

# A Unified Treatment of Selection Rules and Symmetry Relations for Sum-Frequency and Second Harmonic Spectroscopies

Andrew J. Moad and Garth J. Simpson\*

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

Received: May 16, 2003; In Final Form: December 18, 2003

A simplifying treatment is developed for describing the molecular origins of electric dipole allowed sum-frequency generation (SFG) and second harmonic generation (SHG). The full sum-over-states expressions for the nonlinear polarizability simplify tremendously at or near resonance to straightforward formulas easily connected to intuitive molecular properties. For resonance enhancement at the sum or second harmonic frequency, the molecular nonlinear polarizability tensor is shown to be the direct product of the transition moment and the two-photon absorption (TPA) polarizability tensor. To our knowledge, this is the first rigorous mathematical demonstration indicating such a simple relationship directly connecting second harmonic generation with TPA, providing a link between the two fields of inquiry. Under resonance enhancement with one of the incident frequencies, the SFG and SHG nonlinear polarizability tensors similarly are given by the products of the transition moments and the anti-Stokes Raman polarizability tensors (a reasonably well-known result for SFG). Under double-resonance conditions (i.e., resonant with one of the incident frequencies and the sum frequency), the two descriptions for the nonlinear polarizability become mathematically equivalent. Nonlinear optical character tables for both SHG and SFG under all resonance conditions have been compiled for chromophores of  $C_s$ ,  $C_2$ ,  $C_{2v}$ , and  $C_{3v}$  symmetries. Explicit evaluation of the corresponding orientational averages for each allowed transition in each character table assuming a uniaxial macroscopic orientation distribution reveals numerous relationships connecting the microscopic symmetry with the macroscopic nonlinear response. The approaches developed in this work are sufficiently general to allow their use in interpreting electronic, vibrational, and vibronic spectroscopic measurements by SHG and SFG.

## Introduction

The rapid growth in the number and scope of nonlinear optical (NLO) materials and measurements has brought with it a corresponding demand for additional methods to predict second-order nonlinearity in oriented assemblies and to characterize structure at surfaces and in thin films from macroscopic polarization measurements. Clearly, an enormous amount of work has been dedicated toward defining parameters for optimizing molecular hyperpolarizability in NLO materials applications.<sup>1–18</sup> Additionally, remarkable progress has been made in development of methods to use nonlinear polarization measurements to interpret interfacial and molecular structure in second harmonic generation (SHG) and sum-frequency generation (SFG) surface studies.<sup>19–41</sup> Despite this early success in specific applications, the new directions second-order NLO measurements and materials may proceed in the coming years suggest a need for additional tools with the inherent flexibility capable of describing future experiments that have not yet been attempted or conceived.

**SHG of Electronic Transitions.** A solid understanding of the selection rules for a given spectroscopic method is obviously essential for maximizing the information content extractable from a given set of experimental measurements. For this reason,

considerable theoretical effort has already been focused on understanding the selection rules for emerging NLO spectroscopies.<sup>1,3,6,11–13,42–59</sup>

The materials science and surface science literature has a rich history of theoretical methods for assessing NLO properties. For practical reasons, the primary emphasis has been on studying the role of electronic transitions. In an early treatment by Oudar and Zyss, it was demonstrated that the nonlinear responses of many chromophores are qualitatively well described by a two-state model (single ground state and single excited state), for which the molecular hyperpolarizability tensor  $\beta$  is constructed entirely from two vectors within the molecular frame, the transition moment  $\mu$ , and the difference in permanent dipole between the excited and ground state  $\delta$ .<sup>6,42</sup> Similar conclusions have been drawn by numerous others.<sup>1,3,12,43–47</sup> The general validity of this simple two-state model is supported by numerous experimental demonstrations of large hyperpolarizabilities in charge-transfer chromophores.<sup>11–13,45,47–55</sup>

Although chemically and physically intuitive and reasonably successful experimentally, the two-state model neglects some potentially important elements of the complete sum-over-states expression for the nonlinear response. The total hyperpolarizability generated from perturbation theory is constructed by combining the diagonal contributions arising from this two-level model and the remaining off-diagonal contributions consisting of explicit three-state interactions.<sup>1,43,44,56–59</sup> Kanis, Ratner, and

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

Marks provide a discussion and review of the off-diagonal contributions and compare them to the diagonal contributions.<sup>1,59</sup> For 15 different charge-transfer organic chromophores, molecular-modeling calculations suggest that the off-diagonal contributions are approximately half as large and opposite in sign when compared to the diagonal contributions.<sup>1</sup> Although clearly superior in molecular modeling applications, the full sum-over-states expressions used to evaluate the combined diagonal and off-diagonal contributions are often difficult to relate back to simple, chemically intuitive properties in spectroscopic measurements.

### Infrared–Visible Vibrational Sum-Frequency Generation.

In contrast to SHG, the selection rules for infrared–visible SFG are reasonably well established. In the first experimental demonstration of surface SFG, Shen and co-workers suggested that vibrational modes must be both infrared and Raman active to lead to sum-frequency NLO activity.<sup>60</sup> Hirose and co-workers have confirmed this selection rule mathematically by simplification of the sum-over-states expressions derived from perturbation theory.<sup>20</sup> These infrared–visible SFG selection rules are consistent with numerous experimental measurements,<sup>20,30–32,60–67</sup> and there is little disagreement regarding their general validity in vibrational spectroscopic applications.

More recently, interest has grown in applying sum-frequency spectroscopy in investigations of electronic spectroscopic transitions. Shen and co-workers have performed doubly resonant SFG measurements of systems exhibiting resonance enhancement with both vibrational and electronic transitions.<sup>68,69</sup> Several groups have recently investigated vibrationally and/or electronically resonant SFG in randomly oriented chiral media, both theoretically and experimentally<sup>70–81</sup> and in oriented thin films.<sup>77</sup>

The emergence of these exciting new spectroscopic techniques highlights numerous unresolved key issues regarding the molecular origins of the SFG and SHG nonlinear response. For example, it is not immediately clear whether the established infrared–visible SFG selection rules requiring both a nonzero transition moment and a nonzero anti-Stokes Raman polarizability are equally applicable in electronic spectroscopic investigations. Furthermore, since SHG is actually a specific case of SFG, it stands to reason that the widely observed trend indicating that SHG is largely dependent on the transition moment and the difference in state dipole should follow directly from standard SFG selection rules. At a first pass, it is not obvious precisely how this correspondence is achieved given the apparently incongruent dependence of the two spectroscopic techniques on the molecular properties. We present here a single, unified treatment of SHG and SFG that provides a smooth transition between these two apparently disparate conditions and introduces the importance of the two-photon absorption (TPA) polarizability tensor in SHG and SFG.

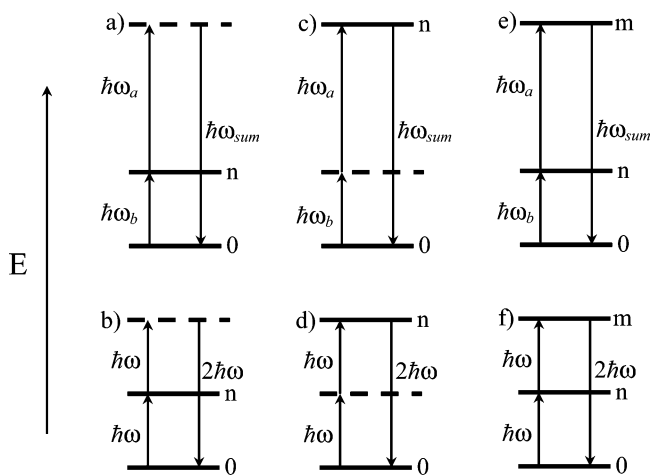
### Theory

Sum-over-states expressions derived from perturbation theory are considered the most generally applicable for treating SFG and SHG at the molecular level. The sum-over-states expression for the second-order nonlinear polarizability for SFG is given by<sup>43,56,82</sup>

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b) = \frac{-1}{4\hbar^2} \sum_{n,m} \left\{ \mu_{0m}^i \mu_{mn}^k \mu_{n0}^j \left[ \frac{1}{(\omega_m + \omega_{\text{sum}} + i\Gamma_m)(\omega_n + \omega_a + i\Gamma_n)} + \frac{1}{(\omega_m - \omega_{\text{sum}} - i\Gamma_m)(\omega_n - \omega_a - i\Gamma_n)} \right] + \mu_{0m}^j \mu_{mn}^k \mu_{n0}^i \left[ \frac{1}{(\omega_m - \omega_a - i\Gamma_m)(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} + \frac{1}{(\omega_m + \omega_a + i\Gamma_m)(\omega_n + \omega_{\text{sum}} + i\Gamma_n)} \right] + \mu_{0m}^i \mu_{mn}^j \mu_{n0}^k \left[ \frac{1}{(\omega_m + \omega_{\text{sum}} + i\Gamma_m)(\omega_n + \omega_b + i\Gamma_n)} + \frac{1}{(\omega_m - \omega_{\text{sum}} - i\Gamma_m)(\omega_n - \omega_b - i\Gamma_n)} \right] + \mu_{0m}^k \mu_{mn}^j \mu_{n0}^i \left[ \frac{1}{(\omega_m - \omega_b - i\Gamma_m)(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} + \frac{1}{(\omega_m + \omega_b + i\Gamma_m)(\omega_n + \omega_{\text{sum}} + i\Gamma_n)} \right] + \mu_{0m}^k \mu_{mn}^i \mu_{n0}^j \left[ \frac{1}{(\omega_m - \omega_b - i\Gamma_m)(\omega_n + \omega_a + i\Gamma_n)} + \frac{1}{(\omega_m + \omega_b + i\Gamma_m)(\omega_n - \omega_a - i\Gamma_n)} \right] + \mu_{0m}^j \mu_{mn}^i \mu_{n0}^k \left[ \frac{1}{(\omega_m - \omega_a - i\Gamma_m)(\omega_n + \omega_b + i\Gamma_n)} + \frac{1}{(\omega_m + \omega_a + i\Gamma_m)(\omega_n - \omega_b - i\Gamma_n)} \right] \right\} \quad (1)$$

In all equations, the complex damping coefficients are included in the frequency denominators, such that  $\omega_{n0} = \omega_{n0} - i\Gamma_{n0}$  and  $\omega_{n0}^* = \omega_{n0} + i\Gamma_{n0}$ .<sup>43,47,56,83</sup> It is worth noting that considerable debate has arisen recently regarding the appropriate sign convention for use in the frequency denominators in SHG, SFG, and Raman polarizability tensors.<sup>84–88</sup> The calculations presented here utilize the more ubiquitous alternate sign convention, although it is straightforward to re-express them using the same sign convention. As has been alluded to by Andrews et al., both conventions yield similar predictions under the most common experimental conditions.<sup>88</sup> Most importantly for the present purposes, we have confirmed that both conventions yield identical mathematical results near resonance in the six cases considered here (resonant near an incident frequency for SFG and SHG, resonant near the sum frequency for SFG and SHG, and doubly resonant for SFG and SHG).

Although the expression in eq 1 is sufficiently general to describe the sum-frequency polarizability of an isolated chromophore under all common experimental conditions (i.e., on resonance, off resonance, double resonance, etc.), it is presented in a form that obscures many relationships between the nonlinearity of the chromophore and intuitive molecular properties. In spectroscopic applications, resonance enhancement is expected with one or all of the incident frequencies. In these instances, the general expression in eq 1 can be greatly simplified.



**Figure 1.** Energy-level diagrams for six resonance cases. Solid lines indicate a real state, and dashed lines indicate a virtual state. (a) Case 1, SFG resonance with one incident frequency; (b) Case 2, SHG resonance with the fundamental frequency; (c) Case 3, SFG resonance at the sum frequency; (d) Case 4, SHG resonance at the second harmonic frequency; (e) Case 5, SFG double resonance; (f) Case 6, SHG double resonance.

