M^{(2)}$ can be replaced by the purely polarized Jones form, since all depolarization effects arise from propagation prior to and following frequency conversion.

$$M_{\text{net}}^{(2)} = M^{2\omega} [A \cdot (\chi_J^{(2)*} \otimes \chi_J^{(2)}) : A^{-1} A^{-1}]^{(2)} : M^{\omega} M^{\omega} \\ = [(M^{2\omega} A) \cdot (\chi_J^{(2)*} \otimes \chi_J^{(2)}) : (A^{-1} M^{\omega})(A^{-1} M^{\omega})]^{(2)} \quad (22)$$

Using this toolkit, the complexity of the nonlinear optical problem has been reduced to a level similar to that of the linear problem. Independent measurements or estimations of the Mueller matrices for propagation to and from the source allow the Mueller tensor to be simplified directly to the Jones formalism while still accommodating partial or complete depolarization.

II.C.1. Model 1 – Completely Depolarized Component—Among the simplest analytical models is one in which the detected Stokes vector for the doubled light is expressed as a linear combination of a purely polarized component and a completely depolarized component (e.g., illustrated in Figure 1C). The purely polarized component can be described using the Jones/Mueller relations derived in the preceding section. In the limit of complete depolarization, the detected Stokes vector contains only s_0 at the nonzero element and is dependent only on the intensity but not the polarization state of the incident light. This model corresponds to depolarization of both the incident and doubled light, consistent with the following Mueller matrices for $M^{2\omega}$ and M^{ω} in eq 22.

$$M_{\alpha}^{2\omega} = M_{\alpha}^{\omega} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (23)$$

The subscript α in eq 23 indicates the depolarized component of the signal. In this limit, the net Mueller tensor for the depolarized component $M_{\alpha}^{(2)}$ contains only a single nonzero element M_{000} .

$$M_{\text{net}}^{(2)} = (1 - \alpha) [A \cdot (\chi_J^{(2)*} \otimes \chi_J^{(2)}) : A^{-1} A^{-1}] + \alpha M_{\alpha}^{(2)} \quad (24)$$

As introduced in the description of linear optical interactions and justified based on the same rationale, the parameter α is defined to be a scaling factor for the relative contributions of purely polarized ($\alpha = 0$) and completely depolarized ($\alpha = 1$) SHG.

This model for depolarization can be connected back to the measured degree of polarization for the Stokes vector describing the detected SHG. In SHG measurements, the DoP of the detected light depends on the polarization state of the incident light, the DoP of the incident light, and the Mueller tensor itself. According to the expression in eq 24, the detected Stokes vector for this model will adopt the following form, with subscripts J indicating the purely polarized component and α the depolarized component.

$$s_{\text{net}}^{2\omega} = (1 - \alpha) M_J^{(2)} : s^{\omega} s^{\omega} + \alpha M_\alpha^{(2)} : s^{\omega} s^{\omega} \quad (25)$$

$$\begin{bmatrix} s_0^{2\omega} \\ s_1^{2\omega} \\ s_2^{2\omega} \\ s_3^{2\omega} \end{bmatrix}_{\text{net}} = (1 - \alpha) \begin{bmatrix} s_0^{2\omega} \\ s_1^{2\omega} \\ s_2^{2\omega} \\ s_3^{2\omega} \end{bmatrix}_J + \alpha \begin{bmatrix} s_0^{2\omega} \\ 0 \\ 0 \\ 0 \end{bmatrix}_\alpha = \begin{bmatrix} s_0^{2\omega} \\ (1 - \alpha) s_1^{2\omega} \\ (1 - \alpha) s_2^{2\omega} \\ (1 - \alpha) s_3^{2\omega} \end{bmatrix} \quad (26)$$

The DoP can be written in terms of α by substitution, taking advantage of the fact that the DoP approaches 1 in the limit of purely polarized light (corresponding to the Jones component).

$$\text{DoP} = (1 - \alpha) \quad (27)$$

In words, the degree of polarization in the limit of an isotropic model for depolarization of the incident and detected light is trivially connected to the parameter α .

II.C.2. Model 2 – Purely Polarized Incident Light, Partially Depolarized

Detected Light—In this limit (illustrated in Figure 1A and B), the driving light remains purely polarized, with the detected light containing both a purely polarized component and a depolarized component. A common example includes epi-detection in measurements of turbid media and/or tissues, in which the signal consists of an epi-propagating polarized component and a forward propagating but backward scattered component. For structures greater in thickness than the forward coherence length, the forward propagating signal can be significantly greater than the epi-propagating signal, such that the backward scattered contributions are non-negligible.

This case also includes epi or transmission measurements in which the frequency-doubled light undergoes significant scattering prior to detection. The most obvious scenario is one in which SHG is produced after only a short propagation through a turbid medium, followed by a longer path length prior to detection. However, it also applies more generally to broad classes of common measurements. Since only the unscattered “ballistic” incident light surviving the journey to the focal plane contributes to the detected signal, optical scatter and depolarization do not impact the incident light as dramatically as the detected light. The corresponding Mueller matrices describing linear propagation to and from the source in eq 22 are distinctly different from those in the preceding model, with the incident Mueller matrix for the scattered component given by the identity matrix.

$$M_{\alpha}^{2\omega} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}; \quad M_{\alpha}^{\omega} = I \quad (28)$$

In this limit, the process can be viewed as the stepwise production of a purely polarized Jones vector describing the SHG produced immediately at the sample, followed by partial depolarization upon propagation to the detector. Fortunately, we have already solved for the linear propagation in the presence of partial isotropic depolarization in eq 8. Substituting the identity matrix for the purely polarized Mueller matrix in eq 8 yields the following Stokes vector for the SHG.

$$\begin{aligned} \vec{s}_{\text{net}}^{2\omega} &= M_{\text{net}}^{(2)} : \vec{s}^{\omega} \vec{s}^{\omega} \\ &= \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 - \alpha & 0 & 0 \\ 0 & 0 & 1 - \alpha & 0 \\ 0 & 0 & 0 & 1 - \alpha \end{bmatrix} \cdot \\ &[A \cdot (\chi_j^{(2)*} \otimes \chi_j^{(2)}) : A^{-1} A^{-1}]^{(2)} : \vec{s}^{\omega} \vec{s}^{\omega} \end{aligned} \quad (29)$$

As in model 1, the DoP is again trivially related to α for all incident polarization states through eq 27. However, the interpretation of the corresponding Stokes vector and the recovery of the Jones and/or local frame tensor elements for the two models correspond to quite different mathematical operations.

In this model, the value of α in eq 29 is derived from the linear Mueller matrix in eq 8. If α can be determined independently (e.g., by turbidity measurements or from linear measurements of the Mueller matrix describing the medium between the source and detector), the expression in eq 29 can be used directly to relate the set of observables back to the local structure and orientation of the SHG-active source. Alternatively, α can potentially serve as another free parameter in a multiparameter fit of the measured polarization dependence. In this manner, the impact of depolarization can be directly integrated with the rest of the polarization analysis, provided covariance between the different parameters is sufficiently small to enable determination of each parameter.

II.D. Coordinate Rotation of the Mueller Tensor

Rotation of Mueller matrices and tensors by an arbitrary set of Euler angles in three dimensions is ill-defined, since the Mueller tensor is defined relative to just two spatial coordinates. However, if just azimuthal rotation is considered, in which objects are oriented at some rotation angle ϕ within the field of view, rotation of both a Stokes vector and a Mueller matrix/tensor becomes tractable.

The azimuthal rotation of the local-frame Stokes vector $\vec{s}_l$ to the laboratory frame Stokes vector $\vec{s}_L$ is well established, the origins of which are detailed in Appendix V.

$$\vec{s}_L = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(2\phi) & \sin(2\phi) & 0 \\ 0 & -\sin(2\phi) & \cos(2\phi) & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \cdot \vec{s}_l = \mathcal{R}_\phi \cdot \vec{s}_l \quad (30)$$

Analogously, the corresponding rotation from the laboratory frame to the local frame is given by multiplication by the inverse of $\mathcal{R}_\phi$.

$$\vec{s}_l = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(2\phi) & -\sin(2\phi) & 0 \\ 0 & \sin(2\phi) & \cos(2\phi) & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \cdot \vec{s}_L = \mathcal{R}_\phi^{-1} \cdot \vec{s}_L = \mathcal{R}_{-\phi} \cdot \vec{s}_L \quad (31)$$

Using this set of operations, the laboratory-frame Mueller tensor $M_L^{(2)}$ in an azimuthally rotated frame is given in the following expressions.

$$\vec{s}_L^{2\omega} = M_L^{(2)} : \vec{s}_L^\omega \vec{s}_L^\omega \\ \vec{s}_L^{2\omega} = \mathcal{R}_\phi \cdot M_l^{(2)} : (\mathcal{R}_{-\phi} \cdot \vec{s}_L^\omega) (\mathcal{R}_{-\phi} \cdot \vec{s}_L^\omega) \quad (32)$$

Using the identity relation $A \cdot B^{(2)} : (CD)(EF) = (A \cdot B^{(2)} : CD)^{(2)} : DF$ from Appendix III, the preceding equation can be rewritten in the following form.

$$\vec{s}_L^{2\omega} = (\mathcal{R}_\phi \cdot M_l^{(2)} : \mathcal{R}_{-\phi} \mathcal{R}_{-\phi})^{(2)} : \vec{s}_L^\omega \vec{s}_L^\omega \quad (33)$$

The laboratory and local Mueller tensors for azimuthal rotation are then given by the following expression.

$$M_L^{(2)} = (\mathcal{R}_\phi \cdot M_l^{(2)} : \mathcal{R}_{-\phi} \mathcal{R}_{-\phi})^{(2)} \quad (34)$$

As can be shown with more rigor through the use of vectorization operations in the next section, it should nevertheless already be intuitively obvious that the local-frame tensor can be similarly expressed in terms of the laboratory-frame measurement.

$$M_l^{(2)} = (\mathcal{R}_{-\phi} \cdot M_L^{(2)} : \mathcal{R}_\phi \mathcal{R}_\phi)^{(2)} \quad (35)$$

II.E. Vectorization and Measurement Inversion

The preceding mathematical framework is designed to intuitively connect the Mueller and Jones tensor descriptions in nonlinear optics, in which the measured Stokes vector can be expressed in terms of the incident Stokes vectors and the Mueller tensor. Knowledge of the Mueller tensor allows prediction of all possible polarization-dependent nonlinear optical observables in a particular polarization-dependent measurement. However, in practice, it is usually the opposite operation that interests us most. Namely, how does one recover the Mueller tensor elements from measurements of the polarized SHG intensity as a function of the incident polarization state?

In previous studies by Shi, McClain, and Harris,⁴⁰ the frequency degeneracy in SHG was shown to reduce the number of unique elements in the Mueller tensor to 36, which could be isolated from measurements of the Stokes vectors for the doubled frequency acquired for a set of incident Stokes vectors. However, this approach does not take full advantage of the additional reductions in unique parameters associated with adoption of a particular model for the depolarization through connection to the Jones formalism, potentially reducing the number of unique unknowns to just six Jones tensor elements in combination with the parameter α . Furthermore, the influence of local-frame symmetry in the Mueller and/or Jones frames can significantly reduce further the number of unique nonzero elements to be recovered.

Consequently, a more general strategy is presented herein, in which symmetry in the local frame and ultimately in the molecular frame can be easily integrated into the mathematical inversion problem. In this manner, the same set of measurements can be inverted to solve for the laboratory-frame Mueller tensor elements, a smaller set of local-frame symmetry-allowed Mueller tensor elements, a smaller set of laboratory-frame Jones tensor elements, and ultimately a smaller set of molecular-frame tensor elements and/or information on the molecular orientation distribution about the local-frame coordinates. Alternatively, inversions that recover a smaller set of parameters can be performed on the basis of a smaller set of measurements than required to perform complete inversion of the Mueller tensor in the most general case of SHG and TPEF. The vectorization approach adopted in this section provides a convenient framework for isolating the Mueller tensor in a linear algebra expression amenable to subsequent inversion.

