# Molecular and surface hyperpolarizability of oriented chromophores of low symmetry

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In chromophores of low symmetry, including chiral species, modeling calculations generally do not produce the most convenient set of coordinates for evaluating the molecular second order nonlinear polarizability tensor  $\beta^{(2)}$ . By referencing the internal coordinate axes with respect to a single, dominant transition, the number of significant electric-dipole allowed  $\beta^{(2)}$  tensor elements can be reduced from 18 in second harmonic generation (SHG) to at most 3, with the complete removal of all chiral elements. This coordinate transformation reduces the complexity of SHG measurements of oriented chiral systems to a level consistent with chromophores of significantly higher symmetry and provides a straightforward approach for extracting orientation information from polarization measurements.

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## INTRODUCTION

The continuing expansion of surface-selective nonlinear optical methods into studies of biological systems requires the development of new methods to interpret polarization measurements of chiral films. To date, second harmonic generation polarization measurements designed to interpret molecular orientation have been primarily performed on films of dye molecules of reasonably high symmetry (often  $C_{2V}$  or higher).<sup>1-8</sup> In these instances, the number of unique nonzero elements of the second order nonlinear optical tensor  $\beta^{(2)}$  of the isolated chromophore reduces to only a few (e.g., only  $\beta_{z'z'z'}$ ,  $\beta_{z'x'x'}$ , and  $\beta_{x'x'z'}$  remain for chromophores with  $C_{2V}$  symmetry), with one element often dominating the nonlinear response. Notable exceptions include studies by Corn, Higgins, and co-workers and others, in which methods of treating chromophores with nonzero  $\beta_{z'x'x'}$  and  $\beta_{z'z'z'}$  contributions were presented.<sup>3,5</sup> In the limiting cases in which only one or two elements of the  $\beta^{(2)}$ tensor are significant, the measured nonlinearity of the surface film (described by the  $\chi^{(2)}$  tensor) can be used to interpret parameters related to molecular orientation using fairly simple expressions.<sup>1–7,9–11</sup> In contrast, chromophores of low symmetry generally have unique nonzero values for all 18 independent elements of the  $\beta^{(2)}$  tensor for second harmonic generation and all 27 for sum frequency generation (SFG). This striking increase in the number of contributing elements of the  $\beta^{(2)}$  tensor has restricted meaningful extraction of orientation information in systems of low symmetry, including chiral films.

The importance of reliable polarization interpretation in oriented chiral systems is highlighted by the pioneering work of Hicks and co-workers<sup>12–14</sup> and Persoons and co-workers,<sup>15–17</sup> in which both groups independently demonstrated the presence of anomalously large chiral effects in nonlinear optical measurements of ultrathin surface films. Second harmonic generation circular dichroism (SHG-CD) experiments yielded dichroic ratios approaching and exceeding 100%, values several orders of magnitude greater than typically observed in the linear analog of absorbance circular

dichroism.<sup>12,14,17–20</sup> Following the development of SHG-CD, several intimately related chiral effects were observed. Hicks and co-workers<sup>13,20</sup> have developed a nonlinear optical analog of optical rotary dispersion. Persoons and co-workers have demonstrated linear dichroism in SHG (SHG-LD), which is the difference in detected SHG intensity for light linearly polarized at  $+45^{\circ}$  vs  $-45^{\circ}$  and has no analog in absorbance measurements.<sup>21</sup> Verbiest, Kauranen, Persoons, and co-workers demonstrated that nonlinear optical activity can occur in surface films of achiral chromophores exhibiting in-plane anisotropy, provided the measurement is performed in an experimental geometry with no mirror plane.<sup>22–25</sup> Sum frequency generation in chiral liquids has also been recently demonstrated as a novel probe of molecular chirality.<sup>26–32</sup>

This remarkable sensitivity to chirality suggests nonlinear optical techniques such as SHG and SFG should be particular useful in structural studies, provided the chiral response can be correlated with surface and molecular organization. Maki and Persoons,<sup>33</sup> Hache, Mesnil, and Schanne-Klein,<sup>34</sup> and Hicks and co-workers<sup>14</sup> have reported theoretical modeling studies focused primarily on understanding the molecular origins of the second-order nonlinear optical response. In previous work from this laboratory,<sup>35</sup> an alternative potential source of chiral effects in SHG measurements was theorized, in which SHG-CD can arise from surface orientation and packing rather than directly from chromophore chirality. As a general tool for interpreting nonlinear optical polarization measurements in oriented chiral and achiral systems, the present work describes a procedure for expressing the molecular hyperpolarizability using any arbitrary internal coordinate system, with significant simplification achieved by referencing the coordinates with respect to a single transition dominating the nonlinear response at a given incident wavelength.

#### THEORY

The complex hyperpolarizability tensor elements of individual chromophores may be evaluated explicitly from sumover-states expressions.<sup>11,36–39</sup> The treatment presented here focuses exclusively on second harmonic generation as experimental observations of large  $\chi^{(2)}$  nonlinear optical circular dichroism have not been routinely observed in infraredvisible SFG surface experiments. Although SFG has been predicted and observed in the bulk from chiral solutions, the intensity of the nonlinear field attributed to chiral interactions was typically four to six orders of magnitude weaker than for analogous SHG measurements of oriented chiral surface systems.<sup>27,29–31</sup> The relative values of all nonzero elements of the complex  $\beta^{(2)}$  tensor can be determined by summing together the contributions from all the excited states and projection onto the internal molecular coordinates:<sup>11,36</sup>

$$\boldsymbol{\beta}_{ijk}^{(2)}(-2\omega;\omega,\omega) = \sum_{n',n} (\boldsymbol{\beta}_{ijk})_{n'n}, \qquad (1)$$

$$\begin{split} (\beta_{ijk})_{n'n} \\ &\equiv -\frac{1}{8\hbar^2} \{ \mu^i_{n'n} (\mu^j_{0n} \mu^k_{on'} + \mu^j_{0n'} \mu^k_{n0}) [f(\bar{1},1) + f(1,\bar{1})] \\ &+ \mu^i_{n0} (\mu^j_{0n'} \mu^k_{n'n} + \mu^j_{n'n} \mu^k_{n'0}) [f(\bar{1},\bar{3}) + f(1,3)] \\ &+ \mu^i_{0n'} (\mu^j_{n'n} \mu^k_{n0} + \mu^j_{n0} \mu^k_{n'n}) [f(3,1) + f(\bar{3},\bar{1})] \}. \end{split}$$

