

Optimization of the molecular hyperpolarizability for second harmonic generation in chiral media

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Abstract

Molecular properties leading to second harmonic generation in chiral media in the electric dipole approximation for the cases of axial and biaxial symmetry are described. The components of the hyperpolarizability tensor that transform like a second-rank pseudotensor ($L=2$) and a third-rank tensor ($L=3$) contribute. The sum-over-states quantum formula for the hyperpolarizability is used to illuminate the molecular features necessary for optimizing the second-rank pseudotensor for dipolar molecules including orthogonal moments and high frequency. The example of C_{2v} , appropriate for a Λ -shaped molecules, is examined in more detail. Results of the measurements of these components in representative molecules using hyper-Rayleigh scattering are presented. Two compounds in which the delocalized pi-system is two-dimensional, a camphorquinone derivative and crystal violet are found to exhibit sizable $L=2$ and $L=3$ components.

1. Introduction

Second order nonlinear optics requires a noncentrosymmetric material. Consequently, much effort has gone into the development of polar materials that exploit the dipolar (vector) component of the molecular hyperpolarizability based on a push-pull conjugated model.¹ However, it has been recognized for a long time that even isotropic fluids containing chiral molecules can exhibit second order nonlinear optical effects.² Second harmonic generation is not observed in such isotropic chiral media, but it may be observed in chiral materials that are at least uniaxially aligned. Since dipoles minimize their energy when aligned antiparallel, polar macroscopic materials are generally more difficult to align and maintain alignment, whereas the nonpolar but axial alignment required in chiral media do not bear these costs in energy since they are aligned by simple steric means. Because of this and intrinsic interest in chirality in general, there has been a recent increase of activity involving the macroscopic nonlinear optical properties of chiral materials.³ However, in contrast little has appeared discussing the molecular aspects necessary for obtaining a large nonlinear response in chiral media.^{4,5}

In chiral media, both electric and magnetic dipoles may contribute. In fact, several workers have examined magnetic effects in chiral media and found that they can be substantial.^{6,7} In this work, we will limit our analysis to the electric dipole approximation. It is anticipated that *optimized* electric dipole contributions will possess the largest magnitude of chiral nonlinear responses, and we will present results indicating very large relevant responses in crystal violet that suggest that this may be so. In any case, we will limit our discussion here to features of chirality in the electric dipole approximation.

A chiral isotropic fluid (symmetry group $\infty\infty$) does not exhibit second harmonic generation in the electric dipole approximation. However, materials with several non-polar symmetry groups can exhibit second harmonic generation. The symmetry group D_∞ , which consists of a nonpolar axis and no mirror planes, is the easiest to achieve in disordered materials, and the group D_2 , which has three two-fold axes and no mirror planes, is also a candidate. The D_∞ symmetry can be created by a single axial stretch of a polymer containing chiral molecules, and is also characteristic of a nematic, columnar, or smectic A liquid crystal.^{8,9} The D_2 symmetry can be obtained by using a two-axis stretch or shear alignment of a polymer containing chiral molecules. The yet smaller (and polar) group C_2 is characteristic of many tilted columnar, smectic, and other biaxial phase liquid crystal phases. Because the polarity and the polar hyperpolarizability are often small in these C_2 phases, the description of nonpolar chiral nonlinear optical susceptibilities presented here may be most appropriate for optimizing chiral nonlinear responses. Thus, symmetries in which non-polar hyperpolarizabilities will result in nonlinear optical susceptibilities can be easily and robustly fabricated.¹⁰ This analysis can also be applied to surfaces where the surface normal and/or an axis in the surface can define the unique axes.¹¹

In this work, we present initial data and analysis of the molecular hyperpolarizability in order to obtain the largest second harmonic response in macroscopic chiral media in the electric dipole approximation. These are based on a new experimental technique utilizing hyper-Rayleigh scattering and theoretical analysis of a quantum mechanical model. We believe the systematic measurement and analysis of the relevant molecular quantities described here will result in technologically interesting

chiral nonlinear optical materials. As in the case of optimizing polar materials, the molecular aspects that couple to the macroscopic response depend both on the details of the molecular structure and of the macroscopic symmetry group to which the molecule couples.

2. Theoretical considerations

To begin to understand how to optimize the molecular properties that can be exploited in these chiral media, we express the molecular hyperpolarizability in terms of the irreducible representation of the rotation group. The hyperpolarizability is a rank-3 tensor that transforms as the product of three rank-1 vectors. This can be reduced through the formalism of the addition of angular momenta.¹² In the most general case of parametric light scattering, the hyperpolarizability, β_{pls} , transforms as follows:

$$\begin{aligned} \mathbf{b}_{pls} &\sim 1 \otimes 1 \otimes 1 \\ &\sim 0 \oplus (1 \oplus 1 \oplus 1) \oplus (2 \oplus 2) \oplus 3 \end{aligned} \quad (1)$$

Eq. (1) shows that β consists of 1 antisymmetric pseudo-scalar ($L=0$), 1 fully symmetric rank-3 tensor ($L=3$), 3 vectors ($L=1$) and 2 pseudo-tensors ($L=2$). One of the rank-1 objects is fully symmetric, the remaining two of rank-1 and rank-2 components transform as the mixed representation of the permutation group of three objects. In the case of second harmonic generation, the tensor is symmetric in the last two indices because the input fields are identical:¹³

$$\begin{aligned} \mathbf{b}_{SHG} &\sim 1 \otimes (1 \otimes 1)_{sym} \\ &\sim 1 \otimes (0 \oplus 2) \\ &\sim 1 \oplus 1 \oplus 2 \oplus 3 \end{aligned} \quad (2)$$

This operation leaves 2 vectors, 1 rank-2 pseudo-tensor and 1 rank-3 tensor. In the fully symmetric case of Kleinman (full permutation) symmetry¹⁴, the hyperpolarizability consists of just two components:

$$\mathbf{b}_{sym} \sim 1 \oplus 3 \quad (3)$$

These two components correspond the vector term (measured in EFISH) and the octupolar contribution.