Vectorized Mueller Matrices and Stokes Vectors—Consistent with the method adopted in the preceding section, vectorization operations will first be considered for conventional linear Mueller matrices prior to extension to nonlinear optics. A review of established vectorization operations vec for matrices is provided in Appendix I, along with the definition of the ascending vectorization operation asc to be used later in tensor manipulations. As described in Appendix I, $asc(A) = vec(A^T)$ if A is a matrix. Using the relation $(ABC)^T = (C^T B^T A^T)$, eq 7 can be rewritten as follows.

$$\begin{aligned}
\vec{M} &= \text{vec}(M^T) = \text{vec}[(A^{-1})^T (\chi_J^{(1)*} \otimes \chi_J^{(1)})^T A^T] \\
&= [(A^T)^T \otimes (A^{-1})^T] \cdot \text{vec}[(\chi_J^{(1)*} \otimes \chi_J^{(1)})^T] \\
&= [A \otimes (A^{-1})^T] \cdot \text{asc}(\chi_J^{(1)*} \otimes \chi_J^{(1)}) \quad (36)
\end{aligned}$$

Vectorization of Mueller and Jones Tensors—By analogy with the linear case in eq 148, the expressions in eq 12 can be written as follows using the identity relations in eq 92.

$$\begin{aligned}
\vec{M} &= \text{asc}(M^{(2)}) = \text{asc}[A \cdot (\chi_J^{(2)*} \otimes \chi_J^{(2)}) : A^{-1} A^{-1}] \\
&= [A \otimes (A^{-1})^T \otimes (A^{-1})^T] \cdot \text{asc}(\chi_J^{(2)*} \otimes \chi_J^{(2)}) \quad (37)
\end{aligned}$$

In both the linear and nonlinear cases described in Appendix IV, the vectorized Mueller tensor can be described in terms of the individual vectorized Jones tensors through introduction of an elementary matrix E , such that $\text{asc}(\chi_J^{(2)*} \otimes \chi_J^{(2)}) = E \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J)$. While the change in ordering associated with the matrix E is not a fundamental necessity and is a tedious additional step, reordering the indices into the $\vec{\chi}_J^* \otimes \vec{\chi}_J$ form has two key practical advantages: (i) the location of any particular combination of Jones tensor elements can be easily identified by simple binary counting as described in Appendix IV, and (ii) expressions connecting the $\vec{\chi}_J^* \otimes \vec{\chi}_J$ ordering to laboratory-frame observables for several different experimental designs are already well-established.^{19,46,47} Substitution leads to the following concise expression connecting the Jones and Mueller tensors for rank three nonlinear optical processes.

$$\vec{M} = [A \otimes (A^{-1})^T \otimes (A^{-1})^T] \cdot E \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \quad (38)$$

II.F. Symmetry Reduction of the Local Frame Mueller Tensor: SHG and TPEF

The effective number of free parameters required to construct the Mueller tensor is generally significantly less than the total number of 64 possible in the most general case of sum-frequency generation from a source of low symmetry. In the case of SHG and TPEF, the degeneracy of the incident frequency reduces the number of unique elements within the Mueller tensor by almost half to 40. In addition, symmetry within the local frame has the potential to reduce the number of elements yet further. Indeed, symmetry reduction of the Mueller tensor in the local frame arguably represents one of the key advantages of coordinate transformation operation described in the preceding section.

The application of local symmetry follows closely that of coordinate transformation detailed in Appendix V and will be illustrated by a mirror-plane reflection about the horizontal axis. In both the Jones and Mueller descriptions, polarizations are all defined in two spatial dimensions, such that symmetry operations are as well. Even if the local electric fields in the region adjacent to the focal volume exhibit components in all three spatial dimensions, the

far-field polarization-dependent observables are still defined for detection of plane wave light in a two-dimensional polarization space. In the Jones reference frame, the reflection operation is described by the following matrix.

$$\vec{e}' = \sigma_H \cdot \vec{e} ; \sigma_H = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \quad (39)$$

As illustrated in Appendix V, the corresponding symmetry operation for the Stokes vector is given by the following relationship.

$$\Sigma_H = A(\sigma_H^* \otimes \sigma_H)A^{-1} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \quad (40)$$

Application of this symmetry operation on the Mueller tensor is performed using the following two expressions, in tensor and vector notations, respectively.

$$M^{(2)'} = \Sigma_H \cdot M^{(2)} : \Sigma_H^{-1} \Sigma_H^{-1} \quad (41)$$

$$\vec{M}' = [\Sigma_H \otimes (\Sigma_H^{-1})^T \otimes (\Sigma_H^{-1})^T] \cdot \vec{M} \quad (42)$$

In the present case, both the transpose and the inverse leave Σ_H unchanged, but the operators are still included in eq 42 to illustrate the process for alternative symmetries.

Worked Example: Local Uniaxial Symmetry—Both SHG and TPEF microscopy have found widespread use in the imaging of biological fibers and cell membranes, both of which routinely exhibit local uniaxial symmetry. Before we can fully take advantage of this local symmetry for simplification of the Mueller tensor, we find ourselves in a similar ill-posed problem as faced in the initial discussion of coordinate system transformation; the Mueller and Jones reference frames are inherently defined in 2D, while the local object exists in 3D. Two routes will be taken. First, symmetry will be applied very generally to the Mueller tensor, which contains both pure and partially depolarized contributions. Second, a complementary bottom-up approach will cast the purely polarized component of the local-frame Mueller tensor in terms of the symmetry-allowed elements in the Cartesian and Jones tensors.

Model-Independent Symmetry Reduction of the Mueller Tensor—Irrespective of the detailed molecular interactions of the uniaxial SHG-active source, the 2D projection in the object plane of a uniaxial, achiral assembly will exhibit mirror-plane symmetry about the

axis of projection, defined to be the H'_l -axis (illustrated in Figure 2). As such, the simplifications described in eq 42 can be used to determine the remaining symmetry-allowed elements in the local-frame Mueller tensor for both SHG and TPEF that is independent of any particular model for the linear and nonlinear optical interactions.

The matrix in brackets in eq 42 directly identifies the tensor elements that survive the mirror-plane symmetry operation. From the 64 initial elements within the Mueller tensor, half become zero-valued in the presence of mirror-plane symmetry. The remaining set of 32 elements is summarized below, using a numbering system in which only the set of three indices is written to indicate the corresponding Mueller tensor element (e.g., 123 corresponds to M_{123}).

$$\begin{pmatrix} 000 & 100 & 202 & 302 \\ 001 & 101 & 203 & 303 \\ 010 & 110 & 212 & 312 \\ 011 & 111 & 213 & 313 \\ 022 & 122 & 220 & 320 \\ 023 & 123 & 221 & 321 \\ 032 & 132 & 230 & 330 \\ 033 & 133 & 231 & 331 \end{pmatrix} \quad (43)$$

If these nonzero elements are combined with the equalities from interchangeability of the right-most two indices for SHG and TPEF with a single incident beam, the number of unique nonzero elements in the Mueller tensor is reduced to 20.

$$\begin{pmatrix} 000 & 100 & 202 = 220 & 302 = 320 \\ 001 = 010 & 101 = 110 & 203 = 230 & 303 = 330 \\ 011 & 111 & 212 = 221 & 312 = 321 \\ 022 & 122 & 213 = 231 & 313 = 331 \\ 023 = 032 & 123 = 132 & & \\ 033 & 133 & & \end{pmatrix} \quad (44)$$

A symmetry matrix Q_M can be introduced to populate the full suite of 64 elements within $\vec{M}'_l$ from a smaller subset of n unique nonzero values within the unprimed version $\vec{M}_l$.

$$\vec{M}'_l = Q_M \cdot \vec{M}_l \quad (45)$$

In the present case, $n = 20$ and Q_M is a sparse 64×20 matrix containing only 1's and 0's that expands the size of all things to the right of Q_M from the 20 that are unique and nonzero to the full set of 64 possible elements. By analogy with the case of the symmetry matrices for Jones tensors based on binary counting in Appendix IV, the decimal nonzero entries in Q_M can be generated by base-four counting.

The local-frame vectorized tensor $\vec{M}_l'$ can be subsequently connected back to the laboratory frame Mueller tensor through coordinate rotation, as described in section II.C. The rotation operation in eq 34 in vectorized form is given by analogy with eq 37.

$$\begin{aligned}\vec{M}_L &= (\mathcal{R}_\phi \otimes \mathcal{R}_\phi \otimes \mathcal{R}_\phi) \cdot \vec{M}_l' \\ &= (\mathcal{R}_\phi \otimes \mathcal{R}_\phi \otimes \mathcal{R}_\phi) \cdot Q_M \cdot \vec{M}_l\end{aligned}\quad (46)$$

Using eq 46, the full set of 64 elements in the laboratory-frame Mueller tensor can be linked back to the much smaller set of symmetry-allowed Mueller tensor elements in the local frame (in this case, 20), provided the orientation angle ϕ is either known or can be independently deduced from the measurements.

II.G. Connection to Molecular Properties: SHG

Even greater simplification of just the purely polarized component can be obtained in SHG from a bottom-up consideration of the local-frame Cartesian tensor, projected into the object plane. Consistent with the previous section and illustrated in Figure 2, the following discussion will be limited to structures exhibiting local uniaxial symmetry. In the limit of gentle focusing, such that the laboratory Z -component of the local electric fields within the object plane can be considered negligible, only the projection of the uniaxial object onto the (H, V) plane is experimentally accessible. In Cartesian coordinates, an object with local C_∞ symmetry (i.e., the Z -axis) will generally exhibit 12 nonzero tensor elements, four of which are unique: χ_{ZZZ} , $\chi_{ZXX} = \chi_{ZYY}$, $\chi_{XXZ} = \chi_{XZX} = \chi_{YYZ} = \chi_{YZY}$, and $\chi_{XYZ} = \chi_{XZY} = -\chi_{YZX} = -\chi_{ZYX}$. Now, let us consider the projection onto the (H, V) object plane. If the in-plane $\vec{H}_l'$ axis is defined to lie coparallel with the projection of the C_∞ symmetry axis (as illustrated in Figure 2), the projection will contain four total and three unique 2D symmetry-allowed tensor elements in the local (H', V') frame: $\chi_{H'H'H'}$, $\chi_{H'V'V'}$, and $\chi_{V'V'H'} = \chi_{V'H'V'}$, with the other four possible arrangements of H' and V' indices forbidden by symmetry.

$$\begin{bmatrix} \chi_{H'H'H'} \\ \chi_{H'H'V'} \\ \chi_{H'V'H'} \\ \chi_{H'V'V'} \\ \chi_{V'H'H'} \\ \chi_{V'H'V'} \\ \chi_{V'V'H'} \\ \chi_{V'V'V'} \end{bmatrix}' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \chi_{H'H'H'} \\ \chi_{H'V'V'} \\ \chi_{V'H'V'} \end{bmatrix} = Q_J \cdot \vec{\chi}_l \quad (47)$$

The vector $\vec{\chi}_l$ contains the unique set of three local-frame Jones tensor elements allowed by symmetry. The nonzero elements of the corresponding purely polarized component of the full 64-element Mueller tensor in the same local frame can be generated from substitution using eq 38.

$$\begin{aligned} \vec{M}_l &= [A \otimes (A^{-1})^T \otimes (A^{-1})^T] \cdot E \cdot [(Q_J \cdot \vec{\chi}_l) * \otimes (Q_J \cdot \vec{\chi}_l)] \\ &= [A \otimes (A^{-1})^T \otimes (A^{-1})^T] \cdot E \cdot (Q_J \otimes Q_J) \cdot (\vec{\chi}_l^* \otimes \vec{\chi}_l) \quad (48) \end{aligned}$$

Coordinate rotation by ϕ to connect the laboratory-frame Mueller tensor to the nine unique products of the local-frame Jones tensor is accomplished through eq 46.

$$\vec{M}_L = (\mathcal{R}_\phi \otimes \mathcal{R}_\phi \otimes \mathcal{R}_\phi) \cdot \vec{M}_l' \quad (49)$$

Using the expression in eq 49, the purely polarized component of the 64-element laboratory-frame Mueller tensor for any azimuthal orientation angle ϕ is unambiguously dependent on only three parameters for locally uniaxial assemblies: $\chi_{H'H'H'}$, $\chi_{H'V'V'}$, and $\chi_{V'V'H'} = \chi_{V'H'V'}$. Furthermore, analogous simplifications for structures of arbitrary symmetry can be directly determined using the framework described herein.

When we were considering in-plane orientations of the local-frame object, we had the luxury of only needing a 2×2 rotation matrix to bridge the local and laboratory frames, such that the local-frame Jones tensor could be described by a $2 \times 2 \times 2$ tensor $\vec{\chi}_l'$. Alas, our foray into the molecular frame will require expansion into the third dimension. In this case, $\vec{\chi}_{c,l}'$ includes all 27 elements present in a Cartesian coordinate system defined relative to the local frame.

In the case of coherent SHG in the limit of identical, uncoupled oscillators, all molecules within the source coherently contribute to the net electric field produced in the propagating beam immediately produced within the focal plane.

$$\overset{\rightarrow}{\chi}_{C,l}^{2\omega'} = N_b \cdot (L^{2\omega} \otimes L^\omega \otimes L^\omega) \cdot \langle R \otimes R \otimes R \rangle_{\theta\psi\phi} \cdot \overset{\rightarrow}{\beta}^{2\omega'} \quad (50)$$

In this equation, N_b is the bulk number density of chromophores contributing to the coherent SHG signal, each L is a 3×3 matrix of local-field correction factors accounting for the local dielectric environment,⁵⁸ the factor $\langle R \otimes R \otimes R \rangle_{\theta\psi\phi}$ is a Kronecker product of three Euler

rotation matrices dependent on the Euler angles θ , ψ , and ϕ , and $\overset{\rightarrow}{\beta}^{2\omega'}$ is the molecular hyperpolarizability tensor, in ascending vectorized form. We will neglect the local-field correction factors for the moment, and reinsert them in the final expression. Since the purely polarized component of the Mueller tensor ultimately scales with the Kronecker product of local-frame Jones tensor elements, that product can be regrouped as follows.

$$\begin{aligned} (\overset{\rightarrow}{\chi}_{C,l}^{2\omega*} \otimes \overset{\rightarrow}{\chi}_{C,l}^{2\omega})' &= N_b^2 \cdot (\langle R \otimes R \otimes R \rangle_{\theta\psi\phi} \cdot \overset{\rightarrow}{\beta}^{2\omega'})^* \\ &\quad \otimes (\langle R \otimes R \otimes R \rangle_{\theta\psi\phi} \cdot \overset{\rightarrow}{\beta}^{2\omega'}) \\ &= N_b^2 \cdot (\langle R \otimes R \otimes R \rangle_{\theta\psi\phi} \otimes \langle R \otimes R \otimes R \rangle_{\theta\psi\phi}) \cdot \\ &\quad (\overset{\rightarrow}{\beta}^{2\omega*} \otimes \overset{\rightarrow}{\beta}^{2\omega'}) \\ &= N_b^2 \cdot (\langle R \otimes R \otimes R \rangle_{\theta\psi\phi} \otimes \langle R \otimes R \otimes R \rangle_{\theta\psi\phi}) \cdot \\ &\quad (S \otimes S) \cdot (\overset{\rightarrow}{\beta}^{2\omega*} \otimes \overset{\rightarrow}{\beta}^{2\omega}) \end{aligned} \quad (51)$$

The symmetry matrix S serves an analogous role as the symmetry matrix Q in eqs 47 and 45, connecting the full set of 27 tensor elements to a smaller subset of unique, nonzero

symmetry-allowed values within the molecular tensor $\overset{\rightarrow}{\beta}^{2\omega}$ (unprimed to indicate the reduced subset). Using a shorthand notation for many of the Kronecker products, the final expression can be written in the following form, in which the matrix $\mathbf{L} \equiv (L^{2\omega*} \otimes L^{\omega*} \otimes L^{\omega*} \otimes L^{2\omega} \otimes L^\omega \otimes L^\omega)$ has been reintroduced.

$$(\overset{\rightarrow}{\chi}_l^{2\omega*} \otimes \overset{\rightarrow}{\chi}_l^{2\omega})' = N_b^2 \cdot \mathbf{L} \cdot \langle \mathbf{R} \rangle_{\theta\psi\phi} \cdot \mathbf{S} \cdot (\overset{\rightarrow}{\beta}^{2\omega*} \otimes \overset{\rightarrow}{\beta}^{2\omega}) \quad (52)$$

Nevertheless, we still have a dimensionality problem. The local-frame tensor $\overset{\rightarrow}{\chi}_{C,l}^{2\omega'}$ defined in eq 52 contains $3^3 = 27$ elements in a Cartesian frame, but $\overset{\rightarrow}{\chi}_J^{2\omega'}$ contains just $2^3 = 8$ in the Jones/Mueller frame. The connection between the Cartesian local frame and the Jones laboratory frame is made by removing the polarization component paralleling the Poynting vector of the incident and detected light.

