Picosecond Light-Induced Noncentrosymmetry in a Dye Solution

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By means of a phase-conjugation experiment by nondegenerate six-wave mixing, we demonstrate a transient $\chi^{(2)}$ grating induced by a nonzero E^3 time average in a solution of noncentrosymmetric dye molecules. The origin of the induced phase-matched second-harmonic generation is found in an orientational hole-burning effect. Its lifetime, limited by molecule rotation, is 210 ± 10 psec and the $\chi^{(2)}$ magnitude reaches 2.5×10^{-3} pm/V for 1 GW cm^{-2} pumps at 1064 nm.

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In a centrosymmetric material, even-order optical nonlinearities (such as second-harmonic generation, SHG) are dipolar forbidden for symmetry reasons [1]. Though SHG is possible in centrosymmetric mixtures of chiral molecules via magnetic or quadrupolar effects [2], the dipolar symmetry requirements can be modified by a nonsymmetric external action such as the application of a dc electric field. Efficient electric-field-induced second-harmonic generation (EFISH) is then observed in centrosymmetric materials, e.g., solutions of molecules with large permanent dipole moment and second-order hyperpolarizability β, via the third-order nonlinear susceptibility $\chi^{(3)}(2\omega;\omega,\omega,0)$ [3]. Such an induced noncentrosymmetry can remain after the dc electric field is switched off, as in poled polymers [4]. In such systems, the partial alignment of initially randomly oriented chromophores with large β results in a nonzero macroscopic second-order susceptibility $\chi^{(2)}$.

The observation of second-harmonic generation in optical fibers prepared by an intense light at 1064 nm [5] or with a simultaneous seeding light at the doubled frequency (532 nm) [6] revealed the possibility of inducing a $\chi^{(2)}$ by light in a centrosymmetric material. The mechanism involves the nonzero time average, at a given point, of the third power of the optical field, $\langle E^3\rangle \neq 0$. For the superposition of a light wave and its second harmonic, $\langle E^3\rangle$ oscillates in space and generates a $\chi^{(2)}$ grating. Hence, the whole write-and-read process can be viewed as a six-wave-mixing (SWM) process [7,8]. In this Letter we report on a phase-conjugation experiment based on such a SWM interaction which demonstrates the induction of a self-phase-matched transient $\chi^{(2)}$ grating by light in a centrosymmetric solution of dye molecules with large β.

In such processes, $\chi^{(2)}(2\omega;\omega,\omega)$ is induced by a combination of two beams at frequencies ω and 2ω. $\chi^{(2)}$ at a given **M** of the material is proportional to $\langle E^3\rangle = E_\omega^{*2}E_{2\omega} + E_\omega^2 E_{2\omega}^*$, where E_ω is the amplitude of the field at frequency ω at point **M**. Now, if we probe this $\chi^{(2)}$ by frequency doubling on a third beam at frequency ω with amplitude E'_ω, the measured 2ω polarization amplitude is $\chi^{(2)}E_\omega'^2$ and is proportional to $E_\omega'^2 E_\omega^{*2}E_{2\omega} + E_\omega'^2 E_\omega^2 E_{2\omega}^*$. Thus, the whole write-and-read process contributes to the fifth-order susceptibilities $\chi^{(5)}(2\omega;\omega,\omega,-\omega,-\omega,2\omega)$ and $\chi^{(5)}(2\omega;\omega,\omega,\omega,\omega,-2\omega)$, respectively. Contributions to the first coefficient comes from $\langle E^3\rangle$-induced $\chi^{(2)}$ but also from $\langle E^4\rangle$-induced index variations [7]. So we focus here on the second term, which can represent only an induced $\chi^{(2)}$. Figure 1 shows the beam arrangement for the measurement of $\chi^{(5)}(2\omega;\omega,\omega,\omega,\omega,-2\omega)$ in a phase-conjugation configuration. Beams 1 and 2, at fundamental frequency ω, are counterpropagating plane waves (complex amplitudes E_1 and E_2, wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, $\mathbf{k}_1+\mathbf{k}_2=0$). The frequency of beam 3 (E_3) is 2ω. The nonlinear polarization at 2ω generated at a point **M** of the material by $\chi^{(5)}(2\omega;\omega,\omega,\omega,\omega,-2\omega)$ contains a term whose spatial dependences in $\exp(i\mathbf{k}_1\cdot\mathbf{M})$ and $\exp(i\mathbf{k}_2\cdot\mathbf{M})$ cancel exactly, keeping only the spatial dependence of E_3^*. This term is

$$P_4(2\omega) = 30\varepsilon_0\chi^{(5)}(2\omega;\omega,\omega,\omega,\omega,-2\omega)E_1^2(\omega)E_2^2(\omega)E_3^*(2\omega)\,. \tag{1}$$

