Experimental observation of a five-wave nonlinear optical process in an optically active liquid: a second-harmonic generation which is sensitive to the mirror asymmetry of biomolecules

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The generation of a noncollinear second harmonic in the five-wave process $2\omega=\omega+\omega+\omega-\omega$ in an optically active liquid has been studied experimentally. An estimate $|\chi^{(4)D}|\approx 10^{-23}$ esu is found for an *l*-arabinose solution. Some new spectroscopic schemes based on measurements of the fourth-order nonlinear susceptibility $\chi^{(4)D}$ are analyzed for the case of isotropic media lacking an inversion center.

1. In this letter we report the results of the first experimental observation of a nonlinear five-wave optical process in which a second harmonic is generated on the basis of the fourth-order dipole nonlinearity in a $2\omega=\omega+\omega+\omega-\omega$ mixing in an optically active isotropic liquid (aqueous solutions of the sugars *d*- and *l*-arabinose). This effect is sensitive to the right-left mirror asymmetry of the molecules in the solution. It does not occur in a racemic solution of chiral molecules (i.e., in a solution which contains equal concentrations of the two mirror components of the biomolecules).

2. The macroscopic symmetry of a continuous medium imposes limitations on the nature of the nonlinear processes which can occur.[1,2] For example, second-harmonic generation and other processes which involve dipole nonlinear susceptibilities of second and higher even orders are forbidden in homogeneous, isotropic media without an inversion center.[3] These effects arise only when quadrupole and magnetic-dipole nonlinear susceptibilities are taken into account. If the solution is dominated by one of the two mirror molecular isomers, however, an isotropic medium lacks an inversion center, and nonlinear dipole optical susceptibilities of even orders are no longer zero.

A first experiment to observe an effect associated with a nonlinear dipole susceptibility of second order in a nonracemic solution of chiral molecules was described by Rentzepis *et al.*[4] They studied a noncollinear, unmatched generation of the sum frequency.[5]

It has been shown previously[6,7] that nonzero dipole nonlinearities of higher orders make possible some new spectroscopic processes which are sensitive to the mirror asymmetry of the medium of interest. In the present letter we describe two experimental schemes for five-wave mixing: second-harmonic generation ($2\omega=3\omega-\omega$; the completely frequency-degenerate case) and difference-frequency generation ($\omega_3=3\omega_1-\omega_2$; the partially degenerate case). We have also carried out an experimental study of one of these processes: the second-harmonic generation.

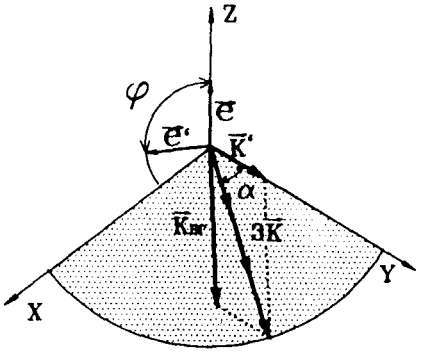

FIG. 1. Vector diagram of the second-harmonic generation $2\omega=\omega+\omega+\omega-\omega$.

In the partially frequency-degenerate case, the matched five-wave mixing in a noncentrally symmetric solution can be described by $\omega_3=\omega_1+\omega_1+\omega_1-\omega_2$. In the completely degenerate (and simplest) case of second-harmonic generation we would have $\omega_1=\omega_2=\omega$. The phase matching is achieved at an angle α between the beams. Figure 1 shows the experimental geometry (including the polarizations of the beams).

The effect which we are considering here corresponds to the following fourth-order nonlinear dipole polarization:

$$P_i^{(4)D}(2\omega)=\chi_{ijklm}^{(4)D}(2\omega;\omega,\omega,\omega,-\omega')E_jE_kE_lE_m^{*\prime}, \tag{1}$$

where $\chi_{ijklm}^{(r)D}$ are the components of the fourth-order nonlinear dipole susceptibility tensor.

A direct summation in (1) leads to the following invariant expression for the vector $\mathbf{P}^{(4)D}(2\omega)$, which is responsible for the second-harmonic generation:

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

Here A,A' and $\mathbf{e},\mathbf{e}'$ are the complex amplitudes and polarization unit vectors of the two beams at the fundamental frequency (ω); we will refer to these beams below as the $3\mathbf{k}$ and $\mathbf{k}'$ beams, respectively. Square brackets mean the vector product, while parentheses mean the scalar product. The factor of 4 corresponds to the case of complete frequency degeneracy.

3. We can find a crude numerical estimate of the peak power of the second-harmonic signal in the approximation of focused Gaussian beams which are interacting over the phase-matching distance:[6,7]

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

Here w_0 are the waist radii of the focused beams $3\mathbf{k}$ and $\mathbf{k}'$, which are assumed to be the same for the two interacting waves, P and P' are the peak power levels of the waves, $n_{2\omega}$ and n_ω are the refractive indices, c is the velocity of light in vacuum, and I_{SH} is the intensity of the second-harmonic wave.

