

Second Harmonic Generation in Non-Polar Chiral Materials: Relationship Between Molecular and Macroscopic Properties

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An oriented gas model for the second order nonlinear optical response for optical second harmonic generation in axially aligned nonlinear optical chromophores in chiral media is presented. Design criteria for the alignment of chromophores possessing Kleinman disallowed traceless symmetric second rank tensor hyperpolarizabilities β resulting in large nonlinear optical susceptibilities $\chi^{(2)}$ are enumerated. These chromophores could be oriented in high density, highly ordered structures due to the absence of dipolar interactions resulting in exceptionally large $\chi^{(2)}$ values. The alignment of chromophores that have C_{2v} or D_n ($n > 2$) symmetry in two chiral non-polar symmetry groups for the medium, D_∞ and D_2 are considered. Criteria for response optimization, and several physical examples are described. Additionally, certain non-polar symmetry groups for the medium, of which the most easily realizable is probably D_2 , also admit Kleinman allowed octupolar susceptibilities for which the optimum chromophore alignment is discussed.

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1 Introduction

Materials for second order nonlinear applications such as second harmonic generation and the linear electro-optic switching must satisfy certain requirements imposed by symmetry, such as the absence of an inversion center. It has been known and recognized that the absence of mirror planes is sufficient for the second-order nonlinear optical susceptibility $\chi^{(2)}$ (for sum and difference frequency generation) to have nonzero value [1]. Moreover, in media without full rotation symmetry, the lack of mirror planes will often increase the number of allowed components of $\chi^{(2)}$. In chiral media, in which the molecular structure does not allow for any mirror symmetries, appropriate conditions for the second order nonlinear optical response, including second harmonic generation and the electro-optic effect, can be easily created by alignment of the chromophores. A chiral, uniaxial non-polar alignment is consistent with non-zero second harmonic generation and electro-optic effects. The main advantage of non-polar alignment over polar ones is that polar order is often accompanied by an increase in free energy due to the dipole-dipole interaction energy between individual chromophore molecules. In consequence, it is difficult to produce robust, high density and highly aligned materials that fully exploit the large hyperpolarizabilities that are often accompanied by a large dipole moment.

The $\chi^{(2)}$ of polar materials is traceable to the part of β that transforms like a vector (first-rank tensor). This component must average to zero in the absence of polar order. Generally, the second harmonic hyperpolarizability tensor can be decomposed into four components, two of which transform under three-dimensional rotations as traceless

symmetric second- and third-rank tensors. These components of higher rank are responsible for the macroscopic second-order nonlinear properties of materials with non-polar order. Since, alignment of the third rank (octupolar) tensor in non-chiral media for high symmetry two-dimensional chromophores has been discussed by others (e.g. [2]), we will mainly focus on the second rank tensor contribution. The second order tensor is most relevant to chiral media, but alignment of certain components of the octupolar tensor can also be achieved in chiral media suggesting new methods for exploiting these hyperpolarizabilities in bulk materials.

Hyperpolarizabilities that contribute to the nonlinear optical response in chiral media are not Kleinman symmetric, that is, are not invariant under the interchange of all indices. We have shown that these hyperpolarizability components, in particular, those that contribute to second harmonic generation and the Pockels effect can be quite large, and, in fact, are generally as large as the components well known in polar media. [3] This suggests that these Kleinman nonsymmetric components may be exploited in high density, highly aligned materials to produce materials with exceptionally large $\chi^{(2)}$.

Our recent study suggested a scheme to optimize the molecular properties of multidimensional NLO chromophores for use in chiral nonlinear materials, which involves molecular engineering, sum-over-states quantum-mechanical calculation and measurements of the rotational invariants of β by means of Kleinman-disallowed hyper-Rayleigh scattering (KD-HRS) [3]. It is evident that molecules that have Kleinman-disallowed hyperpolarizabilities must have electrons that move in at least two dimensions since one-dimensional molecules are necessarily Kleinman symmetric. From the

quantum-mechanical standpoint, molecules appropriate for the alignment discussed here should have a low-lying excited electronic state with a transition dipole moment perpendicular or close to perpendicular to the change in the molecular dipole. This is realized naturally if the molecule has a two-fold rotation axis. The electric dipole moment is constrained to be along this axis and, if the excited state symmetry belongs to the B -type irreducible representation, the transition dipole matrix element is then constrained to be perpendicular to this dipole moment. This predicts a sizable contribution of the second-rank irreducible component of the molecular hyperpolarizability \mathbf{b} . In the "anomalous dispersion" regime, in which the fundamental light has an energy less than that of the excited state but the second harmonic light has an energy in excess of the excited state energy the Kleinman disallowed hyperpolarizability may even exceed the Kleinman allowed hyperpolarizability.

The weight of different irreducible components can be measured by means of KD-HRS [4, 5]. At present, promising candidate molecules include Λ -shaped π -conjugated chromophores that consist of two electron donors (or acceptors) at the ends connected to one acceptor (or donor) at the Λ 's vertex. Λ -shaped molecules generically have C_{2v} or C_2 symmetry that allow existence of states belonging to a B -type irreducible representation, and some such molecules have shown strong non-vector components of the hyperpolarizability tensor that indicated the presence of such B -type states.[6] We also found that Crystal Violet, which may have a symmetry similar to D_3 , possesses a large figure of merit for axially aligned chiral nonlinear optical materials.

As is well known, chromophores with vector hyperpolarizabilities need to be aligned with a nonvanishing dipole in order to result in non-zero $\chi^{(2)}$. In this paper we

consider the geometrical arrangement or alignment required for chromophores with second rank tensor hyperpolarizabilities and discuss how to create highly efficient chiral axial, but non-polar structures for NLO on the basis of Kleinman non-symmetric chromophores. Given a chromophore that has a Kleinman-disallowed irreducible component of hyperpolarizability, we will develop the criteria for axial alignment that efficiently utilizes the molecular nonlinearity, while avoiding polar ordering. We also consider the non-polar D_2 alignment of octupolar molecules.

