Nonlinear Stokes-Mueller polarimetry

Masood Samim, Serguei Krouglov, and Virginijus Barzda*
Department of Chemical and Physical Sciences, Department of Physics and Institute for Optical Sciences, University of Toronto, 3359 Mississauga Road North, Mississauga, Ontario L5L1C6, Canada
(Received 13 August 2015; published 25 January 2016)

The Stokes-Mueller polarimetry is generalized to include nonlinear optical processes such as second- and third-harmonic generation, sum- and difference-frequency generations with Kleinman symmetry. The overall algebraic form of the polarimetry is preserved, where the incoming and outgoing radiations are represented by column vectors and the intervening medium is represented by a matrix. Expressions for the generalized nonlinear Stokes vector and the Mueller matrix are provided in terms of coherency and correlation matrices, expanded by higher-dimensional analogues of Pauli matrices. In all cases, the outgoing radiation is represented by the conventional 4×1 Stokes vector, while dimensions of the incoming radiation Stokes vector and Mueller matrix depend on the order of the process being examined. In addition, the relations between components of nonlinear susceptibility tensor and Mueller matrix are explicitly provided. The approach of combining linear and nonlinear optical elements is discussed within the context of polarimetry.

DOI: 10.1103/PhysRevA.93.013847

I. INTRODUCTION

Polarimetry techniques employ the measurement of polarization state of outgoing radiation from a medium for a defined polarization of incoming radiation. Linear optical polarimetry is a well-established measurement technique that found applications in different research fields including material science and biomedical imaging [1–7]. Polarimetry can also be employed for nonlinear optical techniques, such as second-harmonic generation (SHG), third-harmonic generation (THG), and coherent anti-Stokes Raman scattering (CARS) [8–15].

In an optical setup the polarization-dependent interaction of light with matter can be described using Stokes-Mueller, Poincaré, or Jones formalism [16–18]. Each formalism has unique advantages conveniently applicable for different circumstance. In the linear Stokes-Mueller formalism, the light is represented by a four-element Stokes vector, and its interaction with matter is represented by a 4×4 Mueller matrix. The Stokes vector can describe partially or completely polarized light and operates with intensities, which are real numbers and thus observables in an experiment. On the other hand, Jones formalism is used to describe purely polarized states retaining the phase relations of the electric fields and requires working with complex variables.

Recently, attempts have been made to deal with the nonlinear polarization measurements in a linear fashion. For example, SHG signal from a sample as well as the incoming fundamental beam radiation have been characterized by a 4×1 Stokes vector [19,20]. However, the characterization of the sample remains unresolved, mainly because of the nonlinear relationship between the incoming and outgoing radiations. Meanwhile, the 4×1 Stokes vector has been used to describe the polarization states of beams for nonlinear effects in the pump-probe phenomena and for isotropic medium subjected to a nonlinear dc electric field [21,22]. In ellipsometry, for two-photon processes some nonlinear relationships have been derived by using a quantum-mechanical framework and a Jones-Stokes approach [23,24]. The Jones formalism can be used to describe nonlinear light-matter interaction using higher-order susceptibilities and pure polarization states. However, often media, including biological tissue, are highly heterogeneous scattering materials; therefore, the Stokes-Mueller formalism allows accounting for the scattering contribution in nonlinear optical responses. These efforts demonstrate the need for a unifying and general framework for nonlinear optical Stokes-Mueller polarimetry.

The principles of linear polarimetry measurement techniques can be applied for the nonlinear polarimetry experiments. For example, the degree of polarization of an optical radiation is a useful parameter to quantify the extent of scattering contribution to the radiation. In addition, various filtering mechanisms exist to separate the polarized components of a radiation from scattering contributions [25,26]. In this paper, we develop the theoretical framework for nonlinear optical polarimetry in Sec. II by using the classical description of electric fields, nonlinear susceptibilities, and optical radiations polarizations. In our approach to the multiphoton polarimetry, the nonlinear Jones and Stokes-Mueller formalism is analogous to the conventional linear polarimetry, where the polarization state of light as well as the response of a material is described with real-valued parameters. Higher-dimensional Stokes-Mueller algebra is derived to describe the nonlinear interactions of the optical radiations and the media. The Mueller matrix for an ensemble of nonlinear susceptibility tensor elements is also presented.