Working from experimental data on a lithium formate crystal,[8] we can suggest an order-of-magnitude estimate of the nonlinear susceptibility: $|\chi^{(4)}| \approx 10^{-21}$ esu. Using the experimental conditions specified below, we find the estimate $\approx 3 \times 10^{-14}$ W for the average power of the second-harmonic signal. This power level corresponds to about 10^3 photons per second; this level might be completely sufficient for reliable detection.

4. Since there is a large linear optical rotation, and since there are two natural mirror isomers, we used aqueous solutions of *d*- and *l*-arabinose in our experiments, as in the experiments described by Rentzepis *et al.*[4] These solutions were prepared by a standard procedure[9] with a molarity $M=2.46$ (1 part of arabinose per 2 parts of water), with refractive indices of 1.375, 1.394, and 1.415 at wavelengths of 532, 355, and 266 nm, respectively. The solutions were filtered. All measurements were carried out at least 2 h after the solutions were prepared, so that there would be an equilibrium distribution of the different isomers of arabinose in the solution.[9] To prevent racemization of the solution by the laser light, we used a magnetic stirrer.

The experiments on second-harmonic generation were carried out on a picosecond spectrometer[10] in which the laser oscillator was a cw-pumped Nd:YAG laser with acoustooptic mode locking and Q switching (the wavelength was 1.064 μm, the pulse length was 100 ps, the pulse repetition frequency was 1 kHz, and the average power was 5 W). Conversion into the second harmonic ($\lambda=0.532$ nm) occurred in two KTP crystals, so that two independent channels, with power levels of 100 and 80 mW, would be formed [these were beam 1 ($3\mathbf{k}$) and beam 2 ($\mathbf{k}'$), respectively]. The beams were focused by two lenses with a focal length of 80 mm into the solution of *d*-, *l*, or *dl*-arabinose at the phase-matching angle $\alpha=15.5°$ between the $3\mathbf{k}$ and $\mathbf{k}'$ beams. The waist diameters of the beams in the cell were 120 and 100 μm, respectively. The polarization of the first beam was held vertical; that of the second beam could be varied by means of a double Fresnel rhombus. An optical delay was placed in beam 1 for measurements of the autocorrelation function signal. After spatial and spectral filtering, the second-harmonic light which was generated was detected by a time-correlated photon-counting system with a resolving time of 150 ps.

5. Our first step was to reproduce the experiments on the three-wave mixing $\omega_S=\omega_1+\omega_2$ which were first described in Ref. 4. In addition to the aqueous solutions of *l*- and *d*-arabinose which we mentioned above, we studied a solution of α-cyclodextrin in pyridine (1.0 M). We observed a fairly intense signal at the wavelength $\lambda=355$ nm [ω_1 is the fundamental frequency of the Nd:YAG laser (1.064 μm), and ω_2 is its second harmonic (0.532 μm)]. Working from the estimate of $\chi^{(2)D}$ from Ref. 4, we estimate that $|\chi^{(2)D}|$ for α-cyclodextrin is four times that for *d*-arabinose.

In a next series of experiments on five-wave mixing we observed a matched second harmonic with a wavelength $\lambda=266$ nm and with the time dependence predicted theoretically (Fig. 2).

To determine the nature of the collimated second-harmonic signal, we studied the signal intensity as a function of the polarization of the $\mathbf{k}'$ beam. Figure 3a shows the second-harmonic signal versus the angle φ, between the polarization planes of the $\mathbf{k}'$ and $3\mathbf{k}$ beams, for a 2.4 M solution of *l*-arabinose. Obviously, the $I_{SH}(\varphi)$ (curve *a*)

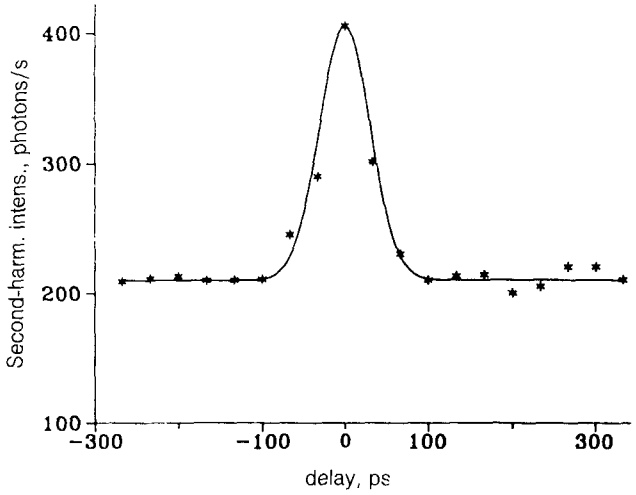

FIG. 2. Autocorrelation function of the second-harmonic signal. The 3**k** and **k**′ beams are linearly polarized in perpendicular planes. The solid line corresponds to a Gaussian profile.

