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"Quadrupoled" Materials for Second-Order Nonlinear Optics

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ABSTRACT

We describe a new approach to second-order nonlinear optical materials, namely quadrupoling. This approach is valid in the regime of Kleinman (full permutation) symmetry breaking, and thus requires a two- or three dimensional microscopic nonlinearity at wavelengths away from material resonances. This "quadrupolar" nonlinearity arises from the second rank pseudotensor of the rotationally invariant representation of the second-order nonlinear optical tensor. We have experimentally investigated candidate molecules comprised of chiral camphorquinone derivatives by measuring the scalar invariant associated with the rank two pseudotensor using hyper-Rayleigh scattering. We have found sizable scalar figures of merit for several compounds using light for which the second harmonic wavelengths are greater than 100 nm longer than the absorption peak location. At these wavelengths, the quadrupolar scalar is as large as the polar (EFISH) scalar of p-nitroaniline. Prospects for applications are discussed.

1. INTRODUCTION

Second-order nonlinear optics has been intensely studied in polymers, and has led to the development of commercial electro-optic devices. [1] Most of this work, aimed at applications, has centered on poled polymeric materials. In this scheme, nonlinear optical molecules incorporated into polymeric hosts are aligned through an electric field poling process, and thus the coupling occurs through the dipolar contribution to the hyperpolarizability. A typical molecule in this application has a large dipole moment to couple to the poling field, and often exhibits a "one-dimensional" response. In this case, full permutation symmetry known as Kleinman symmetry applies, and one has an anisotropic response for all second-order processes.

More recently, the octupolar component of the nonlinear response has been investigated. [2] As with dipolar schemes, this case corresponds to both Kleinman symmetric and unsymmetric species. However, a one dimensional response does not suffice in this case. In both dipolar and octupolar materials, one arranges for a large dipolar or octupolar response in the molecular constituents, and then applies the appropriate macroscopic symmetry using electric field poling or octupoling in the respective cases. For the dipoling case, polar macroscopic alignment is attained with electric field poling or by optical poling techniques. For octupoling, optical poling can be used to achieve the required order.

As we show here, another component based on the rotational invariants of the molecular hyperpolarizability tensor can be used to generate second-order effects. This is the "quadrupolar" contribution, and is possible only when Kleinman symmetry is broken. Kleinman symmetry breaking has been discussed

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theoretically in the past [4,5]. If the π electrons in a molecule are conjugated in one dimension, Kleinman symmetry is required. Thus, molecules must feature electrons which are delocalized in two or three dimensions to be considered good candidate materials in which a violation of Kleinman symmetry can be examined. [6,7] Molecules exhibiting chiral symmetries and excitations are examples of multidimensional molecules which would be expected to exhibit Kleinman symmetry breaking, and are the subject of study here. The enantiomers we will discuss showed significant optical rotary power which indicate the possibility of three-dimensional delocalization [8]. We will present results of quantum mechanical calculations and experimental results which provide additional support for the idea of a nonplanar electronic structure in these chiral conjugated molecules.

The appropriate macroscopic symmetry is attained through the "quadrupoling process" which imparts axial order on the material. Potential materials are uniaxially and biaxially stretched polymers and elastomers, and liquid crystal materials. In all cases, the axial order parameters determine the relationship between the microscopic and macroscopic responses. [2] Axial order is considerably easier to achieve and more persistent than either polar or octupolar order.

In this paper, we report on measurement of the quadrupolar figure of merit for a series of chiral camphorquinone molecules as measured by hyper-Rayleigh scattering. The appropriate theory is briefly presented, followed by a description of the experiment, results, and a discussion of the prospects of these materials and techniques.