II. THEORY OF NONLINEAR STOKES-MUELLER POLARIMETRY

The general nonlinear Stokes-Mueller equation, describing the relationship between the generated nonlinear signal radiation, the nonlinear properties of the media, and the incoming radiations can be written as follows:

$$s'(\omega_\sigma) = \mathcal{M}^{(n)} S(\omega_1, \omega_2, \ldots, \omega_n), \tag{1}$$

where s' is the 4×1 Stokes vector describing the polarization of generated radiation at ω_σ frequency and prime signifies the measured outgoing signal, $\mathcal{M}^{(n)}$ is the nonlinear Mueller matrix of the nth-order light-matter interaction, while S is

*virgis.barzda@utoronto.ca

a $(n+1)^2 \times 1$ vector representing the polarization states of incoming fundamental radiations responsible for generation of outgoing radiation via nonlinear interactions. Henceforth, the s' and S are called the polarization state vectors for outgoing and incoming radiations, respectively.

The following assumptions have been made regarding the experimental applicability of the nonlinear Stokes-Mueller polarimetry theory: (i) the nonlinear Stokes-Mueller polarimetry formalism is applicable for nonionizing radiation in the optical range, where the applied electric field strength is much smaller than the characteristic atomic electric field strength (i.e., $I_{\text{laser}} \ll I_{\text{atomic}} = 4 \times 10^{20}$ W/m^2) [27], (ii) the nonlinear susceptibilities are independent of applied intensities; thus, intensity-dependent susceptibilities are not considered, which may take place at resonant frequencies of atomic and molecular transitions, occurring, for example, due to the ground-state depletion in saturable absorption effect [27]), (iii) the direction of the light propagation is assumed to be perpendicular to the polarization vector plane, (iv) only electric field components of the radiation and dipolar effects are considered, (v) it is assumed that the sample is thin, where the phase-matching effects are ignored, (vi) the incoming radiation is coherent, for example, from a laser source, (vii) the nonlinear Stokes-Mueller polarimetry equations will be derived with harmonic generation processes in mind (i.e., SHG and THG), but also are valid for other nonlinear processes where Kleinman symmetry is applicable. Otherwise, the value of n has to be increased to account for the higher number of observable independent susceptibility tensor components. However, the underlying algebra for the derivations remains valid.

The electric field E of the incident radiation induces a nonlinear polarization $P^{(n)}$ in the material, which is characterized by the nonlinear susceptibility tensor $\chi^{(n)}$:

$$P_i^{(n)} = \chi_{ijk\cdots m}^{(n)} E_j E_k \ldots E_m = \chi_{iA}^{(n)} \psi_A^{(n)}, \tag{2}$$

where (Einstein) summation is assumed over the repeated indices. The index, i, represents the orientation of the outgoing radiation polarization and the remaining indices represent the direction of polarization for incoming electric fields. The incident electric fields can be described as the state function ψ_A, where the relation between the index A and $j,k,\ldots,m$ is specific for a given nonlinear process. Essentially, for an nth-order nonlinear optical phenomena, A runs from 1 to $n+1$, and i represents the two orthogonal vectors expanding the plane of polarization perpendicular to the direction of light propagation [28].

The Stokes vector can be obtained by measuring the light intensities at different polarization orientations and depends on the susceptibility of the materials and the polarization state of the interacting electric fields according to the following equation:

$$I \propto P_i P_i^* \propto \chi_{iA} \chi_{iB}^* \psi_A \psi_B^* \tag{3}$$

where summation over repeated indices is assumed, and the asterisks * denotes the complex conjugate. Thus, by comparing Eqs. (1) and (3) we see that the Stokes vector and Mueller matrix components are composed of products of electric fields vectors and products of susceptibilities components, respectively. At the level of individual electric fields, the outgoing field, denoted by the state vector Φ', is related to the products of incoming electric fields, denoted by the state vector $\psi^{(n)}$, and the susceptibility $\chi^{(n)}$:

$$\Phi'(\omega_\sigma) = \chi^{(n)} \psi^{(n)}(\omega_1, \omega_2, \ldots, \omega_n). \tag{4}$$

The state vector for the fundamental nonlinearly interacting electric fields is

$$\psi^{(n)}(\omega_1, \omega_2, \cdots, \omega_n) = \begin{pmatrix} \psi_1^{(n)} \\ \psi_2^{(n)} \\ \vdots \\ \psi_{n+1}^{(n)} \end{pmatrix}. \tag{5}$$

Each element of the state vector $\psi_A^{(n)}$ $(A = 1, \ldots, n+1)$ is an nth-order function of one or more electric fields oscillations at particular frequencies, and the state vector has $n+1$ components.