The role of Kleinman symmetry is also apparent in the Cartesian representation of the rank-3 symmetric tensor (Eq. (2)) in its irreducible form:

$$\mathbf{b}_{ijk} = \mathbf{b}_{ijk}^{(3s)} + \mathbf{b}_{ijk}^{(2m)} + \mathbf{b}_{ijk}^{(1s)} + \mathbf{b}_{ijk}^{(1m)} \quad (4)$$

Here two vectors and rank-2 pseudo-tensor are embedded into the rank-3 tensor space as follows:

$$\mathbf{b}_{ijk}^{(1s)} = \frac{1}{5} \left[\mathbf{b}_i^{(1s)} \mathbf{d}_j \mathbf{d}_k + \mathbf{b}_j^{(1s)} \mathbf{d}_i \mathbf{d}_k + \mathbf{b}_k^{(1s)} \mathbf{d}_i \mathbf{d}_j \right]$$

$$\mathbf{b}_{ijk}^{(1m)} = \frac{1}{4} \left[2\mathbf{b}_i^{(1m)} \mathbf{d}_j \mathbf{d}_k - \mathbf{b}_j^{(1m)} \mathbf{d}_i \mathbf{d}_k - \mathbf{b}_k^{(1m)} \mathbf{d}_i \mathbf{d}_j \right]$$

$$\mathbf{b}_{ijk}^{(2m)} = \frac{1}{3} \left[2\mathbf{e}_{ijl} \mathbf{b}_l^{(2m)} + \mathbf{b}_{il}^{(2m)} \mathbf{e}_{ljk} \right]$$

Here δ_{ij} is the Kronecker delta, ϵ_{ijk} is the totally anti-symmetric third rank tensor (Levi-Civita tensor) and $\beta^{(Ls)}$ is the rank- L irreducible tensor component of the rank-3 tensor, β . Each component also has a certain permutation symmetry \mathbf{s} (s = symmetric, m = mixed symmetry). It is apparent in Eq. (4) that the $\beta^{(1m)}$ and $\beta^{(2m)}$ terms are forbidden in the Kleinman-allowed regime and, therefore, cannot contribute in the ‘‘one-dimensional’’ case where $i=j=k$.

When the molecular components are averaged consistent with the macroscopic point groups of interest here, the contributing invariants are found, and they are given in Table 1. The active components and the molecular alignment are also given in this table. It is clear that only the $L=2$ and $L=3$ components contribute in the point groups of interest here. *We should emphasize at this point that chirality is not necessary to observe or optimize the $L=2$ or $L=3$ hyperpolarizabilities. Instead, optimized $L=2$ and $L=3$ components along with chirality are necessary to optimize the nonlinear optical response of chiral media possessing D_2 and D_∞ symmetry.* Thus, to optimize the macroscopic response, one must optimize these molecular components as well as orient the molecules in a chiral fashion in the macroscopic medium. Optimization of the $L=3$ component on the molecular level (more widely known as the octupolar component) has already been discussed previously in the literature.¹⁵ We note here that Table 1 indicates that chiral materials represent a new application for octupolar molecules.

The method of optimizing molecular hyperpolarizabilities and the $L=2$ component of interest here, can be understood by considering the quantum mechanical expression for the parts that transform like various irreducible representations of the rotation group, that is like various traceless symmetric tensors. The expression for β in

terms of microscopic parameters of the molecule can be written down as a perturbative solution to the appropriate Schrödinger equation ¹⁶:

$$\mathbf{b}_{ijk}(2\mathbf{w}; \mathbf{w}, \mathbf{w}) = \frac{1}{2\mathbf{h}^2} \sum_{m,n} \left(\frac{\mathbf{m}_{gn}^j (\mathbf{m}_{nm}^j \mathbf{m}_{mg}^k + \mathbf{m}_{nm}^k \mathbf{m}_{mg}^j)}{(\mathbf{w}_{ng} - 2\mathbf{w})(\mathbf{w}_{mg} - \mathbf{w})} + \frac{\mathbf{m}_{nm}^j (\mathbf{m}_{gn}^j \mathbf{m}_{mg}^k + \mathbf{m}_{gn}^k \mathbf{m}_{mg}^j)}{(\mathbf{w}_{ng}^* + \mathbf{w})(\mathbf{w}_{mg} - \mathbf{w})} \right. \\ \left. + \frac{\mathbf{m}_{mg}^j (\mathbf{m}_{gn}^j \mathbf{m}_{nm}^k + \mathbf{m}_{gn}^k \mathbf{m}_{nm}^j)}{(\mathbf{w}_{ng}^* + \mathbf{w})(\mathbf{w}_{mg}^* + 2\mathbf{w})} \right) \quad (5)$$

Eq. (5) is a simplified form for the special case of second harmonic generation and the symmetry with respect to last two indices permutation is intrinsic. The ground state is denoted by g and n and m run over all available quantum states. Dissipation is taken into account by introducing complex-valued transition frequencies