**Diagonal Two-State Contributions to  $\beta^{(2)}$ .** The expression for the diagonal two-state contributions (from the two-level model) to  $\beta^{(2)}$  in SFG can be evaluated using an approach similar to that detailed in previous work for SHG.<sup>1,6,43,89</sup> Although many of the mathematical manipulations used to simplify the diagonal contributions to the nonlinear polarizability are fairly well established,<sup>1,6,43,89</sup> they are included in Appendix I for completeness. In brief, the summation over states  $m$  and  $n$  yields the following diagonal contributions to the  $\beta^{(2)}$  tensor

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_{n=m,0} = \frac{-1}{2\hbar^2} \sum_n \left\{ \delta_{n0}^i \mu_{0n}^k \mu_{n0}^j \left( \frac{1}{(\omega_n + \omega_b + i\Gamma_n)(\omega_n - \omega_a - i\Gamma_n)} + \frac{1}{(\omega_n - \omega_b - i\Gamma_n)(\omega_n + \omega_a + i\Gamma_n)} \right) + \delta_{n0}^j \mu_{0n}^i \mu_{n0}^k \left( \frac{1}{(\omega_n + \omega_b + i\Gamma_n)(\omega_n + \omega_{\text{sum}} + i\Gamma_n)} + \frac{1}{(\omega_n - \omega_b - i\Gamma_n)(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} \right) + \delta_{n0}^k \mu_{0n}^i \mu_{n0}^j \left( \frac{1}{(\omega_n + \omega_a + i\Gamma_n)(\omega_n + \omega_{\text{sum}} + i\Gamma_n)} + \frac{1}{(\omega_n - \omega_a - i\Gamma_n)(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} \right) \right\} \quad (2)$$

In eq 2,  $\delta_{n0}$  is defined to be the difference in permanent electric dipoles between the excited state and the ground state,  $\mu_{nn} - \mu_{00}$ . The double sum over multiple permutations of multiple excited states has been replaced with a single sum over particular excited states, indicated by the index  $n$ . Resonance enhancement in the diagonal elements of  $\beta^{(2)}$  are expected to occur if  $\omega_a$ ,  $\omega_b$ , and/or  $(\omega_a + \omega_b)$  is resonant with a real state within the chromophore. Equation 2 simplifies to the well-known expression for SHG, derived by Oudar and Zyss, in the limit of  $\omega_a = \omega_b$  and by dividing by 2.<sup>1,6,43,89</sup>

**Off-Diagonal Contributions to  $\beta^{(2)}$ .** The remaining off-diagonal elements of the double sum combine to yield the following expression

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_{n \neq m \neq 0} = \frac{-1}{4\hbar^2} \sum_{n \neq m \neq 0} \times \left\{ \mu_{0m}^i \mu_{mn}^k \mu_{n0}^j \left[ \frac{1}{(\omega_m + \omega_{\text{sum}} + i\Gamma_m)(\omega_n + \omega_a + i\Gamma_n)} + \frac{1}{(\omega_m - \omega_{\text{sum}} - i\Gamma_m)(\omega_n - \omega_a - i\Gamma_n)} \right] + \mu_{0m}^j \mu_{mn}^k \mu_{n0}^i \left[ \frac{1}{(\omega_m - \omega_a - i\Gamma_m)(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} + \frac{1}{(\omega_m + \omega_a + i\Gamma_m)(\omega_n + \omega_{\text{sum}} + i\Gamma_n)} \right] + \mu_{0m}^i \mu_{mn}^j \mu_{n0}^k \left[ \frac{1}{(\omega_m + \omega_{\text{sum}} + i\Gamma_m)(\omega_n + \omega_b + i\Gamma_n)} + \frac{1}{(\omega_m - \omega_{\text{sum}} - i\Gamma_m)(\omega_n - \omega_b - i\Gamma_n)} \right] + \mu_{0m}^k \mu_{mn}^j \mu_{n0}^i \left[ \frac{1}{(\omega_m - \omega_b - i\Gamma_m)(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} + \frac{1}{(\omega_m + \omega_b + i\Gamma_m)(\omega_n + \omega_{\text{sum}} + i\Gamma_n)} \right] + \mu_{0m}^k \mu_{mn}^i \mu_{n0}^j \left[ \frac{1}{(\omega_m - \omega_b - i\Gamma_m)(\omega_n + \omega_a + i\Gamma_n)} + \frac{1}{(\omega_m + \omega_b + i\Gamma_m)(\omega_n - \omega_a - i\Gamma_n)} \right] + \mu_{0m}^j \mu_{mn}^i \mu_{n0}^k \left[ \frac{1}{(\omega_m - \omega_a - i\Gamma_m)(\omega_n + \omega_b + i\Gamma_n)} + \frac{1}{(\omega_m + \omega_a + i\Gamma_m)(\omega_n - \omega_b - i\Gamma_n)} \right] \right\} \quad (3)$$

The sum of the expressions in eqs 2 and 3 is equivalent to the double-sum expression in eq 1. In addition to the mathematical simplification, the separation of the sum-over-states expression into diagonal and off-diagonal contributions provides a convenient means for further symmetry analysis in spectroscopic SHG and SFG investigations.

**Resonance-Enhanced Spectroscopic Measurements. Case 1: Sum-Frequency Spectroscopy with a Transition Resonant with One of the Incident Frequencies.** For SFG measurements in which one of the incident frequencies is resonant with a real transition within the molecule (Figure 1a), including infrared–visible SFG, the expressions in eqs 2 and 3 can be considerably simplified. In the following derivation, it is assumed that  $\omega_b$  is near resonance with a particular excited state  $n$  with a transition frequency  $\omega_n$  and that  $\omega_a$  and  $\omega_{\text{sum}}$  are far from resonance. This instance, depicted in Figure 1a, includes but is not limited to the standard infrared–visible sum-frequency spectroscopy condition. Only the terms with  $\omega_{n,m} - \omega_b - i\Gamma_n$  in the denominator are resonance enhanced under these conditions.

The off-diagonal contributions to  $\beta^{(2)}$  are derived by including only the terms with  $\omega_{n,m} - \omega_b - i\Gamma_n$  in the denominator

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_n = \frac{-1}{4\hbar^2} \sum_{n \neq m \neq 0} \times \left\{ \frac{\mu_{n0}^k}{(\omega_n - \omega_b - i\Gamma_n)} \left[ \frac{\mu_{0m}^i \mu_{mn}^j}{(\omega_m - \omega_{\text{sum}} - i\Gamma_m)} + \frac{\mu_{0m}^j \mu_{mn}^i}{(\omega_m + \omega_a + i\Gamma_m)} \right] + \frac{\mu_{0m}^k}{(\omega_m - \omega_b - i\Gamma_m)} \left[ \frac{\mu_{mn}^j \mu_{n0}^i}{(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} + \frac{\mu_{mn}^i \mu_{n0}^j}{(\omega_n + \omega_a + i\Gamma_n)} \right] \right\} \quad (4)$$

The underscore under  $\omega_b$  indicates resonance enhancement with that frequency. Note that the last term in eq 4 is the complex conjugate of the first term. Equation 4 can be simplified further by taking the wave functions to be real. For real or time-averaged wave functions, the transition moments are real values, such that the addition of the complex conjugate yields a factor of 2<sup>90</sup>

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_n = \frac{-\mu_{n0}^k}{2\hbar(\omega_n - \omega_b - i\Gamma_n)} \times \left\{ \frac{1}{\hbar} \sum_{m \neq n \neq 0} \left[ \frac{\mu_{0m}^i \mu_{mn}^j}{(\omega_m - \omega_{\text{sum}} - i\Gamma_n)} + \frac{\mu_{0m}^j \mu_{mn}^i}{(\omega_m + \omega_a + i\Gamma_n)} \right] \right\} \quad (5)$$

The term within the brackets is remarkably similar to the definition of the Raman polarizability tensor for an anti-Stokes transition at an incident frequency of  $\omega_a$ .<sup>90-92</sup> In fact, including the diagonal contributions back into the sum-over-states recovers the full Raman polarizability tensor. Straightforward simplification of the diagonal contributions in eq 2 leads to the following generalized expression for sum-frequency spectroscopy in the case of resonance enhancement with one of the incident frequencies (in this case,  $\omega_b$ )

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_n = \frac{-\mu_{n0}^k}{2\hbar(\omega_n - \omega_b - i\Gamma_n)} \left\{ (\alpha_{0n}^{ij})'_{\text{AR}} + \frac{\delta_{n0}^i \mu_{n0}^j}{\hbar\omega_{\text{sum}}} - \frac{\mu_{n0}^i \delta_{n0}^j}{\hbar\omega_a} \right\} \quad (6)$$

A prime on the Raman polarizability tensor indicates that it is evaluated explicitly excluding the diagonal contributions (i.e., it is a reduced Raman polarizability tensor). For infrared transitions, the diagonal contributions in eq 6 are orders of magnitude smaller than the reduced Raman polarizability and can be categorically neglected.<sup>90,93</sup> However, these diagonal charge-transfer contributions may be significant and possibly dominant when considering electronic Raman transitions.<sup>90</sup> Since the diagonal and off-diagonal contributions can exhibit different symmetry properties, it is useful to explicitly consider them both. The total Raman polarizability tensor is given by the summation of all terms within the brackets in eq 6, leading to the following generalized expression for sum-frequency spectroscopy in the case of resonance enhancement with one of the incident frequencies (in this case,  $\omega_b$ )

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_n = \frac{-\mu_{n0}^k (\alpha_{0n}^{ij})_{\text{AR}}}{2\hbar(\omega_n - \omega_b - i\Gamma_n)} \quad (7)$$

A similar expression is generated under conditions of resonance

enhancement with  $\omega_a$ , in which case  $\omega_a$  replaces  $\omega_b$  in the resonant denominator and the  $j$  and  $k$  indices are interchanged.

The total frequency-dependent resonant nonlinear response is given by the combined contributions of all the transitions resonant or near resonant with  $\hbar\omega_b$  accessed for a given set of incident and exigent frequencies (e.g., for Raman spectra with multiple overlapping transitions)

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b) = \frac{-1}{2\hbar} \sum_n \frac{\mu_{n0}^k (\alpha_{0n}^{ij})_{\text{AR}}}{(\omega_n - \omega_b - i\Gamma_n)} \quad (8)$$

The expression in eq 8 is complete in that it contains the full sum-over-states information in eq 1 evaluated in the limit of resonance enhancement with  $\omega_b$ . Furthermore, it is conceptually in agreement with the simple energy-level diagram shown in Figure 1a, suggesting that the SFG response is given by the product of an absorptive transition and an anti-Stokes Raman transition. Of course, the relationship between the Raman polarizability, the transition moment, and the sum-frequency nonlinear polarizability described in eq 7 for these resonance conditions is not new; Hirose et al. derived a comparable expression in an earlier work.<sup>20</sup> Nevertheless, it provides a mathematical framework for interpreting other resonance conditions in both SHG and SFG.

**Case 2: SHG with Resonance Enhancement at the Fundamental Frequency.** The selection rules for SHG with resonance enhancement at the incident frequency (Figure 1b) can be derived from the selection rules for SFG by setting the two incident frequencies equal in eqs 2 and 3 followed by simplification similar to that described in the previous section. An additional factor of  $1/2$  must also be included to correct for a double counting in the perturbation theory used to derive the  $\beta^{(2)}$  tensor.<sup>43,56</sup> The diagonal contributions for resonance enhancement with the  $n$  excited state are given by the following

$$\beta^{ijk}(-2\omega; \omega, \omega)_n = \frac{-1}{4\hbar(\omega_n - \omega - i\Gamma_n)} \times \left( \frac{\delta_{n0}^i \mu_{n0}^k \mu_{n0}^j}{2\hbar\omega} - \frac{\delta_{n0}^j \mu_{n0}^i \mu_{n0}^k}{\hbar\omega} + \frac{\delta_{n0}^i \mu_{n0}^k \mu_{n0}^j}{2\hbar\omega} - \frac{\delta_{n0}^k \mu_{n0}^i \mu_{n0}^j}{\hbar\omega} \right) \quad (9)$$

Explicit evaluation of the double sum in eq 3 yields the following off-diagonal contributions to the resonance-enhanced  $\beta^{(2)}$  tensor

$$\beta^{ijk}(-2\omega; \omega, \omega) = \frac{-1}{8\hbar^2} \sum_{n \neq m \neq 0} \left\{ \left( \frac{\mu_{0m}^i \mu_{mn}^k \mu_{n0}^j}{(\omega_m - 2\omega - i\Gamma_m)(\omega_n - \omega - i\Gamma_n)} + \frac{\mu_{0m}^k \mu_{mn}^i \mu_{n0}^j}{(\omega_m + \omega + i\Gamma_m)(\omega_n - \omega - i\Gamma_n)} + \frac{\mu_{0m}^i \mu_{mn}^j \mu_{n0}^k}{(\omega_m - 2\omega - i\Gamma_m)(\omega_n - \omega - i\Gamma_n)} + \frac{\mu_{0m}^j \mu_{mn}^i \mu_{n0}^k}{(\omega_m + \omega + i\Gamma_m)(\omega_n - \omega - i\Gamma_n)} \right) + \text{complex conjugate} \right\} \quad (10)$$

Simplification of eq 10 assuming purely real or time-averaged



wave functions yields the following expression

$$\beta^{ijk}(-2\omega; \omega, \omega)_n = \frac{-1}{4\hbar(\omega_n - \omega - i\Gamma_n)} \times \left\{ \mu_{n0}^j \left[ \frac{1}{\hbar} \sum_{m \neq n} \frac{\mu_{0m}^i \mu_{mn}^k}{\omega_m - 2\omega - i\Gamma_m} + \frac{\mu_{0m}^k \mu_{mn}^i}{\omega_m + \omega + i\Gamma_m} \right] + \mu_{n0}^k \left[ \frac{1}{\hbar} \sum_{m \neq n} \frac{\mu_{0m}^i \mu_{mn}^j}{\omega_m - 2\omega - i\Gamma_m} + \frac{\mu_{0m}^j \mu_{mn}^i}{\omega_m + \omega + i\Gamma_m} \right] \right\} \quad (11)$$

As in the case of SFG, the terms in brackets can be replaced by the corresponding anti-Stokes reduced Raman polarizability tensors evaluated for an incident frequency of  $\omega$ . Analogous to Case 1, combining both the diagonal and off-diagonal contributions and summing over all the accessible excited states yields the following generalized expression

$$\beta^{ijk}(-2\omega; \omega, \omega) = \sum_n \frac{-1}{4\hbar(\omega_n - \omega - i\Gamma_n)} \times \left\{ \mu_{n0}^j \left[ (\alpha_{0n}^{ik})'_{AR} + \frac{\delta_{n0}^i \mu_{0n}^k}{2\hbar\omega} - \frac{\delta_{n0}^k \mu_{0n}^i}{\hbar\omega} \right] + \mu_{n0}^k \left[ (\alpha_{0n}^{ij})'_{AR} + \frac{\delta_{n0}^i \mu_{0n}^j}{2\hbar\omega} - \frac{\delta_{n0}^j \mu_{0n}^i}{\hbar\omega} \right] \right\} \quad (12)$$

Equation 12 can be rewritten in the following form

$$\beta^{ijk}(-2\omega; \omega, \omega) = \frac{-1}{4\hbar} \sum_n \frac{\mu_{n0}^j (\alpha_{0n}^{ik})'_{AR} + \mu_{n0}^k (\alpha_{0n}^{ij})'_{AR}}{(\omega_n - \omega - i\Gamma_n)} \quad (13)$$

As in Case 1, the expression in eq 13 is complete in the sense that it contains the full information of the original sum-over-states expression in eq 1, evaluated for SHG with resonance enhancement near the fundamental frequency.