If it is assumed that the unique Cartesian z -axis lies within the plane and coparallel with the local frame $\vec{H}_l$ -axis, this dimension reduction operation can be done by introduction of another matrix $\mathbf{J}$, which serves to remove the component of the field along the propagation

direction of the beam, which does not contribute to the Jones or Mueller observables. In the reference frame described, the local-frame Cartesian z -axis lies parallel to the local-frame $\vec{H}_l'$ -axis and the Cartesian y -axis coparallel with the $\vec{V}_l'$ -axis.⁴⁹ The corresponding expression for the local-frame Mueller tensor is given by the following.

$$\vec{M}_l' = N_b^{-2} \cdot [A \otimes (A^{-1})^T \otimes (A^{-1})^T] \cdot \mathbf{J} \cdot \mathbf{L} \cdot \langle \mathbf{R} \rangle_{\theta\psi\phi} \cdot \mathbf{S} \cdot \begin{pmatrix} \vec{2\omega^*} & \vec{2\omega} \\ \beta & \beta \end{pmatrix} \quad (53)$$

$$\mathbf{J} = \left(\begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \right. \\ \left. \otimes \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \right) \quad (54)$$

From eq 53, the vectorized form for the laboratory frame Mueller tensor can be easily generated through multiplication by $(\mathcal{R}_\phi \otimes \mathcal{R}_\phi \otimes \mathcal{R}_\phi)$, as demonstrated in eq 49.

II.H. Connection to Molecular Properties: TPEF

The treatment for TPEF shares many similarities with SHG but differs in three key respects: (i) the molecular-frame properties driving the detected intensity, (ii) the orientational averages connecting the molecular and ensemble responses, and (iii) the presence of a partially depolarized component even in the absence of optical scattering. Of course, all three of these differences are intimately intertwined. Because the TPEF is an incoherent, stochastic process, the fields from different sources are random in phase and time and do not coherently interfere. As such, the detected light is only partially polarized. Similarly, the incoherent nature of the detected signal significantly affects the orientational averages, and correspondingly the dependence of TPEF on local symmetry.

To aid in drawing parallels between the treatments in SHG and TPEF, the process of fluorescence will be described using notation as similar to that used for SHG as possible. If it is assumed that the TPEF fluorophores undergo internal dynamics and reorientation over time scales that are slow relative to the fluorescence lifetime, the transition moment is fixed relative to the matrix describing two-photon absorption. In this limit, the mathematical expressions describing SHG can be easily adapted to include TPEF through the introduction of an effective hyperpolarizability tensor $(\beta^{(2)})_{\text{eff}}^{\text{TPEF}}$, which will subsequently be defined in terms of the tensor for two-photon absorption and the transition moment for emission. In the case of TPEF, the orientation averages are evaluated over the full 6-fold Kronecker product prior to evaluation.

$$\begin{aligned}
 & (\overset{\rightarrow}{\chi}_l^{\text{TPEF}*} \otimes \overset{\rightarrow}{\chi}_l^{\text{TPEF}})' = N_b \cdot \\
 & \langle (R \otimes R \otimes R \cdot \overset{\rightarrow}{\beta}_{\text{eff}}^{\text{TPEF}'}) * \otimes (R \otimes R \otimes R \cdot \overset{\rightarrow}{\beta}_{\text{eff}}^{\text{TPEF}'}) \rangle_{\theta\psi\phi} \\
 & = N_b \cdot \langle R \otimes R \otimes R \otimes R \otimes R \otimes R \rangle_{\theta\psi\phi} \\
 & \quad (\overset{\rightarrow}{\beta}_{\text{eff}}^{\text{TPEF}*'} \otimes \overset{\rightarrow}{\beta}_{\text{eff}}^{\text{TPEF}'})
 \end{aligned} \tag{55}$$

In eq 55, both $\overset{\rightarrow}{\chi}_l^{\text{TPEF}}$ and $\overset{\rightarrow}{\beta}_{\text{eff}}^{\text{TPEF}'}$, are used as placeholders to help clarify the connections between SHG and TPEF, and are not meant to represent genuine nonlinear susceptibilities or hyperpolarizabilities in the formal sense. The 27-element effective molecular hyperpolarizability is related to the 3-element transition moment for fluorescence emission and the 9-element matrix describing two-photon absorption through the relationship below, which bears clear analogies to expressions for the molecular hyperpolarizability describing SHG.⁵⁹

$$\beta_{\text{eff}}^{\text{TPEF}}(-\omega^f; \omega, \omega) \cong \text{Im} \left[\frac{-1}{\hbar} \frac{\mu_{fm}^f \otimes \alpha_{n0}^{\text{TPA}}}{(\omega_n - 2\omega - i\Gamma_n)} \right] \tag{56}$$

The terms $\overset{\rightarrow}{\mu}^f$ and $\overset{\rightarrow}{\alpha}^{\text{TPA}}$ refer to the 3-element fluorescence emission transition moment and the 9-element matrix for two-photon absorption (TPA), respectively, expressed within the molecular frame coordinate system. If $S_n^{2\omega}$ is defined to be the line shape function for two-photon resonance enhancement to state n , the effective “susceptibility” describing the polarization dependence of TPEF can be cast solely in terms of $\overset{\rightarrow}{\mu}^f$ and $\overset{\rightarrow}{\alpha}^{\text{TPA}}$.

$$\begin{aligned}
 & (\overset{\rightarrow}{\chi}_l^{\text{TPEF}*} \otimes \overset{\rightarrow}{\chi}_l^{\text{TPEF}})' \\
 & = (N_b \cdot S_n^{2\omega}) \cdot \langle R \otimes R \otimes R \otimes R \otimes R \otimes R \rangle_{\theta\psi\phi} \cdot \\
 & \quad (\overset{\rightarrow}{\mu}^{f*} \otimes \overset{\rightarrow}{\alpha}^{\text{TPA}*} \otimes \overset{\rightarrow}{\mu}^{f*} \otimes \overset{\rightarrow}{\alpha}^{\text{TPA}})'
 \end{aligned} \tag{57}$$

In the presence of symmetry, or when using coordinates defined on the basis of the transition moment and/or the principal moments of the TPA matrix, a significantly smaller subset of elements are nonzero within the right-most Kronecker product of eq 55. By analogy with eq 52, a shorthand notation has been used to represent the local-field correction factor matrix **L**, the rotation matrix **R**, and the symmetry matrix **S**. Furthermore, only the nonzero elements are included in the new (unprimed) definitions for $\overset{\rightarrow}{\mu}^f$ and $\overset{\rightarrow}{\alpha}^{\text{TPA}}$.

$$\begin{aligned}
 & (\overset{\rightarrow}{\chi}_l^{\text{TPEF}*} \otimes \overset{\rightarrow}{\chi}_l^{\text{TPEF}})' \\
 & = (N_b \cdot S_n^{2\omega}) \cdot \mathbf{L} \cdot \langle \mathbf{R} \rangle_{\theta\psi\phi} \cdot \mathbf{S} \cdot (\overset{\rightarrow}{\mu}^{f*} \otimes \overset{\rightarrow}{\alpha}^{\text{TPA}*} \otimes \overset{\rightarrow}{\mu}^f \otimes \overset{\rightarrow}{\alpha}^{\text{TPA}})
 \end{aligned} \tag{58}$$

The expressions for the local-frame tensors can now be connected all the way back to the experimental observables by analogy with eq 53 for $(\overset{\rightarrow}{\chi}_l^{2\omega*} \otimes \overset{\rightarrow}{\chi}_l^{2\omega})'$.

$$\vec{M}_l = (N_b \cdot S_n^{2\omega}) \cdot [A \otimes (A^{-1})^T \otimes (A^{-1})^T] \cdot \mathbf{J} \cdot \mathbf{L} \cdot \langle \mathbf{R} \rangle_{\theta\psi\phi} \cdot \mathbf{S} \cdot (\overset{\rightarrow}{\mu}^{f*} \otimes \overset{\rightarrow}{\alpha}^{\text{TPA}*} \otimes \overset{\rightarrow}{\mu}^f \otimes \overset{\rightarrow}{\alpha}^{\text{TPA}}) \quad (59)$$

The two key differences between eqs 53 and 59 are in the molecular properties driving the interaction within the rightmost parenthetical, and the definition of $\langle \mathbf{R} \rangle_{\theta\psi\phi}$. In TPEF, $\langle \mathbf{R} \rangle_{\theta\psi\phi} = \langle R \otimes R \otimes R \otimes R \otimes R \otimes R \rangle_{\theta\psi\phi}$ corresponding to incoherent light generation averaged over 6-fold Kronecker products of rotation matrices, while, in SHG, $\langle \mathbf{R} \rangle_{\theta\psi\phi} = \langle R \otimes R \otimes R \rangle_{\theta\psi\phi} \otimes \langle R \otimes R \otimes R \rangle_{\theta\psi\phi}$, with the orientational averaging arising over 3-fold Kronecker products. That difference between the even and odd number of Kronecker products underpins the different symmetry dependencies of the measurements.

Modeling Depolarization Effects in TPEF—By expressing depolarization effects for section II.C in terms of Mueller matrices, the expressions derived for SHG are also directly applicable without modification for describing TPEF, in which the initial source contains a partially depolarized component even in the absence of scattering. As such, eqs 24 and 29 are equally valid for both SHG and TPEF. However, the equality for the degree of polarization given in eq 27 will no longer hold, as it was derived assuming that the degree of polarization for the source was unity for SHG.

II.I. Polarization Dependent Intensities for SHG and TPEF

The General Case: Mueller Tensor—The total number of methods available for polarization analysis are almost as varied as the number of investigators making such measurements. A detailed description of the observables accessible in SHG and TPEF microscopy measurements under the most common measurement configurations has been discussed previously.⁶⁰ Arguably, the most common polarization-dependent SHG microscopy measurements are acquired with purely polarized inputs and outputs (e.g., horizontally and/or vertically polarized detection for horizontally and/or vertically polarized incident light). This collective set of measurements can be generally described by a more general instrumental design, in which the intensity of n-polarized SHG or TPEF is measured in a single-beam experiment as a function of the incident polarization rotation angle γ for a linearly polarized input (Figure 3). If a half-wave plate is used for polarization rotation, γ corresponds to twice the rotation angle of the wave plate. The Jones vector for the electric field of the fundamental beam is given by the following.

$$\vec{e}^{\omega} = \begin{bmatrix} \cos\gamma \\ \sin\gamma \end{bmatrix} \quad (60)$$

The SHG and/or TPEF intensity scales with the square of the incident intensity, or quartically with the field described in eq 60.⁶¹ As a result, combinations ranging from $\cos^4$

γ through $\sin^4 \gamma$ will generally contribute to the detected SHG and/or TPEF, such that the measured n-polarized intensity as a function of the polarization rotation angle γ results in five unique observables, corresponding to the five quartic combinations of field components.

$$I_n^{2\omega} = A_n \cos^4 \gamma + B_n \cos^3 \gamma \sin \gamma + C_n \cos^2 \gamma \sin^2 \gamma + D_n \cos \gamma \sin^3 \gamma + E_n \sin^4 \gamma \quad (61)$$