2. CONCEPT AND THEORY

The concept of quadrupoling becomes apparent in the decomposition of the molecular hyperpolarizability tensor, β into its rotational invariants. The hyperpolarizability, β , is a rank-3 tensor which is formed by combining three rank-1 vectors. These tensors combine through a formalism analogous to the addition of angular momenta [3]. In the most general case of parametric light scattering, the hyperpolarizability, β_{pls} , transforms as follows:

$$\begin{aligned}\beta_{pls} &\sim 1 \otimes 1 \otimes 1 \\ &\sim 0 \oplus (1 \oplus 1 \oplus 1) \oplus (2 \oplus 2) \oplus 3\end{aligned}\tag{1}$$

which shows that β consists of 1 antisymmetric pseudo-scalar, 1 fully symmetric rank-3 tensor, 3 vectors, and 2 pseudo-tensors. The 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 so [9],

$$\begin{aligned}\beta_{HRS} &\sim 1 \otimes (1 \otimes 1)_{sym} \\ &\sim 1 \otimes (0 \oplus 2) \\ &\sim 1 \oplus 1 \oplus 2 \oplus 3\end{aligned}\tag{2}$$

leaving 2 vectors, 1 rank-2 pseudo-tensor, and 1 rank-3 tensor. In the fully-symmetric case of Kleinman symmetry, the hyperpolarizability consists of just two components:

$$\beta_{sym} \sim 1 \oplus 3\tag{3}$$

	symmetry group	$s_{ijk} = \chi^{(2)}_{ijk} + \chi^{(2)}_{ikj}$	$a_{ijk} = \chi^{(2)}_{ijk} - \chi^{(2)}_{ikj}$
Chiral liquid		none	$a_{123} = a_{231} = a_{312}$
Uniaxial	D_∞	$s_{123} = -s_{231}$	$a_{123} = a_{231}, a_{312}$
Biaxial	D_2	$s_{123}, s_{213}, s_{312}$	$a_{123}, a_{213}, a_{312}$

TABLE I. Values of $\beta_{1,ss}$ and $\beta_{2,mm}$ (10^{-30} esu) at $\lambda=1265\text{nm}$ and 1350nm .

which 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 in its irreducible form:

$$\beta_{ijk} = \beta_{ijk}^{(3)} + \frac{1}{2} (\epsilon_{ijk} \beta_{lk}^{(2)} + \epsilon_{ikl} \beta_{lj}^{(2)}) + \beta_i^{(1)} \delta_{jk} + \frac{1}{2} (\beta_j^{(1')} \delta_{ik} + \beta_k^{(1')} \delta_{ij}) \quad (4)$$

where δ_{ij} is the Kronecker delta, ϵ_{ijk} is the totally anti-symmetric Levi-Cevita tensor, and $\beta^{(n)}$ is the rank- n irreducible tensor component of the rank-3 tensor, β . It is apparent in Eq. 4 that the $\beta^{(2)}$ terms are forbidden in the Kleinman-valid regime, and, therefore, cannot contribute in the "one-dimensional" case where $i = j = k$.

The concept of quadrupoling activates the second-rank pseudotensor contribution to β . As an example of activating this tensor component, we examine more closely the case of chiral molecules. In chiral molecules, assuming that the excitations responsible for β are highly coupled to the chiral center, a three-dimensional character to β results. Table I indicates how this molecular response for second harmonic generation can be activated by "quadrupoling" the macroscopic material. For nonaligned liquids, second harmonic generation is not allowed since $\chi_{ijk}^{(2)}$ must be symmetric symmetric in j and k so that both the symmetric, s_{ijk} , and antisymmetric, a_{ijk} , part of $\chi_{ijk}^{(2)}$ are zero. The symmetry groups important in axially aligned chiral materials, D_∞ and D_2 , contain contributions to the macroscopic second-order susceptibility of the form $\chi_{ijk}^{(2)}$ with i, j , and k all different and symmetric in the last two indices [8]. These forms are similar to the pseudotensor contribution to the rank-3 tensor β . Thus, the axial order formed by stretching or shearing a polymer or due to intrinsic nematic or smectic A and C order can lead to second harmonic generation. Flow alignment may also be possible. Electro-optic effects have somewhat different symmetry properties with the differences arising from the permutation of degenerate input and output fields rather than two degenerate input fields as in second harmonic generation.