**Case 3: Sum-Frequency Spectroscopy with Resonance Enhancement at the Sum Frequency.** The derivation of the off-diagonal contributions to  $\beta^{(2)}$  in the limit of resonance enhancement at the sum frequency (Figure 1c) is virtually identical to that used to generate eqs 6 and 8. Again, it is useful to separate the contributions of the second-order nonlinear polarizability tensor into diagonal two-state contributions (eq 2) and the remaining off-diagonal three-state contributions (eq 3).<sup>1</sup> The diagonal contributions for resonance enhancement with a particular with state  $n$  are given by eq 14

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_n = \frac{-\mu_{0n}^i}{2\hbar(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} \left[ \frac{\delta_{n0}^j \mu_{n0}^k}{\hbar\omega_a} + \frac{\delta_{n0}^k \mu_{n0}^j}{\hbar\omega_b} \right] \quad (14)$$

The remaining off-diagonal contributions are obtained by simplification of eq 15

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_n = \frac{-\mu_{0n}^i}{2\hbar(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} \times \left[ \frac{1}{\hbar} \sum_{m \neq n} \left( \frac{\mu_{nm}^k \mu_{m0}^j}{(\omega_m - \omega_a - i\Gamma_m)} + \frac{\mu_{nm}^j \mu_{m0}^k}{(\omega_m - \omega_b - i\Gamma_m)} \right) \right] \quad (15)$$

In eq 15, the term in brackets can be replaced by a reduced polarizability tensor (i.e., excluding the diagonal elements for  $m = 0, n$ ), in this instance describing a TPA transition.<sup>94–98</sup> The term in brackets is equal to  $\alpha_{n0}^{jk}(\omega_b, \omega_a)$ , which is by symmetry equal to  $\alpha_{n0}^{jk}(\omega_b, \omega_a)$ . Combining the diagonal and off-diagonal contributions and summing over all the accessible resonant interactions yields the following simplified expression for SFG measurements with resonance enhancement at the sum frequency

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_n = \frac{-\mu_{0n}^i}{2\hbar(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} \left\{ (\alpha_{n0}^{jk})'_{TPA} + \frac{\delta_{n0}^j \mu_{n0}^k}{\hbar\omega_a} + \frac{\delta_{n0}^k \mu_{n0}^j}{\hbar\omega_b} \right\} \quad (16)$$

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_n = \frac{-\mu_{0n}^i (\alpha_{n0}^{jk})'_{TPA}}{2\hbar(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} \quad (17)$$

As can be seen in eq 17, the molecular nonlinear polarizability for sum-frequency spectroscopy (and correspondingly second harmonic spectroscopy) for measurements near resonance at the sum frequency is given by the direct product of the transition moment and the TPA polarizability tensor. Similar to the Raman case, the simple energy-level description of nonlinear polarizability depicted in Figure 1c is in excellent conceptual agreement with the mathematical formalism (specifically that the nonlinear polarizability is described by the product of a TPA transition and a stimulated absorptive/emissive transition).

The corresponding expression for the complete nonlinear polarizability tensor including the appropriate resonant or near-resonant interactions from all the excited states in the systems is recovered by summing the contributions from each state

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b) = \frac{-1}{2\hbar} \sum_n \left\{ \frac{\mu_{0n}^i (\alpha_{n0}^{jk})'_{TPA}}{(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} \right\} \quad (18)$$

As in Cases 1 and 2, the expression in eq 18 is complete in the sense that it contains the full information in eq 1 evaluated in the limit of resonance enhancement at or near the sum frequency.

**Case 4: SHG with Resonance Enhancement at the Second Harmonic Frequency.** The selection rules for SHG with resonance enhancement at the second harmonic frequency (Figure 1d) can be derived from the selection rules for SFG by setting the two incident frequencies equal. As in Case 2, an additional factor of  $1/2$  must also be included to correct for a double counting in the perturbation theory used to derive the  $\beta^{(2)}$  tensor

$$\beta^{ijk}(-2\omega; \omega, \omega) = \frac{-1}{4\hbar} \sum_n \left\{ \frac{\mu_{0n}^i}{(\omega_n - 2\omega - i\Gamma_n)} \left[ (\alpha_{n0}^{jk})'_{TPA} + \frac{\delta_{n0}^j \mu_{n0}^k}{\hbar\omega} + \frac{\delta_{n0}^k \mu_{n0}^j}{\hbar\omega} \right] \right\} \quad (19)$$

$$\beta^{ijk}(-2\omega; \omega, \omega) = \frac{-1}{4\hbar} \sum_n \frac{\mu_{0n}^i (\alpha_{n0}^{jk})'_{TPA}}{(\omega_n - 2\omega - i\Gamma_n)} \quad (20)$$

The TPA polarizability tensor is symmetric for SHG such that the expression in eq 19 satisfies the required symmetry relationship  $\beta_{ijk} = \beta_{ikj}$ .

As with SFG in Case 3, eq 20 indicates that the molecular selection rule for SHG resonant or near resonant at the second

harmonic frequency requires that the excited-state transition be simultaneously active for both one-photon absorption and TPA.

**Case 5: Doubly Resonant SFG.** If an incident frequency  $\omega_b$  is resonant with a real transition frequency  $\omega_n$  and the sum of  $\omega_a + \omega_b$  is resonant with a different real transition frequency  $\omega_m$  (Figure 1e), only the off-diagonal terms in eq 1 are doubly enhanced by the double resonance. Since the diagonal contributions to the molecular nonlinearity arising from the differences in permanent dipole are not doubly resonance enhanced, they may be presumed negligible in most fully resonant measurements

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_{n,m} = \frac{-1}{4\hbar^2} \left\{ \frac{\mu_{0n}^i \mu_{mn}^j \mu_{m0}^k}{(\omega_m - \omega_b - i\Gamma_m)(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} + \frac{\mu_{0m}^i \mu_{mn}^j \mu_{n0}^k}{(\omega_m - \omega_{\text{sum}} - i\Gamma_m)(\omega_n - \omega_b - i\Gamma_n)} \right\} \quad (21)$$

There are two alternative ways to interpret the contributions in eq 21. If referenced with respect to the lower-energy transition,  $\hbar\omega_n$ , eq 21 can be rewritten in the following form

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_{n,m} = \frac{-1}{2\hbar} \left\{ \frac{\mu_{n0}^k}{(\omega_n - \omega_b - i\Gamma_n)} \left[ \frac{\mu_{0m}^i \mu_{mn}^j}{\hbar(\omega_m - \omega_{\text{sum}} - i\Gamma_m)} \right] \right\} \quad (22)$$

Equation 22 can be further simplified by recognizing that the term in brackets is a resonanced-enhanced Raman polarizability

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_{n,m} = \frac{-\mu_{n0}^k (\alpha_{0n}^{ij})_{\text{AR}}}{2\hbar(\omega_n - \omega_b - i\Gamma_n)} \quad (23)$$

In eq 23,  $(\alpha_{0n}^{ij})_{\text{AR}}$  is the resonance-enhanced anti-Stokes Raman polarizability of the  $n$  excited state. Alternatively, the  $\beta^{(2)}$  tensor under conditions of double resonance can be expressed with respect to the higher energy  $\hbar\omega_m$  transition

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_{n,m} = \frac{-1}{2\hbar} \left\{ \frac{\mu_{0m}^i}{(\omega_m - \omega_{\text{sum}} - i\Gamma_m)} \left[ \frac{\mu_{mn}^j \mu_{n0}^k}{\hbar(\omega_n - \omega_b - i\Gamma_n)} \right] \right\} \quad (24)$$

Again, recognizing that the term in brackets is a resonance-enhanced polarizability allows eq 24 to be rewritten

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_{n,m} = \frac{-\mu_{0m}^i (\alpha_{m0}^{jk})_{\text{TPA}}}{2\hbar(\omega_m - \omega_{\text{sum}} - i\Gamma_m)} \quad (25)$$

In eq 25,  $\alpha$  now describes the resonance-enhanced TPA polarizability tensor. The use of eqs 23 or 25 in describing doubly resonant SFG is purely a matter of convenience in a given spectroscopic application. Mathematically, the two descriptions are equivalent.

**Case 6: Doubly Resonant SHG.** For SHG with resonance enhancement at both the fundamental and second harmonic frequencies (Figure 1f), the resonance-enhanced component of the hyperpolarizability in eq 1 is given by the following equation

$$\beta^{ijk}(-2\omega; \omega, \omega)_{n,m} = \frac{-1}{8\hbar^2} \left\{ \frac{\mu_{0m}^j \mu_{mn}^k \mu_{n0}^i}{(\omega_m - \omega - i\Gamma_m)(\omega_n - 2\omega - i\Gamma_n)} + \frac{\mu_{0m}^i \mu_{mn}^k \mu_{n0}^j}{(\omega_m - 2\omega - i\Gamma_m)(\omega_n - \omega - i\Gamma_n)} + \frac{\mu_{0m}^k \mu_{mn}^j \mu_{n0}^i}{(\omega_m - \omega - i\Gamma_m)(\omega_n - 2\omega - i\Gamma_n)} + \frac{\mu_{0m}^k \mu_{mn}^j \mu_{n0}^i}{(\omega_m - \omega - i\Gamma_m)(\omega_n - 2\omega - i\Gamma_n)} \right\} \quad (26)$$

Expressed with respect to the lower-energy transition to state  $n$ , eq 26 can be rewritten

$$\beta^{ijk}(-2\omega; \omega, \omega)_{n,m} = \frac{-[\mu_{n0}^j (\alpha_{0n}^{ik})_{\text{AR}} + \mu_{n0}^k (\alpha_{0n}^{ij})_{\text{AR}}]}{4\hbar(\omega_n - \omega - i\Gamma_n)} \quad (27)$$

Alternatively, the same relation in eq 27 expressed with respect to the higher-energy transition to state  $m$  yields the following

$$\beta^{ijk}(-2\omega; \omega, \omega)_{n,m} = \frac{-\mu_{0m}^i (\alpha_{m0}^{jk})_{\text{TPA}}}{4\hbar(\omega_m - 2\omega - i\Gamma_m)} \quad (28)$$

As in the case of sum-frequency spectroscopy, eqs 27 and 28 for doubly resonant SHG are equivalent, although one or the other may be more convenient for interpreting a given set of measurements.

**Symmetry Considerations.** *Microscopic Susceptibility Relationships.* The arguments of the preceding section demonstrate that the product of the dominant transition moment(s) and the appropriate polarizability tensor can reasonably describe the second-order spectroscopic NLO properties of an isolated chromophore near resonance. For resonance enhancement with one of the incident frequencies, the Raman tensor for the anti-Stokes transition should be used. In the case of resonance enhancement at the sum frequency, the product of the transition moment and the TPA polarizability tensor yields the nonlinear polarizability. Under double-resonance conditions, these two descriptions become equivalent. A summary of each of the key relationships presented in the six cases above is provided in Table 1.

Within this framework, the nonzero elements of the molecular  $\beta^{(2)}$  tensor for SFG and SHG can be easily determined from the combined symmetry properties of each process. A series of NLO character tables has been constructed to aid in interpreting SFG and SHG measurements, given in Tables 2–22. Each of the nonzero elements of the  $\beta^{(2)}$  tensor allowed by symmetry have been compiled for the SHG- and SFG-active transitions for chromophores of  $C_s$ ,  $C_2$ ,  $C_{2v}$ , and  $C_{3v}$  symmetries. These four molecular point groups were chosen because they represent the most common classes of chromophores encountered in SHG and SFG measurements. Tables 2–5, 6–9, 10–13, and 14–17 contain results under resonance conditions of Cases 1–4, respectively. These tables include results for diagonal as well as the full contributions, the latter of which is the sum of the diagonal and off-diagonal. Double-resonance conditions for SHG and SFG (Cases 5 and 6) are compiled in Tables 18–21. The doubly resonant tables do not include a column for the diagonal contributions, since the diagonal two-state contributions are necessarily not enhanced by a double resonance. Finally, a

**TABLE 1: Summary of Important Equations for the Six Resonant Conditions**

$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b); \beta(-2\omega; \omega, \omega)$	nonresonant with $\omega_b/\omega$		resonant with $\omega_b/\omega$
nonresonant with $\omega_{\text{sum}}/2\omega$	SFG	full sum-over-states expression in eq 1	$\frac{-1}{2\hbar} \sum_n \frac{\mu_{n0}^k(\alpha_{0n}^{ij})_{\text{AR}}}{(\omega_n - \omega_b - i\Gamma_n)}$
	SHG	full sum-over-states expression in eq 1	$\frac{-1}{4\hbar} \sum_n \frac{\mu_{n0}^i(\alpha_{0n}^{ik})_{\text{AR}} + \mu_{n0}^k(\alpha_{0n}^{ij})_{\text{AR}}}{(\omega_n - \omega - i\Gamma_n)}$
resonant with $\omega_{\text{sum}}/2\omega$	SFG	$\frac{-1}{2\hbar} \sum_n \frac{\mu_{0n}^i(\alpha_{n0}^{jk})_{\text{TPA}}}{(\omega_n - \omega_{\text{sum}} - i\Gamma_n)}$	$\frac{-\mu_{n0}^k(\alpha_{0n}^{ij})_{\text{AR}}}{2\hbar(\omega_n - \omega_b - i\Gamma_n)} = \frac{-\mu_{0m}^i(\alpha_{m0}^{jk})_{\text{TPA}}}{2\hbar(\omega_m - \omega_{\text{sum}} - i\Gamma_m)}$
	SHG	$\frac{-1}{4\hbar} \sum_n \frac{\mu_{0n}^i(\alpha_{n0}^{jk})_{\text{TPA}}}{(\omega_n - 2\omega - i\Gamma_n)}$	$\frac{-[\mu_{n0}^i(\alpha_{0n}^{ik})_{\text{AR}} + \mu_{n0}^k(\alpha_{0n}^{ij})_{\text{AR}}]}{4\hbar(\omega_n - \omega - i\Gamma_n)} = \frac{-\mu_{0m}^i(\alpha_{m0}^{jk})_{\text{TPA}}}{4\hbar(\omega_m - 2\omega - i\Gamma_m)}$