In eq 61, the intensity of horizontally polarized SHG for a horizontally polarized input is given by A_H , horizontally polarized detection for vertically polarized input by E_H , vertically polarized detection for horizontally polarized input by A_V , and vertically polarized detection with vertically polarized incident light by E_V . For phase modulation, in which the polarization state of the incident light is phase-shifted to cycle between circular, linear, and elliptical polarizations (e.g., using a photoelastic or electro-optic modulator), an analogous expression emerges as a function of the phase shift δ .⁶¹

$$I_n^{2\omega} = A_n \cos^4 \left(\frac{\Delta}{2} \right) + B_n \cos^3 \left(\frac{\Delta}{2} \right) \sin \left(\frac{\Delta}{2} \right) + C_n \cos^2 \left(\frac{\Delta}{2} \right) \sin^2 \left(\frac{\Delta}{2} \right) + D_n \cos \left(\frac{\Delta}{2} \right) \sin^3 \left(\frac{\Delta}{2} \right) + E_n \sin^4 \left(\frac{\Delta}{2} \right) \quad (62)$$

In each case, the set of polynomial coefficients $\vec{A}$ can be connected to a corresponding set of Fourier coefficients $\vec{a}$ by taking advantage of trigonometric identities for quadratic and quartic functions [e.g., $2 \cos^2 x = 1 + \cos(2x)$]. As detailed previously,⁴⁹ a conversion matrix F (and vice versa using F^{-1}) facilitates interconversion between a set of Fourier and polynomial coefficients.

$$I_n^{2\omega}(\gamma) \propto a + b \cos(4\gamma) + c \cos(2\gamma) + d \sin(2\gamma) + e \sin(4\gamma) \quad (63)$$

$$I_n^{2\omega}(\Delta) \propto a + b \cos(2\Delta) + c \cos(\Delta) + d \sin(\Delta) + e \sin(2\Delta) \quad (64)$$

$$\begin{bmatrix} a \\ b \\ c \\ d \\ e \end{bmatrix}_n = \frac{1}{8} \begin{bmatrix} 3 & 0 & 1 & 0 & 3 \\ 1 & 0 & -1 & 0 & 1 \\ 4 & 0 & 0 & 0 & -4 \\ 0 & 2 & 0 & 2 & 0 \\ 0 & 1 & 0 & -1 & 0 \end{bmatrix} \cdot \begin{bmatrix} A \\ B \\ C \\ D \\ E \end{bmatrix} = F \cdot \vec{A}_n \quad (65)$$

In the limit of pure incident polarizations, these observables are related to the corresponding Jones tensor elements. For polarization rotation measurements, the set of coefficients is connected back to the Jones tensor through the following expression.

$$\begin{aligned} A_n &= |\chi_{nHH}|^2 \\ B_n &= 4\text{Re}[(\chi_{nHH}^*)(\chi_{nVH})] \\ C_n &= 4|\chi_{nVH}|^2 + \text{Re}[(\chi_{nHH}^*)(\chi_{nVV})] \\ D_n &= 4\text{Re}[(\chi_{nVV}^*)(\chi_{nVH})] \\ E_n &= |\chi_{nVV}|^2 \end{aligned} \quad (66)$$

It is important to note that the expressions in eq 66 hold both for SHG and TPEF. In the case of TPEF, the orientational averages corresponding to the “susceptibility” products are analogous to those given by eq 57. For phase modulation, a different set of equalities emerges.

$$\begin{aligned} A_n &= |\chi_{nHH}|^2 \\ B_n &= -4\text{Im}[(\chi_{nHH}^*)(\chi_{nVH})] \\ C_n &= 4|\chi_{nVH}|^2 - 2\text{Re}[(\chi_{nHH}^*)(\chi_{nVV})] \\ D_n &= 4\text{Im}[(\chi_{nVV}^*)(\chi_{nVH})] \\ E_n &= |\chi_{nVV}|^2 \end{aligned} \quad (67)$$

In each case, these 10 simultaneously accessible observables (five for each polarization) can be stacked to form a 10-element vector $\vec{A}_{\text{obs}}$ connected back to the 64-element Jones tensor product through the 10×64 element sparse matrix P (only 32 elements of which are nonzero), defined explicitly in Appendix III for polarization rotation measurements. In brief, P includes the equalities described analytically by the expressions in eq 66.

$$\vec{A}_{\text{obs}} = \begin{bmatrix} A_H \\ B_H \\ \vdots \\ E_V \end{bmatrix} = P \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \quad (68)$$

The above expression can be related directly back to the laboratory-frame Mueller tensor by inversion of eq 38 and substitution for $(\vec{\chi}_J^* \otimes \vec{\chi}_J)$.

$$\vec{A}_{\text{obs}} = P \cdot E^{-1} \cdot [A^{-1} \otimes A^T \otimes A^T] \cdot \vec{M} \quad (69)$$

The number of symmetry-allowed unique elements in the Mueller tensor can be significantly reduced in the local frame, such that eq 69 can be rewritten in terms of just the subset of unique, symmetry-allowed local-frame Mueller tensor elements using eq 46

$$\vec{A}_{\text{obs}} = P \cdot E^{-1} \cdot [A^{-1} \otimes A^T \otimes A^T] \cdot (\mathcal{R}_\phi \otimes \mathcal{R}_\phi \otimes \mathcal{R}_\phi) \cdot Q_M \cdot \vec{M}_l \quad (70)$$

Again, the expression in eq 70 in terms of the local-frame Mueller tensor is quite general and holds both for SHG and for TPEF. The two measurements differ only in subsequent interpretations.

In the specific case of measurements performed for locally uniaxial assemblies, it was demonstrated that the Mueller tensor contains 20 unique, nonzero elements, while only 10 observables are present within $\vec{A}_{\text{obs}}$ for a given location. As such, the expression in eq 70 cannot in general be inverted in this case to unambiguously determine the local Mueller tensor elements. There are three obvious routes forward: (i) increase the number of locations/pixels used in the analysis and pool the results, (ii) increase the number of polarization states, (iii) reduce the number of free parameters within $\vec{M}_l$. While all three strategies have real merit, the next section will focus on the last of the three, since the first two can vary widely across laboratories depending on the measurement objectives and instrumentation.

Model 1. SHG with Partial Depolarization of Both the Fundamental and Second Harmonic—The local-frame Mueller tensor can be significantly simplified by connecting it back to molecular properties. For model 1, in which only the SHG exhibits significant depolarization following generation, the net laboratory-frame Mueller tensor is given by the following expression.

$$\vec{M}_{\text{net}} = (1 - \alpha) [A \otimes (A^{-1})^T \otimes (A^{-1})^T] \cdot E \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) + \alpha M_{000} \quad (71)$$

Rotation to the local frame and application of symmetry allows the total net local-frame Mueller tensor to be done by two equivalent methods. First, the Mueller tensor can be determined and then rotated, as illustrated in eq 70. However, it turns out to be simpler computationally and equivalent mathematically to rotate the Jones tensor to the laboratory frame rather than the Mueller tensor. An expanded Jones rotation matrix is introduced, $\mathbf{R}_\phi =$

$[R_\phi \otimes R_\phi \otimes R_\phi \otimes R_\phi \otimes R_\phi \otimes R_\phi]$, where R_ϕ is the 2×2 Jones rotation matrix given in eq 152.

$$\begin{aligned} \vec{A}_{\text{obs}}^{2\omega} = & (1 - \alpha) P \cdot \mathbf{R}_\phi \cdot \mathbf{J} \cdot (Q \otimes Q) \cdot (\vec{\chi}_l^* \otimes \vec{\chi}_l) \\ & + \alpha P \cdot E^{-1} \cdot [A^{-1} \otimes A^T \otimes A^T] \cdot \vec{M}_\alpha \end{aligned} \quad (72)$$

Explicit evaluation of the product to the right considering only the M_{000} element in $\vec{M}_\alpha$ leads to the following form

$$\begin{aligned} \vec{A}_{\text{obs}}^{2\omega} = & (1 - \alpha) P \cdot \mathbf{R}_\phi \cdot \mathbf{J} \cdot (Q \otimes Q) \cdot (\vec{\chi}_l^* \otimes \vec{\chi}_l) \\ & + \frac{1}{32} \alpha [3 \ 0 \ 1 \ 0 \ 3 \ 3 \ 0 \ 1 \ 0 \ 3]^T \end{aligned} \quad (73)$$

Alternatively, the observables can be connected instead all the way back to the molecular orientation distribution about the local-frame structure by substitution for the local-frame tensor.

$$\begin{aligned} \vec{A}_{\text{obs}}^{2\omega} = & (1 - \alpha) N_b^2 \cdot P \cdot \mathbf{R}_\phi \cdot \mathbf{J} \cdot \mathbf{L} \cdot \langle \mathbf{R} \rangle_{\theta\psi\phi} \cdot \mathbf{S} \cdot (\vec{\beta}^{2\omega*} \otimes \vec{\beta}^{2\omega}) \\ & + \frac{1}{32} \alpha [3 \ 0 \ 1 \ 0 \ 3 \ 3 \ 0 \ 1 \ 0 \ 3]^T \end{aligned} \quad (74)$$

Using eqs 73 and 74, the unique elements in the local-frame Jones tensor $\vec{\chi}_l$ or the molecular frame $\vec{\beta}^{2\omega}$ tensor can be connected back to the experimental observables through the azimuthal orientation angle ϕ and the molecular orientation distribution about the local uniaxial axis given by $\langle \mathbf{R} \rangle_{\theta\psi\phi}$.

The parameter α in eq 74 can be obtained either from independent measurements of sample turbidity or from the degree of polarization measurements described in eq 27.

Model 2. SHG with Partial Depolarization of Only the Second Harmonic—In this limit, the process can be viewed as the stepwise production of a purely polarized Jones vector describing the SHG produced immediately at the sample, followed by partial depolarization upon propagation to the detector. This model is consistent with a mechanism in which only the “ballistic” nondepolarized light surviving to the focal plane contributes to the detected SHG production. In the limit of complete depolarization of the doubled light, both the horizontally and vertically polarized detectors will access equal intensities of SHG. The 10-element vector $\vec{A}_{\text{obs}}^{2\omega}$ can be broken up into two five-element vectors, as described by eq 67 or 66, with the limit of depolarization of the output resulting in $\vec{A}_H^{\text{det}} = \vec{A}_V^{\text{det}}$ (or equivalently, any orthogonal set of accessible polarizations). If we define $\vec{A}_H^{\text{det}}$ and $\vec{A}_V^{\text{det}}$ to be the set of polynomial coefficients generated immediately within the focal plane, a linear

scaling factor of α can again be used to indicate the detected fraction α of depolarized SHG relative to the fraction $(1 - \alpha)$ of purely polarized detected light.

$$\begin{aligned} \vec{A}_{\text{obs}}^{\text{det}} &= \begin{bmatrix} \vec{A}_H^{\text{det}} \\ \vec{A}_V^{\text{det}} \end{bmatrix} = (1 - \alpha) \begin{bmatrix} \vec{A}_H^0 \\ \vec{A}_V^0 \end{bmatrix} + \frac{\alpha}{2} \left(\begin{bmatrix} \vec{A}_H^0 \\ \vec{A}_V^0 \end{bmatrix} + \begin{bmatrix} \vec{A}_Y^0 \\ \vec{A}_H^0 \end{bmatrix} \right) \\ &= \begin{bmatrix} (1 - \frac{\alpha}{2}) & \frac{\alpha}{2} \\ \frac{\alpha}{2} & (1 - \frac{\alpha}{2}) \end{bmatrix} \begin{bmatrix} \vec{A}_H^0 \\ \vec{A}_V^0 \end{bmatrix} = \left(\begin{bmatrix} (1 - \frac{\alpha}{2}) & \frac{\alpha}{2} \\ \frac{\alpha}{2} & (1 - \frac{\alpha}{2}) \end{bmatrix} \otimes I_5 \right) \vec{A}_{\text{obs}}^0 \end{aligned} \quad (75)$$

The Kronecker product with the 5×5 identity matrix I_5 expands the 2×2 to match the dimensions of $\vec{A}_{\text{obs}}^0$. Substitution for the purely polarized components in the $\vec{A}_H^0$ and $\vec{A}_V^0$ yield the following expression connecting the observables to the local-frame Jones tensors for the purely polarized signals.

$$\vec{A}_{\text{obs}}^{\text{det}} = \left(\begin{bmatrix} (1 - \frac{\alpha}{2}) & \frac{\alpha}{2} \\ \frac{\alpha}{2} & (1 - \frac{\alpha}{2}) \end{bmatrix} \otimes I_5 \right) \cdot P \cdot \mathbf{R}_\phi \cdot \mathbf{J} \cdot (Q \otimes Q) \cdot (\vec{\chi}_l^* \otimes \vec{\chi}_l) \quad (76)$$

In turn, the observables can be connected back to the symmetry-allowed elements in the molecular frame.

$$\vec{A}_{\text{obs}}^{\text{det}} = N_b^2 \cdot \left(\begin{bmatrix} (1 - \frac{\alpha}{2}) & \frac{\alpha}{2} \\ \frac{\alpha}{2} & (1 - \frac{\alpha}{2}) \end{bmatrix} \otimes I_5 \right) \cdot P \cdot \mathbf{R}_\phi \cdot \mathbf{J} \cdot \mathbf{L} \cdot \langle \mathbf{R} \rangle_{\theta\psi\phi} \cdot \mathbf{S} \cdot \begin{pmatrix} \vec{\beta}^{2\omega*} & \vec{\beta}^{2\omega} \end{pmatrix} \quad (77)$$

If α can be determined independently, the expressions in eqs 75 and 77 can be used directly to relate the set of observables back to the local structure and orientation of the SHG-active source. In the case of SHG, the DoP provides a convenient route to recover α directly from the SHG measurements themselves, as has been demonstrated nicely by Barzda and co-workers.⁴¹ Alternatively, independent measurements of turbidity can potentially be used to recover or estimate α . Finally, α can potentially serve as another free parameter in a multiparameter fit of the measured polarization dependence. In this manner, the impact of depolarization can be directly integrated with the rest of the polarization analysis, provided covariance between the different parameters is sufficiently small to enable determination of each parameter.