The *ijk* lowercase subscripts and superscripts refer to the molecular coordinate axes, with  $\mu_{ba}^{i}$  representing the projection along the *i* axis of the transition moment between states

*a* and *b*. Equation (1) simply states that the total hyperpolarizability of an isolated chromophore is a coherent sum of combined pairwise interactions between the ground and the excited states. A shorthand notation has been adopted, in which  $(\beta_{ijk})_{n'n}$  is an  $N \times N$  square matrix with each element describing the nonlinear contributions from the respective two or three state interactions for a given set of *ijk* coordinates for all *N* excited states. The notation of Pugh and Morley has been used for the *f* functions, which contain frequency dependencies and phase information.<sup>11</sup>

It is convenient to distinguish between the diagonal contributions to  $\beta^{(2)}$ , in which n' = n, and the off-diagonal contributions, in which  $n' \neq n \neq 0$ . Expressions for the individual diagonal [Eq. (2)] and off-diagonal [Eq. (3)] matrix elements including complex damping terms have been derived in an earlier work:<sup>11,35</sup>

$$(\beta_{ijk})_{n'=n} = \frac{-1}{2\hbar^2} \left\{ \frac{\delta_{n0}^i \mu_{n0}^j \mu_{n0}^k}{\omega_{n0}^2 - (\omega + i\Gamma_{n0})^2} + \frac{\mu_{n0}^i (\delta_{n0}^j \mu_{n0}^k + \mu_{n0}^j \delta_{n0}^k) (\omega_{n0}^2 + 2\omega^2)}{[\omega_{n0}^2 - (2\omega + i\Gamma_{n0})^2][\omega_{n0}^2 - (\omega + i\Gamma_{n0})^2]} \right\},$$
(2)

$$(\beta_{ijk})_{n'\neq n\neq 0} = \frac{-1}{4\hbar^2} \left\{ \begin{array}{c} \frac{\mu_{nn'}^{i}(\mu_{n0}^{j}\mu_{n'0}^{k} + \mu_{n'0}^{j}\mu_{n0}^{k})(\omega_{n0}\omega_{n'0} + \omega^{2})}{[\omega_{n'0}^{2} - (\omega + i\Gamma_{n'0})^{2}][\omega_{n0}^{2} - (\omega + i\Gamma_{n0})^{2}]} \\ + \frac{\mu_{n0}^{i}(\mu_{n'0}^{j}\mu_{n'n}^{k} + \mu_{n'n}^{j}\mu_{n'0}^{k})(\omega_{n0}\omega_{n'0} + 2\omega^{2})}{[\omega_{n'0}^{2} - (\omega + i\Gamma_{n'0})^{2}][\omega_{n0}^{2} - (2\omega + i\Gamma_{n0})^{2}]} \\ + \frac{\mu_{n'0}^{i}(\mu_{n0}^{j}\mu_{n'n}^{k} + \mu_{n'n}^{j}\mu_{n0}^{k})(\omega_{n0}\omega_{n'0} + 2\omega^{2})}{[\omega_{n'0}^{2} - (2\omega + i\Gamma_{n'0})^{2}][\omega_{n0}^{2} - (\omega + i\Gamma_{n0})^{2}]} \end{array} \right\}.$$
(3)

In Eqs. (2) and (3),  $\omega_{ba}$  is the resonant frequency of the transition between states *a* and *b* with 0 indicating the ground state,  $\Gamma_{ba}$  is the corresponding damping constant,  $\omega$  is the fundamental frequency, and  $\delta_{ba}^{i}$  is the projection along the *i* axis of the difference in permanent dipole between states *a* and *b*.

In general, both diagonal and off-diagonal contributions to  $\beta^{(2)}$  must be considered at a given incident frequency. In the specific instance of a chromophore with strong resonance enhancement with state *n* at the second harmonic frequency, Eq. (1) reduces to the expression

$$\beta_{ijk}^{(2)}(-2\omega;\omega,\omega) \approx \frac{-\mu_{n0}^{i}}{\hbar^{2}[\omega_{n0}^{2}-(2\omega+i\Gamma_{n0})^{2}]} \times \left[ \begin{pmatrix} (\delta_{n0}^{j}\mu_{n0}^{k}+\mu_{n0}^{j}\delta_{n0}^{k}) \\ +\sum_{n'} \left(\frac{\omega}{\omega_{n'0}-\omega}\right)(\mu_{n'0}^{j}\mu_{n'n}^{k}+\mu_{n'n}^{j}\mu_{n'0}^{k}) \right].$$
(4)