**TABLE 2: NLO Character for SFG,  $C_s$  Symmetry, with a Transition Resonant with One of the Incident Frequencies (Case 1)<sup>a,b</sup>**

SFG	$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , resonant with $\omega_b$	
$C_s$	diagonal	full
A'	$\beta_{x'x'x'}$ $\beta_{y'y'y'}$ $\beta_{x'y'x'} + \beta_{y'x'x'} - \beta_{x'x'y'} = \beta_{x'x'y'} \left( \frac{\delta^y \mu^{x'}}{\delta^x \mu^{y'}} \right)$ $\beta_{x'y'y'} + \beta_{y'x'y'} - \beta_{y'y'x'} = \beta_{y'y'x'} \left( \frac{\delta^x \mu^{y'}}{\delta^y \mu^{x'}} \right)$	$\beta_{x'x'x'}$ $\beta_{x'x'y'}$ $\beta_{y'y'x'}$ $\beta_{y'y'y'}$ $\beta_{x'x'x'}$ $\beta_{x'x'y'}$ $\beta_{y'y'x'}$ $\beta_{y'y'y'}$ $\beta_{x'x'x'}$ $\beta_{x'x'y'}$ $\beta_{y'y'x'}$ $\beta_{y'y'y'}$ $\chi_{XYZ} = \chi_{XZY} - \chi_{ZXY}$
A''	$\beta_{x'x'x'} = -\beta_{x'x'x'}(\omega_a/\omega_{\text{sum}})$ $\beta_{y'y'y'} = -\beta_{y'y'y'}(\omega_a/\omega_{\text{sum}})$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{ZZZ} = \frac{-2(\omega_{\text{sum}}\chi_{ZXX} + \omega_a\chi_{XZX})}{\omega_{\text{sum}} + \omega_a}$ $\chi_{XYZ} = \chi_{XZY} - \chi_{ZXY}$ $\chi_{XZY} = -\chi_{ZXY}(\omega_a/\omega_{\text{sum}})$	$\beta_{x'x'x'}$ $\beta_{x'x'y'}$ $\beta_{y'y'x'}$ $\beta_{y'y'y'}$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{XYZ} = \chi_{XZY} - \chi_{ZXY}$

<sup>a</sup> The  $\beta^{(2)}$  tensor elements not listed are zero by symmetry. <sup>b</sup> The tabulated relationships between the  $\chi^{(2)}$  tensor elements are in addition to those imposed by the uniaxial symmetry:  $\chi_{ZZZ}, \chi_{ZXX} = \chi_{ZYY}, \chi_{XZX} = \chi_{YZY}, \chi_{XXZ} = \chi_{YYZ}, \chi_{XYZ} = -\chi_{YXZ}, \chi_{XZY} = -\chi_{YZX}$ , and  $\chi_{ZXY} = -\chi_{ZYX}$ .

separate table summarizing the key relationships between the elements of the  $\beta^{(2)}$  tensor for the specific case of infrared-visible vibrational SFG is given in Table 22. The results in Table 22 differ from the more general SFG symmetry properties in Tables 2–5 in that the Raman polarizability tensor was assumed to be symmetric (a reasonable approximation for vibrational Raman spectroscopy, but not necessarily true for electronic Raman spectroscopy).<sup>90</sup>

**Macroscopic Susceptibility Relationships.** The simplifications in the  $\beta^{(2)}$  tensor arising from symmetry considerations impose relationships on the macroscopic  $\chi^{(2)}$  tensor. Within the electric dipole approximation for light and assuming identical noninteracting chromophores, the macroscopic  $\chi^{(2)}$  tensor is related to the nonlinear polarizability tensor of the chromophore  $\beta^{(2)}$  through orientational averages<sup>19,29,82,99,100</sup>

$$\chi_{IJK}^{(2)} = \sum_{i'j'k'=x'y'z'} N_s \langle R_{Ii'} R_{Jj'} R_{Kk'} \rangle \beta_{i'j'k'}^{(2)} \quad (29)$$

In eq 29,  $N_s$  is the number density of chromophores and  $R_{\Lambda\lambda'}$  are elements of the Euler rotation matrix relating the molecular coordinate system to the macroscopic coordinate system.

**TABLE 3: NLO Character for SFG,  $C_2$  Symmetry, with a Transition Resonant with One of the Incident Frequencies (Case 1)**

SFG	$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , resonant with $\omega_b$	
$C_2$	diagonal	full
A	$\beta_{x'x'x'}$ $\chi_{ZXX} = \chi_{XZX} = \chi_{XXZ}$ $\chi_{XYZ} = \chi_{XZY} = \chi_{ZXY} = 0$	$\beta_{x'x'x'}$ $\beta_{x'x'y'}$ $\beta_{y'y'x'}$ $\beta_{y'y'y'}$ $\beta_{x'x'x'}$ $\beta_{x'x'y'}$ $\beta_{y'y'x'}$ $\beta_{y'y'y'}$ $\chi_{ZXX} = \chi_{XZX}$
B	$\beta_{x'x'x'} = -\beta_{x'x'x'}(\omega_a/\omega_{\text{sum}})$ $\beta_{x'x'y'} = -\beta_{x'x'y'}(\omega_a/\omega_{\text{sum}})$ $\beta_{y'y'x'} = -\beta_{y'y'x'}(\omega_a/\omega_{\text{sum}})$ $\beta_{y'y'y'} = -\beta_{y'y'y'}(\omega_a/\omega_{\text{sum}})$ $\beta_{x'x'x'} = \beta_{x'x'y'}$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{ZZZ} = \frac{-2(\omega_{\text{sum}}\chi_{ZXX} + \omega_a\chi_{XZX})}{\omega_{\text{sum}} + \omega_a}$ $\chi_{XYZ} = \chi_{XZY} - \chi_{ZXY}$ $\chi_{XZY} = -\chi_{ZXY}(\omega_a/\omega_{\text{sum}})$	$\beta_{x'x'x'}$ $\beta_{x'x'y'}$ $\beta_{y'y'x'}$ $\beta_{y'y'y'}$ $\beta_{x'x'x'}$ $\beta_{x'x'y'}$ $\beta_{y'y'x'}$ $\beta_{y'y'y'}$ $-2\chi_{XXZ} = \chi_{ZZZ}$

**TABLE 4: NLO Character for SFG,  $C_{2v}$  Symmetry, with a Transition Resonant with One of the Incident Frequencies (Case 1)**

SFG	$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , resonant with $\omega_b$	
$C_{2v}$	diagonal	full
A <sub>1</sub>	$\beta_{x'x'x'}$ $\chi_{ZXX} = \chi_{XZX} = \chi_{XXZ}$ $\chi_{XYZ} = \chi_{XZY} = \chi_{ZXY} = 0$	$\beta_{x'x'x'}, \beta_{y'y'x'}, \beta_{z'z'x'}$ $\chi_{ZXX} = \chi_{XZX}$ $\chi_{XYZ} = 0$ $\chi_{XZY} = \chi_{ZXY}$
A <sub>2</sub>	0	0
B <sub>1</sub>	$\beta_{x'x'x'} = -\beta_{x'x'x'}(\omega_a/\omega_{\text{sum}})$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{ZZZ} = \frac{-2(\omega_{\text{sum}}\chi_{ZXX} + \omega_a\chi_{XZX})}{\omega_{\text{sum}} + \omega_a}$ $\chi_{XYZ} = \chi_{XZY} - \chi_{ZXY}$ $\chi_{XZY} = -\chi_{ZXY}(\omega_a/\omega_{\text{sum}})$	$\beta_{x'x'x'}, \beta_{z'z'x'}$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{XYZ} = \chi_{XZY} - \chi_{ZXY}$
B <sub>2</sub>	$\beta_{y'y'y'} = -\beta_{y'y'y'}(\omega_a/\omega_{\text{sum}})$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{ZZZ} = \frac{-2(\omega_{\text{sum}}\chi_{ZXX} + \omega_a\chi_{XZX})}{\omega_{\text{sum}} + \omega_a}$ $\chi_{XYZ} = \chi_{XZY} - \chi_{ZXY}$ $\chi_{XZY} = -\chi_{ZXY}(\omega_a/\omega_{\text{sum}})$	$\beta_{y'y'y'}, \beta_{z'z'y'}$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{XYZ} = \chi_{XZY} - \chi_{ZXY}$

The appropriate orientation averages were evaluated for each of the transitions considered in Tables 2–22, assuming a single unique orientation axis (i.e., assuming a random distribution in

**TABLE 5: NLO Character for SFG,  $C_{3v}$  Symmetry, with a Transition Resonant with One of the Incident Frequencies (Case 1)**

SFG	$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , resonant with $\omega_b$	
$C_{3v}$	diagonal	full
A <sub>1</sub>	$\beta_{zzz}$ $\chi_{zxx} = \chi_{xzx} = \chi_{xxz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zyx} = 0$	$\beta_{xxx} = \beta_{yyy}$ $\beta_{zzz}$ $\chi_{zxx} = \chi_{xzx}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zyx} = 0$
A <sub>2</sub>	0	0
E	$\beta_{xxz} = -\beta_{xxz}(\omega_d/\omega_{\text{sum}})$ $\beta_{yyz} = \beta_{yyz}$ $\beta_{zzz} = \beta_{zzz}$ $-2\chi_{xxz} = \chi_{zzz}$ $\chi_{zzz} = \frac{-2(\omega_{\text{sum}}\chi_{zxx} + \omega_d\chi_{xzx})}{\omega_{\text{sum}} + \omega_a}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zyx} = 0$	$\beta_{xxz} = \beta_{yyz}$ $\beta_{zzz} = \beta_{zzz}$ $-\beta_{xxz} = \beta_{yyz} = \beta_{zzz} = \beta_{zzz}$ $-2\chi_{xxz} = \chi_{zzz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zyx} = 0$

**TABLE 6: NLO Character for SHG,  $C_s$  Symmetry, with a Transition Resonant with the Fundamental (Case 2)<sup>a,b</sup>**

SHG	$\beta(-2\omega; \omega, \omega)$	
$C_s$	diagonal	full
A'	$\beta_{xxx}$ $\beta_{yyy}$ $\beta_{xxy}$ $\beta_{yyx}$ $\beta_{xxz} = \beta_{yyz}$ $\beta_{yxx} = \beta_{xyy}$ —	$\beta_{xxx}$ $\beta_{yyy}$ $\beta_{xxy}$ $\beta_{yyx}$ $\beta_{xxz} = \beta_{yyz}$ $\beta_{yxx} = \beta_{xyy}$ $\beta_{zzz} = \beta_{zzz}$ $\beta_{zzx} = \beta_{zzx}$ $\beta_{zzx} = \beta_{zzx}$ —
A''	$-\beta_{xxz} = \beta_{zzx} = \beta_{zzx}$ $-\beta_{yyz} = \beta_{zzx} = \beta_{zzx}$ —	$\beta_{xxz}$ $\beta_{yyz}$ $\beta_{zzx} = \beta_{zzx}$ $\beta_{zzx} = \beta_{zzx}$ —

<sup>a</sup> The  $\beta^{(2)}$  tensor elements not listed are zero by symmetry. <sup>b</sup> The tabulated relationships between the  $\chi^{(2)}$  tensor elements are in addition to those imposed by the uniaxial symmetry:  $\chi_{zzz}, \chi_{zxx} = \chi_{zyy}, \chi_{xzx} = \chi_{yzy} = \chi_{xxz} = \chi_{yyz}$ , and  $\chi_{xyz} = -\chi_{yxz} = \chi_{xzy} = -\chi_{yzx}$ .

**TABLE 7: NLO Character for SHG,  $C_2$  Symmetry, with a Transition Resonant with the Fundamental (Case 2)**

SHG	$\beta(-2\omega; \omega, \omega)$	
$C_2$	diagonal	full
A	$\beta_{zzz}$ $\chi_{zxx} = \chi_{xxz}$ $\chi_{xyz} = 0$	$\beta_{zzz},$ $\beta_{xxx} = \beta_{xxx}$ $\beta_{yyy} = \beta_{yyy}$ $\beta_{xxy} = \beta_{xxy}$ $\beta_{yyx} = \beta_{yyx}$ —
B	$\beta_{xxz} = \beta_{xxz}$ $\beta_{yyz} = \beta_{yyz}$ $\beta_{zzx} = \beta_{zzx}$ $\beta_{xxy} = \beta_{xxy}$ $\beta_{yyx} = \beta_{yyx}$ $\beta_{xxz} = \beta_{xxz}$ $\beta_{yyz} = \beta_{yyz}$ —	$\beta_{xxz} = \beta_{xxz}$ $\beta_{yyz} = \beta_{yyz}$ $\beta_{zzx} = \beta_{zzx}$ $\beta_{xxy} = \beta_{xxy}$ $\beta_{yyx} = \beta_{yyx}$ $\beta_{xxz} = \beta_{xxz}$ $\beta_{yyz} = \beta_{yyz}$ —

the in-plane rotation angle  $\phi$ , yielding  $C_\infty$  macroscopic symmetry), consistent with the vast majority of systems investigated by second harmonic and sum-frequency generation measurements. An example of this procedure is given in Appendix II for the case of SFG of a chromophore with  $C_{2v}$  symmetry considering only the diagonal contributions of a B<sub>1</sub> excited state