3. HYPER-RAYLEIGH SCATTERING

In this section, we describe how hyper-Rayleigh scattering can be used to measure the scalar figure of merit associated with the second-rank pseudotensor part of β . To do this we consider the same rotationally

invariant formalism as described in the previous section. Considerable theoretical effort has gone into the transformation from the laboratory to molecule-fixed frames for nonlinear light scattering [10]- [13]. For the experiments here, the problem is conveniently approached by considering the rotational invariants of the irreducible tensor components [14]. The complete theory, which is presented elsewhere, provides the detailed form of the irreducible tensors and connects directly with experiment. [14] Here we merely summarize. This treatment allows a more transparent decomposition of the scattered signal into the molecular contributions of different symmetry. It also makes clearer inequalities which must be satisfied by the various components of the scattering tensor. As the magnitude of various components of the tensor depends on the underlying molecular symmetry, this allows us both to design more sensitive experiments and to check error estimates by comparing results with the inequalities.

If two optical fields, E_1 and E_2 of frequency ω_1 and ω_2 , respectively, are incident on an isotropic medium of randomly oriented nonlinear optical molecules, the scattered intensity, I^{ω_3} , at the sum-frequency, ω_3 , is [15]:

$$I_{IL}^{\omega_3} = GNB_{IJKLMN}^2(\omega_3 = -\omega_2 - \omega_1; \omega_2, \omega_1)(E_{1,J}^{\omega_1})(E_{1,K}^{\omega_1})^*(E_{2,M}^{\omega_2})(E_{2,N}^{\omega_2})^* \quad (5)$$

where G is a factor incorporating experimental geometries and local fields, N is the number density of nonlinear optical chromophores, and B^2 is an average squared molecular susceptibility tensor at the indicated frequencies. The indices I, J, K, L, M , and N correspond to fixed axes in the laboratory frame of reference. The tensor is given by:

$$B_{IJKLMN}^2(\omega_3 = -\omega_2 - \omega_1; \omega_2, \omega_1) = \langle \beta_{IJK}(\omega_3; \omega_1, \omega_2) \beta_{LMN}^*(\omega_3; \omega_1, \omega_2) \rangle \quad (6)$$

where β is the first hyperpolarizability. We note that $Re(B^2)$ is a symmetric tensor as $IJK \mapsto LMN$ and $Im(B^2)$ is anti-symmetric under this interchange. The problem of transforming the average squared hyperpolarizability, B^2 , between laboratory-fixed and molecule-fixed reference frames is best approached by decomposing the tensor into rotational invariants [14].

The tensor, B_{IJKLMN}^2 , is the physical quantity measured in a nonlinear light scattering experiment. We now consider the rotational invariants of the irreducible tensor components. The transformation between frames is not necessary if the rotational invariants are represented by scalars. Eq. 6 can be rewritten in terms of scalar quantities:

$$B_{IJKLMN}^2 = \sum_{\mathcal{L}} \Delta_{IJK,LMN}(\mathcal{L}) \beta^2(\mathcal{L}) \quad (7)$$

where $\mathcal{L}$ specifies the tensor rank and index-exchange symmetry for each term, $\Delta_{IJK,LMN}$ is a rotationally invariant tensor, $\beta^2(\mathcal{L})$ is the averaged scalar invariant coefficient of the squared hyperpolarizability component, and $\mathcal{L}$ is described below. It is useful to form Δ 's according to the representation of the rotation group $L = 0, 1, 2, 3$ according to which the corresponding β 's transform. When there is more than one β which transforms like any given representation, then, in addition to the tensors corresponding to the square of each β , there are two additional tensors corresponding the real and imaginary parts of the interference between the tensors. Thus $\mathcal{L}$ consists of the set $\{L, \sigma, \sigma', \pm\}$. Here σ and σ' are one of s, a, m , and m' , giving the index-exchange or Kleinman symmetry of the two β 's which describe are involved in this Δ . The completely symmetric β is indexed s , the completely antisymmetric β is indexed a and the two mixed representations under index exchange are indexed m and m' . These mixed representations were chosen so that m is symmetric under interchange of the incoming fields, and m' is antisymmetric under

interchange of these fields. This is convenient for specializing to hyper-Rayleigh scattering. The $\pm$ is given only if $\sigma \neq \sigma'$. $+$ is the real part of the tensor (symmetric under interchange of IJK and LMN) and $-$ is imaginary part of the tensor which is antisymmetric under this interchange.

