

Second Harmonic Generation in an Optically Active Liquid: Experimental Observation of a Fourth-Order Optical Nonlinearity Due to Molecular Chirality

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(Received 21 October 1992)

Molecular left-right asymmetry is an origin of nonvanishing even-order optical nonlinear susceptibilities of nonracemic solutions of chiral molecules. Though second harmonic generation (SHG) due to quadratic dipolar nonlinearity is still symmetry forbidden in optically active liquids yet we have succeeded in experimental observation, for the first time, of noncollinear SHG due to a five-wave mixing process according to a scheme $2\omega = 3\omega - \omega$, governed by a fourth-order susceptibility tensor $\chi^{(4)D}$. The SHG signal is found to be well collimated and quasi-phase-matched; it shows theoretically predicted polarization, intensity, spectral, and temporal properties.

PACS numbers: 42.65.Ky, 42.50.Md, 42.65.Hw, 42.65.Vh

A real challenge for scientists is to understand the origin of the exceptional chiral purity of living nature [1–3]. Nonlinear optical methods, together with others, can provide needed instrumentation for the investigation of this intriguing phenomenon [4–6].

In a centrosymmetrical media [for instance, in a racemic water solution of left-right asymmetric (chiral) molecules] even-order optical effects [such as second harmonic generation (SHG)] are dipolar forbidden for symmetry reasons [7]. SHG is possible in such substances via magnetic dipole or electric quadrupolar effects, or it may be caused by a dipolar fifth-order nonlinearity. These effects are small, phase-mismatched, and critically dependent on the presence of elliptically polarized light [8]. Alternatively, they demand the introduction of an external second-harmonic signal which perturbs the inversion symmetry of the liquid [9].

If only one of the left-right isomers of chiral molecules is dominant in a solution, thus breaking the center of inversion of the isotropic liquid, the even-order dipolar nonlinearities are allowed [4,10,11]. Rentzepis, Giordmaine, and Wecht [12] have succeeded in the first experimental observation of a second-order dipolar nonlinear effect in a nonracemic solution of chiral molecules, an optical sum-frequency generation in a noncollinear, phase-mismatched geometry. However, dipolar SHG is still forbidden in such liquids because of the permutation symmetry [10,11]. Some time ago one of us (N.I.K.) showed that the higher-order dipolar nonlinearity (namely, the fourth-order one) does allow the SHG of linearly polarized beams to occur in a nonracemic isotropic solution of chiral molecules, in a phase-matched noncollinear scheme [4,5].

Here we report on the first experimental observation of this phenomenon in an optically active water solution of *d*- and *l*-arabinose.

The phase-matched five-wave mixing process in a noncentrosymmetric liquid can be symbolically depicted as $2\omega = \omega + \omega + \omega - \omega$ (Fig. 1 shows the beam arrangement for this process), where the first three (positive) ω 's on

the right-hand side correspond to a laser beam with the wave vector \mathbf{k} and the frequency ω (beam 1), and the latter (negative) ω represents photons from the second beam of the same fundamental frequency and with wave vector \mathbf{k}' (beam 2) crossing the first beam at a phase-matching angle α .

The vector of light-induced polarization of the liquid, according to Bloembergen [7], can be represented as a sum of dipole (D) and quadrupole (Q) (magnetic dipole) contributions,

$$P_i = P_i^D + P_i^Q, \quad (1)$$

where both D and Q terms contain linear (L) and nonlinear (NL) (with respect to laser field amplitudes) parts:

$$P_i^{D,Q} = P_i^{D,Q(L)} + P_i^{D,Q(NL)}, \quad (2)$$

where

$$P_i^{D(L)} = \chi_{ij}^{(1)D} E_j, \quad (3)$$

$$P_i^{D(NL)} = \chi_{ijk}^{(2)D} E_j E_k + \chi_{ijkl}^{(3)D} E_j E_k E_l + \chi_{ijklm}^{(4)D} E_j E_k E_l E_m + \dots,$$

$$P_i^{Q(L,NL)} = -\nabla_j Q_{ij}^{(L,NL)}, \quad Q_{ij}^{(L)} = \chi_{ijk}^{(1)Q} E_k, \quad (4)$$

$$Q_{ij}^{(NL)} = \chi_{ijkl}^{(2)Q} E_k E_l + \chi_{ijklm}^{(3)Q} E_k E_l E_m + \dots$$