Any nonlinear susceptibility which gives a spatial dependence in E_3^* is of the form $\chi^{(n)}(2\omega;\ldots,-2\omega)$. The fifth-order susceptibility in Eq. (1) is the lowest order of this form (with the same frequency sum after and before the semicolon) which gives a spatial dependence in E_3^*. Any lower-order effect [e.g., $\chi^{(3)}(2\omega;\omega,-\omega,2\omega)$ [9]] generates signals in other directions. The polarization (1) generates the phase conjugate of beam 3 at the same frequency 2ω and with exact phase matching. The phase matching of the term (1) permits us to use thick samples and to have large angles between beams 1 and 3 so that the signal is largely separated from other possible direc-

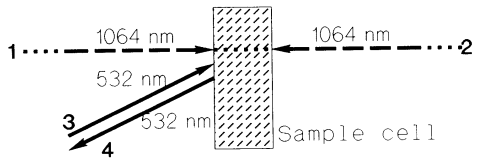

FIG. 1. Beam arrangement for phase conjugation by nondegenerate six-wave mixing in a $\chi^{(5)}(2\omega;\omega,\omega,\omega,\omega,-2\omega)$ medium.

tions of diffraction.

In the experimental setup, the source was a passively and actively mode-locked Nd^{3+}:YAG laser delivering 33-psec pulses at 1064 nm at a repetition rate of 10 Hz. The beam waist diameter at the sample location was 2 mm. The energy in each beam 1 and 2 was 1 mJ per shot. This gives a fluence of 1 GW/cm^2. Beam 3 was obtained by frequency doubling in a potassium dihydrogen phosphate (KDP) crystal, on a separate arm. It made an angle of 8° with beam 1. The remaining 1064-nm wavelength was eliminated by a KG5 Schott glass. The energy at 532 nm was 0.1 mJ per shot. Beams 1 and 3 were polarized vertically. The beam-2 polarization was varied using a half-wave plate. The phase-conjugate signal was extracted from the beam-3 path using a 50% beam splitter inserted after the KDP crystal. It was detected behind a polarization analyzer using a photomultiplier tube (PMT). The PMT signal was held by a fast sampler and averaged over fifty laser shots. For lifetime measurements, the sampler was synchronized on the delayed readout beam. The sample was a 1-mm-thick cell filled with a solution of 4-diethylamino-4'-nitrostilbene (DEANS) in tetrahydrofuran (THF). Both solute and solvent molecules are nonchiral. DEANS has been synthesized by condensation of diethyl 4-nitrobenzyl phosphonate with 4-(diethylamino)benzaldehyde, and crystalized in toluene. Its melting point was 175°C. The maximum-absorption wavelength in THF is 445 nm with $\log_{10}(\varepsilon)=4.46$. The sample concentration was 6.5×10^{-3} mol/dm^3 (2 g/dm^3) and its transmission at 532 nm was $10^{-2.07}$.

When all beams are synchronized, the green signal from the solution is clearly visible as a spot on a white screen. Its shape remains unchanged by inserting a phase object (a spherical mirror used off axis) on the beam-3 path. This proves the phase-conjugation process. No signal is measurable in the neat solvent. Figure 2 shows the evolution of the phase-conjugate signal in DEANS as a function of 1064-nm-beam delays for parallel polarizations. The scattering of beam 3 on the sample appears as a noise level for negative delays lower than -100 psec. In the delay range considered here, the signal is 1 to 4 orders of magnitude larger than the noise. The maximum phase-conjugate reflectivity is 8×10^{-7} at zero delay. The same time dependence is observed with respect to beam-1 and beam-2 delays: a pulse-width-limited peak around zero delay followed by an exponential decay characterized by a time constant $T=105\pm5$ psec. When the probe beam is delayed any 2ω signal has to come from a net second-harmonic generation. The signal at 2ω is then observed to be simultaneous with the probe pulse at ω. Using calibrated optical densities, we have verified that the signal was linear with beam-3 intensity and quadratic with intensities of beams 1 and 2: This is expected from the lowest-order allowed $\chi^{(5)}$ nonlinearity (1) of the studied process.