Clearly, for systems with real states resonant at both the fun-

damental and second harmonic frequencies (i.e., if  $\omega_{n0}$ )  $\approx 2\omega$  and  $\omega_{n'0} \approx \omega$ ), the off-diagonal coherent couplings between excited states indicated in the summation in Eq. (6)become doubly-resonant and are expected to dominate the hyperpolarizability.<sup>38,40–42</sup> Without the double resonance, the situation is not as obvious. Resonance enhancement with a strong charge transfer transition such as in donor/acceptor dyes will exhibit a strong transition moment  $\mu$  and large change in permanent dipole  $\delta$ , suggesting the hyperpolarizability will be dominated by diagonal interactions. Certainly, the relatively large second-order nonlinearity of chargetransfer chromophores has been well established for decades.<sup>37,43-46</sup> Ålthough hyperpolarizability contributions from off-diagonal three-state couplings are routinely much smaller than the diagonal contributions in organic chromophores,<sup>43</sup> these terms cannot be dismissed out of hand and may be significant in some instances (e.g., for double resonances). Given the prolific use of charge-transfer chromophores in nonlinear optical organic thin films and since discussion of internal coordinates in systems dominated by coherent three-state off-diagonal couplings has been detailed in other work,<sup>35</sup> the following discussion will focus exclusively on chromophores dominated by diagonal, two-state interactions.

The surface second-order nonlinear optical tensor  $\chi^{(2)}$  is derived by summing the  $\beta^{(2)}$  tensor contributions from all the oriented chromophores at the interface:

$$\chi_{IJK}^{(2)} = \sum_{ijk=x'y'z'} N_s \langle R_{Ii} R_{Jj} R_{Kk} \rangle \beta_{ijk} \,. \tag{5}$$

 $N_s$  is the number density of surface chromophores and  $R_{\Lambda\lambda'}$ are elements of the Euler rotation matrix relating the molecular coordinate system (indicated by lowercase primed letters) to the surface coordinate system (indicated by uppercase letters). The surface X and Y axes are identical in SHG measurements with a single incident beam and a surface system invariant to rotation about the surface normal (i.e., uniaxial with  $C_{\infty}$  symmetry). Combining this relation with the symmetry condition that the right two indices in  $\chi_{IIK}$  are interchangeable in SHG leads to only four nonzero independent elements of  $\chi^{(2)}$  remaining in uniaxial films (i.e., with one unique axis normal to the surface):  $\chi_{ZZZ}$ ,  $\chi_{ZXX} = \chi_{ZYY}$ ,  $\chi_{XXZ} = \chi_{XZX} = \chi_{YYZ} = \chi_{YZY}$ , and  $\chi_{XYZ} = \chi_{XZY} = -\chi_{YXZ} = -\chi_{YZX}$ .<sup>47</sup> Implicit in Eq. (5) is the assumption that every chromophore is identical for all orientation angles and surface concentrations. Although this approximation routinely fails at high surface coverages (e.g., from aggregation<sup>48-51</sup> and/or reorientation<sup>10,11,49-56</sup>), it has been shown to be reasonably reliable in a broad variety of submonolayer films.<sup>5,11,57–59</sup>

In the most general case of molecular  $C_1$  symmetry, all 27 elements of the molecular hyperpolarizability tensor  $\beta^{(2)}$ may be nonzero, 18 of which are unique in second harmonic generation. Each of the four independent nonzero elements of  $\chi^{(2)}$  present in uniaxially oriented systems can contain contributions from up to 18 different unique  $\beta^{(2)}$  tensor elements. Explicit evaluation of Eq. (5) followed by simplification yields the following generalized expressions for uniaxial systems:

$$\chi_{ZZZ} = N_s \left\{ \begin{array}{c} \langle \cos^3 \theta \rangle \beta_{z'z'z'} - \langle \sin^2 \theta \cos \theta \sin \psi \cos \psi \rangle (2\beta_{x'y'z'} + 2\beta_{y'x'z'} + 2\beta_{z'x'y'}) \\ + \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (2\beta_{x'x'z'} + \beta_{z'x'x'}) + \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (2\beta_{y'y'z'} + \beta_{z'y'y'}) \\ + \langle \sin \theta \sin \psi \rangle (2\beta_{z'y'z'} + \beta_{y'z'z'}) - \langle \sin \theta \cos \psi \rangle (2\beta_{z'x'z'} + \beta_{z'z'z'}) \\ + \langle \sin^3 \theta \sin \psi \rangle (2\beta_{x'x'y'} + \beta_{y'x'x'} - 2\beta_{z'y'z'} - \beta_{y'z'z'}) \\ - \langle \sin^3 \theta \cos \psi \rangle (2\beta_{y'x'y'} + \beta_{x'y'y'} - 2\beta_{z'x'z'} - \beta_{x'z'z'}) \\ + \langle \sin^3 \theta \sin^3 \psi \rangle (\beta_{y'y'y'} - \beta_{y'x'x'} - 2\beta_{x'x'y'}) - \langle \sin^3 \theta \cos^3 \psi \rangle (\beta_{x'x'x'} - \beta_{x'y'y'} - 2\beta_{y'x'y'}) \right\}, \quad (6a)$$