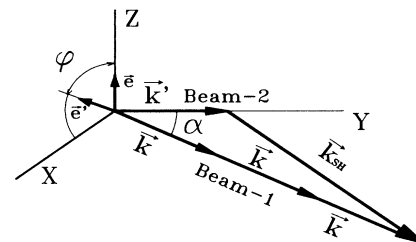


FIG. 1. Beam arrangement for the five-wave mixing process $2\omega = \omega + \omega + \omega - \omega$. All wave vectors of interacting beams lie on the X - Y plane.

are, respectively, components of the vectors of dipole and quadrupole polarizations, arising in each unit cell in the volume of the liquid under the action of optical field. Here and below repeated indices are summed over from 1 to 3; E_j , E_k , etc., are components of electric field vector of the incident light wave.

The last term on the right-hand side of Eq. (3) is responsible for the effect under study:

$$P_i^{(4)D}(2\omega) = \chi_{ijklm}^{(4)D}(2\omega; \omega, \omega, \omega, -\omega') E_j E_k E_l E_m^* \quad (5)$$

It can be easily shown (see Ref. [4]) that, for a symmetry reason, the fifth-rank tensor $\chi_{ijklm}^{(4)D}$ in an isotropic liquid has, in general, only 60 nonvanishing components out of 243, only 6 of them being independent. They are as follows:

$$\chi_{23111}, \chi_{31121}, \chi_{11123}, \chi_{13112}, \chi_{13121}, \chi_{31112}.$$

The direct summation of Eq. (5) leads to the following covariant expression for the vector $\mathbf{P}^{(4)D}(2\omega)$ responsible for the SHG process:

$$\mathbf{P}^{(4)}(2\omega) = 4A^3 A'^* \chi_{31112}^{(4)D}(2\omega; \omega, \omega, \omega, -\omega) (\mathbf{e}\mathbf{e}) [\mathbf{e}, \mathbf{e}'^*] \quad (6)$$

Here A , A' , and \mathbf{e}, \mathbf{e}' are complex amplitudes and unit polarization vectors of the two beams of fundamental frequency (ω), to be further cited as $3\mathbf{k}$ and \mathbf{k}' , respectively. Square brackets stand for vectorial product, and parentheses for scalar product of vectors inside; factor 4 reflects the partial degeneracy among frequency arguments of the fourth-order nonlinear susceptibility tensor components $\chi_{31112}^{(4)D}$. As is easily seen from Eq. (6), the SHG process vanishes when the $3\mathbf{k}$ beam is circularly polarized.

A simple numerical estimate can be made for the peak power of the SHG signal in the approximation of the focused linearly polarized Gaussian beams, interacting along the phase-matching direction [4,5]:

$$P_{SH} \approx \pi w_0^2 I_{SH} \approx \frac{\pi^2 w_0^2 \omega^2}{2c^2 n} 4w_0^2 |\mathbf{P}^{(4)}(2\omega)|^2 \approx \frac{2^{15} \pi^4 |\chi^{(4)D}|^2 P^3 P'}{\lambda^2 c^3 n_{2\omega}^4 n_\omega w_0^4} \quad (7)$$

Here w_0 are the radii of the beam waists of focused beams $3\mathbf{k}, \mathbf{k}'$, which are assumed to be the same for both interacting waves, with peak powers P, P' , crossing inside the liquid with refracting indexes $n_{2\omega}, n_\omega$; c is the speed of light in vacuum; I_{SH} stands for the intensity of the second harmonic wave; and $\lambda = 2\pi c/\omega$.

An order-of-magnitude estimate for the $|\chi^{(4)}|$ can be extracted from the experiments [13] to be in the order of 10^{-21} esu or less. Taking realistic parameters of our experimental setup (see below) from Eq. (7) we get for the average power $P_{SH} \approx 3 \times 10^{-7}$ esu, which corresponds to approximately 10^3 photons per second, which is enough for reliable detection.

A water solution of arabinose was used in our experiments [14], as it was in those of Rentzepis, Giordmaine, and Wecht [12], because of its high specific rotation and availability of its d and l isomers. Solutions were prepared at a concentration of 1 part arabinose to 2 parts water, and had molarity $M=2.46$ and refractive indexes 1.375, 1.394, and 1.415 at 532, 355, and 266 nm, respectively. Our solutions were filtered to ensure an equilibrium distribution of different isomers of arabinose introduced by mutarotation. All measurements were made at least a few hours after the preparation of the solutions. To avoid the accumulation of the racemization of the arabinose solution under the laser irradiation we used a magnetic mixer, so that the substance in the probed volume could be refreshed for each successive excitation pulse train in the focal area of the beams.