**TABLE 8: NLO Character for SHG,  $C_{2v}$  Symmetry, with a Transition Resonant with the Fundamental (Case 2)**

SHG	$\beta(-2\omega; \omega, \omega)$	
$C_{2v}$	diagonal	full
A <sub>1</sub>	$\beta_{zzz}$ $\chi_{zxx} = \chi_{xxz}$ $\chi_{xyz} = 0$	$\beta_{xxx} = \beta_{xxx}$ $\beta_{yyy} = \beta_{yyy}$ $\beta_{zzz}$ —
A <sub>2</sub>	0	0
B <sub>1</sub>	$-\beta_{xxz} = \beta_{xxz} = \beta_{xxz}$ $\chi_{zzz} = -\chi_{xxz} - \chi_{zxx}$	$\beta_{xxz} = \beta_{xxz}$ $\beta_{zzz}$ —
B <sub>2</sub>	$-\beta_{yyz} = \beta_{yyz} = \beta_{yyz}$ $\chi_{zzz} = -\chi_{yyz} - \chi_{zxx}$	$\beta_{yyz} = \beta_{yyz}$ $\beta_{zzz}$ —

**TABLE 9: NLO Character for SHG,  $C_{3v}$  Symmetry, with a Transition Resonant with the Fundamental (Case 2)**

SHG	$\beta(-2\omega; \omega, \omega)$	
$C_{3v}$	diagonal	full
A <sub>1</sub>	$\beta_{zzz}$ $\chi_{zxx} = \chi_{xxz}$ $\chi_{xyz} = 0$	$\beta_{xxx} = \beta_{xxx} = \beta_{yyy} = \beta_{yyy}$ $\beta_{zzz}$ $\chi_{xyz} = 0$
A <sub>2</sub>	0	0
E	$\beta_{xxz} = \beta_{xxz} = \beta_{yyz} = \beta_{yyz}$ $\beta_{zzx} = \beta_{zzx}$ $\chi_{xyz} = 0$	$\beta_{xxz} = \beta_{xxz} = \beta_{yyz} = \beta_{yyz}$ $\beta_{zzx} = \beta_{zzx}$ $-\beta_{xxz} = \beta_{yyz} = \beta_{zzx} = \beta_{zzx}$ $\chi_{xyz} = 0$

**TABLE 10: NLO Character for SFG,  $C_s$  Symmetry, with a Transition Resonant with the Sum-Frequency (Case 3)**

SFG	$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , resonant with $\omega_{\text{sum}}$	
$C_s$	diagonal	full
A'	$\beta_{xxx}$ $\beta_{yyy}$ $\beta_{xxz} + \beta_{yyz} - \beta_{zzx} = \beta_{zzx} \left( \frac{\delta' \mu^x}{\delta'' \mu^y} \right)$ $\beta_{yyx} + \beta_{xxy} - \beta_{xxy} = \beta_{xxy} \left( \frac{\delta' \mu^y}{\delta'' \mu^x} \right)$ $\chi_{xyz} = \chi_{xzy} - \chi_{zxy}$	$\beta_{xxx}$ $\beta_{yyy}$ $\beta_{xxy}$ $\beta_{yyx}$ $\beta_{zzz}$ $\beta_{xxx}$ $\beta_{yyy}$ $\beta_{zzx}$ $\chi_{xyz} = \chi_{xzy} - \chi_{zxy}$
A''	$\beta_{xxz} = -\beta_{xxz}(\omega_d/\omega_b)$ $\beta_{yyz} = -\beta_{yyz}(\omega_d/\omega_b)$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{zzz} = \frac{-2(\omega_d\chi_{xzx} - \omega_b\chi_{xxz})}{\omega_a + \omega_b}$ $\chi_{xyz} = \chi_{xzy} - \chi_{zxy}$ $\chi_{xzy} = \chi_{xzy}(\omega_d/\omega_b)$	$\beta_{xxz}$ $\beta_{yyz}$ $\beta_{zzx}$ $\beta_{zzx}$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{xyz} = \chi_{xzy} - \chi_{zxy}$

with resonance at  $\omega_{\text{sum}}$ . Inspection of the resulting simplified sets of orientational averages revealed proportionalities between the  $\chi^{(2)}$  tensor elements. The tabulated relations between the  $\chi^{(2)}$  tensor elements are *in addition* to the equalities inherently imposed by the presence of uniaxial macroscopic symmetry. For SFG,  $\chi_{zzz}, \chi_{zxx} = \chi_{zyy}, \chi_{xzx} = \chi_{yzy}, \chi_{xxz} = \chi_{yyz}, \chi_{xyz} = -\chi_{yxz}, \chi_{xzy} = -\chi_{yzx}, \chi_{zxy} = -\chi_{zyx}$ , and the remaining tensor elements are zero. For SHG,  $\chi_{zzz}, \chi_{zxx} = \chi_{zyy}, \chi_{xzx} = \chi_{yzy} = \chi_{xxz} = \chi_{yyz}, \chi_{xyz} = -\chi_{yxz} = \chi_{xzy} = -\chi_{yzx}$ , and the remaining



**TABLE 11: NLO Character for SFG,  $C_2$  Symmetry, with a Transition Resonant with the Sum-Frequency (Case 3)**

SFG	$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , resonant with $\omega_{\text{sum}}$	
$C_2$	diagonal	full
A	$\beta_{zzz}$	$\beta_{zzz}$ $\beta_{zzx}$ $\beta_{zxx}$ $\beta_{zzx}$ $\beta_{zzz}$ $\chi_{zxx} = \chi_{xxz} = \chi_{xxz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zyx} = 0$
B	$\beta_{zzz} = \beta_{zzz}(\omega_a/\omega_b)$ $\beta_{zzx} = \beta_{zzx}(\omega_a/\omega_b)$ $\beta_{zxx} = \beta_{zxx}(\omega_a/\omega_b)$ $\beta_{zzx} = \beta_{zzx}(\omega_a/\omega_b)$ $\beta_{zzx} = \beta_{zzx}$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{zzz} = \frac{-2(\omega_a \chi_{xxz} - \omega_b \chi_{xxz})}{\omega_a - \omega_b}$ $\chi_{xyz} = \chi_{xzy} - \chi_{zyx}$ $\chi_{xzy} = \chi_{xzy}(\omega_a/\omega_b)$	$\beta_{zzz}$ $\beta_{zzx}$ $\beta_{zxx}$ $\beta_{zzx}$ $\beta_{zzz}$ $\chi_{zxx} = \chi_{xxz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zyx}$ $-2\chi_{zxx} = \chi_{zzz}$

**TABLE 12: NLO Character for SFG,  $C_{2v}$  Symmetry, with a Transition Resonant with the Sum-Frequency (Case 3)**

SFG	$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , resonant with $\omega_{\text{sum}}$	
$C_{2v}$	diagonal	full
A <sub>1</sub>	$\beta_{zzz}$	$\beta_{zzz}$ $\beta_{zzx}$ $\beta_{zxx}$ $\beta_{zzx}$ $\chi_{zxx} = \chi_{xxz} = \chi_{xxz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zyx} = 0$
A <sub>2</sub>	0	0
B <sub>1</sub>	$\beta_{zzz} = \beta_{zzz}(\omega_a/\omega_b)$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{zzz} = \frac{-2(\omega_a \chi_{xxz} - \omega_b \chi_{xxz})}{\omega_a - \omega_b}$ $\chi_{xyz} = \chi_{xzy} - \chi_{zyx}$ $\chi_{xzy} = \chi_{xzy}(\omega_a/\omega_b)$	$\beta_{zzz}, \beta_{zzx}$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{xyz} = \chi_{xzy} - \chi_{zyx}$
B <sub>2</sub>	$\beta_{zzx} = \beta_{zzx}(\omega_a/\omega_b)$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{zzz} = \frac{-2(\omega_a \chi_{xxz} - \omega_b \chi_{xxz})}{\omega_a - \omega_b}$ $\chi_{xyz} = \chi_{xzy} - \chi_{zyx}$ $\chi_{xzy} = \chi_{xzy}(\omega_a/\omega_b)$	$\beta_{zzx}, \beta_{zxx}$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{xyz} = \chi_{xzy} - \chi_{zyx}$

**TABLE 13: NLO Character for SFG,  $C_{3v}$  Symmetry, with a Transition Resonant with the Sum-Frequency (Case 3)**

SFG	$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , resonant with $\omega_{\text{sum}}$	
$C_{3v}$	diagonal	full
A <sub>1</sub>	$\beta_{zzz}$	$\beta_{zzz} = \beta_{zzx}$ $\beta_{zzz}$ $\chi_{zxx} = \chi_{xxz} = \chi_{xxz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zyx} = 0$
A <sub>2</sub>	0	0
E	$\beta_{zzz} = \beta_{zzz}(\omega_a/\omega_b)$ $\beta_{zzx} = \beta_{zzx}$ $\beta_{zxx} = \beta_{zxx}$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{zzz} = \frac{-2(\omega_a \chi_{xxz} - \omega_b \chi_{xxz})}{\omega_a - \omega_b}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zyx} = 0$	$\beta_{zzz} = \beta_{zzx}$ $\beta_{zzz}$ $\beta_{zzx} = \beta_{zxx} = \beta_{zxx}$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zyx} = 0$

tensor elements are zero. Key relationships between the different  $\chi^{(2)}$  tensor elements for a given transition in a chromophore of

**TABLE 14: NLO Character for SHG,  $C_s$  Symmetry, with a Transition Resonant at the Second Harmonic Frequency (Case 4)**

SHG	$\beta(-2\omega; \omega, \omega)$	
$C_s$	diagonal	full
A'	$\beta_{zzz}$ $\beta_{zzx}$ $\beta_{zxx}$ $\beta_{zzx}$ $\beta_{zzz}$ $\beta_{zzx} = \beta_{zxx}$ $\beta_{zxx} = \beta_{zzx}$ —	$\beta_{zzz}$ $\beta_{zzx}$ $\beta_{zxx}$ $\beta_{zzx}$ $\beta_{zzz}$ $\beta_{zzx} = \beta_{zxx}$ $\beta_{zxx} = \beta_{zzx}$ —
A''	$\beta_{zzz} = \beta_{zzz}$ $\beta_{zzx} = \beta_{zzx}$ $-2\chi_{zxx} = \chi_{zzz}$	$\beta_{zzz} = \beta_{zzz}$ $\beta_{zzx} = \beta_{zzx}$ $-2\chi_{zxx} = \chi_{zzz}$

**TABLE 15: NLO Character for SHG,  $C_2$  Symmetry, with a Transition Resonant at the Second Harmonic Frequency (Case 4)**

SHG	$\beta(-2\omega; \omega, \omega)$	
$C_2$	diagonal	full
A	$\beta_{zzz}$	$\beta_{zzz}$ $\beta_{zzx}$ $\beta_{zxx}$ $\beta_{zzx} = \beta_{zxx}$ $\chi_{zxx} = \chi_{xxz}$ $\chi_{xyz} = 0$
B	$\beta_{zzz} = \beta_{zzz}$ $\beta_{zzx} = \beta_{zzx}$ $\beta_{zxx} = \beta_{zxx}$ $\beta_{zzx} = \beta_{zxx}$ $-2\chi_{zxx} = \chi_{zzz}$	$\beta_{zzz} = \beta_{zzz}$ $\beta_{zzx} = \beta_{zzx}$ $\beta_{zxx} = \beta_{zxx}$ $\beta_{zzx} = \beta_{zxx}$ $-2\chi_{zxx} = \chi_{zzz}$

**TABLE 16: NLO Character for SHG,  $C_{2v}$  Symmetry, with a Transition Resonant at the Second Harmonic Frequency (Case 4)**

SHG	$\beta(-2\omega; \omega, \omega)$	
$C_{2v}$	diagonal	full
A <sub>1</sub>	$\beta_{zzz}$	$\beta_{zzz}$ $\beta_{zzx}$ $\beta_{zxx}$ $\beta_{zzx}$ $\chi_{zxx} = \chi_{xxz}$ $\chi_{xyz} = 0$
A <sub>2</sub>	0	0
B <sub>1</sub>	$\beta_{zzz} = \beta_{zzz}$ $-2\chi_{zxx} = \chi_{zzz}$	$\beta_{zzz} = \beta_{zzz}$ $-2\chi_{zxx} = \chi_{zzz}$
B <sub>2</sub>	$\beta_{zzx} = \beta_{zzx}$ $-2\chi_{zxx} = \chi_{zzz}$	$\beta_{zzx} = \beta_{zzx}$ $-2\chi_{zxx} = \chi_{zzz}$

**TABLE 17: NLO Character for SHG,  $C_{3v}$  Symmetry, with a Transition Resonant at the Second Harmonic Frequency (Case 4)**

SHG	$\beta(-2\omega; \omega, \omega)$	
$C_{3v}$	diagonal	full
A <sub>1</sub>	$\beta_{zzz}$	$\beta_{zzz} = \beta_{zzx}$ $\beta_{zzz}$ $\chi_{zxx} = \chi_{xxz}$ $\chi_{xyz} = 0$
A <sub>2</sub>	0	0
E	$\beta_{zzz} = \beta_{zzz}$ $\beta_{zzx} = \beta_{zzx}$ $\beta_{zxx} = \beta_{zxx}$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{xyz} = 0$	$\beta_{zzz} = \beta_{zzz}$ $\beta_{zzx} = \beta_{zzx}$ $\beta_{zxx} = \beta_{zxx}$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{xyz} = 0$

a particular symmetry are reported below the  $\beta^{(2)}$  tensor elements in all of the second-order nonlinear character tables. The tabulated relationships between the  $\chi^{(2)}$  tensor elements are expected to hold for uniaxially oriented surface films with low