 $\chi_{XXZ}$ 

$$= \frac{1}{2}N_{s} \begin{cases} \langle \sin^{2}\theta\cos\theta\rangle\beta_{z'z'z'} + \langle \cos\theta\rangle(\beta_{x'x'z'} + \beta_{y'y'z'}) \\ -\langle \sin^{2}\theta\cos\theta\cos^{2}\psi\rangle(2\beta_{x'x'z'} + \beta_{z'x'y'}) - \langle \sin^{2}\theta\cos\theta\sin^{2}\psi\rangle(2\beta_{y'y'z'} + \beta_{z'y'y'}) \\ +\langle \sin^{2}\theta\cos\theta\sin\psi\cos\psi\rangle(2\beta_{x'y'z'} + 2\beta_{y'x'z'} + 2\beta_{z'x'y'}) + \langle \sin\theta\cos\psi\rangle(\beta_{y'y'y'} - \beta_{y'z'z'}) + (\beta_{x'x'y'} - \beta_{z'y'z'}) \\ -\langle \sin\theta\cos\psi\rangle(\beta_{x'x'x'} - \beta_{x'z'z'} + \beta_{y'x'y'} - \beta_{z'x'y'}) \\ +\langle \sin^{3}\theta\sin\psi\rangle(\beta_{y'z'z'} - \beta_{y'y'y'} + 2\beta_{z'x'y'} - 2\beta_{y'x'y'}) \\ -\langle \sin^{3}\theta\cos\psi\rangle(\beta_{x'z'z'} - \beta_{x'y'y'} + 2\beta_{z'x'y'} - 2\beta_{y'x'y'}) \\ +\langle \sin^{3}\theta\sin^{3}\psi\rangle(\beta_{y'x'x'} + \beta_{x'x'y'} - \beta_{y'y'y'}) - \langle \sin^{3}\theta\cos^{3}\psi\rangle(\beta_{x'y'y'} + \beta_{y'x'y'} - \beta_{x'x'x'}) \end{cases} \right\},$$

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$$\chi_{ZXX} = \frac{1}{2} N_s \begin{cases} \langle \cos^2 \theta \rangle (\beta_{z'y'y'} - 2\beta_{x'x'z'}) + \langle \cos \theta \sin^2 \psi \rangle (\beta_{z'x'x'} - 2\beta_{y'y'z'}) \\ + \langle \cos^3 \theta \cos^2 \psi \rangle (2\beta_{x'x'z'} + \beta_{z'x'x'}) + \langle \cos^3 \theta \sin^2 \psi \rangle (2\beta_{y'y'z'} + \beta_{z'y'y'}) \\ + \langle \sin^2 \theta \cos \theta \rangle \beta_{z'z'z'} + \langle \sin^2 \theta \cos \theta \sin \psi \cos \psi \rangle (2\beta_{x'y'z'} + 2\beta_{y'x'z'} + 2\beta_{z'x'y'}) \\ + \langle \sin \theta \cos \psi \rangle (2\beta_{z'x'z'} - \beta_{x'y'y'} - \beta_{x'x'x'}) \\ + \langle \sin^3 \theta \cos \psi \rangle (2\beta_{y'x'y'} + \beta_{x'y'y'} - 2\beta_{z'x'z'} - \beta_{x'z'z'}) \\ - \langle \sin \theta \sin \psi \rangle (2\beta_{z'y'z'} - \beta_{y'x'z'} - \beta_{y'y'y'}) \\ - \langle \sin^3 \theta \sin \psi \rangle (2\beta_{x'x'y'} + \beta_{y'x'x'} - 2\beta_{z'y'z'} - \beta_{y'z'z'}) \\ + \langle \sin^3 \theta \cos^3 \psi \rangle (\beta_{x'x'x'} - \beta_{x'y'y'} - 2\beta_{y'x'y'}) \\ - \langle \sin^3 \theta \sin^3 \psi \rangle (\beta_{x'y'y'} - \beta_{x'x'x'} - 2\beta_{x'x'y'}) \\ - \langle \sin^3 \theta \sin^3 \psi \rangle (\beta_{x'y'y'} - \beta_{y'x'z'} - \beta_{y'z'z'}) \\ + \langle \sin^2 \theta \cos^2 \psi \rangle (\beta_{x'y'y'} + \beta_{z'x'z'} - \beta_{x'z'z'} - \beta_{y'z'y'}) \\ + \langle \sin^2 \theta \cos^2 \psi \rangle (\beta_{y'x'z'} - \beta_{z'x'y'}) - \langle \sin^2 \theta \sin^2 \psi \rangle (\beta_{x'y'z'} - \beta_{z'x'y'}) \\ \end{pmatrix} \right\}.$$
(6c)

Internal coordinates. The relations in Eq. (6) will hold irrespective of the internal coordinate system of the chromophores used to generate the  $\beta^{(2)}$  tensor. Many modeling calculations assign coordinate axes along the internal moments of inertia. In systems of high symmetry, these same internal coordinates often serendipitously correspond to convenient symmetry axes for describing electronic excitations. However, in general, the coordinate systems assigned from modeling calculations are not necessarily the simplest to use in hyperpolarizability calculations in systems of low symmetry. A more convenient set of internal coordinates is proposed, in which the coordinates are referenced with respect to a single excited state that dominates the hyperpolarizability at a given set of wavelengths.<sup>35</sup>

Within the validity of the two-state approximation, the molecular hyperpolarizability can be constructed from two vectors inside the molecular frame  $\delta$  and  $\mu$ . It is convenient to construct a coordinate system referenced with respect to these two vectors such that the internal z' axis is defined to be parallel to the change in permanent dipole  $\delta$  between the ground state and the reference excited state and the x' axis is defined such that it contains the transition moment  $\mu$ . Using these  $\delta - \mu$  coordinates, all projections of  $\mu$  onto the molecular y' axis are zero and all projections of  $\delta$  onto the x' or y' axes are zero. By redefining the coordinates in this manner, it is immediately apparent that all  $\beta^{(2)}$  elements with y indices must vanish in two-state chromophores. The additional requirement that  $\delta^{x'} = 0$  limits the number of nonzero independent elements of  $\beta^{(2)}$  to just three;  $\beta_{z'z'z'}$ ,  $\beta_{z'x'x'}$ , and  $\beta_{x'x'z'}$ . In the  $\delta$ - $\mu$  coordinate system, the expressions in Eq. (6) reduce to those in Eq. (7):<sup>35</sup>