There are a very limited number of molecule symmetries that are consistent with traceless symmetric second rank pseudo tensors and hence a very limited number of cases that need to be considered for alignment of Kleinman disallowed chromophores. The allowed chromophore symmetries are D_n , D_{2d} , C_{2v} , C_2 , C_s , and C_1 . We will discuss the chromophore symmetries D_n ($n > 2$) and C_{2v} in detail below. We will also comment briefly on C_2 , C_s and C_1 . We know of no chromophores of interest with D_2 or D_{2d} symmetry and so do not discuss this possibility further below. Similarly we will discuss only D_{∞} and D_2 symmetries of the medium, as we believe that these are easiest to realize experimentally. Another possible symmetry of the medium, C_2 , that of the chiral smectic C liquid crystal, is also reasonably easy to realize. The analysis of this situation, while similar, is complicated and less clear, and will not be discussed. In any case, most Smectic C's, from the point of view of tensor order parameters, are close to uniaxial, and are also polar. Hence, this is a special case and will not be discussed here.

In previous publications, we presented the decomposition of the hyper-Rayleigh scattering tensor into its rotational invariants in order to provide a scheme for measuring all of the figures of merit associated with the invariant tensors using incoherent second

harmonic generation. Thus, we studied the properties of the $\langle \mathbf{b}^2 \rangle$ tensor. Here, we analyze coherent second harmonic generation in terms of this formalism in order to provide the connection between the molecular and bulk response. This is aimed at producing a prescription for optimizing the nonlinear optical response of nonpolar organic media. This paper is organized as follows. In section 2, we present detailed symmetry criteria. In section 3, we will discuss, using examples of chiral NLO chromophores and polymers described in the literature, how the schemes of optimal alignment defined in section 2 can be applied to real-world systems. We will also propose alternative methods to align Λ -shaped chromophores in chiral fashion.

2 Symmetry considerations

The second harmonic generation hyperpolarizability is a third-rank tensor symmetric under permutation of the last two indices. Group theory provides a mechanism for decomposing it into a sum of four irreducible parts whose components do not mix under three-dimensional rotation due to their different rotational or permutation symmetry. In Cartesian coordinates, the decomposition can be written as follows:

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

Two components ($1s$ and $1m$) transform as vectors, $2m$ – as a second-rank traceless symmetric pseudo-tensor, and $3s$ – as a third-rank traceless symmetric tensor. The irreducible tensor components are obtained by contracting the hyperpolarizability tensor with the appropriate Kronecker delta and Levi-Civita tensors. The terms in Eq. (1) are properly embedded in third-rank tensors. The rotationally invariant tensor forms (unembedded) will be denoted below with a tilde. The decomposition into irreducible

parts facilitates the analysis of $\chi^{(2)}$ as the latter is defined through rotational averages of \mathbf{b} . The tensor parts in Eq. (1) belong to different irreducible representation of the permutation group of three objects and thus have different permutation symmetry. After being rotationally averaged they will compose corresponding components of the macroscopic tensor $\chi^{(2)}$ with the same permutation symmetry that can be classified in a similar fashion to Eq. (1), thus

$$\begin{aligned} \mathbf{c}_{IJK} &\propto \langle \mathbf{b}_{ijk} \rangle_{IJK} = \langle \mathbf{b}_{ijk}^{(3s)} \rangle_{IJK} + \langle \mathbf{b}_{ijk}^{(2m)} \rangle_{IJK} + \langle \mathbf{b}_{ijk}^{(1m)} \rangle_{IJK} + \langle \mathbf{b}_{ijk}^{(1s)} \rangle_{IJK} . \\ &\propto \mathbf{c}_{IJK}^{(3s)} + \mathbf{c}_{IJK}^{(2m)} + \mathbf{c}_{IJK}^{(1m)} + \mathbf{c}_{IJK}^{(1s)} \end{aligned} \quad (2)$$

Here, each irreducible component of the bulk nonlinear susceptibility $\chi^{(2)}$ results from components of the hyperpolarizability tensor \mathbf{b} having the same symmetry and not the others. Consequently, it is possible to define optimization conditions for each part of $\chi^{(2)}$ separately without knowing the precise form of the orientational distribution function. The knowledge of the symmetry group of the chromophore *and* the medium can predict that some of the four parts in Eq. (2) must vanish identically. For example, if the symmetry of the aligned medium is such that $\chi^{(2)}$ automatically satisfies Kleinman (full permutation) symmetry, the Kleinman non-symmetric parts $2m$ and $1m$ in Eq. (2) must vanish due to alignment, even if the corresponding molecular hyperpolarizabilities are not zero. Since the goal of this study is to achieve optimization of the NLO response through nonpolar alignment, the main focus of this discussion will be the non-vector irreducible components of $\chi^{(2)}$. We will consider two important cases of chiral axial systems –

uniaxially aligned media with D_∞ symmetry, and a biaxial system with D_2 symmetry. These two types of alignment are chosen because they represent a wide range of physical systems that can be easily fabricated. The first type of alignment can be realized in stretched polymers or in uniaxial liquid crystal phases (e.g. nematic, columnar, or smectic A). The second alignment scheme occurs in more ordered systems like biaxial liquid crystal phases (e.g. smectic C) or liquid-crystalline polymers where two distinct directions are defined by polymer's backbone and liquid-crystalline side-chain moieties. Clearly, due to the chirality of both symmetry groups, certain measures should be taken to assure the absence of the mirror plane symmetry in the bulk. Chirality of the bulk does not require chiral chromophores, and can be achieved by aligning achiral chromophores in a chiral fashion, as will be demonstrated below.