As concerns polarization properties of the response, Fig. 3 shows the variations of the amplitudes of vertically and horizontally polarized signal components as a function of beam-2 to beam-3 polarization angle. The signal polarization is vertical for both vertical and horizontal beam-2 polarization ($\varphi=0$ and 90°). This reflects the general symmetry properties of a $\chi^{(5)}$ tensor in an isotropic material (whereas the y-reversal symmetry imposes $\chi^{(3)}_{xxyx}=0$). The signal amplitude is decreased by a factor of 5 from parallel to crossed 1064-nm-pump polarizations. For $\varphi=90°$, we have rotated a 532-nm half-wave plate in the common path of beam 3 and the signal. The signal remains constant. This means that we get perfect polarization-maintaining phase conjugation.

No conclusion can be drawn on an eventual short-lived $\chi^{(2)}$ from the zero-delay peak since the process leads to a strong coherence artifact. As a matter of fact, in the pulsed regime, if we denote the slowly varying amplitude

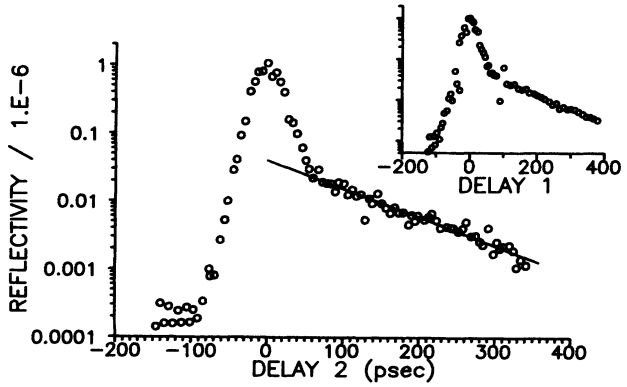

FIG. 2. Phase-conjugate reflectivity (ratio of signal intensity to beam-3 intensity) as a function of beam-2 delay (in inset, beam-1 delay). All polarizations are parallel. The solid line represents a 105-psec exponential decay rate. The same decay rate is observed for both delays.

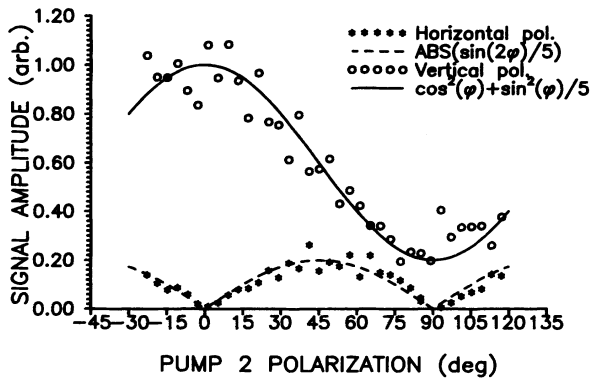

FIG. 3. Horizontally (stars) and vertically (open circles) polarized signal amplitude as a function of beam-2 polarization angle φ. Beams 1 and 3 are polarized vertically. The fitting curves (solid and broken lines) are derived from theoretical expressions (7) and (8).

of beam i by $\tilde{E}_i(t)$, the 2ω polarization generated at time t by the induced $\chi^{(2)}$ may be written as $P_{2\omega}(t) = \varepsilon_0 \chi^{(2)}(t) \tilde{E}_\omega(t)^2$ with $\tilde{E}_\omega(t) = \tilde{E}_1(t) + \tilde{E}_2(t)$. The signal detected is proportional to the integral on t of $P_{2\omega}^2(t)$. Now, assuming an exponential decay, the induced $\chi^{(2)}$ at time t can be written as

$$\chi^{(2)}(t) = \int_{-\infty}^{t} 5\Gamma \chi^{(5)} e^{-\Gamma(t-\tau)} \tilde{E}_\omega(\tau)^2 \tilde{E}_{2\omega}^*(\tau) d\tau , \tag{2}$$