A. Outgoing radiation Stokes vector

The Stokes vector s' for the outgoing electric field $E(\omega_\sigma)$ is characterized by a 4×1 vector just as in the case for conventional Stokes vector. Let $C'(\omega_\sigma) = \langle \Phi'(\omega_\sigma) \cdot \Phi'^{\dagger}(\omega_\sigma) \rangle$ be the coherency matrix composed from the dyad of Φ', where $\Phi'(\omega_\sigma)$ is the state (or simply the electric field) vector of the outgoing beam. The symbol dagger $\dagger$ denotes the complex conjugation and transposition. $\langle \cdot \rangle$ signifies a time average over an interval long enough to make the time-averaging independent of the interval and fluctuations. Then, in terms of its coherency matrix and Pauli matrices the outgoing field Stokes vector is [18,29]

$$s'_t = \text{Tr}(C'\tau_t) = C'_{ab}(\tau_t)_{ba} = \langle \Phi'_a \Phi'^*_b \rangle (\tau_t)_{ba} = \langle \Phi'^{\dagger} \tau_t \Phi' \rangle, \tag{6}$$

where a and b each run from 1 to 2, representing the orthogonal outgoing polarization orientations perpendicular to the propagation direction. τ_t $(t = 0 \ldots 3)$ denotes the 2×2 identity and Pauli matrices:

$$\tau_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \tau_1 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \tau_2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \tau_3 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{7}$$

Thus, the so-called degree of polarization $\mathscr{P}'$ is defined as follows [30]:

$$\mathscr{P}' = \sqrt{s_1'^2 + s_2'^2 + s_3'^2}/s'_0. \tag{8}$$

The values of $\mathscr{P}'$ range from 0 to 1, and the parameter can be used to measure the amount of scattered light in the radiation.

B. Real-valued vector for incoming radiation

The incoming electric fields have a $(n+1) \times (n+1)$ coherency matrix, which is defined as

$$\rho^{(n)}(\omega_1, \omega_2, \ldots, \omega_n) = \langle \psi^{(n)} \cdot \psi^{(n)\dagger} \rangle = \begin{pmatrix} \langle \psi_1^{(n)} \psi_1^{(n)*} \rangle & \cdots & \langle \psi_1^{(n)} \psi_{n+1}^{(n)*} \rangle \\ \vdots & \ddots & \vdots \\ \langle \psi_{n+1}^{(n)} \psi_1^{(n)*} \rangle & \cdots & \langle \psi_{n+1}^{(n)} \psi_{n+1}^{(n)*} \rangle \end{pmatrix}. \tag{9}$$

For nonlinear interaction of electric fields, the coefficients of expansion for the coherency matrix forms a real-valued vector similar to the Stokes vector. The coherency matrix for incoming radiation can be expanded by basis that have higher dimensions than the Pauli's matrices. Leaving aside the details of the dimension for now, and simply denoting this set as η, the vector for the incoming signal can be written as

$$S_N = \mathrm{Tr}(\rho\,\eta_{_N}) = \langle \psi_A \psi_B^*)(\eta_{_N})_{BA} = \langle \psi^\dagger \eta_{_N} \psi\rangle, \tag{10}$$

where $N = 1,\ldots,(n+1)^2$ for each element of the incoming radiation representing the nth-order electric fields. The η matrices similar to Pauli's expand higher dimension states. A subset of properties of η matrices essential for describing an nth-order process are as follows:

(1) They are square matrices with dimension $(n+1)\times(n+1)$.

(2) They are Hermitian: $\eta^\dagger = \eta$.

(3) There are $(n+1)^2$ of η matrices which form the basis.

(4) They obey the orthogonality $\mathrm{Tr}(\eta_\mu \eta_\nu) = c_\eta \delta_{\mu\nu}$ where c_η is a constant and real number, and $\delta_{\mu\nu}$ is the Kronecker δ ($\delta_{\mu\nu} = 1$ when $\mu = \nu$, and 0 otherwise).

The constant c_η can be chosen to be the same and equal to 2 for any order of interaction, similar to the linear case (for Pauli matrices $\mathrm{Tr}(\tau_\mu \tau_\nu) = 2\delta_{\mu\nu}$). The recipe for finding these matrices is given in the Appendix: η Matrices for nonlinear polarimetry.

Similar to the linear Stokes parameters, the vector for the incoming radiation generating the nonlinear signal obeys the following relation [31]:

$$n\,S_1^2 \geqslant \sum_{N=2}^{(n+1)^2} S_N^2, \tag{11}$$

where the equality is valid for the purely polarized state. Therefore, it is helpful to use the degree of polarization $\mathscr{P}^{(2)}$ parameter to characterize the scattered and polarized contribution of the fundamental incoming radiation:

$$\mathscr{P}^{(2)}(\omega_1,\omega_2,\ldots,\omega_n) = \sqrt{\sum_{N=2}^{(n+1)^2} S_N^2/n S_1^2}, \tag{12}$$

where $\mathscr{P}^{(2)}$ ranges from 0 to 1 for unpolarized to fully polarized fundamental radiation, respectively.