In general, there can be a macroscopic susceptibility arising from the $2m$ terms only if (a) the chromophores have a symmetry such that there is at least one traceless symmetric second rank pseudo-tensor which does not change under all the allowed symmetry elements and (b) if the same is true of the macroscopic medium. In more technical group-theoretical terms the representation of the traceless symmetric second rank pseudotensor must contain the trivial representation at least once in the symmetry groups of both the chromophore and the medium. It is easy to see (either systematically or by trial and error) that there are only a small number of cases. If the group is D_n with $n > 2$ there is only one traceless symmetric second rank pseudotensor, $t_{zz} = -2t_{xx} = -2t_{yy}$, where z is the n -fold axis. If the group is C_{2v} , then there is again only one such allowed tensor t_{xy} where x and y are the normals to the mirror planes. If the group is C_2 then there are three such tensors, which can be thought of as both of the above together with

$t_{xx} = -t_{yy}$. Alternatively only $t_{zz} = -2t_{xx} = -2t_{yy}$ and t_{xy} need be included except that the direction of x and y cannot be determined *a priori* and must be guessed, measured or calculated from the chromophore structure. However, x and y are both perpendicular both to each other and the molecular dipole. In approximately planar π -conjugated chromophores with well-separated excited states, when the energy of the second harmonic light is not too close to the energy of any state except the lowest lying excited state, x is (approximately) parallel to the transition dipole matrix element of the lowest lying excited state. This situation is similar to that of ordinary vector hyperpolarizabilities: the vector hyperpolarizability in non-symmetric molecules such as disperse red one or dialkylaminonitrostyrene (DANS) are routinely hypothesized to be parallel to the molecular dipoles. Similarly in the approximately planar π -conjugated Λ -shaped molecules which are (as a group) relatively easy to synthesize and which have been shown to have large $2m$ components and generally have C_2 symmetry and *approximate* C_{2v} symmetry we expect that the large $2m$ component is the t_{xy} component, with x the normal to the molecular plane.

2.1 Uniaxial alignment of L-chromophores – C_{2v} chromophore and $D_{\infty h}$ symmetry of the medium

In the uniaxial alignment scheme D_{∞} , the nonlinear susceptibility is fully defined by one value. In Cartesian coordinates (with z being the unique axis) this is $\tilde{c}(D_{\infty}) = c_{xyz} = c_{xzy} = -c_{yxz} = -c_{yzx}$, while all the other components vanish. The analysis of the irreducible content of the susceptibility tensor $\chi^{(2)}$ shows that there is only the second-rank component that is non-zero in the decomposition (2):

$$\tilde{\mathbf{c}}^{(2m)} = \mathbf{c}_{XYZ} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad (3)$$

where $\tilde{\mathbf{c}}^{(2m)}$ is the irreducible second-rank tensor component. The optimization of nonlinear response of a D_∞ medium can only be achieved by maximizing the second-rank hyperpolarizability of the chromophore and by choosing the type of alignment that is compatible with the symmetry of this component.

First, consider the more general case of an arbitrary chromophore being aligned into D_∞ bulk. The only requirement imposed on the molecule is the existence of non-zero $\mathbf{b}^{(2m)}$. Using the permutation properties of $\tilde{\mathbf{c}}(D_\infty)$, one can write it as

$$\tilde{\mathbf{c}}_{D_\infty}^{(2m)} = \frac{1}{6} (2\tilde{\mathbf{c}}_{ZZ} - \tilde{\mathbf{c}}_{XX} - \tilde{\mathbf{c}}_{YY}) = \frac{1}{6} N \langle 2R_{Zi}R_{Zj} - R_{Xi}R_{Xj} - R_{Yi}R_{Yj} \rangle \tilde{\mathbf{b}}_{ij}^{(2m)} \quad (4)$$

Here, the hyperpolarizability invariant second-rank tensor, $\tilde{\mathbf{b}}_{ij}^{(2m)}$, given in the molecular frame is transformed into laboratory coordinates with orthogonal rotation matrix $\tilde{R}_{ij} = \hat{I} \cdot \hat{j}$ (\hat{I} and \hat{j} stand for basis vectors of the laboratory and molecular frame respectively). In writing Eq. (4) we could have chosen to calculate any non-zero combination of the tensor hyperpolarizability. The particular form that we chose above, which explicitly projects the specific traceless symmetric tensor that is non-zero in this macroscopic medium, is convenient as it makes the nature of the average more evident in subsequent steps.

More specific knowledge of the chromophore's hyperpolarizability or the constraints imposed thereon by symmetry allows one to draw conclusions about alignment from Eq. (4). As was mentioned above, Λ -shaped chromophores may exhibit rather strong Kleinman-disallowed hyperpolarizabilities. Most Λ -shaped molecules can

be well approximated by a planar (2-dimensional) C_{2v} object so that the only nonzero Cartesian components of \mathbf{b} are $\mathbf{b}_{zzz}, \mathbf{b}_{zxx}, \mathbf{b}_{xxz} = \mathbf{b}_{xzx}$ (assuming z – the two-fold axis and zx – the plane of the molecule). The second-rank tensor part is given by

$$\tilde{\mathbf{b}}_{C_{2v}}^{(2m)} = \begin{pmatrix} 0 & \Delta\mathbf{b}/2 & 0 \\ \Delta\mathbf{b}/2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \Delta\mathbf{b} = \mathbf{b}_{zxx} - \mathbf{b}_{xxz} \quad (5)$$

Combining Eqs. (4) and (5) together results in the expression for $\tilde{\mathbf{b}}(C_{2v}) \rightarrow \tilde{\mathbf{c}}(D_\infty)$ alignment scheme. The rotation matrix R can be defined in terms of Euler angles thus making the order parameter a function of three orientation angles of the chromophore in the bulk. The convention for Euler angles and the orientation of the molecular symmetry axis of a Λ -shaped molecule are shown in Fig. 1. So, the nonlinear susceptibility defined in Eq. (4) is now given by

$$\begin{aligned} \tilde{\mathbf{c}}^{(2m)}(C_{2v} \rightarrow D_\infty) &= \frac{1}{6} N \Delta\mathbf{b} \langle 2R_{Zx}R_{Zy} - R_{Xx}R_{Xy} - R_{Yx}R_{Yy} \rangle \\ &= \frac{1}{6} N \Delta\mathbf{b} \langle 2(\hat{Z} \cdot \hat{x})(\hat{Z} \cdot \hat{y}) - (\hat{X} \cdot \hat{x})(\hat{X} \cdot \hat{y}) - (\hat{Y} \cdot \hat{x})(\hat{Y} \cdot \hat{y}) \rangle \quad (6) \\ &= \frac{1}{4} N \Delta\mathbf{b} \langle \sin^2(\mathbf{q}) \sin(2\mathbf{y}) \rangle \end{aligned}$$