In general, there are 15 terms in Eq. 7. However, for hyper-Rayleigh scattering, there are 6 corresponding to $\mathcal{L} = (1, ss); (1, mm); (1, sm)_+; (1, sm)_-; (2, mm)$ which are the 6 measurables. The scalar invariant quantities $\beta^2(\mathcal{L})$ are the figures of merit we wish to measure using hyper-Rayleigh scattering, and they are related to the macroscopic scattering tensor B_{IJKLMN}^2 through the rotationally invariant tensors $\Delta_{IJK,LMN}$. The exact form of the tensors are quite involved and are listed elsewhere. [14] The scalar invariant $\beta^2(1, ss)$ is the dipolar term also measured in EFISH. It is the figure of merit for poled materials. The quantity $\beta^2(3, ss)$ is the figure of merit for octupoling, while $\beta^2(2, mm)$ is the figure of merit of interest here for quadrupoling.

The physical quantities, $\beta(\mathcal{L})$, can be deduced from polarization studies of the scattering cross-section. A theoretical development as above can be used to design the hyper-Rayleigh scattering experiments. The observed intensity can be expressed for a given geometry of output polarizers by simply multiplying the scattering tensor of Eq. 5 by the polarization vectors of the scattered light as follows:

$$I = I_{IL} e_{o,I}^* e_{o,L} \quad (8)$$

where $e_{o,I}$ is the I^{th} component of the polarization vector of the output light. The applied incident fields from Eq. 5 are of the form, $E_1 = e_i \exp(i\omega_1 t)$ and $E_2 = e_{i'} \exp(i\omega_2 t)$, so the observed intensity is

$$I = B_{IJKLMN}^2 e_{o,I}^* e_{i,J} e_{i',K} e_{o,L} e_{i,M}^* e_{i',N} \quad (9)$$

$$= \sum_{\mathcal{L}} \Delta(\mathcal{L}, \mathcal{P}_1, \mathcal{P}_2) \beta(\mathcal{L})^2 \quad (10)$$

The $\Delta_{IJK,LMN}$ tensors are rotationally invariant, so the indices must be equal in pairs for the case of hyper-Rayleigh scattering. Applying this constraint in Eq. 9 shows that the scalar Δ coefficients can be expressed as scalar products of the unit polarization vectors, e_i , $e_{i'}$, e_o , and the complex conjugates. We can explicitly show these intensities for the simplified case of hyper-Rayleigh scattering where, $e_i = e_{i'}$. In this case, the 15 tensors reduce to 6 unique coefficients.

To apply the above formalism, our experiments use the surface of an optical table as the $\hat{x}\hat{z}$ plane, and all polarizer and waveplate angles are defined with the left-hand rule using $\hat{y}$ as the zero-degree position. The polarization of an optical field e_i incident in the $\hat{z}$ -direction on a linear polarizer at angle α_i and a quarter-waveplate at angle γ_i is given by

$$e_i = \cos(\alpha_i - \gamma_i)(\sin \gamma_i \hat{y} + \cos \gamma_i \hat{x}) + i \sin(\gamma_i - \alpha_i)(\cos \gamma_i \hat{y} - \sin \gamma_i \hat{x}). \quad (11)$$

If the scattering is at angle θ in the $\hat{x}\hat{z}$ -plane and then goes through a quarter-waveplate at angle γ_o and a linear polarizer at angle α_o , the resulting field is:

$$e_o = \cos(\alpha_o - \gamma_o)[\sin \gamma_o \hat{y} + \cos \gamma_o(\hat{z} \sin \theta + \hat{x} \cos \theta)] + i \sin(\gamma_o - \alpha_o)[\cos \gamma_o \hat{y} - \sin \gamma_o(\hat{z} \sin \theta + \hat{x} \cos \theta)]. \quad (12)$$

FIG. 1. Chiral molecules used in this study with λ_{max} values determined with a UV-VIS spectrophotometer.

The six invariants can be measured by appropriate choice of the experimental scheme. Two different measurements were required to yield reliable results as described below. We used an iterative fitting technique to determine β^2 by considering only the largest or most active Δ 's from each experiment. We were able to reproduce randomly generated sets of β^2 values generally to within 20% from numerically simulated data even when inserting a signal-to-noise ratio of 1:1. The largest errors came in the $\beta_{1,mm}$ and $\beta_{2,mm}$ where the error could be as high as 50% in the cases when they were very small. We did note, however, that we could accurately determine $(\beta_{1,mm} + \beta_{2,mm})$ to within 20% in every case.

