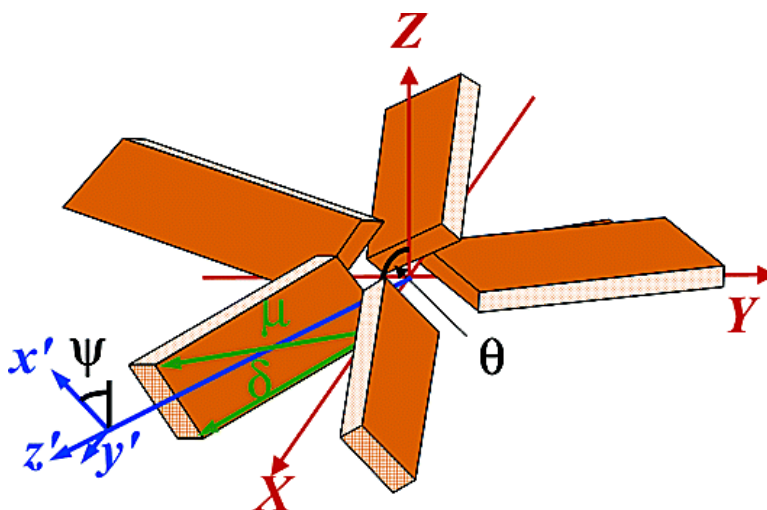Article

Experimental Confirmation of the Importance of Orientation in the Anomalous Chiral Sensitivity of Second Harmonic Generation

Brian J. Burke, Andrew J. Moad, Mark A. Polizzi, and Garth J. Simpson

$$\chi_{XYZ} = \tfrac{1}{2} N_s \left[\langle \sin^2 \theta \sin \psi \cos \psi \rangle \left(\beta_{x'x'z'} - \beta_{z'x'x'} \right) \right]$$

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Experimental Confirmation of the Importance of Orientation in the Anomalous Chiral Sensitivity of Second Harmonic Generation

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Abstract: Macromolecular interactions were demonstrated to yield large chiroptical effects in second harmonic generation measurements of ultrathin surface films. Second harmonic generation (SHG) has recently shown to be several orders of magnitude more sensitive to chirality in oriented systems than common linear methods, including absorbance circular dichroism (CD) and optical rotary dispersion (ORD). Numerous mechanisms have been developed to explain this anomalous sensitivity, with a general emphasis on understanding the molecular origins of the chromophore chirality. In this work, orientational effects alone are shown to be the dominant factor for generating large SHG chiral dichroic ratios in many surface systems. Three distinct uniaxial surface films of SHG-active achiral chromophores oriented at chiral templated surfaces were observed to yield chiral dichroic ratios as great as 40% in magnitude.

Understanding the origins of the remarkable sensitivity of second-order nonlinear optical phenomena to chirality is a crucial hurdle for the construction of novel chiral materials for efficient nonlinear optical photonic applications and for the meaningful interpretation of molecular-scale structure from second harmonic and sum frequency surface spectroscopic measurements of oriented chiral systems (including biological interfaces). In the mid-1990s, Hicks and co-workers and Persoons and co-workers both independently measured circular and linear chiral dichroic ratios approaching and exceeding 100% in nonlinear optical measurements of chiral surface films (i.e., more than 3 orders of magnitude greater than in absorbance circular dichroism).[1-6] Since this pioneering work, a plethora of molecular mechanisms has arisen to explain these effects.

From the more than 40 experimental and theoretical publications on the topic of chirality in SHG and SFG, three general models have emerged. In work led by Persoons and co-workers and by Schanne-Klein and co-workers, magnetic dipole contributions and/or interference between electric and magnetic dipole contributions have been suggested as potential candidates for generating large chiral effects in SHG and SFG.[2,3,6-17]

Alternatively, a number of groups have focused on explanations exclusively involving electric dipole-allowed contributions arising from chirality within the chromophore,[1,4,5,11,18-39] often

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through the presence of at least one pair of coupled oscillators.[18,25,28,30,31,38,39] More recently, theoretical work from this laboratory for surfaces[39,40] and by Ostroverkhov et al. for bulk media[41-44] suggests that macromolecular orientation can potentially generate significant chiral effects in uniaxial surface systems without the need for multiple coupled oscillators or even chiral chromophores at all.

