Three-Wave Mixing in Chiral Liquids

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Second-order nonlinear optical frequency conversion in isotropic systems is only dipole allowed for sum- and difference-frequency generation in chiral media. We develop a single-center chiral model of the three-wave mixing (sum-frequency generation) nonlinearity and estimate its magnitude. We also report results from *ab initio* calculations and from three- and four-wave mixing experiments in support of the theoretical estimates. We show that the second-order susceptibility in chiral liquids is much smaller than previously thought.

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Coherent three-wave mixing in second-order nonlinear optical processes is, in the electric dipole approximation, only symmetry allowed in noncentrosymmetric media, such as crystals, poled polymers, and interfaces. However, the intrinsic symmetry breaking due to molecular chirality allows sum- and difference-frequency generation even for isotropic systems, such as liquids, gases, and optically isotropic polycrystalline materials [1,2]. Apart from their importance in chemistry and biology, chiral liquids offer attractions as nonlinear optical media, as they are self-healing, lend themselves to "wet" synthetic methods, and do not require the growth of crystals.

A high second-order nonlinearity due to chirality was reported over thirty years ago for sum-frequency generation (SFG) from chiral sugar solutions where the sum-frequency susceptibility was found to be comparable to that of low refractive index piezoelectric crystals, such as quartz (~17% of $d_{111}^{\mathrm{SiO}_2}$) [3,4].

In this Letter we present a model of the second-order nonlinear optical properties of simple chiral liquids. The estimates from the model, and the results from high-level *ab initio* computations, suggest that three-wave mixing in chiral liquids is much smaller than previously thought [1,3–5]. We report three- and four-wave mixing experiments in chiral liquids, providing a limit on the magnitude of the sum-frequency nonlinearity in support of our theoretical estimates.

First we consider the theoretical basis for three-wave mixing in chiral liquids. The observables for natural optical rotation and for electric-dipolar sum-frequency generation in a chiral liquid are both time-even pseudoscalars; however, the two phenomena are distinct. The rotational strength $\mathcal{R}$ which determines optical rotation and circular dichroism (CD) near a transition $k \leftarrow g$ is defined by $\mathcal{R} = \mathrm{Im}\{\langle g|\hat{\boldsymbol{\mu}}|k\rangle \cdot \langle k|\hat{\mathbf{m}}|g\rangle\}$ and requires a magnetic-dipole transition moment $\langle k|\hat{\mathbf{m}}|g\rangle$, whereas the sum-frequency generator is purely electric dipolar. It follows that the three-wave mixing susceptibility is a polar tensor of rank three. Its isotropic component is completely antisymmetric

$$\langle \chi^{(2)}_{\alpha\beta\gamma} \rangle = \chi^{(2)} \epsilon_{\alpha\beta\gamma}\,, \tag{1}$$

where the angular brackets denote an orientational average and α, β, and γ label Cartesian indices in the laboratory frame. $\chi^{(2)}$ is given by

$$\chi^{(2)} = \frac{N}{2\epsilon_0}\,\frac{1}{6}\,\epsilon_{\xi\eta\nu}\beta_{\xi\eta\nu} \equiv \frac{N}{2\epsilon_0}\,\overline{\beta}\,. \tag{2}$$

N is the number density, $\epsilon_{\alpha\beta\gamma}$ the unit skew-symmetric tensor, and $\beta_{\xi\eta\nu}$ a molecular hyperpolarizability. For sum-frequency generation with $\omega_3 = \omega_1 + \omega_2$ the pseudoscalar

$$\begin{aligned}\chi^{(2)}(-\omega_3;\omega_1,\omega_2) = \frac{N}{12\epsilon_0\hbar^2}\sum_{kj}(\hat{\boldsymbol{\mu}}_{gk}\cdot[\hat{\boldsymbol{\mu}}_{kj}\times\hat{\boldsymbol{\mu}}_{jg}])\{&(\tilde{\omega}_{kg}-\omega_3)^{-1}[(\tilde{\omega}_{jg}-\omega_2)^{-1}-(\tilde{\omega}_{jg}-\omega_1)^{-1}]\\ &+(\tilde{\omega}^*_{kg}+\omega_1)^{-1}[(\tilde{\omega}^*_{jg}+\omega_3)^{-1}-(\tilde{\omega}_{jg}-\omega_2)^{-1}]\\ &+(\tilde{\omega}^*_{kg}+\omega_2)^{-1}[(\tilde{\omega}_{jg}-\omega_1)^{-1}-(\tilde{\omega}^*_{jg}+\omega_3)^{-1}]\}.\end{aligned} \tag{3}$$