4. MATERIALS

Our experiments were first calibrated using *p*-nitroaniline (pNA) and disperse red-1 (DR1), two chromophores well-known from EFISH and HRS studies [15–17]. We also studied the chiral dyes shown in Fig. 1. The first dye, Q-NH₂ is imine of 4-aminoaniline and camphorquinone, and the second dye, Q-BNH, is imine of *bis*-(4-aminophenyl)amine and camphorquinone. The other dye shown, Q-KCh, is 3-{4'-N,N-bis-2''-[(7'''-ocenoxy)ethyl]aminophenyl}1R,7,7-trimethylbicyclo(2.2.1)heptan-2-one imine. The dyes were prepared by condensation of camphorquinone with the appropriate amine in the presence of sodium acetate, purified by recrystallization, and characterized by ¹H NMR, UV/Vis spectroscopy and elemental analysis. For example, Q-BNH was prepared by the reaction of 2.5 g of camphorquinone with 2.22 g of bis(4-aminophenyl)amine hemisulfate and 2.16 g of sodium acetate in 40 mL CHCl₃. The reaction

FIG. 2. Wavefunctions of a chiral camphorquinone molecule in the AM1 optimized geometry. The contours of the wavefunction are shown.

was heated at reflux for 3 hours under nitrogen, poured into 100 mL water and extracted with CHCl_3 . The extracts were filtered through Celite 521 to remove black contaminants and the resulting red brown solid that was obtained after solvent evaporation was recrystallized from ethanol. Recrystallization from toluene or THF/hexane worked equally well. All dyes showed good solubility in acetone, and the absorption peak was found for solutions using a UV-vis spectrophotometer, and the wavelength of maximum absorption, λ_{max} , is also shown in Fig. 1.

The quinone dyes were chosen to study the effects of chirality on the first hyperpolarizability. The molecules are rather large and have no point symmetry. As such, there is no global symmetry-defined distinction between π and σ orbitals. Large optical polarization rotation can be a strong indication that there is a π -electron system which is delocalized in three dimensions. A solution of Q-NH₂ of 1.1% by weight in *p*-dioxane rotated the linear polarization of a 632.8nm laser beam by 16° in a 20cm pathlength. Quantum chemical calculations were performed to learn more about the electronic structure. The geometry of Q-NH₂ was optimized with the AM1 semi-empirical basis set using the GAMESS [18] quantum chemistry program. A space-filling model of this optimized geometry is shown in Fig. 2. The Hartree-Fock orbitals in the AM1 optimized geometry were also calculated using both AM1 and the *ab initio* 631G basis sets. The Hartree-Fock orbitals were found to be qualitatively similar in both cases. The wavefunctions for the 631G basis sets are shown for the four frontier wavefunctions, that is, those with energies closest to the Fermi level: the two highest occupied molecular orbitals (HOMO) and the two lowest unoccupied molecular orbitals (LUMO). The wavefunction contours are shown. These figures clearly indicate the largely π -character of these wavefunctions. It is also apparent that the wavefunctions are effectively delocalized in three

FIG. 3. Experimental setup for determining rotational invariants with hyper-Rayleigh scattering. Key: OPO - optical parametric amplifier; OPA - optical parametric amplifier; TC - temperature controller; BS - beamsplitter; M - silvered mirror; F - color filter; Pol. - linear polarizer; WP - quarter-waveplate; BC - Berek compensator; L - lens; QC - quartz crystal; PMT - photomultiplier tube; HV - high-voltage supply; MC - motion controller; OSC - digital oscilloscope; PD - photodiode.

dimensions over the molecular structure with the excitation proceeding also over the three-dimensional camphor moiety.

5. EXPERIMENTAL METHOD

The experimental setup, shown in Fig. 3, is similar to the traditional HRS setup except for the 45° scattering angle. Our optical source was a walkoff-compensated dual-crystal β -BBO optical parametric oscillator which was synchronously pumped by the third-harmonic of a flashlamp-pumped two-stage amplified Nd:YAG system with negative feedback and active/passive modelocking. The second harmonic from the YAG was used to optically pump a temperature tunable Li:NbO₃ parametric amplifier. This source produced pulse trains at 10Hz with each train consisting of about 50 pulses with durations of 1-10 ps and an energy per pulse of at least $2 \mu\text{J}$ tunable through the near-IR to 2 microns [19].