$\mathbf{w}_{ng} \equiv \mathbf{w}_{ng}^0 - i\Gamma_n/2$ with \mathbf{w}_{ng}^0 being a real transition frequency and Γ_n , the dissipation, is inversely proportional to the relaxation time. We can specialize this to the various representations of the rotation group assuming Γ_n is zero, yielding,

$$\mathbf{b}_{ls}^i = \frac{1}{\mathbf{h}^2} \left\{ \sum_{n \neq g} \frac{\mathbf{w}_{ng}^2}{(\mathbf{w}_{ng}^2 - \mathbf{w}^2)(\mathbf{w}_{ng}^2 - 4\mathbf{w}^2)} \left(\Delta \mathbf{m}_{ng}^i |\mathbf{m}_{gn}^{\mathbf{r}}|^2 + 2\mathbf{m}_{gn}^i (\Delta \mathbf{m}_{ng}^{\mathbf{r}} \mathbf{g}_{gn}^{\mathbf{r}}) \right) - \right. \\ \left. - \sum_{m \neq n \neq g} \sum_{n \neq g} \left[\frac{2\mathbf{w}^4 (\mathbf{w}_{mg}^2 - 4\mathbf{w}_{mg} \mathbf{w}_{ng} + \mathbf{w}_{ng}^2) + \mathbf{w}^2 \mathbf{w}_{mg} \mathbf{w}_{ng} (3\mathbf{w}_{mg}^2 - \mathbf{w}_{mg} \mathbf{w}_{ng} + 3\mathbf{w}_{ng}^2) - \mathbf{w}_{mg}^3 \mathbf{w}_{ng}^3}{(\mathbf{w}_{ng}^2 - \mathbf{w}^2)(\mathbf{w}_{ng}^2 - 4\mathbf{w}^2)(\mathbf{w}_{mg}^2 - \mathbf{w}^2)(\mathbf{w}_{mg}^2 - 4\mathbf{w}^2)} \times \right. \right. \\ \left. \left. \times (\mathbf{m}_{nm}^i (\mathbf{m}_{gn}^{\mathbf{r}} \mathbf{g}_{gm}^{\mathbf{r}}) + 2\mathbf{m}_{gn}^i (\mathbf{m}_{nm}^{\mathbf{r}} \mathbf{g}_{gm}^{\mathbf{r}})) \right] \right\} \\ \mathbf{b}_{lm}^i = \frac{2\mathbf{w}^2}{\mathbf{h}^2} \left\{ \sum_{n \neq g} \frac{2}{(\mathbf{w}_{ng}^2 - \mathbf{w}^2)(\mathbf{w}_{ng}^2 - 4\mathbf{w}^2)} \left[\mathbf{m}_{gn}^{\mathbf{r}} \times [\mathbf{m}_{gn}^{\mathbf{r}} \times \Delta \mathbf{m}_{ng}^{\mathbf{r}}] \right]^i + \right. \\ \left. \sum_{m \neq n \neq g} \sum_{n \neq g} \frac{8\mathbf{w}^4 - 2\mathbf{w}^2 (3\mathbf{w}_{mg}^2 + 2\mathbf{w}_{mg} \mathbf{w}_{ng}) - \mathbf{w}_{mg} \mathbf{w}_{ng} (\mathbf{w}_{mg}^2 - \mathbf{w}_{mg} \mathbf{w}_{ng} - 2\mathbf{w}_{ng}^2)}{(\mathbf{w}_{ng}^2 - \mathbf{w}^2)(\mathbf{w}_{ng}^2 - 4\mathbf{w}^2)(\mathbf{w}_{mg}^2 - \mathbf{w}^2)(\mathbf{w}_{mg}^2 - 4\mathbf{w}^2)} \left[\mathbf{m}_{gn}^{\mathbf{r}} \times [\mathbf{m}_{gm}^{\mathbf{r}} \times \mathbf{m}_{nm}^{\mathbf{r}}] \right]^i \right\} \quad (6)$$