**TABLE 18: SFG and SHG NLO Character for  $C_s$  Symmetry under Doubly Resonant Conditions (Cases 5 and 6)**

		$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , double-resonance SFG; $\beta(-2\omega; \omega, \omega)$ , double-resonance SHG	
$C_s$		$m = A'$	$m = A''$
$n = A'$	SFG	$\beta_{x'x'x'}, \beta_{x'x'y'}, \beta_{x'y'x'}, \beta_{y'x'x'}, \beta_{y'y'y'}, \beta_{x'y'y'}, \beta_{y'x'y'}, \beta_{y'y'x'}$	$\beta_{z'z'z'}, \beta_{z'z'y'}$ $-2\chi_{zxx} = -2\chi_{zxz} = \chi_{zzz}, \chi_{xyz} = 0, \chi_{xzy} = \chi_{zxy}$
	SHG	$\beta_{x'x'x'}, \beta_{x'x'y'} = \beta_{x'y'x'}, \beta_{y'x'x'}, \beta_{y'y'y'}, \beta_{x'y'y'}, \beta_{y'x'y'} = \beta_{y'y'x'}$	$\beta_{z'z'x'} = \beta_{z'x'z'}, \beta_{z'z'y'} = \beta_{z'y'z'}$ $-2\chi_{zxx} = \chi_{zzz}$
$n = A''$	SFG	$\beta_{x'x'z'}, \beta_{y'y'z'}$ $-2\chi_{xxz} = -2\chi_{xzx} = \chi_{zzz}, \chi_{xyz} = \chi_{xzy}, \chi_{zxy} = 0$	$\beta_{z'z'z'}, \beta_{z'z'y'}$ $-2\chi_{zxx} = -2\chi_{xxz} = \chi_{zzz}, \chi_{xyz} = -\chi_{xzy}, \chi_{xzy} = 0$
	SHG	$\beta_{x'x'z'}, \beta_{y'y'z'}$ $-2\chi_{xxz} = \chi_{zzz}$	$\beta_{z'z'x'} = \beta_{z'x'z'}, \beta_{z'z'y'} = \beta_{z'y'z'}$ $-2\chi_{zxx} = \chi_{zzz}$

**TABLE 19: SFG and SHG NLO Character for  $C_2$  Symmetry under Doubly Resonant Conditions (Cases 5 and 6)**

		$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , double-resonance SFG; $\beta(-2\omega; \omega, \omega)$ , double-resonance SHG	
$C_2$		$m = A$	$m = B$
$n = A$	SFG	$\beta_{z'z'z'}$ $\chi_{zxx} = \chi_{zxz} = \chi_{xxz}, \chi_{xyz} = \chi_{xzy} = \chi_{zxy} = 0$	$\beta_{x'x'z'}, \beta_{x'y'z'}, \beta_{y'x'z'}, \beta_{y'y'z'}$ $-2\chi_{zxx} = -2\chi_{xxz} = \chi_{zzz}$
	SHG	$\beta_{z'z'z'}$ $\chi_{zxx} = \chi_{xxz}, \chi_{xyz} = 0$	$\beta_{x'x'z'}, \beta_{x'y'z'}, \beta_{y'x'z'} = \beta_{z'z'x'}, \beta_{y'y'z'} = \beta_{z'z'y'}$ $-2\chi_{zxx} = \chi_{zzz}$
$n = B$	SFG	$\beta_{z'x'x'}, \beta_{z'x'y'}, \beta_{z'y'x'}, \beta_{z'y'y'}$ $-2\chi_{xxz} = -2\chi_{xzx} = \chi_{zzz}$	$\beta_{x'x'z'}, \beta_{x'y'z'}, \beta_{y'x'z'}, \beta_{y'y'z'}$ $-2\chi_{zxx} = -2\chi_{xxz} = \chi_{zzz}$
	SHG	$\beta_{z'x'x'}, \beta_{z'x'y'}, \beta_{z'y'x'} = \beta_{z'y'y'}$ $-2\chi_{xxz} = \chi_{zzz}$	$\beta_{x'x'z'} = \beta_{x'x'x'}, \beta_{x'y'z'} = \beta_{x'y'x'}, \beta_{y'x'z'} = \beta_{y'x'x'}, \beta_{y'y'z'} = \beta_{y'y'x'}$ $-2\chi_{zxx} = \chi_{zzz}$

**TABLE 20: SFG and SHG NLO Character Table for  $C_{2v}$  Symmetry under Doubly Resonant Conditions (Cases 5 and 6)**

		$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , double resonance SFG; $\beta(-2\omega; \omega, \omega)$ , double resonance SHG			
$C_{2v}$		$m = A_1$	$m = A_2$	$m = B_1$	$m = B_2$
$n = A_1$	SFG	$\beta_{z'z'z'}$ $\chi_{zxx} = \chi_{zxz} = \chi_{xxz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zxy} = 0$	0 0	$\beta_{x'x'z'}$ $-2\chi_{zxx} = -2\chi_{xxz} = \chi_{zzz}$ $\chi_{xyz} = 0, \chi_{xzy} = \chi_{zxy}$	$\beta_{y'y'z'}$ $-2\chi_{zxx} = -2\chi_{xxz} = \chi_{zzz}$ $\chi_{xyz} = 0, \chi_{xzy} = \chi_{zxy}$
	SHG	$\beta_{z'z'z'}$ $\chi_{zxx} = \chi_{xxz}$ $\chi_{xyz} = 0$	0 0	$\beta_{x'x'z'} = \beta_{x'x'x'}$ $-2\chi_{zxx} = \chi_{zzz}$	$\beta_{y'y'z'} = \beta_{y'y'x'}$ $-2\chi_{zxx} = \chi_{zzz}$
$n = A_2$		0	0	0	0
$n = B_1$	SFG	$\beta_{z'x'x'}$ $-2\chi_{xxz} = -2\chi_{xzx} = \chi_{zzz}$ $\chi_{xyz} = \chi_{xzy}$ $\chi_{zxy} = 0$	0 0	$\beta_{x'x'x'}$ $-2\chi_{zxx} = -2\chi_{xxz} = \chi_{zzz}$ $\chi_{xyz} = -\chi_{xzy}, \chi_{xzy} = 0$	0 0
	SHG	$\beta_{z'x'x'}$ $-2\chi_{xxz} = \chi_{zzz}$	0 0	$\beta_{x'x'z'} = \beta_{x'x'x'}$ $-2\chi_{zxx} = \chi_{zzz}$	0 0
$n = B_2$	SFG	$\beta_{z'y'y'}$ $-2\chi_{xxz} = -2\chi_{xzx} = \chi_{zzz}$ $\chi_{xyz} = \chi_{xzy}$ $\chi_{zxy} = 0$	0 0	0 0	$\beta_{y'y'z'}$ $-2\chi_{zxx} = -2\chi_{xxz} = \chi_{zzz}$ $\chi_{xyz} = -\chi_{xzy}$ $\chi_{xzy} = 0$
	SHG	$\beta_{z'y'y'}$ $-2\chi_{xxz} = \chi_{zzz}$	0 0	0 0	$\beta_{y'y'z'} = \beta_{y'y'x'}$ $-2\chi_{zxx} = \chi_{zzz}$

**TABLE 21: SFG and SHG NLO Character for  $C_{3v}$  Symmetry under Doubly Resonant Conditions (Cases 5 and 6)**

		$\beta(-\omega_{\text{sum}}; \omega_a, \omega_b)$ , double resonance SFG; $\beta(-2\omega; \omega, \omega)$ , double resonance SHG		
$C_{3v}$		$m = A_1$	$m = A_2$	$m = E$
$n = A_1$	SFG	$\beta_{z'z'z'}$ $\chi_{zxx} = \chi_{zxz} = \chi_{xxz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zxy} = 0$	0 0	$\beta_{x'x'z'} = \beta_{y'y'z'}$ $-2\chi_{zxx} = -2\chi_{xxz} = \chi_{zzz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zxy} = 0$
	SHG	$\beta_{z'z'z'}$ $\chi_{zxx} = \chi_{xxz}$ $\chi_{xyz} = 0$	0 0	$\beta_{x'x'z'} = \beta_{x'x'x'}, \beta_{y'y'z'} = \beta_{y'y'x'}$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{xyz} = 0$
$n = A_2$		0	0	0
$n = E$	SFG	$\beta_{z'x'x'} = \beta_{z'y'y'}$ $-2\chi_{xxz} = -2\chi_{xzx} = \chi_{zzz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zxy} = 0$	0 0	$-\beta_{x'x'x'} = \beta_{x'y'y'} = \beta_{y'x'x'} = \beta_{y'y'y'}$ $\beta_{x'x'z'} = \beta_{y'y'z'}$ $-2\chi_{zxx} = -2\chi_{xxz} = \chi_{zzz}$ $\chi_{xyz} = \chi_{xzy} = \chi_{zxy} = 0$
	SHG	$\beta_{z'x'x'} = \beta_{z'y'y'}$ $-2\chi_{xxz} = \chi_{zzz}$ $\chi_{xyz} = 0$	0 0	$\beta_{x'x'z'} = \beta_{x'x'x'}, \beta_{y'y'z'} = \beta_{y'y'x'}$ $-\beta_{x'x'x'} = \beta_{x'y'y'} = \beta_{y'x'x'} = \beta_{y'y'y'}$ $-2\chi_{zxx} = \chi_{zzz}$ $\chi_{xyz} = 0$

chromophore densities and for dilute uniaxial bulk media such as poled polymer films (i.e., within the range of validity of eq 29).

The general expressions for the second harmonic and sum-frequency polarizability tensors summarized in Table 1 provide

**TABLE 22: Infrared–Visible SFG NLO Character for  $C_s$ ,  $C_2$ ,  $C_{2v}$ , and  $C_{3v}$  Symmetries for Resonance with the Infrared Frequency**

IR–vis SFG	$\beta(-\omega_{\text{sum}}; \omega_{\text{vis}}, \omega_{\text{IR}})$ , resonant with $\omega_{\text{IR}}$	
$C_s$	$C_2$	
A'	$\beta_{x'x'x'} = \beta_{y'y'y'}$ $\beta_{x'x'y'} = \beta_{y'y'x'}$ $\beta_{x'x'x'} = \beta_{y'y'y'}$ $\beta_{x'x'y'} = \beta_{y'y'x'}$ $\beta_{y'y'x'} = \beta_{x'x'y'}$ $\beta_{x'x'x'} = \beta_{y'y'y'}$ $\beta_{x'x'y'} = \beta_{y'y'x'}$ $\chi_{ZXX} = \chi_{XZX}$ $\chi_{XYZ} = 0$ $\chi_{XZY} = \chi_{ZXY}$	A $\beta_{x'x'x'} = \beta_{y'y'y'}$ $\beta_{x'x'y'} = \beta_{y'y'x'}$ $\beta_{x'x'x'} = \beta_{y'y'y'}$ $\beta_{x'x'y'} = \beta_{y'y'x'}$ $\chi_{ZXX} = \chi_{XZX}$ $\chi_{XYZ} = 0$ $\chi_{XZY} = \chi_{ZXY}$
A''	$\beta_{x'x'x'} = \beta_{z'z'z'}$ $\beta_{y'y'y'} = \beta_{z'z'z'}$  $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{ZXX} = \chi_{XZX}$ $\chi_{XYZ} = 0$ $\chi_{XZY} = \chi_{ZXY}$	B $\beta_{x'x'x'} = \beta_{z'z'z'}$ $\beta_{y'y'y'} = \beta_{z'z'z'}$ $\beta_{x'x'y'} = \beta_{z'z'y'}$ $\beta_{y'y'x'} = \beta_{z'y'x'}$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{ZXX} = \chi_{XZX}$ $\chi_{XYZ} = 0$ $\chi_{XZY} = \chi_{ZXY}$
$C_{2v}$	$C_{3v}$	
A <sub>1</sub>	$\beta_{x'x'x'} = \beta_{y'y'y'}$ $\beta_{x'x'y'} = \beta_{y'y'x'}$ $\beta_{x'x'x'} = \beta_{y'y'y'}$ $\chi_{ZXX} = \chi_{XZX}$ $\chi_{XYZ} = 0$ $\chi_{XZY} = \chi_{ZXY}$	A <sub>1</sub> $\beta_{x'x'x'} = \beta_{y'y'y'}$ $\beta_{x'x'y'} = \beta_{y'y'x'}$ $\chi_{ZXX} = \chi_{XZX}$ $\chi_{XYZ} = \chi_{XZY} = \chi_{ZXY} = 0$
A <sub>2</sub>	0	A <sub>2</sub> 0
B <sub>1</sub>	$\beta_{x'x'x'} = \beta_{z'z'z'}$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{ZXX} = \chi_{XZX}$ $\chi_{XYZ} = 0$ $\chi_{XZY} = \chi_{ZXY}$	E $\beta_{x'x'x'} = \beta_{z'z'z'} = \beta_{y'y'y'} = \beta_{z'y'z'}$ $-\beta_{x'x'y'} = \beta_{y'y'x'} = \beta_{y'y'x'} = \beta_{y'y'x'}$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{ZXX} = \chi_{XZX}$ $\chi_{XYZ} = \chi_{XZY} = \chi_{ZXY} = 0$
B <sub>2</sub>	$\beta_{y'y'y'} = \beta_{z'z'z'}$ $-2\chi_{XXZ} = \chi_{ZZZ}$ $\chi_{ZXX} = \chi_{XZX}$ $\chi_{XYZ} = 0$ $\chi_{XZY} = \chi_{ZXY}$	

a means to interconnect the apparently disparate selection rules routinely used to interpret SHG and SFG measurements. In infrared–visible SFG of vibrational transitions, it is widely accepted that the transition of interest must be both infrared and Raman active to be SFG active, in excellent agreement with the present study. The off-diagonal contributions in the Raman tensor dominate the measured response by several orders of magnitude; therefore, the diagonal contributions can be categorically neglected.<sup>90,93</sup> In SHG investigations of electronic and vibronic transitions, the diagonal contributions and the off-diagonal contributions will both generally be significant, although often the diagonal terms are greater in magnitude.<sup>1</sup> This trend is in excellent agreement with phenomenological guidelines suggesting that the hyperpolarizability is often reasonably well described by a product of the transition moment and the difference in permanent dipole. By inspection, the well-established selection rules for infrared–visible SFG and the experimentally established guidelines for SHG both follow directly from the general expressions summarized in Table 1.