C. Real-valued matrix for intervening medium

By substituting linear and nonlinear Stokes vector expressions [Eqs. (6) and (10), respectively] into the general nonlinear polarimetry Eq. (1), the following expression is obtained:

$$\langle \Phi'^\dagger\, \tau_t\, \Phi'\rangle = \mathcal{M}_{tN}^{(n)}\, \langle \psi^\dagger\, \eta_{_N}\, \psi\rangle. \tag{13}$$

In this frame, each component of the vector Φ' of the generated electric field is proportional to the polarization of outgoing field, which depends on the susceptibility tensor components of the material and the polarization state of the radiation of incoming electric fields. By substituting explicit expressions of Φ' and $\Phi'^\dagger$ into Eq. (13) in the elemental form the following equation is obtained:

$$\left\langle \chi_{aA}^{(n)*} \psi_A^*(\tau_t)_{ab} \chi_{bB}^{(n)} \psi_B \right\rangle = \mathcal{M}_{tN}^{(n)} \langle \psi_A^*\,(\eta_{_N})_{AB}\,\psi_B\rangle, \tag{14}$$

where A and $B = 1,\ldots,n+1$. Since Eq. (14) is written in terms of individual elements, the state functions of the fundamental radiation can be dropped and the nonlinear Mueller matrix elements $\mathcal{M}_{tN}$ can be written in terms of the nth-order susceptibilities as

$$\chi_{aA}^*(\tau_t)_{ab}\chi_{bB} = \mathcal{M}_{tN}(\eta_{_N})_{AB} \tag{15}$$

Note, in Eq. (15) the signal is assumed to be from a single generator, and an ensemble of scatterers have a similar derivation, which will be shown in later in this Section. Multiplying both sides by $(\eta_{_{N'}})_{BC}$ and after summation over index B, and letting $A = C$:

$$\frac{1}{c_\eta}\chi_{aA}^*(\tau_t)_{ab}\chi_{bB}(\eta_{_N})_{BA} = \mathcal{M}_{tN} \tag{16}$$

where (Einstein) summation is implied over repeated indices (i.e., a, b, A and B). c_η is a real-valued constant and can be set to equal to two as shown in the appendix η matrices for nonlinear polarimetry. Finally, the expression of a real-valued matrix element in terms of the susceptibilities is

$$\mathcal{M}_{tN} = \frac{1}{c_\eta}\mathrm{Tr}(\tau_t\,\chi\,\eta_{_N}\,\chi^\dagger). \tag{17}$$

This expression has a general form and is equivalent to the linear Mueller matrix element expression if the matrices η are replaced with Pauli matrices [from Eq. (7)]. In contrast to the linear Mueller matrix elements, the nonlinear $\mathcal{M}$ is composed of nonlinear susceptibilities and η matrices of higher dimension. Note that for linear polarimetry, the transformation matrix J can also be represented by the linear susceptibility $\chi^{(1)}$, in which case the only difference between linear and nonlinear Mueller matrix elements would be to replace one Pauli matrix with an η matrix [18,32]. This familiar form of Mueller matrix elements can be investigated similar to the linear case. All elements of the matrix for the nonlinear interaction are real, a fact that leads to a very useful and a much desired expression for determining the nonlinear susceptibilities.

In a highly scattering media such as in biological tissue, the system may not be completely coherent, and the source of the signal may be an ensemble of scatterers. Therefore, an ensemble average of individual elements with probability p_e may be more appropriate to consider [32]. The ensemble average of the susceptibility values can be expressed as

$$\sum_e p_e\left(\chi_{aA}^{(n)*}\chi_{bB}^{(n)}\right) = \left\langle \chi_{aA}^{(n)*}\chi_{bB}^{(n)}\right\rangle_e. \tag{18}$$

Consequently, Eq. (16) for the nonlinear Mueller element in the case of an ensemble becomes

$$\mathcal{M}_{tN}^{(n)} = \frac{1}{c_\eta}\left\langle \chi_{aA}^{(n)*}\chi_{bB}^{(n)}\right\rangle_e (\tau_t)_{ab}(\eta_{_N})_{BA}, \tag{19}$$

where $\langle\rangle_e$ stands for the average over the e ensemble. The right-hand side of Eq. (19) has a similar form to Eq. (16), except that here an ensemble of $\chi^{(n)}$ is considered (the order of variables is a nonissue because both equations are in the elemental form). The correlation matrix X forming from $\langle \chi_{aA}^{(n)*}\chi_{bB}^{(n)}\rangle_e$ contains all the information about the ensemble, and in the case of a perfectly homogeneous medium reduces to a single source.

Note that since the generated light is no longer originating from a single source but rather from an ensemble of sources

that may not be necessarily coherent, then the outgoing radiation may not be fully polarized. This result is desired and provides a better representation of experimental data from a heterogeneous medium.