$$\begin{aligned}
\mathbf{b}_{2m}^{rk} = & \frac{3w^2}{4\mathbf{h}^2} \left\{ \sum_{n \neq g} \frac{4}{(w_{ng}^2 - w^2)(w_{ng}^2 - 4w^2)} [\mathbf{m}_{gn}^{\mathbf{r}} \times \Delta \mathbf{m}_{ng}^{\mathbf{r}}]^r \mathbf{m}_{gn}^k + \right. \\
& + \sum_{m \neq n \neq g} \sum_{n \neq g} \left[\frac{2(2w^2 - \mathbf{w}_{mg} \mathbf{w}_{ng} - w_{ng}^2)}{(w_{ng}^2 - w^2)(w_{ng}^2 - 4w^2)(w_{mg}^2 - w^2)} [\mathbf{m}_{nm}^{\mathbf{r}} \times \mathbf{m}_{gn}^{\mathbf{r}}]^r \mathbf{m}_{gm}^k - \right. \\
& \left. \left. - \frac{(2w^2 + \mathbf{w}_{mg} \mathbf{w}_{ng})(w_{mg}^2 - w_{ng}^2)}{2(w_{ng}^2 - w^2)(w_{ng}^2 - 4w^2)(w_{mg}^2 - w^2)(w_{mg}^2 - 4w^2)} [\mathbf{m}_{gm}^{\mathbf{r}} \times \mathbf{m}_{gn}^{\mathbf{r}}]^r \mathbf{m}_{nm}^k \right] + \mathbf{r} \leftrightarrow k \right\} \\
\mathbf{b}_{3s}^{ijk} = & \frac{1}{\mathbf{h}^2} \left\{ \sum_{n \neq g} \frac{w_{ng}^2}{(w_{ng}^2 - w^2)(w_{ng}^2 - 4w^2)} \left[\frac{1}{2} \mathbf{P}(\Delta \mathbf{m}_{ng}^j \mathbf{m}_{gn}^i \mathbf{m}_{gn}^k) - \right. \right. \\
& \left. \left. - \frac{1}{5} \left(|\mathbf{m}_{gn}^{\mathbf{r}}|^2 (\Delta \mathbf{m}_{ng}^j \mathbf{d}^{jk} + \Delta \mathbf{m}_{ng}^i \mathbf{d}^{jk} + \Delta \mathbf{m}_{ng}^k \mathbf{d}^{ij}) + 2(\Delta \mathbf{m}_{ng}^{\mathbf{r}} \mathbf{g}_{gn}^{\mathbf{r}}) (\mathbf{m}_{gn}^i \mathbf{d}^{jk} + \mathbf{m}_{gn}^j \mathbf{d}^{ik} + \mathbf{m}_{gn}^k \mathbf{d}^{ij}) \right) \right] - \right. \\
& \left. - \sum_{m \neq n \neq g} \sum_{n \neq g} \frac{2w^4 (w_{mg}^2 - 4\mathbf{w}_{mg} \mathbf{w}_{ng} + w_{ng}^2) + w^2 \mathbf{w}_{mg} \mathbf{w}_{ng} (3w_{mg}^2 - \mathbf{w}_{mg} \mathbf{w}_{ng} + 3w_{ng}^2) - w_{mg}^3 w_{ng}^3}{(w_{ng}^2 - w^2)(w_{ng}^2 - 4w^2)(w_{mg}^2 - w^2)(w_{mg}^2 - 4w^2)} \times \right. \\
& \times \left(\frac{1}{2} \mathbf{P}(\mathbf{m}_{gn}^i \mathbf{m}_{nm}^j \mathbf{m}_{gm}^k) - \frac{1}{5} \left[(\mathbf{m}_{gn}^{\mathbf{r}} \mathbf{g}_{gm}^{\mathbf{r}}) (\mathbf{m}_{nm}^i \mathbf{d}^{jk} + \mathbf{m}_{nm}^j \mathbf{d}^{ik} + \mathbf{m}_{nm}^k \mathbf{d}^{ij}) + \right. \right. \\
& \left. \left. + 2(\mathbf{m}_{nm}^{\mathbf{r}} \mathbf{g}_{gm}^{\mathbf{r}}) (\mathbf{m}_{gn}^i \mathbf{d}^{jk} + \mathbf{m}_{gn}^j \mathbf{d}^{ik} + \mathbf{m}_{gn}^k \mathbf{d}^{ij}) \right] \right) \left. \right\}
\end{aligned}$$

where $\Delta \mathbf{m}_{ng}^{\mathbf{r}} = \mathbf{m}_{nn}^{\mathbf{r}} - \mathbf{m}_{gg}^{\mathbf{r}}$ is the change in the dipole moment and \mathbf{P} is the permutation operator which interchanges the indices i, j, and k.

The first term in each case contains the two-level contributions, which are well-known to give good descriptions of the nonlinear optical response in many quasi-one-dimensional charge transfer molecules.[17] In general, a multilevel model must be applied, and so this general case will be considered first. Of particular interest is the appearance of both dot and cross products in the various terms. For the $1s$ components, the dot product appears throughout, and thus optimum response is obtained if the various moments for important states are parallel. This feature is well-known in optimizing quasi-one-dimensional push-pull molecules for polar nonlinear optics. The $3s$ component involves differences including various dot products and, moreover, there are advantages to having more than one polarization of light relative to the molecule active in the nonlinear optical behavior. Moreover, there are sum rules involving the transition matrix elements in each direction so that β must have components in more than one direction.

Thus both multidimensional and linear molecules can have large and useful 3s hyperpolarizabilities. We see, however, that cross products appear in the two Kleinman disallowed contributions, the $1m$ and $2m$ components. For the $1m$ and $2m$ components, we see that orthogonal moments are always favored.

A second important feature important for optimization of both Kleinman disallowed terms is the frequency dependence. Here we see that these terms tend to zero for small frequencies since they are multiplied by ω^2 . This implies that frequencies comparable to, but not within the absorption bands are needed to have appreciable Kleinman disallowed components. At large frequency, the Kleinman allowed components fall off as $1/\omega^4$ asymptotically while the Kleinman disallowed components fall off as $1/\omega^2$. This implies that the Kleinman disallowed components grow much faster (or decrease less quickly) with increasing frequency than the Kleinman allowed components. Practically, this suggests that the optimum frequency range is the anomalous dispersion regime where the first molecular excited state is intermediate in energy to the fundamental and harmonic frequencies. Of course, the operation of devices in these regimes requires careful consideration of the potential optical loss. An example of a useful device in the regime of anomalous dispersion for femtosecond laser diagnosis has been reported, as well as other potential uses for harmonic conversion.^{18,19}