Experiments were carried out using an original picosecond spectrometer similar to that described in Ref. [15]. The actively mode-locked cw-pumped neodymium-doped yttrium aluminum garnet ($\text{Nd}^{3+}:\text{YAG}$) laser delivered the sequence of pulse trains (each containing 30–35 pulses of 100 ps duration FWHM) at 1064 nm at a repetition rate of 1.0 kHz. The output of the laser with an average power of 5 W was converted into the green radiation (532 nm) in two potassium-titanyl-phosphate (KTP) crystals. For SHG we used two green beams of different intensity. The more intense laser beam 1 (with the average power 100 mW) travels through an optical delay line and is used as a $3\mathbf{k}$ wave in the SHG process. Less intense beam 2 (with the average power 80 mW) is focused directly into the sample. The beam waist diameters inside the sample were 120 and 100 μm , respectively. After focusing with separate 8 cm lenses, the beams $3\mathbf{k}, \mathbf{k}'$ were made to intersect at a phase-matching angle $\alpha=15.5^\circ$ in a solution of d - and/or l -arabinose. Beam 1 was polarized vertically and fixed. Beam 2 polarization was varied using a Fresnel rotator. After spatial separation, the SHG emission passed through the single monochromator was detected by a fast photomultiplier tube with microchannel plates. A time-correlated single-photon counting technique was used with the resolution of about 150 ps.

In a preliminary set of experiments, we have observed a three-wave process, $\omega_S = \omega_1 + \omega_2$, first reported by Rentzepis, Giordmaine, and Wecht [12], in a 2.4M water solution of l - and d -arabinose and in a 1.0M Pyridine solution of α -cyclodextrine. We have succeeded in detecting a pretty intense signal at $\lambda=355$ nm [ω_1 stands for a fundamental frequency of $\text{Nd}^{3+}:\text{YAG}$ laser (1.064 μm) and ω_2 stands for its second harmonic (0.532 μm)]. A rough estimate of the $|\chi^{(2)}|$ value of α -cyclodextrine gives a value 4 times greater than that of d -arabinose.

In a phase-matched configuration for the five-wave mixing process we have observed, for the first time, second harmonic generation with wavelength $\lambda=266$ nm and with theoretically predicted time characteristic behavior (see Fig. 2).

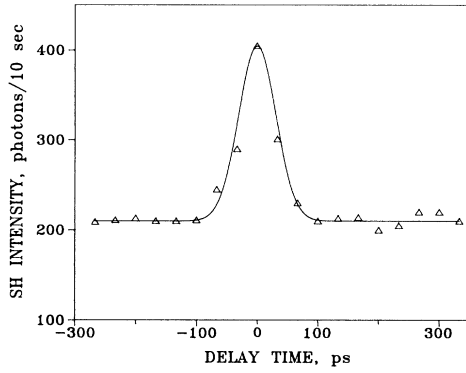


FIG. 2. Time cross-correlation function of SH signal vs the beam 1 delay. The polarizations of the interacting waves are linear and perpendicular to one another. The solid line is the Gaussian fitting with pulse duration $\tau_p = 110$ ps.

A critical test for proving the origin of this well collimated coherent signal was its observed polarization dependence. Figure 3 shows the variation of SH signal from a 2.4M solution of *l*-arabinose with the variation of the angle ϕ between the polarization planes of \mathbf{k}' and $3\mathbf{k}$ beams. It is clearly seen from Fig. 3 (curve *a*) that $I_{SH}(\phi)$ varies in a manner predicted by Eq. (6) (curve *b*). When the equal amount of *d*-arabinose was added to the solution, the polarization dependence became flat (Fig. 3, curve *c*). The intensity of the observed signal was consistent with the estimated above.

However, some residual SH signal was still present after the racemization of the solution. It was coherent, well collimated, dependent on the presence of both beams but almost independent of the orientation of polarization vectors of interacting beams. In a neat water (without solvents) this signal was negligible.