D. Expression of susceptibilities in nonlinear polarimetry

Stokes polarimetry measures the Mueller matrix components, while nonlinear properties of the material are often described by $\chi^{(n)}$ tensor component values. Thus, the next step is to derive expressions for $\chi^{(n)}$ products in terms of $\mathcal{M}_{tN}^{(n)}$ component values. For the derivation we will vectorize the Pauli matrices, τ, as well as the η matrices. We use the trace property $\mathrm{Tr}(AB) = \mathrm{vec}(A^T)^T\mathrm{vec}(B)$, where $\mathrm{vec}(A) = [a_{1,1},...,a_{s,1},a_{1,2},..,a_{s,2},...,a_{1,t},...,a_{s,t}]^T$ is the vectorization of a $s \times t$ matrix A (in other words columns of a matrix are stacked below one another), and its corollary $\mathrm{Tr}(A^T BCD^T) = \mathrm{vec}(A)^T(D \otimes B)\mathrm{vec}(C)$ on the (real) double Mueller elements in Eq. (17) is

$$\begin{aligned}\mathcal{M}_{tN} &= (\mathcal{M}_{tN})^* = \left(\frac{1}{c_\eta}\mathrm{Tr}(\tau_t \chi \eta_N \chi^\dagger)\right)^* \\ &= \frac{1}{c_\eta}\mathrm{Tr}\left(\tau_t^T \chi^* \eta_N^* \chi^T\right) \\ &= \frac{1}{c_\eta}\mathrm{vec}(\tau_t)^T(\chi \otimes \chi^*)\mathrm{vec}(\eta_N^*) \end{aligned} \tag{20}$$

where in going from the first line to the second we took advantage of the Hermitian properties of the τ and η. By letting

$$\mathcal{T} \equiv \begin{pmatrix}\mathrm{vec}(\tau_0)^T \\ \mathrm{vec}(\tau_1)^T \\ \mathrm{vec}(\tau_2)^T \\ \mathrm{vec}(\tau_3)^T\end{pmatrix} = \begin{pmatrix}1 & 0 & 0 & 1 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & i & -i & 0\end{pmatrix}, \tag{21}$$

the matrix $\mathcal{T}$ is invertible and obeys $\mathcal{T}^{-1} = \frac{1}{2}\mathcal{T}^\dagger$. By letting $H^\dagger = [\mathrm{vec}(\eta_1^*),\ldots,\mathrm{vec}(\eta_N^*)]$, we arrive at

$$\mathcal{M} = \mathcal{T} X H^{-1}, \tag{22}$$

where $X = \chi \otimes \chi^*$. Therefore, H should be invertible and obey $H^{-1} = \frac{1}{c_\eta}H^\dagger$. Consequently, the susceptibility products can be easily found as

$$X = \mathcal{T}^{-1}\mathcal{M}H. \tag{23}$$

The relationship between the nonlinear susceptibilities in terms of Mueller matrix derived in Eq. (23) is useful when the Mueller matrix is obtained by the polarimetry measurement of a sample and the explicit values for the corresponding susceptibilities are desired.

In the elemental form $X_{ij} = \frac{1}{2}\mathcal{T}_{it}^\dagger \mathcal{M}_{tN} H_{Nj}$, where $i = (a-1)2 + b$ and $j = (A-1)(n+1) + B$ (a and $b = 1,2$; A and $B = 1,\ldots,n+1$). Since, $\chi_{aA}\chi_{bB}^* = |\chi_{aA}||\chi_{bB}|e^{i(\delta_{aA}-\delta_{bB})}$, then the relative phase between any two susceptibility elements χ_{aA} and χ_{bB} can be found according to

$$\begin{aligned}\delta_{aA} - \delta_{bB} &= \Delta_{aA,bB} \\ &= \tan^{-1}\left(-i\frac{\chi_{aA}\chi_{bB}^* - \chi_{bB}\chi_{aA}^*}{\chi_{aA}\chi_{bB}^* + \chi_{bB}\chi_{aA}^*}\right) \\ &= \tan^{-1}\left(i\frac{\mathrm{X}_{kl} - \mathrm{X}_{ij}}{\mathrm{X}_{kl} + \mathrm{X}_{ij}}\right) \\ &= \tan^{-1}\left(i\frac{\mathcal{T}_{kt}^\dagger \mathcal{M}_{tN} H_{Nl} - \mathcal{T}_{it}^\dagger \mathcal{M}_{tN} H_{Nj}}{\mathcal{T}_{kt}^\dagger \mathcal{M}_{tN} H_{Nl} + \mathcal{T}_{it}^\dagger \mathcal{M}_{tN} H_{Nj}}\right)\end{aligned} \tag{24}$$

where $k = (b-1)2 + a$ and $l = (B-1)(n+1) + A$, and summations over repeated indices are assumed. Equation (24) is important because it shows that by measuring the material matrix for a nonlinear interaction, and using matrices $\mathcal{T}$ in Eq. (21) and H, the relative phase of the susceptibility elements can be obtained.