$$\chi_{ZZZ} = N_{s} [\langle \cos^{3} \theta \rangle \beta_{z'z'z'} + \langle \sin^{2} \theta \cos \theta \sin^{2} \psi \rangle (\beta_{z'x'x'} + 2\beta_{x'x'z'})], \qquad (7a)$$

$$\chi_{ZXX} = \frac{1}{2} N_s \bigg[ \frac{\langle \sin^2 \theta \cos \theta \rangle \beta_{z'z'z'} + \langle \cos \theta \rangle \beta_{z'x'x'}}{-\langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (\beta_{z'x'x'} + 2\beta_{x'x'z'})} \bigg],$$
(7b)

$$\chi_{XXZ} = \frac{1}{2} N_s \begin{bmatrix} \langle \sin^2 \theta \cos \theta \rangle \beta_{z'z'z'} + \langle \cos \theta \rangle \beta_{x'x'z'} \\ - \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (\beta_{z'x'x'} + 2\beta_{x'x'z'}) \end{bmatrix},$$
(7c)

$$\chi_{XYZ} = \frac{1}{2} N_s [\langle \sin^2 \theta \sin \psi \cos \psi \rangle (\beta_{x'x'z'} - \beta_{z'x'x'})].$$
(7d)

For practical reasons, most SHG investigations are performed with the dominating contributions to the hyperpolarizability arising from resonant interactions with a single excited state on or near the second harmonic frequency instead of the fundamental frequency. In this limiting case, contributions to  $\beta^{(2)}$  from  $\beta_{z'x'x'}$  can be safely neglected [Eq. (2)]. If the angle between  $\delta$  and  $\mu$  is defined to be  $\gamma_{\delta\mu}$ , then  $\mu^{x'}$  $= |\mu| \sin \gamma_{\delta\mu}$  and  $\mu^{z'} = |\mu| \cos \gamma_{\delta\mu}$ . Substitution into Eq. (7) allows for further simplification of the  $\chi^{(2)}$  tensor:

$$\chi_{ZZZ} \propto 2 \langle \cos^3 \theta \rangle \cos^2 \gamma_{\delta\mu} + 2 \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle \sin^2 \gamma_{\delta\mu},$$
(8a)

$$\chi_{ZXX} \propto 2 \langle \sin^2 \theta \cos \theta \rangle \cos^2 \gamma_{\delta\mu} - \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle \sin^2 \gamma_{\delta\mu}, \qquad (8b)$$

$$\chi_{XXZ} \propto \langle \sin^2 \theta \cos \theta \rangle \cos^2 \gamma_{\delta\mu} + \frac{1}{2} \langle \cos \theta \rangle \sin^2 \gamma_{\delta\mu} - \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle \sin^2 \gamma_{\delta\mu}, \qquad (8c)$$

$$\chi_{XYZ} \propto \frac{1}{2} \langle \sin^2 \theta \sin \psi \cos \psi \rangle \sin^2 \gamma_{\delta\mu}$$
. (8d)

All phase information in Eq. (8) is contained within the common complex proportionality constant. Simple geometric arguments combined with the relations in Eq. (8) allow for determination of the angle  $\gamma_{\delta\mu}$  from experimental measurements of the relative values of the surface  $\chi^{(2)}$  tensor elements:



FIG. 1. Visible spectrum and chemical structure (inset) of rhodamine 6G ( $10^{-5}$  M in methanol).

$$\tan^{2} \gamma_{\delta \mu} = \frac{2\beta_{x'x'z'}}{\beta_{z'z'z'}} = \frac{4\chi_{XXZ} - 4\chi_{ZXX}}{2\chi_{ZXX} + \chi_{ZZZ}}.$$
 (9)

An analogous expression for  $\gamma_{\delta\mu}$  can be derived to treat systems with isolated transitions resonant with the fundamental frequency, in which case  $\beta_{z'x'x'}$  and  $\beta_{x'x'z'}$  are approximately equal and opposite:

$$\tan^2 \gamma_{\delta\mu} = \frac{\beta_{x'x'z'}}{\beta_{z'z'z'}} = \frac{\chi_{XXZ} - \chi_{ZXX}}{\chi_{XXZ} + \chi_{ZXX} + \chi_{ZZZ}}.$$
 (10)

### MODELING CALCULATIONS

Rhodamine 6G (R6G) was used as a model chromophore primarily because of the wealth of theoretical and experimental work exploring the nonlinear optical properties of rhodamine dye films.<sup>48–50,60–63</sup> Molecular modeling calculations for the rhodamine 6G cation in vacuo were performed using HYPERCHEM with geometry optimization and electronic structure calculations performed using the PM3 numerical method. Potential energy calculations confirmed an optimal twist angle  $\alpha$  of ~90° (used in all calculations), with differences in energy of only a few kcal/mol for  $55^{\circ} \le \alpha \le 115^{\circ}$ . Inspection of the UV-visible spectrum of R6G in methanol in Fig. 1 reveals a dominating absorbance at  $\sim$ 530 nm. Molecular modeling calculations of R6G in vacuum generated different values for the transition energies than those observed in methanol, but the dominating charge-transfer transition at  $\sim$ 530 nm in solution can be assigned to the strong resonance calculated at 466 nm (corresponding to a theoretical  $2\omega$  resonance for a fundamental beam at 932 nm). For incident wavelengths around 1  $\mu$ m, measurements have confirmed that this single resonant feature dominates the nonlinear optical response of rhodamine 6G.<sup>10,11,51</sup>

Hyperpolarizability calculations were performed by explicit evaluation of Eq. (1) using the vectors  $\mu$  and  $\delta$  ob-