Incident pulses travelled through a half-waveplate, whose axis is at an angle γ_i to the vertical, and a linear polarizer, whose axis is at an angle α_i to the vertical, to fix the incident polarization. A silver mirror then turned the pulse $\theta = 45^\circ$ in the plane parallel to the optical table surface. A Berek compensator mounted in a rotation stage was tuned for quarter-wave retardation of the fundamental. Light went through the exact center of the Berek compensator, and very little deflection of the beam

FIG. 4. Polar plots of real data with fitted curves (solid) and Kleinman-allowed (dotted) curves for (a) pNA and (b) Q-KCh.

occurred as the device rotated. The light was then focused at normal incidence onto the hypotenuse of a right-triangular cuvette containing the solution being studied. A detection system was set up with its optical axis parallel to the direction of the incident light before the turning mirror and perpendicular to a short face of the cuvette. Harmonic light was collected and mostly collimated by a short focal length lens with a collection angle of about 15° . Small changes in the numerical aperture of this lens did not appear to significantly affect final results. Collected light passed through a quarter-waveplate, whose axis is at an angle γ_o to the vertical, and a linear polarizer, whose axis is α_o to the vertical, before being focused into a photomultiplier tube. A narrow-band filter was in front of the photomultiplier tube to ensure only harmonic light would be detected. The signal from the tube went to a boxcar integrator. A computer controlled the entire experiment and divided the signal generated by the scattered light with that produced in a photomultiplier tube monitoring second harmonic generation in quartz. Reported data points represent the mean of about 50 weighted averages from the boxcar. The ratio of the two signals was seen to be independent of fundamental energy over a range of $1.25\text{--}2\mu\text{J/pulse}$.

Two experiments with different polarizations were performed at fundamental wavelengths of 1265nm and 1350nm with each dye dissolved in acetone. In each experiment, the incident polarization was 90° (parallel to the optical table) leaving α_o and γ_o as the remaining variables. At 1265nm, the two experiments corresponded to $\alpha_o = \gamma_o = 0^\circ$ and $\alpha_o = 54.7^\circ$ with $\gamma_o = 0^\circ$. At 1350nm, the experiments were $\alpha_o = \gamma_o = 54.7^\circ$ and $\alpha_o = 54.7^\circ$ with $\gamma_o = 0^\circ$. We looked at Q-KCh at both wavelengths with all 3 of these experiments and found the same results. Once the β -tensor was established for pNA and DR1, those dyes could serve as external references for the unknown materials. DR1 was only considered a reliable reference at a long wavelength where the effects of two-photon fluorescence were determined to be negligible.

		Dye				
	λ (nm)	pNA	DR1	Q-KCh	Q-NH ₂	Q-BNH
$\beta_{1,ss}$	1265	11 $\pm$ 2	170 $\pm$ 20	39 $\pm$ 7	12 $\pm$ 5	23 $\pm$ 8
$\beta_{1,ss}$	1350	10 $\pm$ 2	136 $\pm$ 15	32 $\pm$ 6	10 $\pm$ 4	14 $\pm$ 7
$\beta_{2,mm}$	1265	1 $\pm$ 2	20 $\pm$ 30	10 $\pm$ 3	4 $\pm$ 1	4 $\pm$ 4
$\beta_{2,mm}$	1350	0 $\pm$ 2	0 $\pm$ 20	9 $\pm$ 2	2 $\pm$ 2	11 $\pm$ 4

TABLE II. Values of $\beta_{1,ss}$ and $\beta_{2,mm}$ (10^{-30} esu) at $\lambda=1265$ nm and 1350nm.

6. RESULTS

Previous HRS experiments with pNA showed that there are no competing effects when pumped in the near-IR [16]. It was expected, then, that the hyperpolarizability would behave according to Kleinman symmetry, and results would agree with past results for both the vector and octupolar terms [20,21]. Raw data and fits are shown in Fig. 4 which were collected at a fundamental wavelength of 1265 nm with the polarizers set as indicated. Also included in that figure are the expected results for assuming that only the Kleinman-allowed components of β are used in the fit.