where Γ is the decay rate of $\chi^{(2)}$. The contribution of $P_{2\omega}(t)$ to the phase-conjugate signal [i.e., proportional to $(\tilde{E}_1 \tilde{E}_2)^2 \tilde{E}_3^*$] is

$$P_{2\omega}^{PC}(t) = 5\varepsilon_0 \Gamma \chi^{(5)} \left[\tilde{E}_2(t)^2 \int_{-\infty}^{t} e^{-\Gamma(t-\tau)} \tilde{E}_1(\tau)^2 \tilde{E}_3^*(\tau) d\tau + \tilde{E}_1(t)^2 \int_{-\infty}^{t} e^{-\Gamma(t-\tau)} \tilde{E}_2(\tau)^2 \tilde{E}_3^*(\tau) d\tau \right.$$
$$\left. + 4\tilde{E}_1(t) \tilde{E}_2(t) \int_{-\infty}^{t} e^{-\Gamma(t-\tau)} \tilde{E}_1(\tau) \tilde{E}_2(\tau) \tilde{E}_3^*(\tau) d\tau \right] . \tag{3}$$

The first term in Eq. (3) corresponds to a $\chi^{(2)}$ grating written at time τ by the interference of beams 1 and 3, with wave vector $2\mathbf{k}_1 - \mathbf{k}_3$. This $\chi^{(2)}$ grating is probed at time t by frequency doubling of beam 2. The second term corresponds to the grating written by beams 2 and 3, with wave vector $2\mathbf{k}_1 - \mathbf{k}_3$ and probed by beam 1. The third term corresponds to a grating with wave vector $-\mathbf{k}_3$ written by a combination of the three incident beams and probed by both beams 1 and 2. When the beam-2 (beam-1) delay is larger than the pulse width only the first (second) term contributes to the signal. At zero delays all terms contribute to the signal amplitude, which leads to a coherence peak. This could explain the larger signal observed at zero delay in Fig. 2.

Accounting for beam 3 and signal absorption we estimate an amplitude of the induced $\chi^{(2)}$ at a delay of 100 psec of 2.5×10^{-3} pm/V. The decay rate of the $\chi^{(2)}$ amplitude is half that of the signal intensity plotted in Fig. 1, that is, $\Gamma = 1/2T \simeq 1/210$ psec^{-1}. Integration of Eq. (2) accounting for pulse width yields

$$\chi_{\text{expt}}^{(5)} = 5 \times 10^{-37} \text{ m}^4/\text{V}^4 . \tag{4}$$

Two microscopic explanations can be invoked for generation of $\chi^{(2)}$ by light in this material: Poling can be achieved either (a) by a net rotation of the molecules or (b) by an orientation-selective bleaching. Effect (a) has two contributions. One is the interaction of the 2ω seeding field $E_{2\omega}$ with the 2ω dipole moment $[\beta(2\omega;\omega,\omega)E_\omega^2]$ induced by the ω field via $\beta(2\omega;\omega,\omega)$. The other is the interaction of E_ω with the ω dipole moment induced by difference-frequency generation $[2\beta(\omega;2\omega,-\omega)E_{2\omega}E_\omega^*]$. Assuming a one-dimensional β and in the continuous-wave regime, a calculation based on Boltzmann statistics gives for parallel polarizations

$$\chi_a^{(5)}(2\omega;\omega,\omega,\omega,\omega,-2\omega) = f(\omega)^4 f(2\omega)^2 \frac{N}{35\varepsilon_0} \frac{[\beta(2\omega;\omega,\omega) + 2\beta^*(\omega;2\omega,-\omega)]\beta(2\omega;\omega,\omega)}{kT} , \tag{5}$$

where N is the number of molecules per unit volume, k the Boltzmann constant, T the temperature, and $f(\omega)$ the local-field factor at frequency ω. Effect (b) is the electronic contribution previously suggested by Baranova and Zel'dovitch [10]. Here, it corresponds to an orientation-selective excitation of the DEANS molecule which bleaches the hyperpolarizability β of the class of molecules oriented either up or down (depending upon the relative phase of the fields E_ω and $E_{2\omega}$). This thus leaves a nonzero macroscopic $\chi^{(2)}$. Such a process can be referred to as orientational hole burning, by analogy with the widely studied spectral hole burning. The $\chi^{(5)}$ obtained by applying this theory to the classical one-dimensional two-level model of push-pull molecules such as DEANS can be also expressed as a function of β:

$$\chi_b^{(5)}(2\omega;\omega,\omega,\omega,\omega,-2\omega) = f(\omega)^4 f(2\omega)^2 \frac{N}{35\varepsilon_0} \frac{4\gamma}{\Gamma} \frac{\beta^2(2\omega;\omega,\omega)}{\hbar(\omega_{01} - 2\omega + i\gamma)} , \tag{6}$$

where ω_{01} is the transition energy and γ the transverse relaxation rate.

Both models lead to the same polarization properties:

$$\chi_{yxxxxy}^{(5)} = \chi_{xyyxxx}^{(5)} = \chi_{yyxxxx}^{(5)} = \chi_{xyxxxy}^{(5)} = \tfrac{1}{5} \chi_{xxxxxx}^{(5)}(2\omega;\omega,\omega,\omega,\omega,-2\omega) , \tag{7}$$

where indices x and y represent two perpendicular directions of the material. This property can be confirmed by the polarization experiment (Fig. 3). When beams 1 and 3 are polarized vertically (x direction) and beam-2 polarization makes an angle φ, the vertical (x) and horizontal (y) components of the phase-conjugate polarization are (in the continuous-wave regime)

$$P_x = 30\varepsilon_0 E_1^2 E_2^2 E_3^* [\chi_{xyyxxx}^{(5)} \sin^2\varphi + \chi_{xxxxxx}^{(5)} \cos^2\varphi] ,$$
$$P_y = 30\varepsilon_0 E_1^2 E_2^2 E_3^* [2\chi_{yyxxxx}^{(5)} \sin\varphi \cos\varphi] . \tag{8}$$

The fitting curves represented in Fig. 3 are derived from Eq. (8) with account of Eq. (7). The agreement with the experimental points confirms the symmetry properties expressed by Eq. (7). The reduction factor $\frac{1}{5}$ in Eq. (7) is

characteristic of our models and is observed experimentally. It is important to notice that it is replaced by $\frac{1}{3}$ in the case of optical fibers [11]. This indicates a different origin for these effects.

The lifetime of a motional orientation is only limited by the orientational decay time whereas an orientational hole-burning effect is limited both by the orientational decay time and by the excited-state lifetime. Time-resolved absorption and gain spectroscopy of a DEANS solution in benzene exhibits a decay time much larger than 400 psec [12]. The 210-psec $\chi^{(2)}$ decay observed here is thus mainly caused by the loss of molecular orientation. Thus this observation cannot distinguish between the two possible origins (a) and (b) of $\chi^{(5)}$.

A hyperpolarizability $\beta(2\omega;\omega,\omega)$ of 1.7×10^{-48} C m^3/V^2 (450×10^{-30} esu) has been estimated by EFISH experiments for 4-dimethylamino-4'-nitrostilbene (DMANS) [2]. DMANS is analogous to DEANS. Taking the same value for DEANS and neglecting local-field corrections as well as problems linked with inhomogeneous broadening, Eq. (5) gives an order of magnitude estimate: $\chi_a^{(5)}\approx3\times10^{-41}$ m^4/V^4. Similarly, Eq. (6) taken at the exact resonance gives a much larger order of magnitude: $\chi_b^{(5)}\approx3\times10^{-37}$ m^4/V^4. The latter is much closer to the experimental value Eq. (3). We thus conclude that the origin of the light-induced $\chi^{(2)}$ observed here is an orientational hole burning (b).

The experiment presented here gives evidence of light-induced $\chi^{(2)}$ in a solution of noncentrosymmetric dye molecules. The origin of the effect is attributed to an orientational hole burning. Its lifetime is limited by molecular rotation. With our single-pulse preparation, the ratio of oriented molecules is about 0.5%. This suggests new ways of poling organic materials which offers a natural means to obtain the periodicity ensuring phase matching for SHG. This is an alternative to the phase matching achieved artificially by periodic poling using alternate electrodes [13]. This opens new directions of investigation in the search of materials for frequency conversion.

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