FIG. 2. Real (a) and imaginary (b) components of the three nonzero independent elements of the  $\beta^{(2)}$  tensor remaining in the  $\delta$ - $\mu$  coordinate system, determined from molecular modeling calculations of rhodamine 6G (solid= $\beta_{x'x'z'}$ , dashed= $\beta_{z'z'z'}$ , dotted =  $\beta_{z'x'x'}$ ).

tained from molecular modeling. Calculations of  $\beta^{(2)}$  were performed using Eq. (3) in two different coordinate systems, first using the coordinates provided by the modeling program from the moments of inertia [hereby referred to as the inertial coordinates (IC's)] then using the  $\delta \mu$  coordinates referenced with respect to the strong transition at 466 nm. The  $\delta \mu$ coordinates were defined as follows:  $z'_{\delta\mu} = \delta/|\delta|$ ,  $y'_{\delta\mu} = \delta$  $\times \mu/|\delta \times \mu|$ , and  $x'_{\delta\mu} = y'_{\delta\mu} \times z'_{\delta\mu}$ . For all transitions, a damping parameter of  $\Gamma_{n0} = 80$  THz was chosen to generate linewidths comparable to those observed in solution (~20 nm). The line shapes shown in Figs. 2–6 are for illustrative purposes only. Berkovic and co-workers have demonstrated the inadequacies of using Lorenzian line shapes to rigorously describe inhomogeneously broadened Gaussian peaks in nonlinear optical measurements.<sup>39</sup>

In both the inertial and  $\delta$ - $\mu$  molecular coordinate systems,



FIG. 3. Real components of the eighteen nonzero independent elements of the  $\beta^{(2)}$  tensor present when using the inertial coordinate system provided from molecular modeling calculations of rhodamine 6G. solid =  $\beta_{z'x'y'}$ , dashed =  $\beta_{z'x'x'}$ , In (a), dotted =  $\beta_{z'x'z'}$ . (b), solid =  $\beta_{z'y'z'}$ , dashed =  $\beta_{z'y'y'}$ , In dotted =  $\beta_{z'z'z'}$ . In (c), solid =  $\beta_{x'x'z'}$ , dashed =  $\beta_{x'x'y'}$ , dotted =  $\beta_{x'x'x'}$ . In (d), solid =  $\beta_{x'y'z'}$ , dashed =  $\beta_{x'y'y'}$ , dotted =  $\beta_{x'z'z'}$ . In (e), solid =  $\beta_{y'x'z'}$ , dashed =  $\beta_{y'x'x'}$ , dotted =  $\beta_{y'x'y'}$ . In (f), solid =  $\beta_{y'z'z'}$ , dashed =  $\beta_{y'y'y'}$ , dotted =  $\beta_{y'y'z'}$ .

the  $\chi^{(2)}$  surface hyperpolarizability tensor elements were determined using the more generalized expressions in Eq. (6) by summing the complex diagonal contributions from all transitions with non-negligible oscillator strengths (i.e., from the trace of the  $\beta_{ijk}^{n'n}$  matrix). Although the expressions in Eq. (7) should be valid for evaluating  $\chi^{(2)}$  in the  $\delta$ - $\mu$  coordinate system in the spectral region around the dominating resonance (fundamental wavelength of ~932 nm), the more rigorous general expressions in Eq. (5) were used to include contributions from higher-energy resonances.

### **RESULTS/DISCUSSION**

Theoretical values of all 18 nonzero  $\beta^{(2)}$  tensor elements present for SHG measurements are shown in Figs. 2 (real components) and 3 (imaginary components), calculated for rhodamine 6G using the inertial coordinates assigned from the modeling calculations. Analogous calculations, shown in



FIG. 4. Imaginary components of the eighteen nonzero independent elements of the  $\beta^{(2)}$  tensor present when using the inertial coordinate system provided from molecular modeling calculations of rhodamine 6G. The curve labels are identical to those used in Fig. 3.

Fig. 4, were also performed for the three nonzero unique  $\beta^{(2)}$  elements remaining after re-expressing the molecular hyperpolarizability in the  $\delta$ - $\mu$  coordinate system for the same molecule.

Values for the  $\chi^{(2)}$  tensor elements shown in Fig. 5 were calculated using the  $\delta$ - $\mu$  coordinate system for rhodamine 6G oriented with the  $\delta$  axis tilted at an angle  $\theta_{\delta\mu}$  equal to the SHG magic angle of 39.2° (the result obtained for a broad distribution in orientation angles)<sup>10,64</sup> and the twist angle  $\psi_{\delta\mu}$ equal to 0°. This particular choice of  $\psi_{\delta\mu}$  generates a zero value for the chiral tensor element  $\chi_{XYZ}$  in Eq. (7d), consistent with experimental expectations for an achiral surface film. Additionally, use of an apparent polar orientation angle approximately equal to the SHG magic angle and  $\psi_{\delta\mu}$  equal to 0° is consistent with previous experimental SHG polarization measurements of R6G at air/glass interfaces.<sup>42,48,62</sup>

To calculate the values of the same four  $\chi^{(2)}$  tensor elements using the inertial coordinates, the appropriate angles for  $\theta_{\rm IC}$  and  $\psi_{\rm IC}$  were first determined. The new molecular z' and x' axes were expressed with respect to the surface coordinates by first transforming them into the  $\delta$ - $\mu$  coordinate system, and then by transforming them further with the appropriate Euler rotation matrix. This generalized transfor-





FIG. 5. Real (a) and imaginary (b) components of the four independent  $\chi^{(2)}$  tensor elements present in uniaxial films, calculated for rhodamine 6G oriented with the  $\delta$  axis tilted at the SHG magic angle of 39.2° and the twist angle of the  $\mu$  axis oriented at 0° (solid= $\beta_{x'x'z'}$ , dashed= $\beta_{z'z'z'}$ , dotted= $\beta_{z'x'x'}$ ). In the inertial coordinate system, this orientation corresponds to  $\theta_{\rm IC}$ =49.0° and  $\psi_{\rm IC}$ =61.6°.