Model 1. TPEF with Partial Depolarization of Both the Excitation and

Fluorescent Light—In the case of TPEF, the general expression is virtually identical to that for SHG in eq 74.

$$A_{\text{obs}}^{\rightarrow 2\omega} = (1 - \alpha)(N_b \cdot S_n^{2\omega}) \cdot P \cdot \mathbf{R}_\phi \cdot \mathbf{J} \cdot \mathbf{L} \cdot \langle \mathbf{R} \rangle_{\theta\psi\phi} \cdot \mathbf{S} \cdot \left(\begin{matrix} \mu^{\rightarrow f*} & \alpha^{\rightarrow \text{TPA}*} \\ \mu^{\rightarrow f} & \alpha^{\rightarrow \text{TPA}} \end{matrix} \right) + \frac{1}{32}\alpha[3 \ 0 \ 1 \ 0 \ 3 \ 3 \ 0 \ 1 \ 0 \ 3]^T \quad (78)$$

The major differences between the expression in eq 78 relative to the analogous one in eq 74 for SHG are the following: (i) the term $\langle \mathbf{R} \rangle_{\theta\psi\phi}$ is performed over 6-fold products of rotation matrices in TPEF, (ii) the molecular properties are given by the Kronecker products of transition moments and TPA matrices instead of hyperpolarizabilities, (iii) the observable coefficients scale linearly with number density, and (iv) the line shape function is explicitly included in the expression.

Unlike the case of SHG, the degree of polarization does not provide a convenient handle for aiding in disentangling the value of α in TPEF, since the DoP will not be unity even in the absence of scattering. However, α can still be recovered either by independent assessments of turbidity or by integrating α as a free parameter in a multiparameter fit.

Model 2. TPEF with Partial Depolarization of Only the Fluorescence—A similar approach can be taken to describe the set of polarization-dependent coefficients in terms of model 2, in which the only purely polarized “ballistic” component of the incident light contributes to TPEF, with partial depolarization of the fluorescence arising during the propagation from the source to the detector. The expression below describes the set of coefficients expected in a polarization rotation experiment (including pure linear polarizations as a subset).

$$A_{\text{obs}}^{\rightarrow \text{TPEF}} = (N_b \cdot S_n^{2\omega}) \left(\left[\begin{matrix} (1 - \frac{\alpha}{2}) & \frac{\alpha}{2} \\ \frac{\alpha}{2} & (1 - \frac{\alpha}{2}) \end{matrix} \right] \otimes I_5 \right) \cdot P \cdot \mathbf{J} \cdot \mathbf{L} \cdot \langle \mathbf{R} \rangle_{\theta\psi\phi} \cdot \mathbf{S} \cdot \left(\begin{matrix} \mu^{\rightarrow f*} & \alpha^{\rightarrow \text{TPA}*} \\ \mu^{\rightarrow f} & \alpha^{\rightarrow \text{TPA}} \end{matrix} \right) \quad (79)$$

As in the case of model 1, the TPEF expression differs primarily in the evaluation of the orientational averages, in the scaling with number density, and in the molecular-frame interactions driving the detected intensities.

III. DISCUSSION

The linear algebra architecture described in the present work has several notable differences from preceding approaches. In the most well-established alternative formulation by Harris and co-workers,^{39,40} the incident Stokes vectors were combined to produce a nine-element “double-Stokes” vector, which in turn was multiplied by a contracted 4×9 “double Mueller” matrix, loosely analogous to the “piezoelectric contraction” used to simplify SHG measurements. This early work by Harris and co-workers is an elegant bottom-up treatise,^{39,40} providing a thorough development of two-photon processes in the limit of single beam measurements, focusing largely on isotropic assemblies. However, a significant

limitation of the prior approach is the absence of a connection between the Mueller and Jones descriptions. Without that bridge, analytical models for treating optical scattering effects are challenging to construct and partially polarized measurements difficult to interpret. Correspondingly, the physical connections between material properties and the different elements within the Mueller tensor become challenging to intuitively navigate, reducing the benefits of this early Stokes–Mueller treatment. In contrast, the link connecting the Jones and Mueller tensors derived herein and given in eqs 16 and 38 is remarkably simple and intuitive, with clear connections to established analogues in linear optics. Furthermore, the Mueller tensor presented in this manner is easily generalizable to higher order processes and sum-frequency generation incorporating multiple incident beams.

The mathematical framework presented easily allows simplifications arising from symmetry in the local-frame response. In the common case of a real or effective mirror plane within the field of view (e.g., for uniaxial assemblies), the total set of unique nonzero symmetry-allowed elements in the model-independent Mueller tensor is reduced to 20 for both SHG and TPEF. Incorporation of a rotation matrix allows the laboratory-frame observables to be easily connected back to these local-frame tensor elements, significantly reducing the number of parameters required to describe the Mueller tensor. Furthermore, the approach is straightforward to extend to include multiple symmetry operations for the local-frame response. The vectorization approach developed in this work provides a very general route to inversion and recovery of the local-frame tensor irrespective of the local-frame symmetry, which represents a significant advantage over the “double-Mueller” matrix approach originally developed by Shi et al.⁴⁰ Taking advantage of the local-frame symmetry allows substantial reduction in the number of observables required for inversion, which can be easily adapted for any local-frame symmetry through the construction of a symmetry matrix.

The simplicity of the connections between the Mueller and Jones formalisms enabled the development of analytical models to further reduce the number of free parameters required to incorporate the effects of scatter. In brief, effects for partial depolarization of the incident and/or exiting beams were modeled by introducing only a single additional parameter α relative to the Jones treatment with pure polarizations. In contrast, a naïve Mueller tensor built around the Stokes vectors alone without the connection to the Jones framework contains up to 36 potentially independent elements when using a single incident light source (e.g., for SHG and TPEF). In contrast, the analogous Jones transformations depend on just $6 = \sqrt{36}$ independent elements in the most general case. Given the limited number of accessible observables and the benefits of over-determined measurements, there are clear advantages in minimizing the total free parameters by bridging the Mueller and Jones frameworks.

This parameter reduction is particularly advantageous when bridging the laboratory frame Mueller–Jones tensors to the local frame and molecular frame properties. In both the Jones and Stokes–Mueller formalisms, measurements are made in the two dimensions orthogonal to the optical propagation axis but are ultimately linked to local-frame molecular orientation distributions in three-dimensional space. Consequently, it is quite possible for measurements to be highly underdetermined and therefore intractable when the number of unique parameters exceeds the number of independent measured observables. The quadratic

reduction in free parameters afforded by the Jones framework is highly attractive in this context. By connecting the Jones and Mueller approaches, depolarization and partial polarization effects can be measured and treated with the rigor of the Mueller architecture but with only a minor increase in the number of free parameters relative to the simpler Jones framework.

The approach described herein also provides a means of connecting Jones and Mueller tensors measured in the laboratory frame to the corresponding local-frame tensors in a rotated reference frame. This flexibility is important in microscopy measurements, in which the presence of local symmetry can greatly reduce the number of free parameters used to construct the Jones and Mueller tensors. For example, local C_{∞} symmetry reduces the number of unique elements in the local-frame Jones tensor from six down to just three in the case of SHG. However, these simplifications generally do not appear in the laboratory-frame Jones and Mueller tensors. Furthermore, the measured nonlinear optical properties of interest are typically related most directly to the local-frame response, with the laboratory-frame measurements simply providing a means to that end. The vectorization approach described in this work provides a simple and generally applicable means of coordinate transformation to recover local-frame tensors from laboratory-frame measurements. The introduction of either of the proposed analytical models to treat depolarization effects introduces only a single additional parameter to the analysis. For comparison, the four free parameters in describing the polarization-dependent SHG activity of a C_{∞} -symmetry local-frame assembly (three local-frame tensor elements plus one scattering parameter) translate to 36 free parameters (i.e., a 9-fold increase) in the full evaluation of the Mueller tensor in the most general case of SHG when it is not bridged to the Jones formalism in the limit of pure polarizations.

Finally, it is worth emphasizing that the Mueller tensor framework developed in this work is directly compatible with both SHG and TPEF measurements. This generality is particularly noteworthy for two reasons. First, spontaneous TPEF produces incoherent radiation that is inherently incompatible with a conventional Jones tensor formalism. However, TPEF is directly compatible with the Stokes–Mueller tensor platform developed herein. Second, both SHG and TPEF are routinely acquired in parallel in nonlinear optical microscopy, differing only in the wavelength window used for data acquisition. The ability to characterize both methods using a single mathematical framework and a single instrumental platform facilitates efforts to merge the two for combined analysis.^{62,63} In assemblies that are both SHG and TPEF active, the two methods probe different and highly complementary moments of the molecular orientation distribution, as described by eq 51 for SHG and eq 55 for TPEF. Whereas SHG can access the first and third Legendre moments of the molecular orientation distribution, TPEF can access the complementary second, fourth, and sixth moments. Consequently, combined analysis has the potential to substantially improve the determination of molecular orientation distributions by polarization analysis.

CONCLUSIONS

A framework was developed connecting the more general Mueller tensor to the purely polarized Jones tensor formalisms, resulting in substantial reductions in the number of free

parameters required for treating depolarization effects in SHG and TPEF measurements. Connecting these two frameworks was facilitated by the development of several theorems establishing tensor identity relations, many of which are connected through vectorization operations. Nevertheless, the resulting final expressions bridging the two architectures are directly and clearly analogous to corresponding operations in linear optical treatments connecting Stokes vectors, Jones vectors, Mueller matrices, and Jones matrices. A key advantage of the current architecture is the requirement of only a single additional free parameter in the model to allow for corrections arising from depolarization in SHG and TPEF measurements in turbid media. For comparison, the most general naïve Mueller tensor strategies require a complete set of 36 measurements to reconstruct the Mueller tensor, followed by subsequent development of models relating these measurements back to local structure and orientation. By integrating the Mueller tensor measurements with common measurement strategies, the framework developed herein connects routine experimental observables in the laboratory frame all the way to the molecular orientation distribution in the local-frame. Combining both SHG and TPEF in a single computational framework aligns the ease of parallel measurements with the possibility of parallel analysis.

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V. APPENDIX I. VECTORIZATION OPERATIONS

Vectorization operations in linear optics

For the purposes of extension to nonlinear optics, it is worthwhile to introduce an alternative formulation of the same outcome described in eq 7 based on vectorization of the Jones and Mueller matrices. Along the way, we will take advantage of several relationships connecting vectorization and matrix multiplication, which will subsequently be extended for use with tensors.

The vectorization operation vec is given mathematically by column-wise stacking of an $n \times m$ matrix to generate a single vector $(n \cdot m)$ elements long.

$$vec(B) = vec \begin{pmatrix} b_{00} & b_{01} \\ b_{10} & b_{11} \end{pmatrix} = \begin{bmatrix} b_{00} \\ b_{10} \\ b_{01} \\ b_{11} \end{bmatrix} \quad (80)$$

The following identity relationships emerge from the vectorize operation as defined above.

$$vec(ABC) = (C^T \otimes A) \cdot vec(B) \quad (81)$$

$$vec(AB)=(I_m \otimes A)vec(B)=(B^T \otimes I_k)vec(A) \quad (82)$$

$$vec(ABC)=(I_n \otimes AB)vec(C)=(C^T B^T \otimes I_k)vec(A) \quad (83)$$

In this work, a complementary vectorization operation *asc* is introduced, in which the entries appear in ascending order of indices. In the case of a matrix, this operation corresponds to vectorization of the transpose.

$$asc(B)=asc \begin{bmatrix} b_{00} & b_{01} \\ b_{10} & b_{11} \end{bmatrix} = \begin{bmatrix} b_{00} \\ b_{01} \\ b_{10} \\ b_{11} \end{bmatrix} = vec(B^T) \quad (84)$$

Obviously, in the case of matrix vectorization, there is little benefit in introducing the *asc* operation, since it is trivially connected to the *vec* operation by a transpose. However, the value of the *asc* operation will become clearer in subsequent extension to tensors. While there is universal agreement on how to transpose a matrix, similar agreement does not generally exist for transposing tensors, with the *asc* operation removing potential ambiguities associated with element ordering upon vectorizing tensors. Using these definitions, the following relations emerge for the ascending vectorize operation *asc*.

$$asc(ABC)=(A \otimes C^T) \cdot asc(B) \quad (85)$$

$$asc(AB)=(I_m \otimes B^T) \cdot asc(A)=(A \otimes I_k) \cdot asc(B) \quad (86)$$

$$asc(ABC)=(I_n \otimes C^T B^T) \cdot asc(A)=(A^T B^T \otimes I_k) \cdot asc(C) \quad (87)$$

For reasons related to book-keeping in sparse matrices upon subsequent extension to tensor analysis, the preferred vectorized form for the Mueller matrix $\vec{M}$ used in this work is the ascending version.

$$\vec{M}=asc(M)=vec(M^T) \quad (88)$$

Vectorization of tensors and tensor products

In most experimental measurements, the primary goal is experimental determination of the Mueller tensor elements (or functions thereof). In this context, the vectorized form of the tensor has distinct advantages of enabling inversion to isolate the individual elements by linear algebra manipulations. And here's where we run into a potential source of ambiguity. While the vectorize convention is well-established in linear algebra, the corresponding operations for tensors are not. For example, it is not obvious *a priori* how best to stack the different elements in the rank three tensor, with 3! different possible options. As the rank increases, the ambiguity correspondingly increases factorially. This ambiguity is not unique to the vectorize operation, with analogous and related complications arising in evaluating the transpose of a tensor.