The summation is over all excited states k and j, and the electric-dipole transition matrix element $\langle g|\hat{\boldsymbol{\mu}}|k\rangle \equiv \hat{\boldsymbol{\mu}}_{gk}$. By allowing the transition frequency to be the complex quantity $\tilde{\omega}_{kg} \equiv \omega_{kg} - (i/2)\Gamma_{kg}$, where ω_{kg} is the real transition frequency and Γ_{kg} the width at half the maximum height of the transition from the ground state g to the upper level k, Eq. (3) is valid near resonance [6]. The pseudoscalar $\chi^{(2)}$ changes sign with the enantiomer and consequently vanishes for a racemic mixture. It is zero for second-harmonic generation, i.e., when $\omega_1 = \omega_2$. To estimate the magnitude of $\overline{\beta}$ we consider a model system. The simplest chiral molecule consists of a central atom bonded to three different, noncoplanar substituents. The bonding in such a molecule can be represented by four nondegenerate sp^3 hybrid molecular orbitals of the form:

$$(\psi_g, \psi_l, \psi_m, \psi_n) = \begin{bmatrix} 0.93 & 0.10 & 0.20 & 0.30 \\ 0.093 & -0.99 & 0.02 & 0.03 \\ 0.26 & 0 & -0.95 & -0.16 \\ 0.26 & 0 & 0.22 & -0.94 \end{bmatrix} \begin{pmatrix} s \\ p_x \\ p_y \\ p_z \end{pmatrix}, \tag{4}$$

where s, p_x, p_y, and p_z are atomic orbitals on the central atom. We take the transition energies to ψ_l, ψ_m, and ψ_n to be 45 000, 50 000, and 55 000 cm^{-1}, and transition dipole moments to be 1 D, and find $|\overline{\beta}| \sim 0.01$ a.u. [7] for the sum-frequency process $3\omega = 2\omega + \omega$, where ω corresponds to the fundamental of the ruby laser (694 nm). Even near resonance $|\overline{\beta}| < 0.1$ a.u. for linewidths of $\sim$1000 cm^{-1}. Linewidths and transition dipole moments of vibrational transitions are smaller, though here we consider only electronic transitions.

The isotropic part of the sum-frequency hyperpolarizability has also been calculated for monofluoro-oxirane (C_2H_3FO) and propylene oxide (C_3H_6O) using a sum-over-states approach [8,9]; for R-(+)-propylene oxide $\overline{\beta}$ is shown in Fig. 1. The excitation energies and dipole transition moments were evaluated for the first 120 excited states within the configuration interaction singles procedure. All calculations were performed on fully optimized geometries using GAUSSIAN94 [10] and a 6-311++G^{**} basis set. We found that $\overline{\beta}$ converged after inclusion of the first 80 excited states. To account for solvatochromic effects and electron correlation we reduced all excitation energies by $\sim$2.5 eV [11] to fit experimental UV absorption data. As required for a pseudoscalar, the value for $\overline{\beta}$ was found to be independent of the choice of Cartesian axes [11].

Both the simple molecular model and the *ab initio* calculations estimate that the sum-frequency $|\overline{\beta}|$ for small chiral molecules is at least 2 orders of magnitude smaller than that reported experimentally for arabinose (where $|\overline{\beta}|$ corresponds to $\sim$14 a.u. [3]).

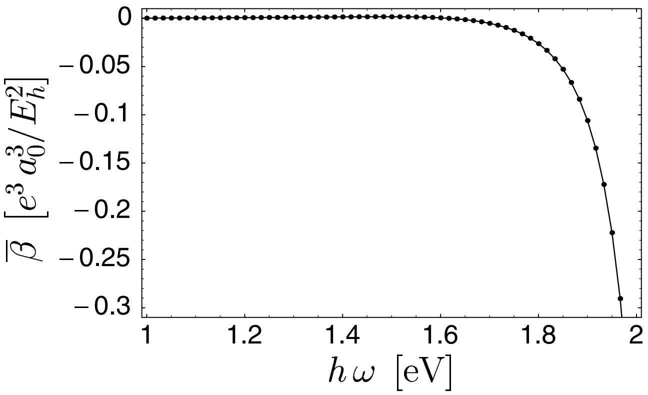

FIG. 1. $\overline{\beta}$ for R-(+)-propylene oxide for the sum-frequency process $3\omega = 2\omega + \omega$. In particular, at 1.165 eV ($\lambda = 1064$ nm) $\overline{\beta} = +0.0006$ a.u., and at 1.786 eV ($\lambda = 694$ nm) $\overline{\beta} = -0.0206$ a.u.