The conditions for maximizing the order parameter of such a system is clear from Eq. (6). The order parameter naturally does not depend on the azimuthal angle ϕ since the system is invariant under this rotation. The macroscopic response of the system is maximized by the combination of the other two angles $\mathbf{q} = \mathbf{p}/2$ and $\mathbf{y} = \pm\mathbf{p}/4$. In terms of molecules' orientation, the situation corresponds to the polar axes of the molecules being perpendicular to the C_∞ -axis of the bulk and the molecules being twisted about their C_2 axes by 45° . Note that the direction of the twist must be the same for the majority

of Λ -chromophore molecules: the sign of ψ has to be predominantly either plus or minus.

The sign of ψ changes under inversion so that equal numbers of positive and negative ψ 's result in an effectively racemic (non-chiral) mixture of twists and cancellation of the (chiral) nonlinear susceptibility we are considering. However, uniformly changing the sign of ψ simply changes the sign of this susceptibility.

2.2 ***Biaxial alignment of L-chromophores – C_{2v} chromophore and D_2 symmetry of the medium***

Consider the second chiral alignment type of interest – D_2 symmetry. The polar axis is absent in this case too so that the vector components in Eq. (2) vanish identically as in the previous case. The second and third rank tensors, however, are allowed in D_2 . The tensor is defined in terms of three values (nonzero Cartesian component $\mathbf{c}_{XYZ} = \mathbf{c}_{XZY}$, $\mathbf{c}_{YZX} = \mathbf{c}_{YXZ}$, and $\mathbf{c}_{ZXY} = \mathbf{c}_{ZYX}$). In terms of irreducible tensors, the fully symmetric octupolar part of the susceptibility tensor is defined by a single value, while the second-rank part carries two others

$$\tilde{\mathbf{c}}^s = \tilde{\mathbf{c}}_{XYZ}^{(3s)} = \tilde{\mathbf{c}}_{YZX}^{(3s)} = \dots = \frac{1}{3}(\mathbf{c}_{XYZ} + \mathbf{c}_{YZX} + \mathbf{c}_{ZXY}) \quad (7)$$

$$\tilde{\mathbf{c}}^{(2m)} = \begin{pmatrix} \mathbf{c}_{YZX} - \mathbf{c}_{ZXY} & 0 & 0 \\ 0 & \mathbf{c}_{ZXY} - \mathbf{c}_{XYZ} & 0 \\ 0 & 0 & \mathbf{c}_{XYZ} - \mathbf{c}_{YZX} \end{pmatrix}$$

The second rank tensor in Eq. (7) can be split into two parts we will call uniaxial and biaxial

$$\tilde{\mathbf{c}}^{(2m)} = \tilde{\mathbf{c}}^u \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \tilde{\mathbf{c}}^b \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (8)$$

$$\tilde{\mathbf{c}}^u = \frac{\mathbf{c}_{XYZ} - \mathbf{c}_{YZX}}{2}; \tilde{\mathbf{c}}^b = \frac{2\mathbf{c}_{ZXY} - \mathbf{c}_{XYZ} - \mathbf{c}_{YZX}}{2}$$

The uniaxial term of Eq. (8) is identical in structure to $\tilde{\mathbf{c}}_{D_\infty}^{(2m)}$ (Eq. (3)) with the exception of a differently defined scalar order parameter (which, in fact, transforms into (3) upon transition of D_2 to D_∞). Therefore, the entire discussion of the optimization of the macroscopic response in D_∞ media is fully applicable to the uniaxial part of $\tilde{\mathbf{c}}^{(2m)}$ so that the conditions for maximizing the order parameter $\tilde{\mathbf{c}}^u$ are given by Eq. (6). The second term of Eq. (8) corresponds to biaxial alignment. The third independent value in $\tilde{\mathbf{c}}(D_2)$ can be defined as follows

$$\tilde{\mathbf{c}}^b = \frac{1}{2} N \langle R_{Yi} R_{Yj} - R_{Xi} R_{Xj} \rangle \tilde{\mathbf{b}}_{ij}^{(2m)} \quad (9)$$

In the special case of C_{2v} chromophores (Eq. (5)), the biaxial part of the second-rank susceptibility is given by

$$\begin{aligned} \tilde{\mathbf{c}}^b &= \frac{1}{2} N \Delta \mathbf{b} \langle R_{Yx} R_{Yy} - R_{Xx} R_{Xy} \rangle = \\ &= \frac{1}{2} N \Delta \mathbf{b} \langle (\hat{Y} \cdot \hat{x})(\hat{Y} \cdot \hat{y}) - (\hat{X} \cdot \hat{x})(\hat{X} \cdot \hat{y}) \rangle \\ &= \frac{1}{16} N \Delta \mathbf{b} \langle 4 \cos(\mathbf{q}) \cos(2\mathbf{y}) \sin(2\mathbf{f}) + (3 + \cos(2\mathbf{q})) \sin(2\mathbf{y}) \cos(2\mathbf{f}) \rangle \end{aligned} \quad (10)$$

The orientational average in Eq. (10) can be maximized if the preferred polar angle of the chromophore θ is close to 0 or π . Eq. (10) reduces to

$$\tilde{\mathbf{c}}^b(\mathbf{q} = 0) = \frac{1}{4} N \Delta \mathbf{b} \langle \sin[2(\mathbf{y} + \mathbf{f})] \rangle$$

$$\tilde{\mathbf{c}}^b(\mathbf{q}=\mathbf{p}) = \frac{1}{4} N \Delta \mathbf{b} \left\langle \sin[2(\mathbf{y}-\mathbf{f})] \right\rangle$$