The vectorized ascending operation *asc* has the advantage of removing this ambiguity in tensor operations by explicitly specifying the element-wise ordering in the resulting vectorized tensor. By analogy with the expressions given in eqs 85–87 and proven explicitly in Appendix II, the following identity relationships emerge in rank 3 tensor operations, in which m is the dimension of the rank three tensor $B^{(2)}$ (e.g., $m = 2$ for the Jones tensor and $m = 4$ for the Mueller tensor).

$$asc(A \cdot B^{(2)}:CD) = (A \otimes C^T \otimes D^T) \cdot asc(B^{(2)}) \quad (89)$$

$$asc(B^{(2)}:CD) = (I_m \otimes C^T \otimes D^T) \cdot asc(B^{(2)}) \quad (90)$$

Generality to tensors of arbitrary rank n is given by the following two relations.

$$\begin{aligned} & asc(A \cdot B^{(n-1)}:C_{(0)}C_{(1)} \dots C_{(n-1)}) \\ &= (A \otimes C_{(0)}^T \otimes C_{(1)}^T \dots \otimes C_{(n-1)}^T) \cdot asc(B^{(n-1)}) \end{aligned} \quad (91)$$

$$\begin{aligned} & asc(B^{(n-1)}:C_{(0)}C_{(1)} \dots C_{(n-1)}) \\ &= (I_m \otimes C_{(0)}^T \otimes C_{(1)}^T \dots \otimes C_{(n-1)}^T) \cdot asc(B^{(n-1)}) \end{aligned} \quad (92)$$

Using the *asc* operation as a convention reference, the *vec* operation can now similarly be unambiguously defined relative to *asc*, which in turn also defines a particular convention for the tensor transpose operation.

$$vec(B^{(2)}) = asc[(B^{(2)})^T] \quad (93)$$

$$(D^T \otimes C^T \otimes A) \cdot \text{vec}(B^{(2)}) = \text{vec}(A \cdot B^{(2)}; CD) \quad (94)$$

$$\text{vec}(B^{(2)}; CD) = (D^T \otimes C^T \otimes I_m) \cdot \text{vec}(B^{(2)}) \quad (95)$$

$$\begin{aligned} & \text{vec}(A \cdot B^{(n-1)}; C_{(0)} C_{(1)} \dots C_{(n-1)}) \\ &= (C_{(n-1)}^T \otimes \dots \otimes C_{(1)}^T \otimes C_{(0)}^T \otimes A) \cdot \text{vec}(B^{(n-1)}) \end{aligned} \quad (96)$$

$$\begin{aligned} & \text{vec}(B^{(n-1)}; C_{(0)} C_{(1)} \dots C_{(n-1)}) \\ &= (C_{(n-1)}^T \otimes \dots \otimes C_{(1)}^T \otimes C_{(0)}^T \otimes I_m) \cdot \text{vec}(B^{(n-1)}) \end{aligned} \quad (97)$$

VI. APPENDIX II. IDENTITY RELATIONSHIPS WITH KRONECKER PRODUCTS OF TENSORS

Theorem 1

Let $B^{(2)}$ be a tensor of dimensions $i \times j \times k$, $\vec{c}$ a vector of dimension j , and $\vec{d}$ a vector of dimension k . The following identity holds.

$$\text{asc}(B^{(2)}; \vec{c} \vec{d}) = (I_i \otimes \vec{c}^T \otimes \vec{d}^T) \cdot \text{asc}(B^{(2)}) \quad (98)$$

$$\text{vec}(B^{(2)}; \vec{c} \vec{d}) = (\vec{d}^T \otimes \vec{c}^T \otimes I_i) \cdot \text{vec}(B^{(2)}) \quad (99)$$

Proof

Let $\vec{x} = B^{(2)}; \vec{c} \vec{d}$. The term inside the parenthetical is equal to the following.

$$B^{(2)}; \vec{c} \vec{d} = \sum_p c_p \sum_q d_q B_{ipq} \quad (100)$$

Explicit expansion of the terms in the summation yields the following.

$$x_n = \begin{pmatrix} c_0 d_0 \\ c_0 d_1 \\ \vdots \\ c_0 d_k \\ c_1 d_0 \\ \vdots \\ c_j d_k \end{pmatrix}^T \cdot \begin{bmatrix} B_{n00} \\ B_{n01} \\ \vdots \\ B_{n0k} \\ B_{n10} \\ \vdots \\ B_{njk} \end{bmatrix} = [\vec{c} \otimes \vec{d}]^T \cdot \begin{bmatrix} B_{n00} \\ B_{n01} \\ \vdots \\ B_{n0k} \\ B_{n10} \\ \vdots \\ B_{njk} \end{bmatrix} \quad (101)$$

This same approach is repeated for each of the j entries in x , the complete set of which can be recovered by a Kronecker product with the identity matrix. The vector B has a last entry of $(i \times j \times k)$, such that the first $j \times k$ entries contribute to x_0 , the next $j \times k$ entries contribute to x_1 , etc. This bookkeeping can be handled most conveniently by multiplication of $[\vec{c} \otimes \vec{d}]^T$ by an identity matrix ending in the index i , producing a stack of the products in the ascending vectorized tensor $B^{(2)}$.

$$\vec{x} = \begin{bmatrix} x_0 \\ x_1 \\ \vdots \\ x_i \end{bmatrix} = I_j \otimes [\vec{c} \otimes \vec{d}]^T \cdot \begin{bmatrix} B_{000} \\ B_{001} \\ \vdots \\ B_{00k} \\ B_{010} \\ \vdots \\ B_{ijk} \end{bmatrix} \quad (102)$$

Since the entries of both x and B are in ascending order in the preceding equation, eq 98 is confirmed.

Theorem 2

Let $B^{(2)}$ be a tensor of dimensions $j \times k \times l$, C a $k \times m$ matrix, and D an $l \times m$ matrix. The following identity holds.

$$asc(B^{(2)}:CD) = (I_j \otimes C^T \otimes D^T) \cdot asc(B^{(2)}) \quad (103)$$

$$vec(B^{(2)}:CD) = (D^T \otimes C^T \otimes I_i) \cdot vec(B^{(2)}) \quad (104)$$

Proof

Extension of Theorem 1 to matrices is straightforward. The matrices C and D can be written as a set of column vectors.

$$B^{(2)}:CD=B^{(2)}:\left(\vec{c}_0 \ \vec{c}_1 \ \dots \ \vec{c}_m\right)\left(\vec{d}_0 \ \vec{d}_1 \ \dots \ \vec{d}_m\right) \quad (105)$$

For every q th column vector in eq 105, the relationship in eq 98 holds, with a corresponding matrix $X=B^{(2)}:CD$ given by the following.

$$X=\begin{bmatrix} x_{00} & x_{01} & \cdots & x_{0m} \\ x_{10} & x_{11} & & \\ \vdots & & \ddots & \vdots \\ x_{j0} & & \cdots & x_{jm} \end{bmatrix}$$

$$=I_j \otimes \left[\left(\vec{c}_0 \ \vec{c}_1 \ \dots \ \vec{c}_m \right) \otimes \left(\vec{d}_0 \ \vec{d}_1 \ \dots \ \vec{d}_m \right) \right]^T \cdot \begin{bmatrix} B_{n00} \\ B_{n01} \\ \vdots \\ B_{n0k} \\ B_{n10} \\ \vdots \\ B_{njk} \end{bmatrix} \quad (106)$$

It is arguably easier to see the connection between the column vectors of C and D by transposing the terms to the right of the equality and taking advantage of the relation $A^T \cdot B = B^T \cdot A$. In this framework, it is straightforward to see that each column of C and D yields a corresponding column in X .

$$X=[\vec{X}_0 \ \vec{X}_1 \ \dots \ \vec{X}_m]$$

$$= \cdot \begin{bmatrix} B_{n00} \\ B_{n01} \\ \vdots \\ B_{n0k} \\ B_{n10} \\ \vdots \\ B_{njk} \end{bmatrix} \cdot I_j \otimes \left[\left(\vec{c}_0 \ \vec{c}_1 \ \dots \ \vec{c}_m \right) \otimes \left(\vec{d}_0 \ \vec{d}_1 \ \dots \ \vec{d}_m \right) \right] \quad (107)$$

From eq 107, $asc(X) = asc(B^{(2)}:CD) = [I \otimes C^T \otimes D^T] \cdot asc(\beta^{(2)})$.

Theorem 3

Let A be a matrix of dimensions $j \times n$ and B a matrix of $n \times k$.

$$I_i \otimes (A \cdot B) = [I_i \otimes A] \cdot [I_i \otimes B] \quad (108)$$

Proof

Expanding the term to the right of the equality yields the following.

$$\begin{aligned}
[I_i \otimes A] \cdot [I_i \otimes B] &= \begin{bmatrix} A & 0 & 0 & 0 \\ 0 & A & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & A \end{bmatrix} \cdot \begin{bmatrix} B & 0 & 0 & 0 \\ 0 & B & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & B \end{bmatrix} \\
&= \begin{bmatrix} \begin{pmatrix} A_{00} & A_{01} & \cdots \\ A_{10} & A_{11} & \\ \vdots & & \ddots \end{pmatrix} & 0 & 0 & 0 \\ 0 & A & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & A \end{bmatrix} \cdot \begin{bmatrix} \begin{pmatrix} B_{00} & A_{01} & \cdots \\ B_{10} & B_{11} & B \\ \vdots & & \ddots \end{pmatrix} & 0 & 0 & 0 \\ 0 & B & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & B \end{bmatrix} \\
&= \begin{bmatrix} AB & 0 & 0 & 0 \\ 0 & AB & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & AB \end{bmatrix} = I_i \otimes (A \cdot B)
\end{aligned} \tag{109}$$

Theorem 4

Let $B^{(2)}$ be a tensor of dimensions $j \times k \times l$, C a $k \times m$ matrix, and D an $m \times n$ matrix, E an $l \times p$ matrix, and F a $p \times q$ matrix.

$$B^{(2)}:(C \cdot D)(E \cdot F) = (B^{(2)}:CE)^{(2)}:DF \tag{110}$$

Proof

From **Theorem 2**, the expression to the left of the equality can be rewritten as follows.

$$B^{(2)}:(C \cdot D)(E \cdot F) = [I_j \otimes (C \cdot D)^T \otimes (E \cdot F)^T] \cdot \vec{B} \tag{111}$$

Using the equality $(C \cdot D) \otimes (E \cdot F) = (C \otimes E) \cdot (D \otimes F)$ allows for the following expression.

$$\begin{aligned}
B^{(2)}:(C \cdot D)(E \cdot F) &= [I_j \otimes (D^T \cdot C^T) \otimes (F^T \cdot E^T)] \cdot \vec{B} \\
&= [I_j \otimes ((D^T \otimes F^T) \cdot (C^T \otimes E^T))] \cdot \vec{B}
\end{aligned} \tag{112}$$

From **Theorem 3**, the Kronecker product with the identity can be expanded.

$$\begin{aligned}
B^{(2)}:(C \cdot D)(E \cdot F) &= [I_j \otimes (D^T \cdot C^T) \otimes (F^T \cdot E^T)] \cdot \vec{B} \\
&= [I_j \otimes D^T \otimes F^T] \cdot [I_j \otimes C^T \otimes E^T] \cdot \vec{B}
\end{aligned} \tag{113}$$

From **Theorem 2**, the preceding equations can be reformulated back into tensor notation.

$$\begin{aligned}
 B^{(2)}:(C \cdot D)(E \cdot F) &= [I_j \otimes (D^T \cdot C^T) \otimes (F^T \cdot E^T)] \cdot \vec{B} \\
 &= ([I_j \otimes C^T \otimes E^T] \cdot \vec{B})^{(2)} : DF \\
 &= (B^{(2)}:CE)^{(2)} : DF
 \end{aligned} \tag{114}$$

The dimensions of the tensor $(B^{(2)}:CE)^{(2)}$ are $i \times m \times p$.

Theorem 5

Let $B^{(2)}$ be a tensor of dimensions $j \times k \times l$, $\vec{a}$ a $j \times 1$ vector, $\vec{c}$ a $k \times 1$ vector, and $\vec{d}$ an $l \times 1$ vector. The following identity holds.

$$asc(\vec{a}^T \cdot B^{(2)} : \vec{c} \cdot \vec{d}) = (\vec{a}^T \otimes \vec{c}^T \otimes \vec{d}^T) \cdot \vec{B} \tag{115}$$

$$vec(\vec{a}^T \cdot B^{(2)} : \vec{c} \cdot \vec{d}) = (\vec{d}^T \otimes \vec{c}^T \otimes \vec{a}^T) \cdot vec(B^{(2)}) \tag{116}$$

Proof

Let the matrix $M = B^{(2)} \cdot \vec{d}$ of dimension $(j \times k)$ with $\vec{d}$ corresponding to the right-most index in $B^{(2)}$.

$$\begin{aligned}
 asc(\vec{a}^T \cdot M \cdot \vec{c}) &= (\vec{a}^T \otimes \vec{c}^T) \cdot asc(M) \\
 &= (\vec{a}^T \otimes \vec{c}^T) \cdot asc(B^{(2)} \cdot \vec{d}) \\
 &= (\vec{a}^T \otimes \vec{c}^T) \cdot [I_{j+k} \otimes \vec{d}^T] \cdot \vec{B}
 \end{aligned} \tag{117}$$

Since the dimensions of I_{j+k} are identical to those of the product $(A \otimes \vec{c}^T)$, the preceding expression can be contracted to remove the identity and recover the expression in eq 115.