The circular dichroic ratio R^{CD} in SHG is defined in eq 1, in which I is the intensity of the second harmonic light measured for left versus right circularly polarized incident beams (indicated by the L and R subscripts, respectively).[1,7,45,46]

$$R^{CD} \equiv \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)} = 4\frac{\text{Im}(FG^*)}{|F|^2 + |G|^2} \quad (1)$$

The right-most expression is a simplified form of the dichroic ratio, valid for uniaxial systems within the electric dipole approximation for light.[3,11,39] For detection of s-polarized SHG, $F_s = s_1\chi_{XXZ}$ and $G_s = -s_2\chi_{XYZ}$, in which each macroscopic hyperpolarizability $\chi^{(2)}$ tensor element describes the efficiency of generating second harmonic radiation under a given set of incident and exigent polarization conditions, indicated by the subscripts. The s_n coefficients are constants related to the experimental geometry and the thin film or material optical properties.[39,47,48] For p-polarized SHG, $F_p = -s_4\chi_{XYZ}$ and $G_p = -s_3\chi_{XXZ} + (s_5 - s_6)\chi_{ZXX} + s_7\chi_{ZZZ}$. In measurements of linear dichroic ratios (R^{LD}), the equations are identical except that the imaginary component in the right-most expression is replaced with the real component of (FG^*) (see Supporting Information).[11] *In uniaxial systems and within the electric dipole approximation for light, a nonzero value of the chiral tensor element χ_{XYZ} is required in order to generate significant chiroptical effects in SHG.* The presence or absence of chirality in SHG and SFG is most easily tested by the presence or absence of linear or circular dichroism. Although these chiral dichroic ratios are difficult to relate directly back to molecular-scale properties, they can serve as useful diagnostics for the presence of significant chiral macroscopic tensor elements.

Within the electric dipole approximation for light and assuming noninteracting chromophores, the second-order nonlinear polarizability tensor of the macroscopic system $\chi^{(2)}$ is related to the nonlinear polarizability tensor of the chromophore $\beta^{(2)}$ through orientational averages.[47,49,50]

$$\chi_{IJK}^{(2)} = \sum_{i'j'k' = x'y'z'} N_s \langle R_{Ii'}R_{Jj'}R_{Kk'}\rangle\beta_{i'j'k'}^{(2)} \quad (2)$$

In eq 2, N_s is the number density of chromophores and $R_{\Lambda\lambda'}$ are elements of the Euler rotation matrix relating the molecular
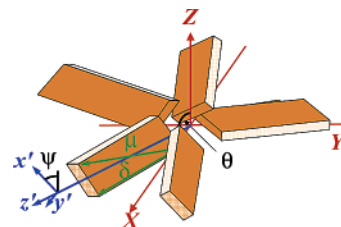
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Figure 1. Depiction of macromolecular surface chirality akin to that in a propeller, constructed from appropriate orientation of achiral "blades". Chiroptical effects in surface SHG can arise even in achiral chromophores if the planes orient with asymmetry in the twist angle ψ as shown in the above drawing and described mathematically in eq 3d.

coordinate system to the laboratory coordinate system. Although higher order effects such as those from magnetic dipoles may be significant in some instances, the electric dipole contributions are the most likely candidates for generating the large surface chiroptical effects routinely observed experimentally.[39]

Within the electric dipole approximation for light and in systems dominated by interactions between a single ground state and a single excited state, all chiral elements of the molecular hyperpolarizability tensor $\beta^{(2)}$ for SHG can be removed by judicious choice of an internal coordinate system, leaving $\beta_{z'z'z'}$, $\beta_{z'x'x'}$, and $\beta_{x'x'z'} = \beta_{x'z'x'}$ as the only three remaining nonzero independent elements.[39,40] Briefly, the second-order nonlinear optical response of a two-state chromophore can be completely defined by two vectors inside the molecular frame (the transition moment μ and the change in permanent dipole δ, as indicated in Figure 1),[39,40,51] introducing effective mirror-plane symmetry. For such systems, explicit evaluation of eq 2 yields the following expressions for the four possible nonzero independent elements of the macroscopic second-order nonlinear polarizability $\chi^{(2)}$ tensor.[39,40,47]

$$\chi_{ZZZ} = N_s[\langle\cos^3\theta\rangle\beta_{z'z'z'} + \langle\sin^2\theta\cos\theta\cos^2\psi\rangle(\beta_{z'x'x'} + 2\beta_{x'x'z'})] \quad (3a)$$