These principles are well-illustrated by considering the example of a donor-acceptor-donor or acceptor-donor-acceptor Λ -shaped molecule, with donors or acceptors at the apex and acceptors or donors (respectively) at the feet. These compounds have been the subject of several recent studies.^{20,21,22} Although these molecules are not inherently chiral, a recent study by Van Elshocht et al. has indicated how such a molecule can be incorporated into a chiral medium, a helical binaphthyl polymer, in this case.²³ They measured a substantial electric dipole chiral component to the optical nonlinear susceptibility. In the example we now consider, the molecular symmetry is a planar C_{2v} . It is well-known that a two-level model reasonably approximates the nonlinear optical response of linear C_{2v} compounds such as p-nitroaniline. It has been shown that, in general, a two-level model cannot describe a multidimensional molecule and certainly not a nonpolar molecule,^{15,22} we find that, in the case of a multidimensional compound with polar C_{2v} symmetry, a two-level model is illustrative of the optimization of the Kleinman

disallowed components. In this symmetry, the tensor components in various representations are given in terms of the Cartesian components by,

$$\begin{aligned}
1s \quad \mathbf{b}_z &= \mathbf{b}_{zzz} + \frac{1}{3}(\mathbf{b}_{zxx} + \mathbf{b}_{xzx} + \mathbf{b}_{xxz}) \\
1m \quad \mathbf{b}_z &= \frac{1}{3}(2\mathbf{b}_{zxx} - \mathbf{b}_{xzx} - \mathbf{b}_{xxz}) \\
2m \quad \mathbf{b}_{yx} &= \frac{1}{2}(\mathbf{b}_{zxx} - \mathbf{b}_{xzx}) \\
3s \quad \mathbf{b}_{zzz} &= \frac{2}{5}\mathbf{b}_{zzz} - \frac{1}{5}(\mathbf{b}_{zxx} + \mathbf{b}_{xxz}) \\
\mathbf{b}_{zxx} &= \mathbf{b}_{xzx} = \mathbf{b}_{xxz} = \frac{4}{15}\mathbf{b}_{zxx} + \frac{8}{15}\mathbf{b}_{xzx} - \frac{1}{5}\mathbf{b}_{zzz}
\end{aligned} \tag{7}$$

It has been established that a minimum of three levels are necessary to describe certain Kleinman allowed components.^{15,22} In C_{2v} symmetry, the excited states must transform either like A states, which are unchanged when the system is rotated by 180° around the 2-fold axis or like B states, which change sign under this rotation. The transition moment must either be parallel (A states) or perpendicular (B states) to the charge transfer axis and the dipole must be along this axis. Thus, in general, the quantum two-level expression corresponding to the ground and a single excited state can result either in non-zero diagonal (\mathbf{b}_{zzz}) or off diagonal (\mathbf{b}_{zxx}) components, but not both. In a linear C_{2v} molecule, only the A state contributes in this Kleinman symmetric case, whereas both the A and B states have been found to contribute in a Λ -shaped molecule.²² Since, in a Λ -shaped molecule, both diagonal and off-diagonal components are measured and observed in the Kleinman allowed invariants, a single pair of states cannot completely describe the nonlinear susceptibility.

However, as Eqs. (6) and (7) indicate, only B excited states with their transition moments orthogonal to the charge transfer axis can contribute to the first (two-level like) term in the $1m$ and $2m$ components, yielding off-diagonal components (zxx, xxz).²⁰ There are also contributions from the intrinsically three-state terms β , but only when one of n and m has a transition moment perpendicular to the charge transfer axis (B state) and the other has a transition moment parallel thereto (A state). However, these terms have

complicated, frequency dependent cancellations. Thus, this situation seems quite analogous to the more usual case of a rod like molecule and it seems reasonable to suppose that, as in that case, the two-level model will aptly describe the essential physics for the Kleinman disallowed component. This two-level model yields for the Kleinman disallowed terms,

$$\begin{aligned}
\mathbf{b}_i^{(1m)} &= \frac{1}{3} (2\mathbf{b}_{ijk} \mathbf{d}_{jk} - \mathbf{b}_{jik} \mathbf{d}_{jk} - \mathbf{b}_{jki} \mathbf{d}_{jk}) = \\
&= 4 \left(\mathbf{w} / \mathbf{w}_{ng}^0 \right)^2 \mathbf{F}(\mathbf{w}, \mathbf{w}_{ng}^0) \left[\mathbf{m}_{gn}^i (\Delta \mathbf{m} \cdot \mathbf{m}_{gn}) - \Delta \mathbf{m}^i (\mathbf{m}_{gn} \cdot \mathbf{m}_{gn}) \right] \\
\mathbf{b}_{ij}^{(2m)} &= \frac{1}{2} (\mathbf{e}_{ikl} \mathbf{b}_{klj} + \mathbf{e}_{jkl} \mathbf{b}_{kli}) = \\
&= 3 \left(\mathbf{w} / \mathbf{w}_{ng}^0 \right)^2 \mathbf{F}(\mathbf{w}, \mathbf{w}_{ng}^0) \left[\mathbf{m}_{gn}^i (\mathbf{m}_{gn} \times \Delta \mathbf{m})^j + (\mathbf{m}_{gn} \times \Delta \mathbf{m})^i \mathbf{m}_{gn}^j \right]
\end{aligned} \tag{8}$$