We believe that this residual SHG signal is due to electric quadrupole interaction of $3\mathbf{k}, \mathbf{k}'$ beams in a racemic mixture of *d*- and *l*-arabinose. Indeed, the covariant vector of quadrupole second-order polarization can be written in the following form [4], following from Eq. (4):

$$\mathbf{P}^{(2)Q}(2\omega) = i2AA'\{\chi_{1122}^{(2)Q}(\mathbf{k} + \mathbf{k}')(\mathbf{e}\mathbf{e}^*) + \chi_{1212}^{(2)Q}[\mathbf{e}^*(\mathbf{k}\mathbf{e}') + \mathbf{e}(\mathbf{k}\mathbf{e}^*)]\}, \quad (8)$$

where quadrupole quadratic optical susceptibility tensor $\chi_{1212}^{(2)Q}$ is defined in Eq. (4).

In a medium with normal dispersion (as it is in our case), this effect is phase mismatched, in the direction $(\mathbf{k} + \mathbf{k}')$ phase mismatch being minimal. Still, along the direction of phase-matched dipolar SHG, the nonlinear source $\mathbf{P}^{(2)Q}$ can give some contribution determined by its normal component. In our experimental situation, the scalar product of \mathbf{k}' and \mathbf{e} is zero, and that of \mathbf{k}, \mathbf{e}' gives $(\mathbf{k}, \mathbf{e}') = k \sin \alpha \sin \phi$. The normal component of the vector, following $\chi_{1122}^{(2)Q}$, is proportional to $k \sin \alpha \cos \phi$. The square

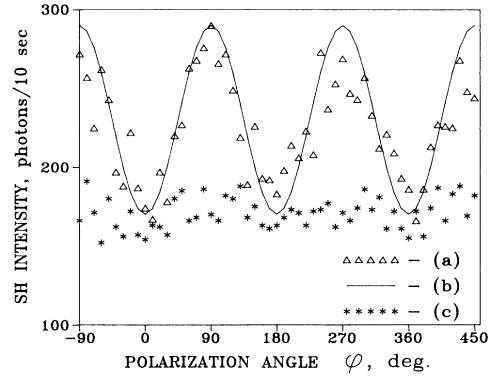


FIG. 3. SH signal amplitude function of beam 2 polarization angle ϕ (curve *a*). Beam 1 is polarized vertically. The fitting curve *b* is derived from theoretical expression (6): $I_{SH}(\phi) = I_{\text{background}} + I_0 \sin^2 \phi$. Polarization dependence from *dl* solution was unobservable (curve *c*).

of absolute value of the projection of $\mathbf{P}^{(2)Q}$ on a plane, normal to the direction of \mathbf{k}_{SH} , which determines the intensity of the residual SH signal, is

$$|\mathbf{P}^{(2)Q}| \approx 4k^2 |AA'|^2 \sin^2 \alpha \{ |\chi_{1122}^{(2)Q}|^2 \cos^2 \phi + |\chi_{1212}^{(2)Q}|^2 \sin^2 \phi \} \approx \frac{4}{3} k^2 \sin^2 \alpha |AA'|^2 |\chi_{1111}^{(2)Q}|^2, \quad (9)$$

being independent on the angle ϕ between \mathbf{e} and \mathbf{e}' (here we take, in accordance with Kleinman's rule [7], $\chi_{1122}^{(2)Q} \approx \chi_{1212}^{(2)Q} \approx \frac{1}{3} \chi_{1111}^{(2)Q}$), in full accordance with the experiment.

In conclusion, we have observed, for the first time, the five-wave mixing process of second harmonic generation, $2\omega = \omega + \omega + \omega - \omega$, in a nonracemic water solution of *d*- and *l*-arabinose. The signal demonstrates predicted polarization, intensity, spectral, and time characteristics. An approximated value of $|\chi^{(4)}|$ can be extracted from our experiments according to Eq. (7). Taking the parameters of the beams used in our experiments from Eq. (7) we get an order-of-magnitude value for $|\chi^{(4)}| \approx 10^{-23}$ esu. The coherent background signal of the same frequency is observed which demonstrates no polarization dependence and insensitivity to the state of chirality of the solution, being determined, predominantly, by a three-wave phase-mismatched quadrupole nonlinearity.

We wish to thank Professor A. K. Yatsemirskii (Chemical Department of MSU) for providing the samples, Dr. A. Yu. Chikishev, Dr. V. A. Makarov, Dr. V. G. Tunkin, and Dr. J. Yaver, for valuable discussions.

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