$$\chi_{ZXX} = (1/2)N_s[\langle\sin^2\theta\cos\theta\rangle\beta_{z'z'z'} + \langle\cos\theta\rangle\beta_{z'x'x'} - \langle\sin^2\theta\cos\theta\cos^2\psi\rangle(\beta_{z'x'x'} + 2\beta_{x'x'z'})] \quad (3b)$$

$$\chi_{XXZ} = \chi_{XZX} = (1/2)N_s[\langle\sin^2\theta\cos\theta\rangle\beta_{z'z'z'} + \langle\cos\theta\rangle\beta_{x'x'z'} - \langle\sin^2\theta\cos\theta\cos^2\psi\rangle(\beta_{z'x'x'} + 2\beta_{x'x'z'})] \quad (3c)$$

$$\chi_{XYZ} = \chi_{XZY} = -\chi_{YXZ} = -\chi_{YZX} = (1/2)N_s[\langle\sin^2\theta\sin\psi\cos\psi\rangle(\beta_{x'x'z'} - \beta_{z'x'x'})] \quad (3d)$$

In eq 3, θ and ψ are the Euler tilt and twist angles as defined in Figure 1 and referenced with respect to the molecular axes δ and μ. The first three expressions in eq 3 were reported over a decade ago by Heinz for achiral uniaxial films of chromophores with C_{2v} symmetry,[47] and the last expression was recently derived in this laboratory for chiral surfaces[39] and by Ostroverkhov et al. for oriented bulk media.[44] Despite the loss

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Table 1. Summary of the s- and p-Polarized SHG-CD and SHG-LD Measurements of Chiral Templated Interfaces[a]

	R_s^{CD}	R_s^{LD}	R_p^{CD}	R_p^{LD}
R6G	5.3% (4.6%)	4.5% (2.9%)	−0.2% (4.9%)	3.6% (8.0%)
system 1: R6G+BSA	−2.1% (3.9%)	−9.5% (7.1%)	−6.0% (3.3%)	36% (11%)
system 2: DTB	7.0% (3.7%)	−4.4% (1.6%)	−4.8% (2.7%)	44.0% (5.8%)
system 3: FITC−BSA	−24.8% (6.9%)	−4.8% (9.8%)	−21% (12%)	0% (12%)

[a] Values in parentheses are standard deviations from multiple measurements over multiple days. R6G: 100 μM aqueous rhodamine 6G solutions, $N =$ 4. System 1: aqueous solutions of ~1 μM BSA with 100 μM aqueous rhodamine 6G, $N = 9$. System 2: adsorbed DTB films, $N = 9$. System 3: aqueous solutions of ~80 μg/mL FITC−BSA, $N = 6$.

of nonlinear optical information regarding chromophore chirality in two-state systems, eq 3d predicts that nonzero values of the χ_{XYZ} tensor elements are still possible from orientational effects related to bulk and/or surface packing. For achiral molecules at achiral interfaces, the twist angle ψ is equally likely to be either positive or negative when averaged over the spot size of a focused optical beam, for which $\langle \sin^2 \theta \sin \psi \cos \psi \rangle = 0$ and $\chi_{XYZ} = 0$. However, for a chromophore interacting with an external chiral architecture or oriented at a chiral interface, asymmetry in the twist angle ψ is generally expected to be present, potentially generating non-negligible values of χ_{XYZ}. A pictorial representation of this type of orientation is shown in Figure 1. This origin of chirality is analogous to that found in a propeller, in which the individual propeller "blades" need not be chiral to generate macroscopic chirality. Indeed, the ability to create macroscopic chiral structures at surfaces from assembly of molecular chiral moieties has been confirmed in recent scanning probe microscopy measurements.[52,53] It is reasonable to suggest that similar effects may be expected in essentially all oriented chiral films.

The greatest benefits of nonlinear optical measurements of oriented chiral systems will be realized when the relative importance of the many possible contributions to the chiroptical nonlinear responses are evaluated for different classes of systems and methods are developed to relate the macroscopic measurements back to the molecular and macromolecular structure. The present work is directed toward elucidating the minimal molecular requirements necessary for generating large chiral effects in SHG. Specifically, the contributions arising from molecular orientation as described mathematically in eq 3d and depicted in Figure 1 were selectively isolated by performing SHG measurements of achiral dye films with strong electric dipole-allowed nonlinearity assembled at chiral templated interfaces.