Theorem 6

Let $B^{(2)}$ be a tensor of dimensions $j \times k \times l$, A an $i \times j$ matrix, C a $k \times i$ matrix, and D an $l \times i$ matrix. The following identity holds.

$$asc(A \cdot B^{(2)} : CD) = (A \otimes C^T \otimes D^T) \cdot \vec{B} \tag{118}$$

$$vec(A \cdot B^{(2)} : CD) = (D^T \otimes C^T \otimes A) \cdot \vec{B} \tag{119}$$

Proof

The proof for this expression follows from the proof for **Theorem 5**, evaluated one column vector at a time. Let the matrix $M = A^T$.

$$A \cdot B^{(2)}:CD = [\vec{m}_0 \cdots \vec{m}_{i-1}]^T \cdot B^{(2)}: [\vec{c}_0 \cdots \vec{c}_{i-1}] \\ [\vec{d}_0 \cdots \vec{d}_{i-1}] \quad (120)$$

From **Theorem 5**, a particular q th set of vectors from the total number of i possible yields the following product.

$$asc(\vec{m}_q^T \cdot B^{(2)}: \vec{c}_q \vec{d}_q) = (\vec{m}_q^T \otimes \vec{c}_q^T \otimes \vec{d}_q^T) \cdot \vec{B} \quad (121)$$

Once in this form, the matrices can be reconstructed one column at a time.

$$asc(A \cdot B^{(2)}:CD) = ([\vec{m}_0 \cdots \vec{m}_{i-1}]^T \otimes [\vec{c}_0 \cdots \vec{c}_{i-1}]^T \\ \otimes [\vec{d}_0 \cdots \vec{d}_{i-1}]^T) \cdot \vec{B} \\ = (M^T \otimes C^T \otimes D^T) \cdot \vec{B} \\ = (M \otimes C^T \otimes D^T) \cdot \vec{B} \quad (122)$$

Theorem 7

Let B be an $i \times j \times k$ tensor, E be an $l \times m \times n$ tensor, C a $j \times p$ matrix, D a $j \times q$ matrix, F an $m \times r$ matrix, and G an $n \times s$ matrix.

$$(B^{(2)}:CD) \otimes (E^{(2)}:FG) = (B^{(2)} \otimes E^{(2)}):(C \otimes F)(D \otimes G) \quad (123)$$

Proof

For a rank three tensor of order 2, the multiplication by C recovers a matrix $M = B^{(2)} \cdot C$, with a similar arrangement arising for $N = E^{(2)} \cdot F$.

$$(M \cdot D) \otimes (N \cdot G) = (M \otimes N) \cdot (D \otimes G) \quad (124)$$

A similar approach can be taken along the orthogonal axis corresponding to C and F .

$$(M \otimes N) \cdot (D \otimes G) \\ = ([B^{(2)} \cdot C] \otimes [E^{(2)} \cdot F]) \cdot (D \otimes G) \\ = (B^{(2)} \otimes E^{(2)}):(C \otimes F)(D \otimes G) \quad (125)$$

Theorem 8

The approach described in Theorem 8 can be directly extended to tensors of arbitrary order.

$$\begin{aligned} & (B^{(n)}:C_1C_2\cdots C_n) \otimes (E^{(n)}:F_1F_2\cdots F_n) \\ & = (B^{(2)} \otimes E^{(2)}):(C_1 \otimes F_1)(C_2 \otimes F_2)\cdots (C_n \otimes F_n) \end{aligned} \quad (126)$$

Proof

The proof follows the derivation in Theorem 8.

$$\begin{aligned} & ([B^{(n)}:C_1C_2\cdots C_{n-1}] \otimes [E^{(n)}:F_1F_2\cdots F_{n-1}]) \cdot (C_n \otimes F_n) \\ & = ([B^{(n)}:C_1C_2\cdots C_{n-2}] \otimes [E^{(n)}:F_1F_2\cdots F_{n-2}]): \\ & \quad (C_{n-1} \otimes F_{n-1})(C_n \otimes F_n) \\ & = (B^{(n)} \otimes E^{(n)}):(C_1 \otimes F_1)(C_2 \otimes F_2)\cdots (C_n \otimes F_n) \end{aligned} \quad (127)$$

VI. APPENDIX III. CONSTRUCTION OF THE MATRIX P FOR LINEAR AND NONLINEAR OPTICS

In this section, the origins of two matrices connecting Jones tensor element combinations with experimental observables are described. The matrix P connects the set of polynomial coefficients introduced in eq 61 to the Jones tensor elements through eq 68. An analogous matrix P_S given by $P_S = A \otimes P$ connects the detected Stokes vectors to the Jones tensor elements. For linearly polarized light rotated an angle γ as defined in Figure 3, the incident light is given by the following.

$$\vec{e}^{\text{in}} = \begin{bmatrix} \cos\gamma \\ \sin\gamma \end{bmatrix}; \quad \vec{e}^{\text{in}*} \otimes \vec{e}^{\text{in}} = \begin{bmatrix} \cos^2\gamma \\ \sin\gamma\cos\gamma \\ \sin\gamma\cos\gamma \\ \sin^2\gamma \end{bmatrix} = \begin{bmatrix} c^2 \\ cs \\ cs \\ s^2 \end{bmatrix}_\gamma \quad (128)$$

Using the identity relationship $as\alpha(A \cdot B) = [I \otimes B^T] \cdot as\alpha(A)$ in eq 5 and breaking down into each of the polynomial coefficients yields the following.

$$\begin{aligned} \vec{e}^{\text{out}*} \otimes \vec{e}^{\text{out}} &= \left\{ \left(I_4 \otimes \begin{bmatrix} c^2 \\ 0 \\ 0 \\ 0 \end{bmatrix} \right)^T + \left(I_4 \otimes \begin{bmatrix} 0 \\ cs \\ cs \\ 0 \end{bmatrix} \right)^T \right. \\ & \quad \left. + \left(I_4 \otimes \begin{bmatrix} 0 \\ 0 \\ 0 \\ s^2 \end{bmatrix} \right)^T \right\} \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \end{aligned} \quad (129)$$

Considering the horizontally polarized intensity, given by $I_H = e_0^{\text{out}*} \cdot e_0^{\text{out}}$ for the first entry in $\vec{e}^{\text{out}*} \otimes \vec{e}^{\text{out}}$, the $\cos^2 \gamma$ dependent term given by A_H in the left-most column within the brackets in eq 129 is given by the following expression.

$$A_H = [1 \ 0 \ 0 \ 0] \cdot \left\{ \left(I_4 \otimes \begin{bmatrix} 1 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{bmatrix} \right)^T \right\} \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \\ = ([1 \ 0 \ 0 \ 0] \otimes [1 \ 0 \ 0 \ 0]) \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \quad (130)$$

A shorthand notation was adopted, in which $c^2 = \cos^2 \gamma$, $cs = \sin \gamma \cos \gamma$, and $s^2 = \sin^2 \gamma$. The left-most set of four entries corresponds to the product $I_H = e_0^{\text{out}*} \cdot e_0^{\text{out}}$, and the right-most set of four to the $\sin^2 \gamma$ term. Using analogous operations for the $\sin \gamma \cos \gamma$ and $\sin^2 \gamma$ terms allows the set of all three polynomial coefficients $\vec{A}_H$ to be generated in matrix notation.

$$\vec{A}_H = \left([1 \ 0 \ 0 \ 0] \otimes \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \right) \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \\ = ([1 \ 0 \ 0 \ 0] \otimes P') \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \quad (131)$$

The term P' corresponds to the transformation matrix for just one of the two pure H or V polarizations. The corresponding set of vertically polarized components is given by changing the left-most set of four entries.

$$\vec{A}_V = ([0 \ 0 \ 0 \ 1] \otimes P') \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \quad (132)$$

For the most common experimental configuration, the two orthogonally polarized intensities are measured experimentally, with the results stacked to make a six element vector.

$$\begin{bmatrix} \vec{A}_H \\ \vec{A}_V \end{bmatrix} = \left(\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \otimes P' \right) \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \\ = P \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \quad (133)$$

If the full set of all four elements in $\vec{e}^{\text{out}*} \otimes \vec{e}^{\text{out}}$ is desired or measured, the definition of the expanded matrix P is altered accordingly to make a 12 element vector.

$$\begin{bmatrix} \vec{A}_H \\ \xrightarrow{(e_0^{\text{out}*} \cdot e_1^{\text{out}})} \\ \xrightarrow{(e_1^{\text{out}*} \cdot e_0^{\text{out}})} \\ \vec{A}_V \end{bmatrix} = \left(\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \otimes P' \right) \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \\ = P \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \quad (134)$$

An analogous set of operations can be used to generate the corresponding set of six independent Stokes vectors by left-multiplication of the identity matrix by A from eq 2, which is mathematically equivalent to replacing I_4 with A . In the limit of pure polarizations, the relationships between the Mueller matrix and the Stokes vectors as a function of γ describing the incident polarization state are given below to generate a transformed 12 element vector $\vec{S}$.

$$\vec{S} = \begin{bmatrix} \vec{s}_0 \\ \vec{s}_1 \\ \vec{s}_2 \\ \vec{s}_3 \end{bmatrix} = (A \otimes P') \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \\ = P_S \cdot [A^{-1} \otimes A^T \otimes A^T] \cdot \vec{M} \quad (135)$$

The notation could be a bit confusing here; $\vec{s}$ refers to a Stokes vector and s_0 the zeroth element of the Stokes vector, whereas the vectorization indicated by $\vec{s}_0$ represents the set of three γ -dependent parameters contributing to the 0th Stokes element s_0 . The substitution was also made with $\mathbf{P}_S = (A \otimes P)$. The vector $\vec{S}$ is a stack of the three γ -dependent parameters for each Stokes element to generate a 12-element combined vector. Using the inverse of the vectorize operation, the stack can also be rewritten in matrix notation.

$$\text{vec}^{-1}(\vec{S}) = \begin{bmatrix} \left(\vec{s} \right)_{c_2} & \left(\vec{s} \right)_{c_s} & \left(\vec{s} \right)_{s_2} \end{bmatrix} \quad (136)$$

The first column in the matrix to the right of the equality in eq 136 corresponds to the Stokes vector generated for a horizontally polarized input, the right-most to a vertically polarized input, and the middle to a mixed polarization. Depending on the measurement architecture and goals, the transposed arrangement may also be advantageous.

$$\text{asc}^{-1}(\vec{S}) = \begin{bmatrix} (s_0)_0 & (s_1)_0 & (s_2)_0 & (s_3)_0 \\ (s_0)_1 & (s_1)_1 & (s_2)_1 & (s_3)_1 \\ (s_0)_2 & (s_1)_2 & (s_2)_2 & (s_3)_2 \end{bmatrix} \quad (137)$$

The zeroth column in eq 137 corresponds to the set of three γ -dependent coefficients measured for s_0 (corresponding to the γ -dependence of the total unpolarized intensity), the next set describing the γ -dependence of s_1 , etc.

It should be clear from eq 137 that the use of linearly polarized light produces a set of 12 observables, which in the most general case depend on 16 possible nonzero elements within the Mueller matrix. As such, eq 135 cannot be inverted to uniquely solve for the elements of the Mueller matrix without either additional measurements or reduction in the number of parameters describing the Mueller matrix.

Extension to SHG

On the basis of the framework described for linear optics, the extension to nonlinear optical interactions is straightforward. The product of $\vec{e}^{\text{sum}*} \otimes \vec{e}^{\text{sum}}$ can be written in multiple manners. Using what is given by the following general expression from Theorem 7 provides a clear bridge to the Mueller tensor framework.

$$\begin{aligned} \vec{e}^{\text{sum}*} \otimes \vec{e}^{\text{sum}} &= (\chi^{(2)} : \vec{e}^{\rightarrow a} \vec{e}^{\rightarrow b}) * \otimes (\chi^{(2)} : \vec{e}^{\rightarrow a} \vec{e}^{\rightarrow b}) \\ &= (\chi^{(2)*} \otimes \chi^{(2)}) : (\vec{e}^{\rightarrow a*} \otimes \vec{e}^{\rightarrow a}) (\vec{e}^{\rightarrow b*} \otimes \vec{e}^{\rightarrow b}) \\ &= [I_4 \otimes (\vec{e}^{\rightarrow a*} \otimes \vec{e}^{\rightarrow a}) \otimes (\vec{e}^{\rightarrow b*} \otimes \vec{e}^{\rightarrow b})] \text{asc}(\chi^{(2)*} \otimes \chi^{(2)}) \quad (138) \end{aligned}$$

Alternatively, the product $\vec{e}^{\text{sum}*} \otimes \vec{e}^{\text{sum}}$ can be connected to the product $\vec{\chi}^* \otimes \vec{\chi}$, rather than $\text{asc}(\chi^{(2)*} \otimes \chi^{(2)})$ by changing the order of substitution.

$$\begin{aligned} \vec{e}^{\text{sum}*} \otimes \vec{e}^{\text{sum}} &= (\chi^{(2)} : \vec{e}^{\rightarrow a} \vec{e}^{\rightarrow b}) * \otimes (\chi^{(2)} : \vec{e}^{\rightarrow a} \vec{e}^{\rightarrow b}) \\ &= ([I_2 \otimes \vec{e}^{\rightarrow a} \otimes \vec{e}^{\rightarrow b}]^T \cdot \vec{\chi}^*) \otimes ([I_2 \otimes \vec{e}^{\rightarrow a} \otimes \vec{e}^{\rightarrow b}]^T \cdot \vec{\chi}) \\ &= [I_2 \otimes \vec{e}^{\rightarrow a*} \otimes \vec{e}^{\rightarrow b*} \otimes I_2 \otimes \vec{e}^{\rightarrow a} \otimes \vec{e}^{\rightarrow b}] \cdot (\vec{\chi}^* \otimes \vec{\chi}) \quad (139) \end{aligned}$$