We now describe sum-frequency generation experiments in chiral liquids. The experimental arrangement allows, symmetry permitting, for the simultaneous observation of spatially separated three- and four-wave mixing. The four-wave mixing (FWM) process is described by a fourth rank tensor and exists for all systems. Using a standard plane-wave analysis [12] the three-wave mixing (TWM) intensity at the sum frequency is

$$I_{\omega_3}(L) = \frac{\omega_3^2}{2 n_1 n_2 n_3 \epsilon_0 c^3} I_{\omega_1} I_{\omega_2} L^2 \times |\boldsymbol{\chi}^{(2)}(-\omega_3; \omega_1, \omega_2)|^2 \mathrm{sinc}^2\left(\frac{\Delta k L}{2}\right), \tag{5}$$

where we have assumed that the waves interact over a length L. $I_{\omega_i} = \frac{1}{2} n_i c \epsilon_0 |\mathbf{E}^{\omega_i}|^2$, n_i is the refractive index at ω_i, and $\mathrm{sinc}x = (\sin x)/x$. Local field corrections have been ignored. From (5) it is seen that minimizing the phase mismatch $\mathbf{\Delta k} \rightarrow \mathbf{0}$ is necessary for efficient nonlinear frequency conversion. For most media the refractive index increases with frequency (*normal dispersion*). In isotropic media the phase-matching condition $\mathbf{\Delta k} \rightarrow \mathbf{0}$ cannot be satisfied for a TWM process, $\mathbf{k_3} - (\mathbf{k_2} + \mathbf{k_1}) = \mathbf{\Delta k}$, except for a small frequency range near resonance (*anomalous dispersion*). The scattering power at the sum frequency is proportional to the square of the polarization, $|P_\alpha^{\omega_3}|^2$, so SFG experiments do not distinguish between optical isomers. The polarization at ω_3 is given by

$$P_\alpha^{\omega_3} = \epsilon_0 \chi^{(2)} \epsilon_{\alpha\beta\gamma} E_\beta^{\omega_1} E_\gamma^{\omega_2}. \tag{6}$$

It follows that the electric field vectors of the three beams at ω_1, ω_2, and ω_3 need to span the x, y, and z axes of a Cartesian frame. If both input beams are plane polarized in the plane of incidence (p polarized) then the sum-frequency signal will be polarized perpendicular to that plane (s polarized). Should one of the input beams be p polarized and the other s polarized then the signal will be p polarized. The former arrangement is expected to yield the stronger signal. For simplicity we ignore the rotation of the plane of polarization due to optical activity and assume the light is linearly polarized in the chiral liquid. SFG is not allowed when both input beams have their electric field vector perpendicular to the plane of incidence. Equation (6) would suggest an arrangement where the two incident beams make a right angle. However, momentum conservation favors a collinear beam geometry. The optimum angle to observe SFG in an optically active fluid is thus a balance of these two requirements and can be determined from (5) by considering

$$\eta_{\mathrm{SFG}} = \sin^2\varphi L^2 \mathrm{sinc}^2\left(\frac{\Delta k L}{2}\right), \tag{7}$$

where the factor $\sin^2\varphi$ reflects the requirement for orthogonal electric field vector components. Figure 2 shows the

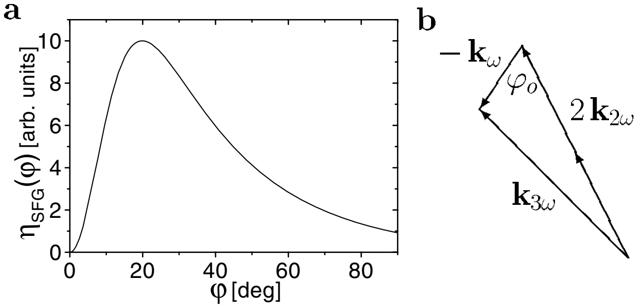

FIG. 2. (a) Dependence of the noncollinear sum-frequency signal on the angle between the incident beams (at 1064 and 532 nm, respectively). We use the refractive index data for arabinose and a typical interaction length L of 1 mm $\gg l_c$, with a coherence length $l_c \sim 5\ \mu$m. (b) Phase-matching triangle for the FWM process $3\omega = 2\omega + 2\omega - \omega$ (not to scale).

envelope of η_{SFG} as a function of the angle between the incident beams.