Experimental Section

Three different interfacial systems were prepared and analyzed to evaluate the relative importance of orientational chiral contributions to the macroscopic chiroptical response. System 1 consisted of rhodamine 6G (R6G, Aldrich, 99%, $\lambda_{max} = 525$ nm) adsorbed on fused silica in the presence or absence of bovine serum albumin (BSA, Sigma). Solutions of either 400 μM R6G alone or ~1 μM BSA and 100 μM R6G were prepared in Nanopure water (Barnstead) and introduced into a sealed sample cell described elsewhere.[54] The surface coverage of rhodamine in both systems was determined from adsorption isotherm measurements to be approximately 60% of a full monolayer (adsorption isotherms are provided in the Supporting Information). System 2 consisted of a solution of 1 mg of a ~10 000 molecular weight

polydextran labeled with tetramethylrhodamine and biotin (DTB, Molecular Probes, on average less than one chromophore per polydextran chain, $\lambda_{max} = 555$ nm) in 1.5 mL of water. System 3 consisted of a solution of 2 mg of fluorescein−isothiocyanate−BSA (FITC−BSA, Sigma, $\lambda_{max} = 503$ nm in a multilayer film) per 25 mL of water. All solutions were used within 4 days. Measurements of system 1 were acquired in equilibrium with the protein and dye solution, the DTB samples in system 2 were rinsed with water before measurements to remove excess dye, while the FITC−BSA was adsorbed to the prism surface. In the experiments using just R6G, four measurements were taken over 3 days, while in system 1, nine measurements were taken over 6 days. In system 2, nine measurements were taken over 3 days, while in system 3, six measurements were taken over 2 days. The prisms were cleaned before each trial using a piranha solution (2 parts concentrated sulfuric acid, 1 part concentrated hydrogen peroxide), rinsed thoroughly with ultrapure water, and dried under a stream of nitrogen. (Piranha solution is a strong oxidant; use with care.) None of the systems investigated yielded detectable absorbance circular dichroism in the visible portion of the spectrum in solution-phase measurements (Jasco Spectrometer).

Circular and linear dichroic ratios from systems 1 and 3 were acquired using 5−7 ns pulses of 1064 nm light from a Nd:YAG laser (Continuum NY60) at a frequency of 10 Hz and ~1 mJ/pulse. The light first passed through a polarizing beam splitting cube, a half-wave plate, a quarter-wave plate set at 45°, and a visible blocking RG695 filter. The appropriately polarized light was then focused on a fused silica right angle prism in a total internal reflection configuration. The frequency-doubled light generated at the surface then passed through a half-wave plate, a polarizing beam splitting cube, an infrared absorbing filter, and a 532 nm interference filter prior to introduction to a Hamamatsu C7169 photomultiplier tube. Intensity data were recorded using a Tektronix TDS 2022 oscilloscope using 128 averages/measurement. Measurements of system 2 were acquired using a similar instrumental design employing a New Wave Research Polaris Nd:YAG laser generating 5−7 ns pulses of 1064 nm light at 20 Hz as previously described.[54] The errors in the dichroic ratios include the measured deviation over multiple days with multiple solutions. Errors within a given set of measurements were considerably lower. Similar dichroic ratios were obtained for multiple locations at the surfaces and for both orientations of the prism within the instrument, indicating the absence of in-plane anisotropy within the sample (the presence of in-plane orientational anisotropy can produce nonzero circular and linear dichroism in nonuniaxial systems through a mechanism independent of surface chirality[55−57]).

Results/Discussion

SHG-CD and -LD Measurements of Chiral Templated Interfaces. SHG-CD and -LD ratios for systems 1, 2, and 3 are summarized in Table 1. Large chiral dichroic ratios were observed for p-polarized SHG-LD in systems 1 and 2 (36% ±

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11% and 44.0% ± 5.8%, respectively) and for both s- and p-polarized SHG-CD in system 3 (−24.8% ± 6.9% and −21.4% ± 12%, respectively). All dichroic ratios were approximately zero for the adsorbed rhodamine/glass interface in the absence of a chiral template. Negligible signals were obtained for the bare prism as well as adsorbed BSA. Adsorption isotherms for system 1 are shown in Figure S1. Circular and linear dichroism measurements were acquired for surface coverages of rhodamine of approximately 60%.