Inspection of Tables 2–17 reveals the presence of symmetry-allowed macroscopic chiral tensor elements (e.g., nonzero  $\chi_{XYZ}$  for SHG and a nonzero  $\chi_{XYZ}$ ,  $\chi_{XZY}$ , or  $\chi_{ZXY}$  for SFG) for molecular point groups with mirror-plane symmetry and no chirality in the molecular  $\beta^{(2)}$  tensor. Furthermore, the diagonal

contributions to the  $\beta^{(2)}$  tensor inherently lack chirality regardless of molecular symmetry, as they depend on only two vectors within the molecular frame.<sup>19,74,76,101</sup> Although derived purely from symmetry arguments, this macromolecular chirality in both of these instances has a simple physical origin. Achiral chromophore planes can assemble to generate macroscopic chirality if appropriately oriented.<sup>8,9,19,44,101,102</sup> Recently, the importance of these orientational contributions has been experimentally confirmed in this laboratory in studies of achiral chromophores assembled at chiral templated interfaces.<sup>103</sup> From Table 22, it is predicted that these chiral effects are also expected to be present in infrared–visible SFG measurements of an oriented chiral system, even for achiral vibrational resonances (e.g., stretching modes of a molecule or fragment with  $C_s$  or  $C_{2v}$  symmetry).

## Conclusions

A simple, unified treatment of the selection rules for sum-frequency and second harmonic spectroscopies was developed. For both vibrational and electronic resonances, it was shown that resonance enhancement with an incident frequency generates a selection rule for SHG and SFG requiring a nonzero transition moment and a nonzero anti-Stokes Raman polarizability. Resonance enhancement at the sum frequency or second harmonic frequency similarly requires a nonzero transition moment and a nonzero polarizability for TPA. In the case of double resonance, the two descriptions become equivalent. For symmetry analysis, it is convenient to separate the contributions into diagonal two-state and off-diagonal three-state terms. In vibrational SFG, the off-diagonal terms dominate, while both are generally significant in electronically resonant systems.

From these simplified expressions for describing SHG and SFG, a series of NLO character tables was generated, summarizing key relationships between the molecular and the macroscopic nonlinear polarizability tensors for uniaxial systems containing chromophores of  $C_s$ ,  $C_2$ ,  $C_{2v}$ , and  $C_{3v}$  symmetry. These four point groups were chosen because they represent the most common chromophore classes encountered in SHG and SFG experiments. Most significantly, the relationships imposed on the macroscopic  $\chi^{(2)}$  tensor elements were shown to be indicative of the molecular symmetry and the symmetry of the resonant transition(s). It is anticipated that these tables will be valuable assets in interpreting current and future experimental polarization measurements in second harmonic and sum-frequency spectroscopic investigations.

One important result from this work is the elucidation of an intimate relationship between molecular hyperpolarizability and TPA. The hyperpolarizability tensor is explicitly given by the simple product of the transition moment and the two-photon polarizability tensor. Consequently, many of the key molecular design properties relevant for optimizing hyperpolarizability should also result in large TPA and vice versa. This finding suggests that the recent efforts toward development of molecules with large TPA cross sections for microscopy applications could gain insight from the wealth of published theoretical and experimental work describing optimization of organic and inorganic moieties with large hyperpolarizabilities for NLO device applications and vice versa.

**Acknowledgment.** The authors gratefully acknowledge financial support from a Camille and Henry Dreyfus New Faculty Award, a Research Corporation Research Innovation Award, and Purdue University.

## Appendix I

The expression in eq 1 can be rewritten in the following shorthand notation

$$\beta^{ijk}(-\omega_{\text{sum}}; \omega_a, \omega_b)_{n=m,0} = \frac{-1}{4\hbar^2} \sum_n (A_{ijk} + B_{ijk} + C_{ijk}) \quad (\text{A1})$$

In eq A1, the  $A$ ,  $B$ , and  $C$  terms are defined as follows

$$A_{ijk} = \left( \frac{2\mu_{0n}^i \mu_{nn}^j \mu_{n0}^k}{(\omega_n - \omega_a - i\Gamma_n)(\omega_n + \omega_b + i\Gamma_n)} + \frac{2\mu_{0n}^j \mu_{nn}^i \mu_{n0}^k}{(\omega_n + \omega_a + i\Gamma_n)(\omega_n - \omega_b - i\Gamma_n)} \right) + \frac{2}{\omega_{\text{sum}}} \left( \frac{\mu_{00}^i \mu_{0n}^k \mu_{n0}^j}{(\omega_n + \omega_a + i\Gamma_n)} - \frac{\mu_{00}^i \mu_{0n}^k \mu_{n0}^j}{(\omega_n - \omega_a - i\Gamma_n)} + \frac{\mu_{00}^j \mu_{0n}^k \mu_{n0}^i}{(\omega_n + \omega_b + i\Gamma_n)} - \frac{\mu_{00}^j \mu_{0n}^k \mu_{n0}^i}{(\omega_n - \omega_b - i\Gamma_n)} \right) \quad (\text{A2})$$

$$B_{ijk} = \left( \frac{2\mu_{0n}^i \mu_{nn}^j \mu_{n0}^k}{(\omega_n + \omega_b + i\Gamma_n)(\omega_n + \omega_{\text{sum}} + i\Gamma_n)} + \frac{2\mu_{0n}^j \mu_{nn}^i \mu_{n0}^k}{(\omega_n - \omega_b - i\Gamma_n)(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} \right) + \frac{2}{\omega_1} \left( \frac{\mu_{00}^j \mu_{0n}^k \mu_{n0}^i}{(\omega_n - \omega_b - i\Gamma_n)} - \frac{\mu_{00}^j \mu_{0n}^k \mu_{n0}^i}{(\omega_n + \omega_b + i\Gamma_n)} + \frac{\mu_{00}^i \mu_{0n}^k \mu_{n0}^j}{(\omega_n + \omega_{\text{sum}} + i\Gamma_n)} - \frac{\mu_{00}^i \mu_{0n}^k \mu_{n0}^j}{(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} \right) \quad (\text{A3})$$

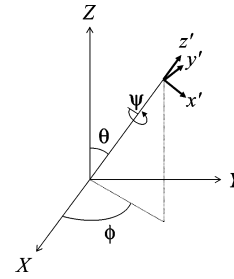
$$C_{ijk} = \left( \frac{2\mu_{0n}^i \mu_{nn}^k \mu_{n0}^j}{(\omega_n + \omega_a + i\Gamma_n)(\omega_n + \omega_{\text{sum}} + i\Gamma_n)} + \frac{2\mu_{0n}^j \mu_{nn}^k \mu_{n0}^i}{(\omega_n - \omega_a - i\Gamma_n)(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} \right) + \frac{2}{\omega_2} \left( \frac{\mu_{00}^k \mu_{0n}^j \mu_{n0}^i}{(\omega_n + \omega_{\text{sum}} + i\Gamma_n)} - \frac{\mu_{00}^k \mu_{0n}^j \mu_{n0}^i}{(\omega_n - \omega_{\text{sum}} - i\Gamma_n)} + \frac{\mu_{00}^k \mu_{0n}^j \mu_{n0}^i}{(\omega_n - \omega_a - i\Gamma_n)} - \frac{\mu_{00}^k \mu_{0n}^j \mu_{n0}^i}{(\omega_n + \omega_a + i\Gamma_n)} \right) \quad (\text{A4})$$

The  $A$ ,  $B$ , and  $C$  terms can be simplified further. An example is given for  $A_{ijk}$

$$A_{ijk} = \left( \frac{2\mu_{0n}^j \mu_{nn}^i \mu_{n0}^k}{(\omega_n - \omega_a - i\Gamma_n)(\omega_n + \omega_b + i\Gamma_n)} + \frac{2\mu_{0n}^j \mu_{nn}^i \mu_{n0}^k}{(\omega_n + \omega_a + i\Gamma_n)(\omega_n - \omega_b - i\Gamma_n)} \right) + \frac{2}{\omega_{\text{sum}}} \left( \frac{\mu_{00}^i \mu_{0n}^k \mu_{n0}^j (\omega_a + \omega_b)}{(\omega_n - \omega_a - i\Gamma_n)(\omega_n + \omega_b + i\Gamma_n)} + \frac{\mu_{00}^i \mu_{0n}^k \mu_{n0}^j (\omega_a + \omega_b)}{(\omega_n + \omega_a + i\Gamma_n)(\omega_n - \omega_b - i\Gamma_n)} \right) \quad (\text{A5})$$

$$A_{ijk} = \left( \frac{2\delta_{n0}^i \mu_{0n}^k \mu_{n0}^j}{(\omega_n + \omega_b + i\Gamma_n)(\omega_n - \omega_a - i\Gamma_n)} + \frac{2\delta_{n0}^i \mu_{0n}^k \mu_{n0}^j}{(\omega_n - \omega_b - i\Gamma_n)(\omega_n + \omega_a + i\Gamma_n)} \right) \quad (\text{A6})$$

Analogous expressions can be derived for  $B_{ijk}$  and  $C_{ijk}$  to generate the simplified expression for the diagonal contributions to  $\beta^{(2)}$  for SFG given in eq 2.



**Figure 2.** Euler angles ( $\theta, \psi, \phi$ ) relating the molecular ( $x', y', z'$ ) and macroscopic ( $X, Y, Z$ ) coordinate systems.

## Appendix II

A derivation of the relationships between different macroscopic hyperpolarizability tensors is presented here for the case of SFG,  $C_{2v}$  symmetry, diagonal,  $\omega_{\text{sum}}$  resonant, and a  $B_1$  excited state. The molecular and laboratory coordinate systems are related through the Euler angles  $\theta$  (tilt angle),  $\psi$  (twist angle), and  $\phi$  (in-plane rotation angle) as defined in Figure 2. Equations A7–A16 are used to build up the general equations for  $\chi^{(2)}$ . For a film with a random orientation distribution within the surface plane (i.e., for a uniaxial film), the average over  $\phi$  is separable, with  $\langle \sin^2 \phi \rangle = \langle \cos^2 \phi \rangle = 1/2$  and  $\langle \sin \phi \cos \phi \rangle = 0$

$$R = \begin{bmatrix} R_{Xx'} & R_{Xy'} & R_{Xz'} \\ R_{Yx'} & R_{Yy'} & R_{Yz'} \\ R_{Zx'} & R_{Zy'} & R_{Zz'} \end{bmatrix} \quad (\text{A7})$$

$$R_{Xx'} = -\sin \psi \sin \phi + \cos \theta \cos \psi \cos \phi \quad (\text{A8})$$

$$R_{Xy'} = -\cos \psi \sin \phi - \cos \theta \sin \psi \cos \phi \quad (\text{A9})$$

$$R_{Xz'} = \sin \theta \cos \phi \quad (\text{A10})$$

$$R_{Yx'} = \sin \psi \cos \phi + \cos \theta \cos \psi \sin \phi \quad (\text{A11})$$

$$R_{Yy'} = \cos \psi \cos \phi - \cos \theta \sin \psi \sin \phi \quad (\text{A12})$$

$$R_{Yz'} = \sin \theta \sin \phi \quad (\text{A13})$$

$$R_{Zx'} = -\sin \theta \cos \psi \quad (\text{A14})$$

$$R_{Zy'} = \sin \theta \sin \psi \quad (\text{A15})$$

$$R_{Zz'} = \cos \theta \quad (\text{A16})$$

Equations A17–A23 are for the most general case of molecular  $C_1$  symmetry. They are derived from evaluation of eq 29 followed by averaging over the in-plane orientation angle  $\phi$ . There are seven unique elements remaining in the  $\chi^{(2)}$  tensor for SFG in uniaxial systems, and they are  $\chi_{ZZZ}$ ,  $\chi_{ZXX} = \chi_{ZYY}$ ,  $\chi_{XZX} = \chi_{YZY}$ ,  $\chi_{XXZ} = \chi_{YYZ}$ ,  $\chi_{XYZ} = -\chi_{YXZ}$ ,  $\chi_{XZY} = -\chi_{YZX}$ , and  $\chi_{ZXY} = -\chi_{ZYX}$

$$\chi_{ZZZ} = N_s \times$$

$$\left\{ \begin{aligned} & \langle \cos^3 \theta \rangle (\beta_{zzz}^z) \\ & + \langle \sin \theta \sin \psi \rangle (\beta_{zzz}^x + \beta_{zzz}^y + \beta_{zzz}^z) \\ & - \langle \sin \theta \cos \psi \rangle (\beta_{zzz}^x + \beta_{zzz}^y + \beta_{zzz}^z) \\ & + \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (\beta_{zzz}^x + \beta_{zzz}^y + \beta_{zzz}^z) \\ & + \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{zzz}^x + \beta_{zzz}^y + \beta_{zzz}^z) \\ & - \langle \sin^2 \theta \cos \theta \sin \psi \cos \psi \rangle (\beta_{zzz}^x + \beta_{zzz}^y + \beta_{zzz}^z + \beta_{zzz}^x + \beta_{zzz}^y + \beta_{zzz}^z) \\ & + \langle \sin^3 \theta \sin \psi \rangle (\beta_{zzz}^x + \beta_{zzz}^y + \beta_{zzz}^z - \beta_{zzz}^x - \beta_{zzz}^y - \beta_{zzz}^z) \\ & + \langle \sin^3 \theta \cos \psi \rangle (\beta_{zzz}^x + \beta_{zzz}^y + \beta_{zzz}^z - \beta_{zzz}^x - \beta_{zzz}^y - \beta_{zzz}^z) \\ & + \langle \sin^3 \theta \sin^3 \psi \rangle (\beta_{zzz}^x - \beta_{zzz}^y - \beta_{zzz}^z - \beta_{zzz}^x) \\ & + \langle \sin^3 \theta \cos^3 \psi \rangle (-\beta_{zzz}^x + \beta_{zzz}^y + \beta_{zzz}^z + \beta_{zzz}^x) \end{aligned} \right\} \quad (\text{A17})$$