We use a Spectra-Physics 3800RA optical regenerative amplifier that is seeded by a mode locked (76 MHz) Antares 90 ps Nd:YAG laser. Frequency doubling in a beta-barium borate (BBO) crystal yields $\sim$100 μJ at 532 nm and $\sim$300 μJ at 1064 nm at a repetition rate of 1 kHz. We use a photomultiplier tube (PMT) and either detect in a photon-counting mode with a Stanford SR400 dual channel gated photon counter or by using a SR510 analog lock-in amplifier. Bandpass filters with combined optical density OD > 20 at 532 nm and OD > 12 at 266 nm ensure that no light from the 2ω beam and its second harmonic is detected.

Figure 3 shows a schematic of the experimental arrangement. The ω and 2ω beams are incident parallel to the optic axis on an achromatic doublet ($f = 15.2$ cm) and cross in the focus of the lens, which ensures spatial overlap. Temporal overlap of the input beams is accomplished with a delay stage. By translating a mirror (TM) the separation between the two incident beams and hence the angle φ between the beams in the focal region can be varied. The beam waists in the focus of the doublet were $\sim$150 μm wide. The PMT is mounted on a rotating arm such that it can be scanned over an arc with the center in the liquid cell. Momentum conservation requires that the 3ω waves propagate in the plane defined by the input beams. Using suitable filters and a mask in front of the PMT housing we ensure that the input beams and the arc the PMT opening describes lie in the same plane.

Whereas it is not possible to phase match TWM in isotropic media for normal dispersion, the FWM process $3\omega = 2\omega + 2\omega - \omega$ can be vector phase matched $\Delta\mathbf{k} = \mathbf{0}$, as shown in Fig. 2. The four-wave mixing can be likened to the nonresonant electronic contribution in coherent anti-Stokes Raman scattering. The phase-matching angle φ_0 is typically of the order of 10° for simple liquids ($\varphi_0 = 11.5°$ for 2.46 M aqueous solutions of arabinose) using the fundamental (1064 nm) of a Nd:YAG laser. If no other nonlinear mixing processes compete with the FWM, and if there is no absorption or depletion of the pumps, then the FWM signal depends quadratically on the intensity of the 2ω beam and linearly on the intensity of the ω beam. Figure 4 shows that these approximations are satisfied in the existing experimental conditions. The same intensity dependence was observed in chiral solutions.

We choose the angle φ between the input beams such that the expected sum-frequency signal is maximized as suggested by Fig. 2 while still allowing for FWM. The latter demonstrates that—provided appropriate beam polarizations are chosen and that the optically active solutions have an appreciable sum-frequency susceptibility—*the right experimental conditions exist for the detection of any sum-frequency signal from the chiral liquid.*

Replacing the liquid sample by a quartz crystal we obtain a strong SFG signal (Fig. 5). Rentzepis *et al.* report a SFG signal from 2.46 M *d*- and *l*-arabinose solutions that is $\sim$250 times weaker than that obtained from the quartz reference [3]. In our experimental arrangement any sum-frequency signal from the chiral solutions [13] was at least 10^5 times weaker than that obtained from our quartz reference (2 mm thick z-cut disk). SFG from the chiral solution is expected at a similar PMT angle as that from the crystal quartz. In some scans we did observe a small peak in this region. However, the intensity of these peaks depended quadratically on that of the 2ω beam and did

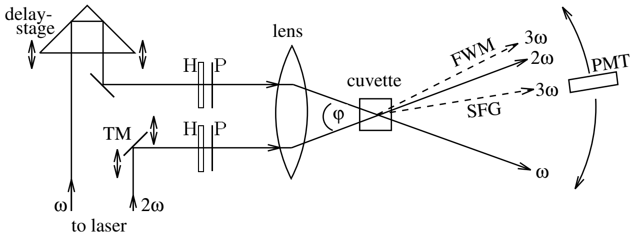

FIG. 3. Experimental arrangement for the simultaneous observation of FWM and SFG. The optical elements shown include a mirror mounted on a translation stage (TM), a half-wave retarder (H), polarizers (P), and a photomultiplier tube (PMT) mounted on a rotating arm. The ω and 2ω make an angle φ in the cuvette.