When the polar angle is zero, the azimuthal rotation and twist about molecule's axis become equivalent so that only the sum $\mathbf{y} + \mathbf{f}$ describes the orientation of the molecule. When $\mathbf{q} = \mathbf{p}$, the molecules are turned up side down between the first and the last rotations. The first and last rotations are also coaxial here, although positive values of ψ correspond to negative values of ϕ and the twist angle is defined as the difference $\mathbf{y} - \mathbf{f}$. Therefore, the maximum of the biaxial component of the susceptibility can be achieved when the molecules are aligned along an axis pointing either up or down with the plane of the molecules twisted 45° in opposite directions for upward and downward pointing species so that their molecular planes (xz - in Fig. 1) are perpendicular. The optimized alignment schemes for uniaxial (both D_∞ and D_2) and biaxial (D_2 only) parts of $\tilde{\mathbf{c}}^{(2m)}$ for Λ -shaped chromophore are summarized in Fig. 2 and Fig. 3(a).

The fully symmetric part of the susceptibility $\tilde{\mathbf{c}}^s$ is allowed in a biaxially (D_2)-aligned medium, so its optimization will be considered here. As in the case of the second-rank component, the octupolar part of the nonlinear susceptibility can occur only due to the octupolar part of the molecular hyperpolarizability $\tilde{\mathbf{b}}^{(3s)}$

$$\tilde{\mathbf{c}}^s = \tilde{\mathbf{c}}_{XYZ}^{(3s)} = \left\langle R_{Xi} R_{Yj} R_{Zk} \right\rangle \tilde{\mathbf{b}}_{ijk}^{(3s)}$$

Nonzero components of $\tilde{\mathbf{b}}^{(3s)}$ for a chromophore with C_{2v} symmetry are

$$\tilde{\mathbf{b}}_{zzz}^{(3s)} = \frac{1}{5} (2\mathbf{b}_{zzz} - 2\mathbf{b}_{.xxz} - \mathbf{b}_{zxx}),$$

$$\tilde{\mathbf{b}}_{zxx}^{(3s)} = \tilde{\mathbf{b}}_{xzx}^{(3s)} = \tilde{\mathbf{b}}_{xxz}^{(3s)} = \frac{1}{15} (8\mathbf{b}_{.xxz} + 4\mathbf{b}_{zxx} - 3\mathbf{b}_{zzz}),$$

$$\tilde{\mathbf{b}}_{zyy}^{(3s)} = \tilde{\mathbf{b}}_{yzy}^{(3s)} = \tilde{\mathbf{b}}_{zyy}^{(3s)} = -\frac{1}{15}(3\mathbf{b}_{zzz} + 2\mathbf{b}_{xxz} + \mathbf{b}_{zxx})$$

where we have assumed a planar π system in which \mathbf{b}_{zyy} is expected to be small, and so has been ignored. After substitution, the value of the octupolar susceptibility can be written as the following rotational average:

$$\begin{aligned} \tilde{\mathbf{c}}^s = N \left\langle \frac{1}{5} \mathbf{b}_{zzz} \left(2R_{xz}R_{yz}R_{zz} - R_{xz}R_{yx}R_{zx} - R_{xz}R_{yz}R_{zx} - R_{xz}R_{yx}R_{zz} \right. \right. \\ \left. \left. - R_{xz}R_{yz}R_{zy} - R_{xy}R_{yz}R_{zy} - R_{xy}R_{yz}R_{zz} \right) \right. \\ \left. + \frac{1}{15} (2\mathbf{b}_{xxz} + \mathbf{b}_{zxx}) \left(4R_{xz}R_{yx}R_{zx} + 4R_{xz}R_{yz}R_{zx} + 4R_{xz}R_{yx}R_{zz} \right. \right. \\ \left. \left. - R_{xz}R_{yz}R_{zy} - R_{xy}R_{yz}R_{zy} - R_{xy}R_{yz}R_{zz} - 3R_{xz}R_{yz}R_{zz} \right) \right\rangle \end{aligned}$$

or in terms of three Euler angles

$$\begin{aligned} \tilde{\mathbf{c}}^s = N \left\langle -\frac{1}{2} \mathbf{b}_{zzz} \cos(\mathbf{q}) \sin^2(\mathbf{q}) \sin(2\mathbf{f}) + \frac{1}{48} (2\mathbf{b}_{xxz} + \mathbf{b}_{zxx}) \times \right. \\ \left. \left[8\cos(2\mathbf{q}) \cos(2\mathbf{f}) \sin(2\mathbf{y}) + 3\cos(3\mathbf{q}) \cos(2\mathbf{y}) \sin(2\mathbf{f}) \right. \right. \\ \left. \left. + 5\cos(\mathbf{q}) \cos(2\mathbf{y}) \sin(2\mathbf{f}) + 3\cos(\mathbf{q}) \sin(2\mathbf{f}) - 3\cos(3\mathbf{q}) \sin(2\mathbf{f}) \right] \right\rangle \end{aligned}$$

The analysis of the last expression is not straightforward even for this simple chromophore symmetry. However, it can be simplified by realizing that this susceptibility is also allowed in a number of other, larger bulk symmetry groups. The largest of these is T_d , the symmetry group of the tetrahedron. This implies that any orientation of the chromophore that can be reached from a “standard” orientation through an element of T_d will make the same contribution to this susceptibility. It also suggests aligning “special” axes of the chromophore along special axes of a tetrahedron is a good way to maximize the susceptibility. Note, moreover, that this alignment is in consequence “optimal” for this susceptibility and any media whose symmetry group is any subgroup of T_d .