In nonlinear polarimetry studies, it is customary to characterize nonlinear optical properties of the material using susceptibility values. Therefore, Eq. (23) provides a mechanism to check and compare nonlinear polarimetry investigations with similar previous studies using conventional nonlinear optics. For example, the ratio of susceptibilities for cylindrically symmetric material can be calculated for a number of biological structures [13,24,33–35].

E. Combining nonlinear and linear optical elements

For a setup, containing a nonlinear optical medium followed by a train of linear optical components, the Mueller-Stokes formalism can be used to relate vector of incoming radiation to the outgoing radiation vector:

$$s'(\omega_\sigma) = M_t \ldots M_1 \mathcal{M}^{(n)} S(\omega_1,\omega_2,\ldots,\omega_n), \tag{25}$$

where $M_1 \ldots M_t$ are the 4×4 linear Mueller matrices that characterize the linear interactions, and $\mathcal{M}^{(n)}$ is the 4×9 for the second-order matrix, 4×16 for the third-order matrix, and $4 \times (n+1)^2$ for the nth-order nonlinear interaction. Therefore, linear and nonlinear Stokes-Mueller formalism can be appropriately combined. As an example, we point to derivation of the so-called polarization-in polarization-out (PIPO) equation for SHG using the double Stokes-Mueller polarimetry [29]. A similar relation also exists for THG intensity equation, which we will show in an upcoming publication.

III. DISCUSSION AND CONCLUSION

The general formalism for nonlinear Stokes-Mueller polarimetry is derived. The derivation stems from the basic nonlinear relationship between the polarization density and the resultant outgoing electric field from an intervening material due to the incoming radiation. In nonlinear polarimetry all three components of the expression including the incoming radiation, the material under study, and the outgoing radiation are characterized by real-valued parameters. The state of the incoming radiations is characterized by $(n+1)^2 \times 1$ vector; the sample is represented by a $4 \times (n+1)^2$ matrix; and the outgoing radiation is simply determined by a conventional 4×1 Stokes vector. States are described in terms of electric fields and the conventional Stokes vectors. The matrix $\mathcal{M}^{(n)}$ for a nonlinear interaction is derived in terms of nonlinear susceptibilities. The theoretical framework is comprehensive (since it encapsulates all aspects of the polarization state for the outgoing radiation) for a given material and an incoming radiation. Previous successful nonlinear polarimetric

studies such as polarization-in polarization-out equations are particular cases of Stokes-Mueller nonlinear polarimetry, where linear polarizations are employed in nonbirefringent and nonabsorbing materials. The theory describes the polarimetry of important two-photon effects such as SHG, SFG, and DFG, as well as three-photon effects including THG and CARS. The dimension of nonlinear Stokes-Mueller formalism for an n th-photon process may be different than their corresponding harmonic generation if Kleinman symmetry is not valid. Nonetheless, for each case the polarization state of incoming radiations as well as the nonlinear optical properties of the intervening material can be described in terms of measurable polarimetric quantities.

The nonlinear Stokes-Mueller polarimetry assumes intensity-independent susceptibilities. Hence, the incident radiation intensity range under which the Stokes-Mueller polarimetry is valid can be tested by measuring the Mueller matrix elements values at different incident intensities. The test has a particular importance at incident radiation frequencies near atomic and molecular transitions.

The coherency matrix is constructed from a vector composed of electric fields of the incoming radiation. The expansion of the coherency matrix is facilitated by a set of matrices with unique properties and form the basis for development of the polarization state vector as well as the susceptibility matrix. Elsewhere the η matrices are shown to be the generalized matrices for group SU$(n+1)$, where an $(n+1)$-dimensional quantum system is described by $(n+1)\times(n+1)$ density matrix [36]. Therefore, these matrices may be used for quantum-mechanical derivation of nonlinear polarimetry. For an nth-order process the overall formalism is the same as long as the Kleinman symmetry is valid. For example, the material matrices for SFG, DFG, and SHG assume similar forms. Similarly, the matrix for three-photon-polarimetry shares the same form for THG and CARS processes. It is conceivable that a similar approach can be taken to express the state for various other frequency mixing techniques including two-photon absorption, coherent Stokes-Raman scattering (CSRS), and stimulated Raman scattering (SRS). For each of these techniques the polarization states needs to be expressed in terms of the electric fields that nonlinearly interact and result in the nonlinear polarization density. For higher-order techniques such as fourth and fifth harmonics the corresponding higher dimension η matrices may be used.