The figures of merit associated with these representations of the rotation group can be derived from the Eqs. (8):²⁴

$$\begin{aligned}
b_{1mm}^2 &= \frac{1}{\sqrt{3}} \sum_{ijk} \left| \mathbf{b}_{ijk}^{(1m)} \right|^2 = \frac{\sqrt{3}}{4} \sum_i \left| \mathbf{b}_i^{(1m)} \right|^2 = \frac{12}{\sqrt{3}} \mathbf{F}^2(\mathbf{w}, \mathbf{w}_{ng}^0) \left(\mathbf{w} / \mathbf{w}_{ng}^0 \right)^4 \mathbf{m}_{gn}^2 \left[(\Delta \mathbf{m})^2 \mathbf{m}_{gn}^2 - (\Delta \mathbf{m} \cdot \mathbf{m}_{gn})^2 \right] = \\
&= \frac{12}{\sqrt{3}} \mathbf{F}^2(\mathbf{w}, \mathbf{w}_{ng}^0) \left(\mathbf{w} / \mathbf{w}_{ng}^0 \right)^4 \mathbf{m}_{gn}^4 (\Delta \mathbf{m})^2 (\sin^2 \mathbf{q})
\end{aligned} \tag{9}$$

$$\begin{aligned}
b_{2mm}^2 &= \frac{1}{\sqrt{5}} \sum_{ijk} \left| \mathbf{b}_{ijk}^{(2m)} \right|^2 = \frac{2}{3\sqrt{5}} \sum_{ij} \left| \mathbf{b}_{ij}^{(2m)} \right|^2 = \frac{12}{\sqrt{5}} \mathbf{F}^2(\mathbf{w}, \mathbf{w}_{ng}^0) \left(\mathbf{w} / \mathbf{w}_{ng}^0 \right)^4 \mathbf{m}_{gn}^2 (\mathbf{m}_{gn} \times \Delta \mathbf{m})^2 = \\
&= \frac{12}{\sqrt{5}} \mathbf{F}^2(\mathbf{w}, \mathbf{w}_{ng}^0) \left(\mathbf{w} / \mathbf{w}_{ng}^0 \right)^4 \mathbf{m}_{gn}^4 (\Delta \mathbf{m})^2 \sin^2 \mathbf{q}
\end{aligned}$$

where

$$\sin \mathbf{q} = \frac{|\mathbf{m}_{gn} \times \Delta \mathbf{m}|}{|\mathbf{m}_{gn}| |\Delta \mathbf{m}|}.$$

Eqs. (9) show that in the simplest case of a two-level system, the figures of merit of the irreducible parts can be expressed in terms of \mathbf{q} , the angle between the transition dipole moment \mathbf{m}_{gn} and difference between the excited and ground state dipole moments $\Delta \mathbf{m}$.

The model suggests that $\mathbf{q} = 90^\circ$ maximizes the $2m$ component. This is a requirement of

C_{2v} (or C_2) symmetry, provided the transition moment of the first excited state is not parallel to the charge transfer axis. Thus Λ -shaped molecules may represent an optimum approach and Van Elshocht et al.'s approach may prove fruitful. It is not clear yet that the particular arrangement of Λ -shaped molecules in their polymer will yield the optimum macroscopic response. These issues are the subject of our current research.

We note that the appearance of $\sin\mathbf{q}$ confirms the idea that motion of the electrons in two or more dimensions is required for Kleinman disallowed hyperpolarizabilities.^{20,25} Figure 1 presents plots of the two-level model for the \mathbf{b}_{2mm}^2 and \mathbf{b}_{1ss}^2 as a function of ω in this example of C_{2v} symmetry for the contribution of the B state only. Damping was neglected since it was to affect these plots only very near resonance. For the $1ss$ component, the A state contributes a similar amount (a factor of 3 more in one example²²), while, as mentioned earlier the A state does not contribute to the $2mm$ component. It is clear that the $2mm$ component is relatively large in the anomalous dispersion regime. Thus, the example of C_{2v} symmetric Λ -shaped molecules illustrates considerations that should hold in more general cases as described above.

We now describe measurements illustrating these principles. In particular, we present results on a chiral Λ -shaped molecule, Q-BNH, and also find an exceptionally large $2m$ component in CV, which we show may also exhibit this symmetry. However, we wish to emphasize that systems, such as nonpolar ones, though not necessarily conforming to a two-level model would require the important features of orthogonal moments, and high frequency in order to optimize the $2m$ component.

3. Experimental results

We have developed an experimental technique to characterize all of the figures of merit for the rotational invariants (Eqs. 4) of the hyperpolarizability tensor using hyper-Rayleigh scattering. We have also used this technique to test some of the molecular design concepts described here as well as to evaluate the efficacy of some chiral and non-chiral chromophores. This technique utilizes the polarization analysis of elliptically polarized fundamental and harmonic light scattered at an oblique angle in order to deduce the complete set of rotational invariants. Spectral analysis and filtering of the scattered light insured that the signal measured was a hyper-Rayleigh signal and not multiphoton

absorption and emission. A complete description of the experiment is discussed elsewhere.^{24,26}

The structures of the compounds we have studied are given in Figure 2. The results of measurements of the four figures of merit for the invariants defined in Eq. (9) are given in Table 2. Magnitudes are normalized to the Is component of p -nitroaniline determined by electric field induced second harmonic generation.²⁴ The compound p -nitroaniline (p NA, **1**) is a simple and well-known π -conjugated molecule whose geometry is fixed linear so that the vector contribution dominates as expected from its one-dimensional nature. As such, it exhibits near Kleinman symmetry with relatively small $\mathbf{b}^{(1m)}$ and $\mathbf{b}^{(2m)}$ components. A low level of Kleinman symmetry breaking in p -NA is predicted by quantum chemical calculations reported by Lalama and Garito.²⁷ We have indicated elsewhere that the deduced depolarization ratio and the ratio of the Kleinman allowed components are consistent with previous findings, confirming the accuracy of these measurements.²⁴ However, the Im component seems larger than it should be, but this may be due to a small systematic error since the error bars indicate that the results are near the limits of signal to noise.