By thinking about the group T_d it is easy to extract the alignment conditions for a purely linear chromophore with a single nonzero component \mathbf{b}_{zzz} . The rotational average is maximized when the polar angle θ satisfies the condition $\cos\theta = \pm 1/\sqrt{3}$ and the azimuthal angle is $\phi = \mp \pi/4; \pm 3\pi/4$. The signs must be chosen consistently so that all contributions to the resultant $\tilde{\mathbf{c}}^s$ are positive (or negative), although the second harmonic intensity depends only on the square of χ . However, the relative signs between θ and ϕ must be chosen as illustrated in Fig. 3 so that the hyperpolarizabilities of the chromophores add constructively. The condition for optimization of a nonlinear medium of D_2 symmetry made of one-dimensional chromophores can be summarized as chromophores pointing in four preferential directions which are $\bar{1}11$, $1\bar{1}1$, $11\bar{1}$, and $\bar{1}\bar{1}\bar{1}$, i.e. towards vertices of a tetrahedron. Similarly, if \mathbf{b}_{xxz} is the dominant hyperpolarizability, it is best to align the molecular z -axis along a 100 direction (a two fold rotation axis of the tetrahedron) and the molecular x -axis along one of the edges of the tetrahedron e.g. 011 or $0\bar{1}\bar{1}$, e.g. in a mirror plane of the tetrahedron. Again, these should be chosen so that the “feet” of the Λ are always along the edges of *one* of the tetrahedron whose two-fold rotation axes correspond to the two-fold rotation axes of the medium. Note that these alignments for the two different possible components of β are inconsistent for C_{2v} molecules: if the molecules are aligned so as to maximize the contribution of one hyperpolarizability there is no contribution from the other. Also note, however, that the alignment of a Λ molecule is consistent with viewing each of the “legs” of the Λ as linear chromophores with large \mathbf{b}_{zzz} along their lengths, which are then

aligned along the three-fold axes of a tetrahedron (Fig. 3). Finally note that this alignment is consistent with the alignment required for the biaxial alignment of Λ chromophores. It is also, in principle, consistent with an arbitrarily small birefringence.

2.3 Propeller-like molecules (D_n chromophores in D_m media, $n, m > 2$)

Another example that we will discuss in relation to the axial alignment of Kleinman asymmetric chromophores is systems built with molecules of D_3 symmetry group that are aligned in D_∞ fashion. Various three-fold propeller-like NLO chromophores have been extensively studied in relation to their use in octupolar NLO media (e.g. Ref. 7, 8, and others). However, if the chromophore is not perfectly flat, its symmetry is compatible with the second-rank irreducible component, which may be rather large as is indicated by our results for Crystal Violet [5] (which, however, does not have its expected D_3 symmetry in the medium in which we have done measurements.) Here we present an alignment scheme where the performance of the material is based on Kleinman-disallowed $\tilde{\mathbf{b}}^{(2m)}$ rather than octupolar part $\tilde{\mathbf{b}}^{(3s)}$.

The symmetry group D_3 is a uniaxial group with the second-rank hyperpolarizability tensor identical by structure to Eq. (3)

$$\tilde{\mathbf{b}}_{D_3}^{(2m)} = \mathbf{b}_{xyz} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

The rotational averages are even more straightforward to interpret in this case:

$$\begin{aligned} \tilde{\mathbf{c}}(D_3 \rightarrow D_\infty) &= \mathbf{c}_{xyz} = \frac{1}{6} N \langle 2R_{Zi}R_{Zj} - R_{Xi}R_{Xj} - R_{Yi}R_{Yj} \rangle \tilde{\mathbf{b}}_{ij}^{D_3} \\ &= \frac{1}{2} N \mathbf{b}_{xyz} \langle 2R_{Zz}R_{Zz} - R_{Xz}R_{Xz} - R_{Yz}R_{Yz} \rangle \\ &= \frac{1}{4} N \mathbf{b}_{xyz} \langle 1 + 3\cos(2\mathbf{q}) \rangle \end{aligned}$$

The optimal response of such a system is achieved with all molecules lying in the plane perpendicular to the symmetry axis of the bulk ($\mathbf{q} = 0, \mathbf{p}$). The azimuthal alignment does not influence this part of the nonlinear susceptibility. The uniaxial alignment makes use of only “chiral” part of the hyperpolarizability of a D_n ($n > 2$) molecule (\mathbf{b}_{xyz}), while the utilization of the other, octupolar, nonzero component ($\mathbf{b}_{xxx} = -\mathbf{b}_{xyy} = -\mathbf{b}_{yyx} = -\mathbf{b}_{yyy}$) would require stricter, three-fold alignment that is generally harder to achieve in molecular media.

Biaxial alignment of propeller molecules is also possible. However, we know of no polymeric materials that plausibly have this symmetry and in consequence do not discuss it.

3 Discussion

The previous section discussed how chiral macroscopic NLO systems could be created via chiral alignment of chromophores that belong to a different symmetry group but contain Kleinman-disallowed (second-rank) contribution in the molecular hyperpolarizability. A set of molecular orientation angles that optimizes the macroscopic response of the material was deduced on the basis of general symmetry considerations for each case of interest. The rotational freedom of the chromophore has to be limited although it may freely rotate in certain direction (uniaxial case). As discussed above, the alignments described can be achieved relatively easily in polymer systems with NLO chromophores incorporated in the backbone or attached as a side chain.

A number of chiral polymeric systems for nonlinear optics have been studied recently. Van Elshocht *et al.* studied NLO response of Langmuir-Blodgett films made of binaphthyl-based chiral helical polymers [9]. However, these systems do not seem to be

optimized in the axial sense discussed here. The authors report the symmetry of the films to be C_∞ , which is supported by the observation that c_{zzz} is the largest component of the susceptibility. Indeed, in the materials presented, the Λ -shaped monomers are attached to each other with their “feet” creating the polymer main chain, so in the aligned state, they would rather have the planes of the molecules aligned parallel to the polymer’s axis than at the 45° angle – the configuration that would favor large nonlinear optical susceptibility resulting from a traceless symmetric second-rank tensor hyperpolarizability.