$$\chi_{ZZX} = \frac{1}{2} N_s \times \left\{ \begin{aligned} &\langle \sin^2 \theta \cos \theta \rangle (\beta_{zzz} + \beta_{zzx} + \beta_{zzx}) \\ &- \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (\beta_{yyz} + \beta_{yyz} + \beta_{yyz}) \\ &- \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^2 \theta \cos \theta \sin \psi \cos \psi \rangle (\beta_{xyx} + \beta_{xyx} + \beta_{xyx} + \beta_{xyx} + \beta_{xyx} + \beta_{xyx}) \\ &+ \langle \sin \theta \sin \psi \rangle (\beta_{yyx} + \beta_{yyx} - \beta_{yyx} - \beta_{yyx}) \\ &+ \langle \sin \theta \cos \psi \rangle (-\beta_{xxz} - \beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^3 \theta \sin \psi \rangle (-\beta_{xxz} - \beta_{xxz} - \beta_{xxz} + \beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^3 \theta \cos \psi \rangle (\beta_{yyx} + \beta_{yyx} + \beta_{yyx} - \beta_{yyx} - \beta_{yyx} - \beta_{yyx}) \\ &+ \langle \sin^3 \theta \sin^3 \psi \rangle (-\beta_{yyx} + \beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^3 \theta \cos^3 \psi \rangle (\beta_{xxz} - \beta_{xxz} - \beta_{xxz} - \beta_{xxz}) \end{aligned} \right\} \quad (A18)$$

$$\chi_{XZX} = \frac{1}{2} N_s \times \left\{ \begin{aligned} &\langle \sin^2 \theta \cos \theta \rangle (\beta_{zzz} + \beta_{zzx} + \beta_{zzx}) \\ &- \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (\beta_{yyz} + \beta_{yyz} + \beta_{yyz}) \\ &- \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^2 \theta \cos \theta \sin \psi \cos \psi \rangle (\beta_{xyx} + \beta_{xyx} + \beta_{xyx} + \beta_{xyx} + \beta_{xyx} + \beta_{xyx}) \\ &+ \langle \sin \theta \sin \psi \rangle (\beta_{yyx} + \beta_{yyx} - \beta_{yyx} - \beta_{yyx}) \\ &+ \langle \sin \theta \cos \psi \rangle (-\beta_{xxz} - \beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^3 \theta \sin \psi \rangle (-\beta_{xxz} - \beta_{xxz} - \beta_{xxz} + \beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^3 \theta \cos \psi \rangle (\beta_{yyx} + \beta_{yyx} + \beta_{yyx} - \beta_{yyx} - \beta_{yyx} - \beta_{yyx}) \\ &+ \langle \sin^3 \theta \sin^3 \psi \rangle (-\beta_{yyx} + \beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^3 \theta \cos^3 \psi \rangle (\beta_{xxz} - \beta_{xxz} - \beta_{xxz} - \beta_{xxz}) \end{aligned} \right\} \quad (A19)$$

$$\chi_{XXZ} = \frac{1}{2} N_s \times \left\{ \begin{aligned} &\langle \sin^2 \theta \cos \theta \rangle (\beta_{zzz} + \beta_{zzx} + \beta_{zzx}) \\ &- \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (\beta_{yyz} + \beta_{yyz} + \beta_{yyz}) \\ &- \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^2 \theta \cos \theta \sin \psi \cos \psi \rangle (\beta_{xyx} + \beta_{xyx} + \beta_{xyx} + \beta_{xyx} + \beta_{xyx} + \beta_{xyx}) \\ &+ \langle \sin \theta \sin \psi \rangle (\beta_{yyx} + \beta_{yyx} - \beta_{yyx} - \beta_{yyx}) \\ &+ \langle \sin \theta \cos \psi \rangle (-\beta_{xxz} - \beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^3 \theta \sin \psi \rangle (-\beta_{xxz} - \beta_{xxz} - \beta_{xxz} + \beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^3 \theta \cos \psi \rangle (\beta_{yyx} + \beta_{yyx} + \beta_{yyx} - \beta_{yyx} - \beta_{yyx} - \beta_{yyx}) \\ &+ \langle \sin^3 \theta \sin^3 \psi \rangle (-\beta_{yyx} + \beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \\ &+ \langle \sin^3 \theta \cos^3 \psi \rangle (\beta_{xxz} - \beta_{xxz} - \beta_{xxz} - \beta_{xxz}) \end{aligned} \right\} \quad (A20)$$

$$\chi_{XYZ} = \frac{1}{2} N_s \times \left\{ \begin{aligned} &\langle \cos^2 \theta \rangle (\beta_{xxz} - \beta_{xxz}) \\ &+ \langle \sin^2 \theta \sin^2 \psi \rangle (\beta_{zzx} - \beta_{zzx}) \\ &+ \langle \sin^2 \theta \cos^2 \psi \rangle (\beta_{yyz} - \beta_{yyz}) \\ &+ \langle \sin^2 \theta \sin \psi \cos \psi \rangle (\beta_{xxz} - \beta_{yyz} - \beta_{xxz} + \beta_{yyz}) \\ &+ \langle \sin \theta \cos \theta \sin \psi \rangle (\beta_{xxz} - \beta_{xxz} - \beta_{yyz} + \beta_{yyz}) \\ &+ \langle \sin \theta \cos \theta \cos \psi \rangle (-\beta_{xxz} + \beta_{yyz} - \beta_{yyz} + \beta_{xxz}) \end{aligned} \right\} \quad (A21)$$

$$\chi_{ZYZ} = \frac{1}{2} N_s \times \left\{ \begin{aligned} &\langle \cos^2 \theta \rangle (\beta_{xxz} - \beta_{xxz}) \\ &+ \langle \sin^2 \theta \sin^2 \psi \rangle (\beta_{zzx} - \beta_{zzx}) \\ &+ \langle \sin^2 \theta \cos^2 \psi \rangle (\beta_{yyz} - \beta_{yyz}) \\ &+ \langle \sin^2 \theta \sin \psi \cos \psi \rangle (\beta_{xxz} - \beta_{yyz} - \beta_{xxz} + \beta_{yyz}) \\ &+ \langle \sin \theta \cos \theta \sin \psi \rangle (\beta_{xxz} - \beta_{xxz} - \beta_{yyz} + \beta_{yyz}) \\ &+ \langle \sin \theta \cos \theta \cos \psi \rangle (-\beta_{xxz} + \beta_{yyz} - \beta_{yyz} + \beta_{xxz}) \end{aligned} \right\} \quad (A22)$$

$$\chi_{ZZY} = \frac{1}{2} N_s \times \left\{ \begin{aligned} &\langle \cos^2 \theta \rangle (\beta_{xxz} - \beta_{xxz}) \\ &+ \langle \sin^2 \theta \sin^2 \psi \rangle (\beta_{yyz} - \beta_{yyz}) \\ &+ \langle \sin^2 \theta \cos^2 \psi \rangle (\beta_{zzx} - \beta_{zzx}) \\ &+ \langle \sin^2 \theta \sin \psi \cos \psi \rangle (\beta_{xxz} - \beta_{xxz} - \beta_{yyz} + \beta_{yyz}) \\ &+ \langle \sin \theta \cos \theta \sin \psi \rangle (\beta_{xxz} - \beta_{xxz} - \beta_{yyz} + \beta_{yyz}) \\ &+ \langle \sin \theta \cos \theta \cos \psi \rangle (-\beta_{xxz} + \beta_{yyz} - \beta_{yyz} + \beta_{xxz}) \end{aligned} \right\} \quad (A23)$$

These general equations can be simplified in systems of chromophores with symmetry greater than  $C_1$ . An example is given for  $C_{2v}$  to illustrate this process. The  $z'$  axis is defined to be parallel to the change in permanent dipole  $\delta$  between the ground state and the reference excited state, which by symmetry is along the  $C_2$  axis

$$(x', y', z') \xrightarrow{C_2} (-x', -y', z') \quad (A24)$$

$$(x', y', z') \xrightarrow{\sigma(xz)} (x', -y', z') \quad (A25)$$

$$(x', y', z') \xrightarrow{\sigma(yz)} (-x', y', z') \quad (A26)$$

These three symmetry operations applied to the  $x'$ ,  $y'$ , and  $z'$  coordinate axes remove, by setting equal to zero, all elements of the  $\beta^{(2)}$  tensor with an odd number of  $x$  and/or  $y$  indices.

Equations A27–A33 are general equations for  $C_{2v}$  symmetry using only the remaining nonzero elements of the  $\beta^{(2)}$  tensor

$$\chi_{ZZZ} = N_s \times \left\{ \begin{aligned} &\langle \cos^3 \theta \rangle (\beta_{zzz} + \beta_{zzx} + \beta_{zzx}) \\ &+ \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (\beta_{yyz} + \beta_{yyz} + \beta_{yyz}) \\ &+ \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \end{aligned} \right\} \quad (A27)$$

$$\chi_{ZXX} = \frac{1}{2} N_s \times \left\{ \begin{aligned} &\langle \sin^2 \theta \cos \theta \rangle (\beta_{zzz} + \beta_{zzx} + \beta_{zzx}) \\ &- \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (\beta_{yyz} + \beta_{yyz} + \beta_{yyz}) \\ &- \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \end{aligned} \right\} \quad (A28)$$

$$\chi_{XZX} = \frac{1}{2} N_s \times \left\{ \begin{aligned} &\langle \sin^2 \theta \cos \theta \rangle (\beta_{zzz} + \beta_{zzx} + \beta_{zzx}) \\ &- \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (\beta_{yyz} + \beta_{yyz} + \beta_{yyz}) \\ &- \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \end{aligned} \right\} \quad (A29)$$

$$\chi_{XXZ} = \frac{1}{2} N_s \times \left\{ \begin{aligned} &\langle \sin^2 \theta \cos \theta \rangle (\beta_{zzz} + \beta_{zzx} + \beta_{zzx}) \\ &- \langle \sin^2 \theta \cos \theta \sin^2 \psi \rangle (\beta_{yyz} + \beta_{yyz} + \beta_{yyz}) \\ &- \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{xxz} + \beta_{xxz} + \beta_{xxz}) \end{aligned} \right\} \quad (A30)$$

$$\chi_{XYZ} = \frac{1}{2} N_s \{ \langle \sin^2 \theta \sin \psi \cos \psi \rangle \times (\beta_{x'x'z'} - \beta_{y'y'z'} - \beta_{z'x'x'} + \beta_{z'y'y'}) \} \quad (\text{A31})$$

$$\chi_{XZY} = \frac{1}{2} N_s \{ \langle \sin^2 \theta \sin \psi \cos \psi \rangle \times (\beta_{x'x'z'} - \beta_{y'y'z'} - \beta_{z'x'x'} + \beta_{z'y'y'}) \} \quad (\text{A32})$$

$$\chi_{ZXY} = \frac{1}{2} N_s \{ \langle \sin^2 \theta \sin \psi \cos \psi \rangle \times (\beta_{x'x'z'} - \beta_{x'z'x'} - \beta_{y'y'z'} + \beta_{y'z'y'}) \} \quad (\text{A33})$$

Equations A27–A33 simplify further considering only the diagonal contributions of a B<sub>1</sub> excited state with resonance at  $\omega_{\text{sum}}$ . By defining the  $x'$  axis to lie parallel with the transition moment, inspection of eq 16 reveals that the only two remaining nonzero elements of the molecular hyperpolarizability are proportional to each other

$$\beta_{x'x'z'} = \beta_{x'z'x'} \left( \frac{\omega_a}{\omega_b} \right) \quad (\text{A34})$$

The equations for the  $\chi^{(2)}$  tensor elements simplify to

$$\chi_{ZZZ} = N_s \{ \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{x'x'z'} + \beta_{x'z'x'}) \} \quad (\text{A35})$$

$$\chi_{ZXX} = \frac{1}{2} N_s \{ -\langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{x'x'z'} + \beta_{x'z'x'}) \} \quad (\text{A36})$$

$$\chi_{XZX} = \frac{1}{2} N_s \{ \langle \cos \theta \rangle (\beta_{x'x'z'} - \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{x'x'z'} + \beta_{x'z'x'})) \} \quad (\text{A37})$$

$$\chi_{XXZ} = \frac{1}{2} N_s \{ \langle \cos \theta \rangle (\beta_{x'x'z'} - \langle \sin^2 \theta \cos \theta \cos^2 \psi \rangle (\beta_{x'x'z'} + \beta_{x'z'x'})) \} \quad (\text{A38})$$

$$\chi_{XYZ} = \frac{1}{2} N_s \{ \langle \sin^2 \theta \sin \psi \cos \psi \rangle (\beta_{x'x'z'}) \} \quad (\text{A39})$$

$$\chi_{XZY} = \frac{1}{2} N_s \{ \langle \sin^2 \theta \sin \psi \cos \psi \rangle (\beta_{x'x'z'}) \} \quad (\text{A40})$$

$$\chi_{ZXY} = \frac{1}{2} N_s \{ \langle \sin^2 \theta \sin \psi \cos \psi \rangle (\beta_{x'x'z'} - \beta_{x'z'x'}) \} \quad (\text{A41})$$

From eqs A35–A41, the following relations can be generated

$$-2\chi_{ZXX} = \chi_{ZZZ} \quad (\text{A42})$$

$$\chi_{ZZZ} = \frac{-2}{\omega_a - \omega_b} (\omega_a \chi_{XZX} - \omega_b \chi_{XXZ}) \quad (\text{A43})$$

$$\chi_{XYZ} = \chi_{XZY} - \chi_{ZXY} \quad (\text{A44})$$

$$\chi_{XZY} = \chi_{XYZ} \left( \frac{\omega_a}{\omega_b} \right) \quad (\text{A45})$$

The relationships between the  $\chi^{(2)}$  tensor elements compiled in Tables 2–22 were generated by repeating this general procedure for each allowed transition in each character table.

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