mation procedure is described mathematically in Eq. (11), in which  $\mathbf{v}'$  is an arbitrary vector expressed with respect to the coordinate system indicated by the subscripts,  $R_{\delta\mu}^{\text{surf}}$  is the Euler rotation matrix transforming the  $\delta$ - $\mu$  coordinate system to the surface coordinates, and  $T_{\text{IC}}^{\delta\mu}$  is the Cartesian transformation matrix relating the inertial and  $\delta$ - $\mu$  coordinates within the chromophore:

$$\mathbf{v}_{\rm surf}' = R_{\delta\mu}^{\rm surf} T_{\rm IC}^{\delta\mu} \mathbf{v}_{\rm IC}'. \tag{11}$$

FIG. 6. Real (a) and imaginary (b) components of the four independent  $\chi^{(2)}$  tensor elements present in uniaxial films, calculated for rhodamine 6G oriented with the  $\delta$  axis tilted at the SHG magic angle of 39.2° and the twist angle of the  $\mu$  axis oriented at 45° (solid= $\beta_{x'x'z'}$ , dashed= $\beta_{z'z'z'}$ , dotted= $\beta_{z'x'x'}$ ). In the inertial coordinate system, this orientation corresponds to  $\theta_{\rm IC}$ =72.6° and  $\psi_{\rm IC}$ =44.0°.

The angle  $\theta_{\rm IC}$  between the molecular z' axis in the IC coordinate system and the surface Z axis was evaluated from the dot product  $z' \cdot Z = \cos \theta_{\rm IC}$ , and the value for  $\psi_{\rm IC}$  from the relation  $x' \cdot Z = -\cos \theta_{\rm IC} \sin \psi_{\rm IC}$ . For  $\theta_{\delta\mu} = 39.2^{\circ}$  and  $\psi_{\delta\mu} = 0^{\circ}$ , the corresponding angles using the IC coordinates for R6G were  $\theta_{\rm IC} = 49.0^{\circ}$  and  $\psi_{\rm IC} = 61.6^{\circ}$ . A twist angle of  $\psi_{\delta\mu} = 0^{\circ}$  (and equivalently  $\psi_{\rm IC} = 61.6^{\circ}$ ) resulted in a zero-valued  $\chi_{XYZ}$  tensor element. Identical values of the four unique  $\chi^{(2)}$  tensor elements were generated using both the inertial and the  $\delta$ - $\mu$  coordinate systems, shown in Fig. 5,

supporting the validity of the expressions in Eqs. (2), (6), and (11) used to evaluate  $\beta^{(2)}$  and  $\chi^{(2)}$ .

A twist angle  $\psi$  equal to 45° in the  $\delta$ - $\mu$  coordinate system was used in Fig. 6 to model the expected surface response for a chiral film. The corresponding angles in the IC coordinate system were  $\theta_{\rm IC}$ =72.6° and  $\psi_{\rm IC}$ =44.0°. Again, both coordinate systems yielded identical results for the  $\chi^{(2)}$  tensor elements.

For a fundamental wavelength of 1064 nm, previous modeling calculations and experimental measurements have demonstrated that the molecular hyperpolarizability of rhodamine 6G is dominated by the  $\beta_{x'x'z'}$  tensor element.<sup>10,11,51</sup> These earlier findings are consistent with the results shown in Figs. 5 and 6 calculated for an incident wavelength around 1  $\mu$ m. In the case of a dominant  $\beta_{x'x'z'}$ tensor element, the relation  $\chi_{ZZZ} = -2\chi_{ZXX}$  should hold for the surface tensor elements. By inspection of Figs. 5 and 6 and by analysis of the corresponding data, this relation was found to be correct for a fundamental wavelength near 930 nm in both figures. The calculations performed using the inertial coordinates were not dominated by the  $\beta_{x'x'z'}$  tensor element for an incident wavelength around 1  $\mu$ m. In fact, almost all other  $\beta^{(2)}$  elements were greater in magnitude than  $\beta_{x'x'z'}$ , including the chiral elements  $\beta_{z'x'y'}$ ,  $\beta_{x'y'z'}$ , and  $\beta_{y'x'z'}$ . Nevertheless, the coherent summation of all  $\beta^{(2)}$  contributions still yielded the same expected  $\chi_{ZZZ} \cong$  $-2\chi_{ZXX}$  relation.

Interestingly, nonzero values of the chiral elements  $\beta_{x'y'z'} = \beta_{x'y'z'}, \ \beta_{y'x'z'} = \beta_{y'z'x'}, \ \text{and} \ \beta_{z'x'y'} = \beta_{z'y'x'} \text{ do}$ not necessarily generate nonzero values of the chiral surface tensor element  $\chi_{XYZ}$ , and vice versa. In Figs. 3 and 4, the molecular  $\beta_{x'y'z'}$  and  $\beta_{z'x'y'}$  elements in the IC coordinate system were greater in magnitude than either the  $\beta_{x'x'z'}$  or  $\beta_{z'z'z'}$  tensor elements, and yet the combined coherent contributions of all 18 unique nonzero  $\beta^{(2)}$  tensor elements still led to a negligible  $\chi_{XYZ}$  tensor element, shown in Fig. 5. For a molecular hyperpolarizability dominated by electric dipole interactions with a single excited state, these chiral elements of  $\beta^{(2)}$  were artifactual in the sense that they could be removed entirely by redefining the internal coordinates. In general, chiral information is lost in two-state chromophores by the ability to express the nonlinear activity of the chromophore entirely within a single internal plane, introducing effective mirror-plane symmetry.