Another work by Kauranen *et al.* presents a study of the NLO properties of helicenebisquinone-based Langmuir-Blodgett films [10]. The enantiomerically pure chiral material aggregates into a film of C_2 symmetry. However, the measurements of the nonlinear susceptibility $\chi^{(2)}$ showed that by far the largest Cartesian components are c_{xyz} and c_{yxz} , i.e. the characteristic components of chiral groups D_∞ and D_2 discussed here. So, one can imagine (at least in rough approximation) that the molecules pack in helical columns creating a structure close to D_∞ symmetry. In this case, the chirality of the bulk is forced directly by the strong chirality of the helicenebisquinone. The molecule is essentially three-dimensional and, although clearly it is not the C_{2v} case discussed in most detail above, the symmetry of the chromophore is a simpler group C_2 that has similar properties. The chromophore can also be thought of as a Λ -shaped chromophore. As they are stacked in columns, the molecules automatically satisfy the condition for the polar angle (pointing perpendicular to the column axis). At the same time, the “plane” of the molecule (i.e. the plane that cuts through the molecule’s mid point – the “vertex” – and two end points – the “feet” of Λ) is naturally twisted by some angle (other than 0° or 90°)

away from the normal to the bulk principal axis due to the pitch of the chiral column. Moreover, the axes x and y discussed above in conjunction with C_2 molecules will be rotated by some hard to discern angle which is likely to vary with frequency of the light from (say) the plane of the central aromatic ring. Thus, given the formalism presented above, the large chiral nonlinearity reported in Ref. 10 can be accounted for by satisfactorily (if not optimally) aligned Λ -shaped molecules of helicerebisquinone.

The desired alignment of Λ -shaped chromophores can be also achieved by other means. For a D_∞ system, a material consisting of long, linear polymers that have Λ -shaped chromophores attached to the backbone with their vertices can be stretched in one direction, so that the molecular dipoles are, generally, perpendicular to the main chain. The linking group must contain a chiral center that favors the rotation of the plane of the chromophore by $\sim 45^\circ$ from the direction of the main-chain of the polymer, with the most important condition being that a preponderance of the chromophores are twisted in the same direction. An alternative scheme is somewhat similar to the system in Ref. 10: the chromophores are attached (again with their vertices) to a helical polymer backbone heading toward the helix axis. The rotation about the molecular axes must still be constrained, although it can be parallel to the local direction of the polymer *chain* and only tilt with respect to the *symmetry axis*. This is created (and even controlled) by pitch of the helix. The two cases are schematically shown in Fig. 2 (a) and (b).

The case of D_2 alignment is slightly more complicated. The structure is similar to the first example of D_∞ alignment from the previous paragraph. The chromophores are incorporated into a linear polymer as side-chain groups with a fixed twist angle. In addition, liquid crystalline moieties are attached to the “feet” of the Λ -shaped

chromophore. When conditions are satisfactory for existence of the nematic phase, the direction of the stretch (along the polymer chain) and director of the nematic phase (perpendicular to the main axis) define two distinct nonpolar axes in the system, forming D_2 symmetry (Fig. 2(c)). When the nematic moieties align parallel to each other, the chromophores will, on average, have to point mostly “up” and “down” favoring only $\mathbf{q} = 0, \mathbf{p}$. Such alignment can also, in principle, be achieved by stretching of an appropriately cross-linked polymer gel in a biaxial fashion.

Finally, the optimized alignment scheme for D_3 chromophores can be physically realized in a discotic nematic or columnar liquid crystals or LC-polymers (Fig. 4). Here the chirality of such systems should originate from the chirality of the chromophores. Hence, an enantiomerically pure chromophore should be used in for the best performance, since the left- and right-handed species, if present simultaneously, will cancel each other’s hyperpolarizability, so that the susceptibility is proportional to the enantiomeric excess. Molecules with a low threshold for the transition between left- and right-handed states (like Crystal Violet) can be stabilized if placed into a matrix (or a host liquid crystal) with a well-defined handedness, or if appropriate, optically unresponsive moieties are attached thereto.

4 Conclusions

In this paper, we have shown how bulk nonlinear susceptibility can be created from an axially aligned arrangement of responsive chromophores in a chiral nonpolar medium. Our theory elucidates the criteria for optimization of the nonlinear response of such chiral media. Based on the conclusions drawn from the theory, several examples of known materials as well as possible physical configurations involving Λ -shaped and

propeller-like chromophores were discussed. This study gives guidelines for the creation of conceptually new materials for second-order nonlinear optics by implementing tensorial properties of the molecular hyperpolarizability and using an appropriate chiral alignment scheme.

Acknowledgments

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Figure captions

Figure 1. (a) Euler angles for transformation between the molecular and bulk reference frames; (b) coordinate system for a Λ -shaped molecule.

Figure 2. Alignment examples for Λ -shaped molecules in a uniaxial macroscopic NLO system of D_∞ symmetry: (a) linearly stretched polymer chain and chromophores twisted by angle ψ ; (b) a helical polymer – the twist of the polymers is defined by the helix pitch.

Figure 3. Alignment in biaxial D_2 symmetry: (a) Λ -shaped molecules – two-fold axes of the bulk are defined by the polymer stretch direction and the director of the nematic side-chain moieties; (b) nonpolar alignment of the 1D chromophores utilizes the octupolar component of β .

Figure 4. Alignment of three-fold propeller-like chromophores in a bulk of D_∞ symmetry.