The algorithm for fitting our data used the gradient search method to first determine $\beta_{1,ss}^2$ and $\beta_{3,ss}^2$ while holding all other components at zero. These two Kleinman-allowed β 's were expected to be the largest in the set of 6 numbers. Conversely, the $\beta_{1,mm}^2$ and $\beta_{2,mm}^2$ are completely Kleinman-disallowed so they were the last quantities to be fit as their Δ -coefficients had the smallest amplitudes. The coefficients of the interference terms, $\beta_{1,sm+}^2$ and $\beta_{1,sm-}^2$ were in the intermediate range. Table II lists the results for the deduced polar and quadrupolar figures of merit for all of the materials. Recall that the standards p-nitroaniline and disperse red 1 are quasi-one dimensional molecules, and the results indicate that the molecules do appear to be Kleinman symmetric with $\beta_{2,mm} = 0$ within experimental error. In fact, all of the Kleinman breaking components are zero in p-nitroaniline, as expected. A small β_{1mm} is found in disperse red 1 which may indicate some deviation from one-dimensionality. The dipolar and octupolar components are found to agree with previous values measured with EFISH and hyper-Rayleigh scattering. The error bars given reflect the uncertainties in the fitting algorithm as well as errors introduced by the finite numerical aperture of the collection system [21]. It is difficult to interpret a true uncertainty in an arbitrary fit, but the uncertainty, σ in a fitted parameter, μ , can be approximated from

$$\sigma_{\mu}^2 \approx \frac{2}{\left(\frac{\partial^2(\chi^2)}{\partial \mu^2}\right)} \quad (13)$$

where σ is taken as standard deviation of the 50 laser shot averages that make up each data point, and (χ^2) is the parameter describing the least squares fitting.

For the camphorquinones, the only Kleinman symmetry breaking components observed are the quadrupolar $\beta_{2,mm}$ terms which are listed in the table. All of the chiral monomers show nonzero $\beta_{2,mm}$ indicating quadrupolar order in the charge transfer system. In particular, Q-BNH has a significant quadrupolar ($J=2$) term at 1350nm. The results with Q-BNH are very different at the shorter wavelength, but the harmonic is just onto the linear absorption tail in that case so the results may be affected by competition with fluorescence [16]. The low available concentrations and low signals from Q-NH₂ made measurement at 1350nm difficult to reliably interpret. However, the shorter wavelength revealed a significant $\beta_{2,mm}$ as the lone Kleinman-breaking element. At the longer wavelength, the Kleinman-allowed terms are the only components which are obviously nonzero. The result is expected because Kleinman symmetry gains validity as the frequency moves away from a material resonance. In fact, the contributions from Kleinman-disallowed tensors were generally smaller at the longer wavelength for cases when fluorescence was not apparent. These results support the predictions discussed earlier (and shown in Fig. 3) that conjugated chiral molecules feature π -electron orbitals which show significant delocalization in three dimensions.

7. CONCLUSIONS

We have measured dispersion of the figure of merit, $\beta_{2,mm}$, for camphorquinone compounds for potential use in quadrupoling by hyper-Rayleigh scattering having developed a scheme for measuring the rotational invariants of β using elliptically polarized light at a 45 deg scattering angle. Measurements were carried out in the near infrared in the Kleinman symmetry breaking regime. Some deduced $\beta_{2,mm}$ contributions in the chiral dyes are comparable with the vector ($\beta_{1,ss}$) part in pNA. This indicates that axially aligned materials containing chiral centers should produce significant second-harmonic generation. Little is known about the design features for multidimensional nonlinearities, and thus further understanding of the role of chirality in second-order nonlinear optics on the molecular level could lead to synthesis of molecules with larger $\beta_{2,mm}$ contributions capable of producing large macroscopic pseudotensor second-order susceptibilities.

Because of the requirement of Kleinman symmetry breaking, use of this concept is limited to near resonant regimes. Thus, absorption losses may preclude the use of quadrupoled materials in waveguide devices. However, the less anisotropic nature of the susceptibility tensor may allow for applications requiring polarization independent response in non-waveguided bulk geometries.

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