Even in the absence of any chiral contributions to  $\beta^{(2)}$ , two-state chromophores can still generate films with nonzero values of the chiral  $\chi_{XYZ}$  surface tensor element, as demonstrated in Fig. 6 and in agreement with earlier predictions.<sup>35</sup> This source of chirality in the  $\chi^{(2)}$  tensor is purely structural in origin, arising from asymmetry in the twist angle  $\psi$  as the chromophores assemble at the interface. In fact, nonzero values of  $\chi_{XYZ}$  are predicted to be possible even in uniaxial films of achiral chromophores appropriately oriented at the interface.<sup>35</sup>

It is interesting to consider how chiral orientations of achiral chromophores may arise in thin surface films. Averaged over a sufficiently large area of the surface, achiral molecules such as rhodamine 6G allowed to assemble at achiral surfaces (e.g., fused silica) would be equally likely to twist positive vs negative in  $\psi$ . If  $\psi$  is an even function for all tilt angles  $\theta$ ,  $\langle \cos^2 \theta \sin \psi \cos \psi \rangle = 0$ ,  $\chi_{XYZ} = 0$ , and the resulting film is achiral. However, the same is not necessarily true for achiral (or effectively achiral) chromophores positioned within the framework of larger chiral structures, arising either from the surface itself or from other, chiral parts of the surface-bound molecules. In these instances, molecular and/or surface chirality can serve as an orientational template directing asymmetry in  $\psi$ .

The results shown in Fig. 6 suggest the possibility of a structural origin of surface SHG-CD in a two-state chromophore that is unique from previous theoretical descriptions by others. Maki and Persoons have developed a model system comprised of a single electron constrained to move along a helical path to describe circular dichroism in SHG.<sup>33</sup> In this model system, the magnetic dipole transition moment contributions resulting from the helical electron motion were found to be comparable to the electric dipole contributions arising from subtle phase differences between  $\chi_{XXZ}$  and  $\chi_{XYZ}$ .<sup>33</sup> Theoretical and experimental nonlinear optical studies by Hache, Mesnil, and Schanne-Klein have considered origins of circular dichroism similar to those present in linear measurements (e.g., absorbance), including electric dipole, magnetic dipole, and coupled-oscillator contributions.<sup>34,65,66</sup> Molecular modeling calculations by Byers et al.<sup>13</sup> considering only electric-dipole contributions have predicted nonzero values of chiral elements of the  $\beta^{(2)}$  tensors a chiral molecule using internal coordinates referenced with respect to a  $C_2$  symmetry axis. In most of these previous studies, the chiral response of the isolated chromophore was assumed to direct the circular dichroism of the surface layers.<sup>13,33,34,65,66</sup> In contrast, Eq. (7d) predicts an additional purely electric dipole-allowed possibility, in which molecular chirality serves to drive asymmetric surface packing of the chromophore. These structural contributions will generally be present for all chiral films and may be sufficient to explain many of the results previously attributed to chromophore chirality.

Molecular Orientation. In chiral surface systems in which the nonlinear optical response is dominated by two-state interactions, the methodology presented in this work allows for extraction of orientation information unavailable in comparable studies of achiral surfaces. Specifically, in the limiting case of a narrow orientation distribution and  $2\omega$  resonance, chiral films produce the four equations in Eq. (8) with the four unknowns  $\theta_{\delta\mu}$ ,  $\psi_{\delta\mu}$ ,  $\gamma_{\delta\mu}$ , and the common proportionality constant. From ratios of the  $\chi^{(2)}$  tensors, it should be possible to extract information on the polar tilt angle, the molecular twist angle, and the internal angle  $\gamma_{\delta\mu}$  between the transition moment and change in permanent dipole. For comparison, SHG studies of achiral films generally yield only a single orientation parameter that is dependent on both  $\theta_{\delta\mu}$  and  $\psi_{\delta\mu}$ .<sup>9,47</sup>

#### CONCLUSIONS

A methodology was presented allowing for interpretation of SHG polarization measurements using any arbitrary molecular coordinate system. The validity of this generalized approach was tested in molecular modeling calculations of rhodamine 6G, in which consistent surface  $\chi^{(2)}$  tensor elements were obtained using two different internal coordinate systems (one provided by molecular modeling calculations and the other using  $\delta$ - $\mu$  coordinates referenced with respect to the dominating transition). The  $\delta$ - $\mu$  coordinate system was shown to yield considerable simplification by effectively introducing a mirror-plane symmetry element, reducing the number of unique nonzero elements of the  $\beta^{(2)}$  tensor from 18 to three with loss of all chiral  $\beta^{(2)}$  elements. Near resonance, the number of significant  $\beta^{(2)}$  elements can be further reduced to only two.

Molecular modeling calculations of rhodamine 6G demonstrated that the presence of chiral contributions to  $\beta^{(2)}$ 

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does not necessarily result in nonzero values for the surface  $\chi_{XYZ}$  tensor element, and the absence of chiral contributions to  $\beta^{(2)}$  does not forbid nonzero values for the surface  $\chi_{XYZ}$  tensor element. Orientational origins of chirality in surface SHG measurements are still electric-dipole allowed, even for achiral chromophores such as rhodamine 6G, provided the chromophores assemble with asymmetry in the twist angle  $\psi$ . These structural contributions will generally be present for all chiral films and may be comparable in magnitude or larger than contributions directly dependent on the chromophore chirality. Work is in progress to assess the relative importance of these structural contributions by performing SHG-CD polarization studies of achiral chromophores adsorbed to chiral templated surfaces.

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