ACKNOWLEDGMENTS

This work was supported by grants from the NSERC and the Canadian Institutes of Health Research. M.S. acknowledges the financial support from the Ontario Graduate Scholarship.

APPENDIX: η MATRICES FOR NONLINEAR POLARIMETRY

The polarization state of incoming radiation S [Eq. (10)] as well as the matrix representing the nonlinear medium $\mathcal{M}$ [Eq. (17)] require the $(n+1)\times(n+1)$ η matrices in order to be defined from the coherency and susceptibility matrices, respectively. The recipe for generating η matrices has two steps: In step 1 the matrix η''_{jk} is defined such that only the value of element jk of the matrix η''_{jk} is 1, and 0 for all other elements (both j and k run from 1 to $n+1$). This creates a two-dimensional set of matrices, where each element of the set is a $(n+1)\times(n+1)$ matrix. Note that the η'' are also independent basis and can expand the coherency matrix. However, they are not Hermitian and therefore the resulting Stokes vector and Mueller matrix will be complex. To obtain the desired Hermitian matrices for an nth-order process the following relation can be used:

$$\eta'_{jk}=\begin{cases}\eta''_{jk}+\eta''_{kj}, & \text{if } j<k\\ i(\eta''_{jk}-\eta''_{kj}), & \text{if } j>k\\ \sqrt{\frac{2}{j^2+j}}\left[\left(\sum_{m=1}^{j}\eta''_{mm}\right)-j\eta''_{j+1,j+1}\right], & \text{if } 1\leqslant k=j<(n+1)\\ \sqrt{\frac{2}{n+1}}\mathcal{I}_{n+1}, & \text{if } j=k=(n+1)\end{cases}\tag{A1}$$

where $\mathcal{I}_{n+1}$ is the $(n+1)\times(n+1)$ identity matrix. In the first case (when $j<k$) the new matrices $\eta'_{jk}=\eta''_{jk}+\eta''_{kj}$ are real valued; in the second case (when $j>k$) the new matrices $\eta'_{jk}=i(\eta''_{jk}-\eta''_{kj})$ are complex valued and have similar nonzero elements as to their real-value counterparts in the first case. In the third case (when $1\leqslant j=k<n+1$), the new matrices are diagonal and real valued. Finally, in the last case an identity matrix is used. In step 2 the two-dimensional η' set is converted to a one-dimensional set of matrices [37]: $\eta'_{jk}\rightarrow\eta_N$.

These matrices satisfy all the requirements as desired for expanding the coherency matrix for the nonlinear polarimetry. In addition, the new matrices defined in Eq. (A1) ensure that η obey $\mathrm{Tr}(\eta_\mu\eta_\nu)=2\delta_{\mu\nu}$. For linear polarimetry $n=2$ and η corresponds to Pauli matrices. For second-order process $n=3$ and therefore the generated matrices are those of Gell-Mann. For the case of three photon polarimetry $n=4$, and there are sixteen 4×4 matrices, which will be shown in a separate manuscript [38], and so forth. A useful relation between these matrices and Stokes-Mueller formalism is the following: The real-valued η generate the Stokes vector components that depend on linear polarization, while the complex valued ones are responsible for circular components. Also, the real-valued ones are in part responsible for nonzero Mueller matrix elements, while the Mueller matrix component constructed from a complex-valued η matrix may be zero if the involved nonlinear susceptibilities are real.

[1] W. S. Bickel, J. F. Davidson, D. R. Huffman, and R. Kilkson, Proc. Nat. Acad. Sci. USA **73**, 486 (1976).

[2] W. S. Bickel and M. E. Stafford, J. Biol. Phys. **9**, 53 (1981).

[3] G. Yao and L. V. Wang, Opt. Lett. **24**, 537 (1999).

[4] S. Jiao, G. Yao, and L. V. Wang, Appl. Opt. **39**, 6318 (2000).

[5] N. Ghosh, I. A. Vitkin, and M. F. G. Wood, J. Biomed. Opt. **13**, 044036 (2008).

[6] N. Ghosh, M. F. Wood, S. H. Li, R. D. Weisel, B. C. Wilson, R. K. Li, and I. A. Vitkin, J. Biophotonics **2**, 145 (2009).

[7] M. F. Wood, N. Ghosh, E. H. Moriyama, B. C. Wilson, and I. A. Vitkin, J. Biomed. Opt. **14**, 014029 (2009).

[8] P. J. Campagnola, M. D. Wei, A. Lewis, and L. M. Loew, Biophys. J. **77**, 3341 (1999).

[9] S. V. Plotnikov, A. C. Millard, P. J. Campagnola, and W. A. Mohler, Biophys. J. **90**, 693 (2006).