Compound **2** is a camphorquinone derivative that was chosen as a basic chiral species in our studies. The chirality in this molecule creates an environment for multidimensional charge transfer near the donor that results in a modest increase in the Kleinman disallowed ($\mathbf{b}^{(1m)}$ and $\mathbf{b}^{(2m)}$) components, and in particular, a $\mathbf{b}^{(2m)}$ component appears. This multidimensional charge transfer was confirmed by the observation of large optical rotation and by quantum chemical calculations.²⁶ The compounds **3**, **4**, and **5** were synthesized to investigate the influence of enhanced dipolar response due to increased acceptor strength and conjugation length. The absorptions of these latter three compounds are shifted toward the red and the Kleinman symmetric components ($\mathbf{b}^{(1s)}$, $\mathbf{b}^{(3s)}$) increase as expected, but the effect on the $\mathbf{b}^{(2m)}$ component is unremarkable. Thus, we see that the multidimensional character required by Eq. 4 for the $\mathbf{b}^{(2m)}$ component is not enhanced by these substitutions probably because they do not affect the region of the molecule where the multidimensional character resides. Note that

the two conformations **3** and **4** have different out-of-plane geometry²⁸ that leads to different contributions of the various components.

The Q-BNH **6** molecule is a dimer counterpart of the basic chiral material **2**. This chromophore includes two chiral camphorquinones and a Λ -shaped acceptor-donor-acceptor structure. There had been indication of Kleinman symmetry breaking in brilliant green, a somewhat similar donor-acceptor-donor Λ -shaped molecule.²⁰ We observe a 50% enhancement of the $\mathbf{b}^{(2m)}$ component in this case over the monomer value. While the Λ shape suggests a 90° angle \mathbf{q} in the quantum model, quantum chemical calculations are necessary to verify how this compound fits with the model. Note that $|\mathbf{b}_{2mm}|$ is about two times as large as the vector part $|\mathbf{b}_{1ss}|$ of pNA. Thus, one can expect that chiral materials can possess macroscopic susceptibilities comparable to efficient dipolar materials. These measurements were not performed in the anomalous dispersion regime, so that we can expect larger $2m$ components when measured in that case.

The compound **7** is another candidate for the $\mathbf{b}^{(2m)}$ nonlinearity. This molecule has more rigid structure than those previously discussed due to its polycyclic steroid-derived ring system. The measurements showed a nonzero $\mathbf{b}^{(2m)}$ component of the hyperpolarizability for this molecule comparable to the camphorquinone monomer. The π -electron system in this case has only a small bend between the donor and the acceptor, so that the angle between the difference in dipole moments and transition matrix element is expected to be rather small. This further illustrates the multidimensional nature required for the $\mathbf{b}^{(2m)}$ component.

Finally, measurements of crystal violet (CV) **8** reveal large Kleinman-disallowed hyperpolarizability components – the two vector components, $\mathbf{b}^{(2m)}$ and $\mathbf{b}^{(3s)}$ components are of the same order of magnitude. All the hyperpolarizability figures of merit for CV are more than an order of magnitude larger than those of pNA in these nearly resonant conditions (but with little multiphoton fluorescence). Such a huge $\mathbf{b}^{(2m)}$ component part makes it reasonable to expect that CV could be effectively used in systems with macroscopic nonlinearity activated by means of axial alignment. Crystal violet probably does possess chiral propeller-like conformations. However, the

enantiomers cannot be stabilized to form chiral macroscopic media, so that stable chiral forms or macroscopic structures must be developed before it would be useful for chiral nonlinear optics.

The shape of the CV molecule, and specifically the electronic delocalization in two dimensions suggests that it may meet the quantum criteria for large $L=2$ components. Unfortunately, understanding these results in detail is made difficult by the fact that the symmetry / ground state structure of CV is not well understood. The “naïve” expected symmetry for CV would be D_3 , which would be consistent with $L=2$ and $L=3$ but not $L=1$ (vector) components, although this symmetry (with a degenerate excited state) would require treatment at least within a three-level model. However, we note that our measurements have detected a dipolar contribution, indicating a different ground state symmetry which could be the sub-groups C_3 , C_2 , or C_1 or even C_{2v} .²⁴ This, along with other details of this measurement is discussed in detail elsewhere; however we note that the deduced depolarization ratios are in agreement with previous work.²⁴ It should also be noted that in this case there is an excitation energy (or possibly two) of the molecule in the anomalous dispersion regime *between* the energy of the fundamental and the second harmonic light. The quantum model suggests that this will result in large Kleinman disallowed (e.g. $L=2$) hyperpolarizabilities. Measurements of the dispersion of the CV hyperpolarizability are in progress so that less resonant values will be reported later.