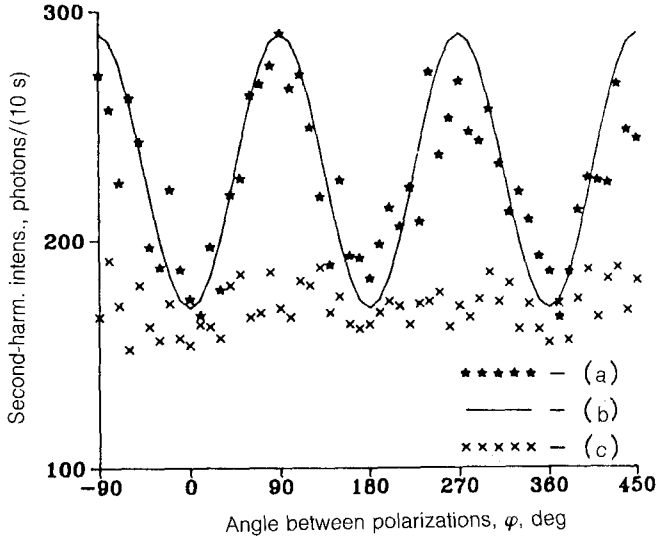

FIG. 3. a—Amplitude of the second-harmonic signal as a function of φ, the angle between the polarization planes of the 3**k** and **k**′ beams (the 3**k** beam is polarized vertically); b—theoretical signal amplitude [Eq. (2)]; c—polarization dependence of the second-harmonic signal in the case of a racemic solution.

agrees with (2) (Fig. 3b). When an equal amount of *d*-arabinose is added to the solution of *l*-arabinose, the polarization dependence disappears (Fig. 3c).

Figure 3c also shows a signal which persists even after the racemization of the solution. This signal is coherent, it is well collimated, it has the frequency of the second harmonic, and it depends on the presence of both beams. On the other hand, it is essentially independent of the angle between the polarization planes of the interacting beams.

6. This residual signal is tentatively attributed to an electric-quadrupole interaction of the $3\mathbf{k}$ and $\mathbf{k}'$ waves in the racemic solution of *d*- and *l*-arabinose. This conclusion can be drawn from the circumstance that the invariant vector of the second-order quadrupole polarization can be written as follows:[6]

$$\mathbf{P}^{(2)Q}(2\omega)=i2AA'[\chi_{1122}^{(2)Q}(\mathbf{k}+\mathbf{k}')(\mathbf{ee}')+\chi_{1212}^{(2)Q}(\mathbf{e}'(\mathbf{k}'\mathbf{e})+\mathbf{e}(\mathbf{ke}'))], \tag{4}$$

where $\chi_{1122}^{(2)Q}$ and $\chi_{1212}^{(2)Q}$ are components of the quadratic optical nonlinearity tensor of the quadrupole type.

In a medium with a normal dispersion (as in the case at hand) this effect does not have a phase-matching direction, but in the matching direction for generation of the dipole second harmonic the nonlinear source $\mathbf{P}^{(2)Q}$ may make a contribution governed by its normal component. The square of the absolute value of the projection of $\mathbf{P}^{(2)Q}$ onto the plane normal to the $\mathbf{k}_{SH}$ direction, which determines the intensity of the residual second-harmonic signal is

$$\begin{aligned}|\mathbf{P}^{(2)Q}| &\approx 4k^2|AA'|^2\sin^2\alpha\{|\chi_{1122}^{(2)Q}|^2\cos^2\varphi+|\chi_{1212}^{(2)Q}|^2\sin^2\varphi\}\\ &\approx\frac{4}{9}k^2\sin^2\alpha|AA'|^2|\chi_{1111}^{(2)Q}|^2.\end{aligned} \tag{5}$$

It is independent of φ, the angle between $\mathbf{e}$ and $\mathbf{e}'$ (in accordance with Kleinman's conjecture, we are assuming $\chi_{1122}^{(2)Q}\approx\chi_{1212}^{(2)Q}\approx\frac{1}{3}\chi_{1111}^{(2)Q}$ here), in total agreement with experiment.

7. In summary, second-harmonic generation in the five-wave mixing $2\omega=\omega+\omega+\omega-\omega$ in a nonracemic aqueous solution of *l*- and *d*-arabinose has been studied in these experiments. The intensity of the signal and its polarization, temporal, and spatial characteristics agree with theoretical predictions. [We can find an order-of-magnitude estimate of $|\chi^{(4)}|$ from (3). Taking into account the characteristics of the beams used in these experiments, we find $|\chi^{(4)D}|\approx 10^{-23}$ esu from (3).] We have also observed a coherent background signal at the same frequency. The latter signal does not depend on the polarization state of the interacting beams or on the chirality of the solution. It has been suggested that this signal is due to a three-wave mixing on the basis of a quadrupole nonlinearity in the absence of phase matching.

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