For a single incident beam linearly polarized with the axis of polarization rotated the angle γ as described by eq 128, the electric field components can be written as follows (written in abbreviated form in which $c = \cos \gamma$ and $s = \sin \gamma$).

$$\begin{aligned} & \left[I_2 \otimes \vec{e}^{\rightarrow a*} \otimes \vec{e}^{\rightarrow b*} \otimes I_2 \otimes \vec{e}^{\rightarrow a} \otimes \vec{e}^{\rightarrow b} \right]^\gamma \\ &= \begin{bmatrix} [c \ s] \otimes [c \ s] & 0 \\ 0 & [c \ s] \otimes [c \ s] \end{bmatrix} \\ & \otimes \begin{bmatrix} [c \ s] \otimes [c \ s] & 0 \\ 0 & [c \ s] \otimes [c \ s] \end{bmatrix} \\ &= \left[I_4 \otimes \begin{bmatrix} c \\ s \end{bmatrix} \otimes \begin{bmatrix} c \\ s \end{bmatrix} \otimes \begin{bmatrix} c \\ s \end{bmatrix} \otimes \begin{bmatrix} c \\ s \end{bmatrix} \right]^T \quad (140) \end{aligned}$$

Breaking the preceding expression up into the five polynomial coefficients allows the product to be described by the following sum.

$$= \begin{bmatrix} c^4 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} \begin{bmatrix} c \\ s \end{bmatrix} \otimes \begin{bmatrix} c \\ s \end{bmatrix} \\ 0 \\ c^3 s \\ c^3 s \\ 0 \\ c^3 s \\ 0 \\ 0 \\ 0 \\ 0 \\ c^3 s \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} \begin{bmatrix} c \\ s \end{bmatrix} \otimes \begin{bmatrix} c \\ s \end{bmatrix} \\ 0 \\ 0 \\ 0 \\ c^2 s^2 \\ 0 \\ c^2 s^2 \\ c^2 s^2 \\ c^2 s^2 \\ 0 \\ 0 \\ c^2 s^2 \\ c^2 s^2 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} \begin{bmatrix} c \\ s \end{bmatrix} \otimes \begin{bmatrix} c \\ s \end{bmatrix} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} \begin{bmatrix} c \\ s \end{bmatrix} \otimes \begin{bmatrix} c \\ s \end{bmatrix} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ s^4 \end{bmatrix} \quad (141)$$

If the five columns in eq 141 are stacked left to right, the matrix P' is given by the transpose by analogy with eq 131.

$$P' = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \quad (142)$$

As in the linear case described in eq 133, the expression for the horizontally and vertically polarized intensities is given by the first and last entries in $\vec{e}^{\text{sum}*} \otimes \vec{e}^{\text{sum}}$.

$$\begin{bmatrix} \vec{A}_H \\ \vec{A}_V \end{bmatrix} = \left(\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \otimes P' \right) \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \\ = P \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \quad (143)$$

Alternatively, the stacked set of 20 components in the Stokes vector (five γ -dependent parameters for each of the four Stokes elements) can be generated using the matrix A from eq 2.

$$\vec{S} = \begin{bmatrix} \vec{s}_0 \\ \vec{s}_1 \\ \vec{s}_2 \\ \vec{s}_3 \end{bmatrix} = (A \otimes P') \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \\ = P_S \cdot E^{-1} \cdot [A^{-1} \otimes A^T \otimes A^T] \cdot \vec{M} \quad (144)$$

As with linear optics, the stack can analogously be unvectorized to generate a set of five γ -dependent parameters for each of the four Stokes elements.

$$asc^{-1}(\vec{S}) = \begin{bmatrix} (s_0)_0 & (s_1)_0 & (s_2)_0 & (s_3)_0 \\ (s_0)_1 & (s_1)_1 & (s_2)_1 & (s_3)_1 \\ (s_0)_2 & (s_1)_2 & (s_2)_2 & (s_3)_2 \\ (s_0)_3 & (s_1)_3 & (s_2)_3 & (s_3)_3 \\ (s_0)_4 & (s_1)_4 & (s_2)_4 & (s_3)_4 \end{bmatrix} \quad (145)$$

The first column in the matrix above corresponds to the total detected intensity produced from a pure linearly polarized input.

APPENDIX IV. EVALUATION OF THE ELEMENTARY TRANSFORMATION MATRIX E

There are subsequent bookkeeping simplicities available if we can re-express the product $asc(\chi_J^* \otimes \chi_J)$ in terms of $asc(\vec{\chi}_J^*) \otimes asc(\vec{\chi}_J) = (\vec{\chi}_J^* \otimes \vec{\chi}_J)$. Both vectorized forms contain the identical set of elements but in different orderings. The latter ordering has two significant advantages in subsequent analyses. First, the introduction of local symmetry and the corresponding reduction in unique, independent elements within the Jones matrix are arguably simpler to integrate on the individual vectorized Jones matrices rather than on the combined product. Second, this latter arrangement of elements facilitates subsequent bookkeeping by compatibility with binary counting. An elementary matrix can be constructed to interconvert from one ordering to the other. Prior to extension to nonlinear optics, the simpler case of linear optics will be considered first to illustrate the approach.

Linear Optics

Introducing an elementary matrix E allows re-ordering of the two different forms for the Kronecker product of the Jones matrices.

$$asc(\chi_J^* \otimes \chi_J) = E \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \quad (146)$$

$$\vec{M} [A \otimes (A^{-1})^T] \cdot E \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J) \quad (147)$$

From eq 36, the ascending vectorized form of the Jones matrix $\vec{\chi}_J$ can be directly related to the ascending vectorized form of the Mueller matrix using the known elements of the transformation matrix A given in eq 2. The relations in eqs 7 and 36 both yield identical results for the elements of M .

Using this ascending vectorized notation, the detected Stokes vector $\vec{s}^{\text{out}}$ is given by the following general expression using the relation in eq 86.

$$\begin{aligned}\vec{s}^{\text{out}} &= M \cdot \vec{s}^{\text{in}} = \left(\vec{s}^{\text{in}} \right)^T \cdot M^T \\ &= \left[I_4 \otimes \left(\vec{s}^{\text{in}} \right)^T \right] \cdot \text{vec}(M^T) \\ &= \left[I_4 \otimes \left(\vec{s}^{\text{in}} \right)^T \right] \cdot \vec{M} = \left[I_4 \otimes \left(\vec{s}^{\text{in}} \right)^T \right] \cdot \left[A \otimes (A^{-1})^T \right] \cdot E \cdot \left(\vec{\chi}_J^* \otimes \vec{\chi}_J \right) \quad (148)\end{aligned}$$

In the linear case of the Mueller matrix, the use of the much clunkier vectorized form is difficult to justify, when established linear algebra manipulations recover such concise expressions such as those in eq 7. However, the potential advantages of vectorization will be more apparent upon consideration of extension to nonlinear optical interactions.

The 16×16 element transformation matrix E relating $\text{asc}(\chi_J^{(1)*} \otimes \chi_J^{(1)}) = E \cdot (\vec{\chi}_J^* \otimes \vec{\chi}_J)$ in the linear Stokes/Mueller formalism is relatively straightforward to produce. The particular product $(\chi_{ij}^* \otimes \chi_{kl})$ in which $ijkl$ are either 0 or 1 is multiplied by the following to recover the product $e_i^{\text{out}*} \otimes e_k^{\text{out}}$.

$$e_i^{\text{out}*} \otimes e_k^{\text{out}} = \left[I_2 \otimes e^{\vec{s}^{\text{in}*}} \otimes I_2 \otimes e^{\vec{s}^{\text{in}}} \right]^T \cdot (\chi_{ij}^* \otimes \chi_{kl}) \quad (149)$$

The same $e_i^{\text{out}*} \otimes e_k^{\text{out}}$ product recovered from $\text{asc}(\chi_J^* \otimes \chi_J)$ arises from the following multiplication.

$$e_i^{\text{out}*} \otimes e_k^{\text{out}} = \left[I_2 \otimes I_2 \otimes e^{\vec{s}^{\text{in}*}} \otimes e^{\vec{s}^{\text{in}}} \right]^T \cdot (\chi_J^* \otimes \chi_J)_{ijkl} \quad (150)$$

The elementary matrix bridging the two vectorized forms is one that swaps the j and k indices throughout. Because the Jones vectors are only two elements in length, we can use some simple tricks from binary counting to assist in the conversion. Using binary numbers, the element $(\chi_{10}^* \otimes \chi_{10})$ in $(\vec{\chi}_J^* \otimes \vec{\chi}_J)$ is connected to its companion through the element $E_{1100,1010} = 1$, in which the two inner indices have been swapped. In terms of position within the matrix E in decimal notation, conversion from binary to decimal yields $E_{12,10} = 1$. This same binary reordering can be repeated for each of the 16 different combinations from 0000 to 1111 to complete the matrix E .

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An exactly analogous strategy can be used to populate E in the case of SHG, illustrated in Figure 4. The two sets of $(ijklmn)$ indices in $(\vec{\chi}_J^* \otimes \vec{\chi}_J)$ are related to the elements in $(\chi_J^{(2)*} \otimes \chi_J^{(2)})$ by the following elementary permutation.

$$\begin{aligned}
 & \left[I_2 \otimes \overset{i}{e} \otimes \overset{j}{e} \otimes \overset{k}{e} \otimes I_2 \otimes \overset{m}{e} \otimes \overset{n}{e} \right]^T \\
 & \left[I_2 \otimes I_2 \otimes \overset{j}{e} \otimes \overset{m}{e} \otimes \overset{k}{e} \otimes \overset{n}{e} \right]^T
 \end{aligned} \quad (151)$$

As in the linear optics example, the particular product of tensor elements encodes the binary number of the corresponding position in $(\vec{\chi}_J^* \otimes \vec{\chi}_J^*)$. For example, the tensor element corresponding to the production of 1-polarized (e.g., vertical) SHG produced with 0-polarized (e.g., horizontal) incident light for both $\overset{a}{e}$ and $\overset{b}{e}$ is given by $(ijklmn) = 100100$ in terms of $(\chi_J^* \otimes \chi_J^*)$. The corresponding decimal number is 36, such that the 36th row (starting at 0) of $(\chi_J^* \otimes \chi_J^*)$ refers to the $\chi_{100}^* \cdot \chi_{100}$ combination. Using the transformation $(ijklmn) \Rightarrow (ikmjln)$, the new position of $\chi_{100}^* \cdot \chi_{100}$ following multiplication by E will be (110000) in $asc(\chi_J^{(2)*} \otimes \chi_J^{(2)})$ from eq 151. Consequently, $E_{110000,100100} = 1$ in binary or $E_{48,36} = 1$ in decimal. This same strategy based on binary counting can be similarly reproduced to populate the remaining 63 nonzero elements of the elementary matrix E .

APPENDIX V. COORDINATE TRANSFORMATION OF THE MUELLER TENSOR

Although the expression for azimuthal rotation of a Stokes vector in eq 30 is already well established, its origin is reviewed here to help provide a framework for more general applications of local-frame symmetry. Extrinsic rotation of a Jones vector from the local frame to the laboratory frame is described by the following rotation matrix.⁵³

$$\vec{e}_L = \begin{bmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{bmatrix} \cdot \vec{e}_l = R_\phi \cdot \vec{e}_l \quad (152)$$

Substitution of this expression into eq 2 yields the following.

$$\begin{aligned}
 \vec{s}_L &= A \cdot [(R_\phi \cdot \vec{e}_l^*) \otimes (R_\phi \cdot \vec{e}_l)] \\
 &= A \cdot (R_\phi \otimes R_\phi) \cdot (\vec{e}_l^* \otimes \vec{e}_l) \quad (153)
 \end{aligned}$$

Incorporation of an identity matrix of the form $A^{-1}A$ allows the above expression to be connected back to the input Stokes vector.

$$\vec{s}_L = [A \cdot (R_\phi \otimes R_\phi) \cdot A^{-1}] \cdot [A \cdot (\vec{e}_l^* \otimes \vec{e}_l)] = \mathcal{R}_\phi \cdot \vec{s}_l \quad (154)$$

Explicit evaluation of the left-most term in brackets yields the expression for $\mathcal{R}_\phi$ given in eq 30.

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Figure 1.

Three complementary models are illustrated for the generation of partially polarized SHG and/or TPEF measurements in turbid media. Measurements illustrated in part A contain both a directly detected epi-generated signal from a cleanly polarized source mixed with a backscattered signal initially propagating in the forward direction. In part B, an analogous situation arises, in which the signal from a cleanly polarized source contains both a purely polarized and partially depolarized component. In part C, it is assumed that the polarization purity of the source is partially degraded prior to arrival at the focal plane, such that the detected signal includes a component that is independent of both the source and the detected polarization.

Figure 2. Application of local-frame symmetry for simplification of the local Mueller tensor. The local (H', V') coordinate system will generally be rotated an angle ϕ relative to the laboratory (H, V) frame.

Figure 3.
Illustration of common polarization-dependent measurements performed with linearly polarized incident light.

Figure 4.

Illustration of the reordering associated with the elementary matrix E , enabling the position in the tensor product to be easily identified on the basis of binary counting.