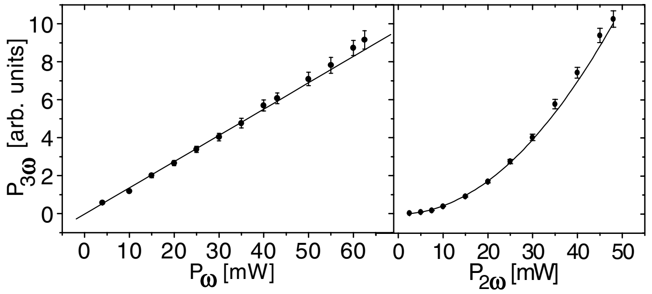

FIG. 4. Dependence of the FWM signal $P_{3\omega}(3\omega = 2\omega + 2\omega - \omega)$ on the pump beam powers P_ω and $P_{2\omega}$ (here measured in CCl_4). The solid lines are linear and quadratic functions, respectively, fitted to the data.

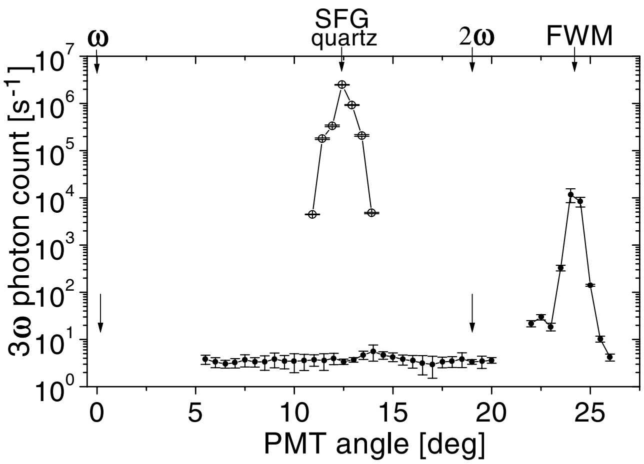

FIG. 5. Angular distribution of 3ω signal in 2.46 M aqueous *l*-arabinose (closed circles). Signal from reference quartz shown with open circles. See text for particulars.

not disappear after racemization of the solution. We attributed these peaks to higher-order Raman effects generated in the focus of the 2ω beam [14]. We did not observe any three-wave mixing in pinene or solutions of arabinose (see Fig. 5) within the sensitivity of the experiment, and thus deduce that $|\overline{\beta}| < 0.8$ a.u. for SFG at 355 nm.

Shkurinov *et al.* [5] observed second-harmonic generation in a five-wave mixing process [15] ($2\omega = \omega + \omega + \omega - \omega$) in 2.46 M solutions of arabinose. In their Letter they report having seen an intense sum-frequency signal ($3\omega = 2\omega + \omega$) in a preliminary set of experiments. The angle between their input beams in the solution was 15.5°. We have demonstrated that the fundamental and its harmonic can give rise to a signal at 3ω via a FWM process with a phase-matching angle $\varphi_0 \approx 12°$. In Fig. 5 it is seen that even with a phase mismatch of several degrees a strong FWM signal is observed.

The wavelengths used in the original SFG experiment (694, 347, and 231 nm) [3] are shorter than in the above experiments. Since $\overline{\beta}$ is enhanced by dispersion, we conducted a series of SFG experiments using the fundamental (1064 nm) and third harmonic (355 nm) of the Nd:YAG laser. Here the FWM mixing signal is not at the same wavelength as the expected sum-frequency signal, and temporal overlap of the input beams was thus confirmed by observing SFG from a thin BBO crystal. We spatially overlapped the input beams using a 200 μm pinhole suspended in the liquid. Again, we did not observe any TWM within the sensitivity of our arrangement. We conclude that $|\overline{\beta}| < 1$ a.u. for SFG at 266 nm in 2.46 M optically active solutions of arabinose.

In this Letter we have estimated the isotropic component of $\beta_{\xi\eta\nu}$ that may give rise to SFG in a chiral liquid and showed that it is much smaller than previously thought. The strong signals reported in [3] might have arisen from supramolecular chiral clusters [16], and the signal at 3ω in [5] was probably due to four-wave mixing.

The sum-frequency signal should be larger near resonance and under phase-matched conditions. Phase matching can be achieved using the anomalous dispersion of a chiral molecule or by adding a suitable dye with a narrow absorption band lying in the ω_1, ω_2, and ω_3 frequency range [1,17].

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