4. Discussion and conclusions

We have begun the development of a regime for the optimization of second-order nonlinear optical response in non-polar or weakly polar chiral media at the molecular level. By relating the rotational invariants and their figures of merit to the point group of the macroscopic media, we find that the $\mathbf{b}^{(2m)}$ and $\mathbf{b}^{(3s)}$ invariant figures of merit will contribute in the point groups of interest. We have analyzed theoretically how to optimize the $\mathbf{b}^{(2m)}$ figure of merit in the quantum expression. We found that both orthogonal matrix elements and operation in the anomalous dispersion regime optimize the $\mathbf{b}^{(2m)}$ hyperpolarizability component. We argued that the two level model is likely to apply well to Kleinman disallowed components for molecules with C_{2v} symmetry. We

have measured a series of compounds illustrating these findings and our measurements and analysis suggest some promising approaches. However, measurements at frequencies both in and out of the anomalous dispersion regime are in progress which will provide a more rigorous test of the theoretical design considerations for the $2m$ component discussed here.

We find that three dimensional, chiral delocalization of the electrons seems *not* to be important to optimizing these hyperpolarizabilities. However, molecules in which the electrons are delocalized in two spatial dimensions, and move appreciably in two different dimensions on being excited from the ground to the first excited state, to degenerate or nearly degenerate excited states seem to have appreciable Kleinman disallowed hyperpolarizability components. Specifically molecules with a Λ -like shape with a donor (or acceptor) at the apex and acceptors (or donors) on the legs are good candidates. Molecules like crystal violet, with a central acceptor (or donor), and two or more “legs” with donors (or acceptors) may be a useful generalization of such molecules. In both these types of molecules there should be important low-lying excited states for which the dipole transition matrix element is close to perpendicular to the charge transfer axis. These molecules, if incorporated into chiral media and appropriately axially aligned, should lead to sizable nonlinear optical coefficients.

Since operation in the anomalous dispersion regime is likely to be useful in increasing the Kleinman disallowed components, a “brilliant” dye is preferred as it must not appreciably absorb *either* the fundamental or the second harmonic light. However, we note that the Kleinman allowed octupolar component contributes in the case of a D_2 chiral material which allows operation at a wider range of wavelengths and suggests a new application for such octupolar chromophores.

Recent results on a binaphthyl helical polymer incorporating non-chiral Λ -shaped chromophores support some of our key conclusions. First, the large chiral nonlinearity they measured was electric dipole in nature, and second that these nonchiral Λ -shaped nonchiral chromophores can be arranged into an efficient chiral media. We anticipate that large $2m$ components in the molecular components contribute to these results. Since $2m$ and $3s$ component contribute to D_∞ , optimized $3s$ components might be most useful

for operation away from the anomalous dispersion regime, while D_2 requires Kleinman disallowed response optimized in the anomalous dispersion regime.

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²⁸ X-ray crystal structures were determined by Dr. C. Barnes at University of Missouri-Columbia.

Table 1. Hyperpolarizability contributions to the chiral point groups of interest in this study. Properties of the macroscopic susceptibility tensor and molecular ordering are also given. The rotation axes and their nature are indicated.

Table 2. Figures of merit of the four irreducible components of β tensor (esu).

	Symmetry group	Non-vanishing components	Invariant parts	Molecular alignment
Chiral liquid	$\infty\infty$	All vanish	$L=1$ $L=2$ $L=3$	
Uniaxial alignment	$D_\infty (\infty 2)$	$\mathbf{c}_{xyz}^{(2)} = \mathbf{c}_{xzy}^{(2)}$ $= -\mathbf{c}_{yxz}^{(2)}$ $= -\mathbf{c}_{yzx}^{(2)} \neq 0$	$L=1$ $L=2$ $L=3$	
Biaxial alignment	$D_2 (222)$	$\mathbf{c}_{xyz}^{(2)} = \mathbf{c}_{xzy}^{(2)} \neq 0$ $\mathbf{c}_{yxz}^{(2)} = \mathbf{c}_{yzx}^{(2)} \neq 0$ $\mathbf{c}_{zxy}^{(2)} = \mathbf{c}_{zyx}^{(2)} \neq 0$	$L=1$ $L=2$ $L=3$	

Material (Wavelength)	$\ \beta_{1ss}\ ,$ $\times 10^{-30}$ esu	$\ \beta_{1mm}\ ,$ $\times 10^{-30}$ esu	$\ \beta_{2mm}\ ,$ $\times 10^{-30}$ esu	$\ \beta_{3ss}\ ,$ $\times 10^{-30}$ esu
1064nm				
1 - pNA	11.2 ±1.6	4.6 ±1.2	2.1 ±2.6	8.2 ±1.2
2	33.2 ±4.8	15.5 ±2.6	10.8 ±2.9	23.9 ±3.5
5	110 ±16	26.8 ±6.0	15.7 ±7.6	70 ±10
6 - Q-BNH	38.3 ±5.9	14.7 ±5.7	16.9 ±3.3	26.3 ±4.3
7	33.6 ±4.7	12.1 ±2.2	9.6 ±1.6	23.9 ±3.4
8 - CV	305 ±58	341 ±72	276 ±52	398 ±81
1340nm				
pNA	8.1 ±1.5	3.4 ±0.8	0.0 ±1.9	5.9 ±1.1
3	44.9 ±7.7	10.2 ±1.9	14.7 ±4.8	30.9 ±5.3
4	78 ±13	25.7 ±4.7	0.0 ±1.0	49.1 ±8.4

Figure 1. Plots of the b_{2mm} and b_{1ss} for the B state two-level model in C_{2v} symmetric molecules as a function of frequency near the anomalous dispersion regime. (Damping is neglected.)

Figure 2. Molecular structures of the studied molecules. Wavelength of the excited state absorption peak is given in parentheses.