[10] V. Nucciotti, C. Stringari, L. Sacconi, F. Vanzi, L. Fusi, M. Linari, G. Piazzesi, V. Lombardi, and F. S. Pavone, Proc. Natl. Acad. Sci. USA **107**, 7763 (2010).

[11] S. Bancelin, C. Aimé, I. Gusachenko, L. Kowalczuk, G. Latour, T. Coradin, and M.-C. Schanne-Klein, Nat. Commun. **5**, 4920 (2014).

[12] T. Boulesteix, E. Beaurepaire, M. P. Sauviat, and M. C. Schanne-Klein, Opt. Lett. **29**, 2031 (2004).

[13] M. Samim, N. Prent, D. Dicenzo, B. Stewart, and V. Barzda, J. Biomed. Opt. **19**, 056005 (2014).

[14] I. Freund and M. Deutsch, Opt. Lett. **11**, 94 (1986).

[15] V. Barzda, C. Greenhalgh, J. A. der Au, J. A. Squier, S. Elmore, and J. H. van Beek, in *Proceedings of SPIE on Commercial and Biomedical Applications of Ultrafast Lasers IV*, Vol. 5340, edited by J. Neev, C. B. Schaffer, and A. Ostendorf (SPIE, 2004), pp. 96–103.

[16] W. A. Shurcliff, *Polarized Light: Production and Use* (Harvard University Press, Cambridge, MA, 1962).

[17] D. S. Kliger, J. W. Lewis, and C. E. Randall, *Polarized Light in Optics and Spectroscopy* (Academic Press, San Diego, CA, 1990).

[18] R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1977).

[19] C.-H. Lien, K. Tilbury, S.-J. Chen, and P. J. Campagnola, Biomed. Opt. Express **4**, 1991 (2013).

[20] N. Mazumder, C.-W. Hu, J. Qiu, M. R. Foreman, C. M. Romero, P. Török, and F.-J. Kao, Methods **66**, 237 (2014).

[21] S. V. Popov, Y. P. Svirko, and N. I. Zheludev, J. Opt. Soc. Am. B **13**, 2729 (1996).

[22] K. L. Sala, Phys. Rev. A **29**, 1944 (1984).

[23] Y. Shi, W. M. McClain, and R. A. Harris, Phys. Rev. A **49**, 1999 (1994).

[24] N. J. Begue, R. M. Everly, V. J. Hall, L. Haupert, and G. J. Simpson, J. Phys. Chem. C **113**, 10166 (2009).

[25] S. R. Cloude, Optik **75**, 26 (1986).

[26] J. J. Gil, Eur. Phys. J. Appl. Phys. **40**, 1 (2007).

[27] R. Boyd, *Nonlinear Optics*, 3rd ed. (Academic Press, Boston, MA, 2008).

[28] Thus, any matrix notation of $\chi_{iA}^{(n)}$ (i.e., with two indices) represents the contracted notation of nth-order nonlinear susceptibilities.

[29] M. Samim, S. Krouglov, and V. Barzda, J. Opt. Soc. Am. B **32**, 451 (2015).

[30] M. Born and E. Wolf, *Principles of Optics*, 7th ed. (Cambridge University Press, Cambridge, MA, 1999).

[31] For any vector ψ of length $n+1$, let $\rho = \psi \otimes \psi^{\dagger}$: then $n[\mathrm{Tr}(\eta_1\rho)]^2 = \sum_{N=2}^{(n+1)^2} [\mathrm{Tr}(\eta_N\rho)]^2$. The set of η matrices are defined in Appendix: η matrices for nonlinear polarimetry.

[32] K. Kim, L. Mandel, and E. Wolf, J. Opt. Soc. Am. A **4**, 433 (1987).

[33] M. Samim, D. Sandkuijl, I. Tretyakov, R. Cisek, and V. Barzda, Int. J. Mol. Sci. **14**, 18520 (2013).

[34] S. Plotnikov, V. Juneja, A. B. Isaacson, W. A. Mohler, and P. J. Campagnola, Biophys. J. **90**, 328 (2006).

[35] S. W. Chu, S. Y. Chen, G. W. Chern, T. H. Tsai, Y. C. Chen, B. L. Lin, and C. K. Sun, Biophys. J. **86**, 3914 (2004).

[36] G. Kimura, Phys. Lett. A **314**, 339 (2003).

[37] This is to simplify the indices and to conform to a Stokes-Mueller notation of vector = matrix × vector. The matrices η' can also be used directly for polarimetry, in which case there will be an additional index for the entity representing the incoming radiation as well as for the entity representing the medium.

[38] M. Samim, S. Krouglov, and V. Barzda, arXiv:1512.09102.