The presence of chiral dichroic ratios well outside of experimental error of zero in all three systems indicates that the chiral and achiral elements of the $\chi^{(2)}$ tensor are comparable in magnitude. The absence of significant SHG from films of BSA alone in systems 1 and 3 indicates that the detected nonlinear responses arose exclusively from interactions with the oriented surface chromophores. Furthermore, the absence of absorbance CD at the wavelengths of relevance and the lack of chiral centers within the chromophores confirm that contributions to the surface nonlinearity from magnetic dipoles and/or other higher order chiral effects (beyond electric dipole) can be categorically excluded. Both the R6G and FITC chromophores exhibit approximately C_{2v} symmetry. Under conditions of resonance-enhancement at the second harmonic frequency with a state of B_1 symmetry (i.e., the long-axis transition in each chromophore), the only elements of the molecular nonlinear polarizability tensor allowed by symmetry are $\beta_{x'x'z'} = \beta_{x'z'x'}$.[58] This symmetry analysis is consistent with previous modeling calculations and experimental measurements.[59,60] Consequently, internal chiral contributions (e.g., from electric dipole-allowed three-state interactions) are symmetry forbidden in R6G and FITC. Through the process of elimination, macromolecular orientation effects are the most likely candidates for generating the large surface chirality exhibited in the templated systems 1, 2, and 3.

The observation of large linear dichroism on-resonance (systems 1 and 2) and large circular dichroism off-resonance (system 3, in which the absorbance of FITC is approximately 5-fold smaller at 532 nm than at the absorbance maximum) is in direct opposition to the expected trends based on previous theoretical treatments considering electric dipole interactions.[12−14,16,17] Equation 1 might initially appear to suggest that nonzero SHG-CD requires complex-valued phase shifts between the chiral χ_{XYZ} and achiral χ_{XXZ} tensor elements, which would not be expected off-resonance within the electric dipole approximation. However, this requirement is valid only for traditional reflection or transmission measurements (i.e., not total internal reflection) in the limit of ultrathin transparent films and substrates.[39] In total internal reflection, for multilayer films, and/or for surface systems with resonance enhancement at the fundamental or second harmonic frequencies, the Fresnel reflection and transmission coefficients, and in turn the s_n coefficients in eq 1, will be complex-valued. In these instances, phase differences between the $\chi^{(2)}$ tensor elements are not required for observation of nonzero circular dichroism in SHG.[39]

Evidence supporting the importance of structural contributions to chirality in SHG of uniaxial films can be found in several previous studies. Although attributed to other mechanisms, large

SHG chiroptical effects were observed in systems with little obvious electronic coupling between the chiral centers and the nonlinear chromophores.[11,12,14,16,17] In studies by Persoons and co-workers,[11,14] SHG-CD was observed in oriented chiral polymers in which the chiral centers were separated from the nonchiral planar chromophores by multiple σ-bonds. They attributed the large observed chiral responses to helical charge displacement along the polymer backbone.[11,14] In studies by Schanne-Klein and co-workers,[12,16,17] large SHG-CD ratios were also measured in systems in which the chiral centers were located in σ-bonded tetrahedral carbons that were not obviously coupled electronically to the achiral nonlinear chromophores.[12,16,17,25] It is tempting to suggest an alternative possible explanation for these previous results, in which the dominating role of the chiral centers was to direct asymmetric orientation within the thin films. In this mechanism, the chiral centers can yield nonzero values of χ_{XYZ} without the need for significant chiral elements within the molecular hyperpolarizability $\beta^{(2)}$ tensors.

Further evidence supporting the importance of molecular orientation in driving the chiral responses of thin surface films can be found in recent sum frequency generation studies of chiral binaphthol (BN) solutions and oriented thin BN films by Belkin, Shen, and co-workers.[18,30,31] Sum frequency spectroscopy of randomly oriented media exclusively probes contributions arising from inherent nonlinear chirality within the molecular frame.[18,29,30,32,34,35] Binaphthol exhibits Davydov exciton splitting from the two adjacent naphthol moieties to generate a chiral pair of coupled oscillators closely spaced in energy.[18] Consequently, BN in solution is a model molecular system for isolating the nonlinear contributions from electric dipole-allowed effects inherent within chiral chromophores. The measured per-molecule $\chi^{(2)}$ nonlinear optical chiral activities of BN solutions were approximately 2 orders of magnitude smaller than values measured in oriented thin BN films and yielded significantly different nonlinear spectra.[30,31] Shen and co-workers attributed the substantial differences between the measured solution and film nonlinearities to orientational effects,[30,31] in excellent qualitative agreement with the proposed mechanism.