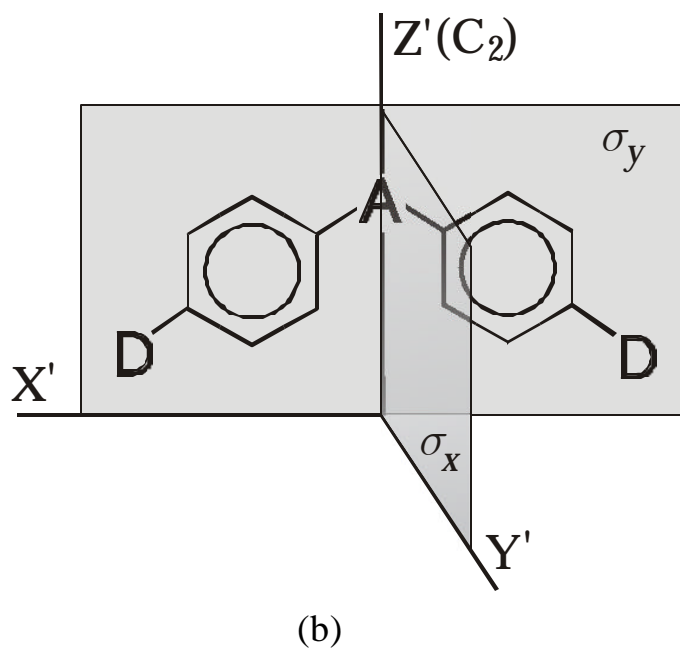
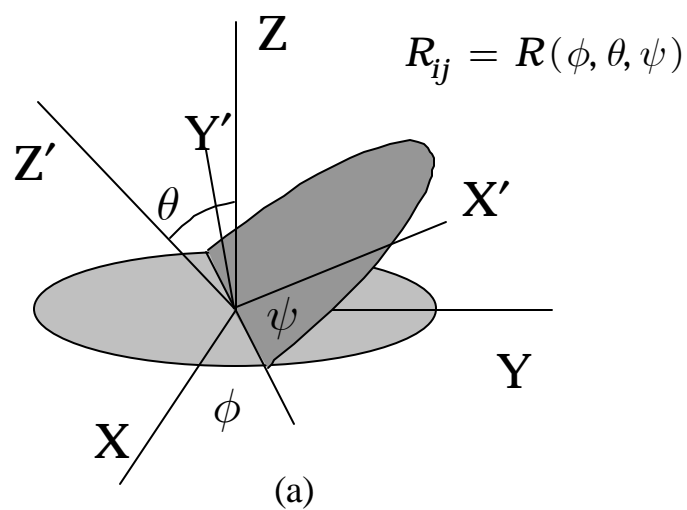


Figure 1

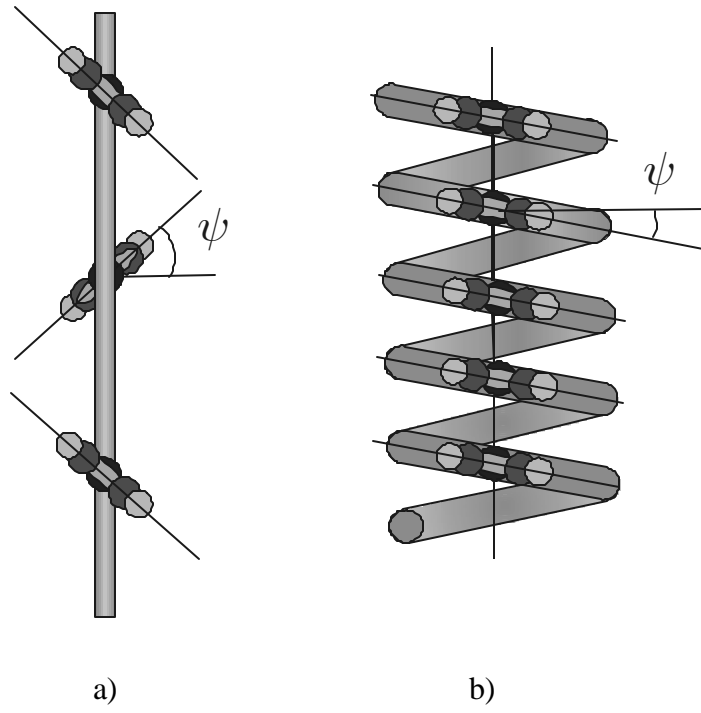


Figure 2

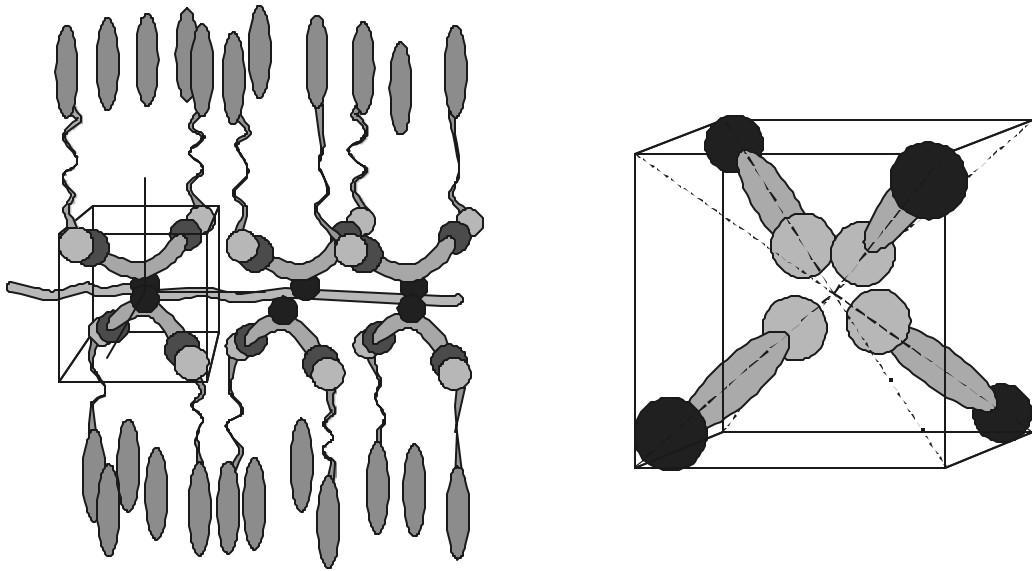


Figure 3

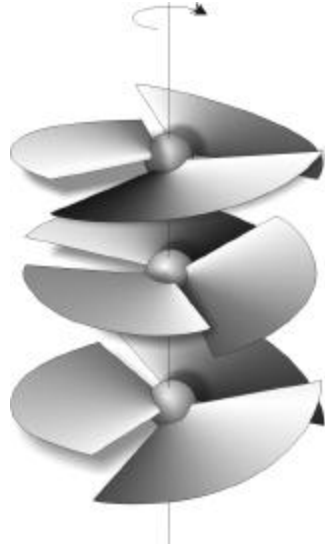


Figure 4.