The remarkable dependence of SHG and SFG on surface orientation suggests rich structural information can be mined from nonlinear optical polarization measurements of chiral materials and films. In systems dominated by two-state electric dipole interactions, the polarization of the nonlinear signal is directly dependent on the tilt and twist angle of the chromophore plane through the simple orientational averages in eq 3. While circular and/or linear dichroism measurements in SHG are useful diagnostic tools for assessing the presence of nonlinear chirality, directly relating the dichroic ratios to molecular-scale structure is nontrivial. Work is currently in progress to apply a newly developed ellipsometric detection approach for SHG to uniquely determine fully complex relative values of all four $\chi^{(2)}$ tensor elements in chiral films to yield information about molecular tilt and twist angles.[54] These measurements should allow for meaningful assessment of the molecular interactions leading to asymmetric orientation in systems 1, 2, and 3.

If molecular orientation is largely responsible for many of the chiroptical effects observed in SHG, similar phenomena should be expected in sum frequency vibrational spectroscopy of oriented chiral interfaces. As has been demonstrated by Shen

(58) Moad, A. J.; Simpson, G. J. *J. Phys. Chem. B*, submitted for publication.
(59) Simpson, G. J.; Rowlen, K. L. *Anal. Chem.* **2000**, *72*, 3407.
(60) Morgenthaler, M. J. E.; Meech, S. R. *J. Phys. Chem.* **1996**, *100*, 3323.

and co-workers, infrared-visible vibrational SFG in chiral solutions requires a breakdown in the Born−Oppenheimer approximation to recover chiral elements in the molecular tensor.[32] However, the results of the present investigation indicate that the chromophore need not be chiral in order to generate macromolecular chirality at interfaces. It is reasonable to suggest that significant chiroptical effects will also be observable in SFG vibrational spectroscopic measurements of oriented chiral interfaces.

Many of the conclusions drawn in the present work may be easily extended to systems of inorganic chromophores and uniaxially oriented materials and polymers. We have recently developed a unified theory for treating symmetry and selection rules in SHG and SFG to assist in interpreting polarization measurements of both organic and inorganic chromophores exhibiting a host of different molecular symmetries.[58] As has been indicated previously,[41,43,44] the observation of significant chiroptical activity in SHG measurements of oriented films of achiral chromophores suggests new potential routes for generating organic and inorganic materials with large optical nonlinearities. In contrast to oriented films of achiral chromophores (which require net polar chromophore orientation), chiral systems with macroscopic D_∞ symmetry (uniaxial but not polar) can still exhibit nonlinear optical activity, providing new design possibilities with greater flexibility in materials properties.[41,43,44]

Conclusions

In summary, large chiral effects in SHG were observed for achiral charge-transfer chromophores assembled at chiral templated interfaces. These results confirm recent predictions of large electric dipole-allowed structurally driven chiral effects in oriented uniaxial films.[39−41,43,44] The measured dichroic ratios for the three chiral templated systems investigated indicate that surface orientation alone is sufficient for generating substantial chiroptical effects in SHG. Furthermore, these orientational

contributions will be present to some degree in essentially all SHG-active uniaxial chiral films and materials.

Given the magnitude of these orientational contributions to surface chirality and their expected ubiquity, it is tempting to suggest that these effects may routinely dominate the SHG and SFG chiral responses in many uniaxially oriented surface systems. Although alternative internal origins of chirality may indeed be present, particularly if chirality is intimately linked to the chromophore itself,[4,18−20,22,25,26,28−31,33−35,38] orientational contributions will generally exist for all uniaxially oriented chiral systems. Work is already underway in this laboratory toward quantitative assessment of the relative importance of these internal versus orientational effects.

The importance of orientation in driving the chiral responses of oriented uniaxial systems suggests straightforward algorithms can be developed for determining orientation from SHG and SFG nonlinear polarization measurements in systems in which these contributions dominate. Methods are being developed to overcome many of the current limitations of circular and linear dichroism measurements by extending a novel ellipsometric detection approach for analyzing nonlinear polarization measurements.[54]

Supporting Information Available: Equations S1−S8 describe the derivation of compact formulas for linear and circular dichroic ratios in SHG, while the figure contains adsorption isotherms for rhodamine 6G at the water/glass and water/BSA/glass interfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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