

# Light-induced second-harmonic generation in an octupolar dye

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Quasi-permanent light-induced second-order susceptibility  $\chi^{(2)}$  of octupolar molecules is demonstrated. The octupolar molecule Ethyl Violet was oriented in a solgel matrix by a purely optical poling technique. The method consists of a seeding process based on a nonclassical holographic process with coherent two-frequency mixing. The growth of the induced  $\chi^{(2)}$  is monitored in real time by frequency doubling of the fundamental beam in the sample. The polarization dependence of the signal is used to demonstrate the octupolar symmetry of the induced  $\chi^{(2)}$ . © 1995 Optical Society of America

Most molecular systems considered so far as candidates for use in quadratic nonlinear optics have been inspired by the molecular diode template as exemplified by the *para*-nitroaniline prototype donor–acceptor molecule. This perspective was recently enlarged<sup>1</sup> by the proposal of multipolar systems for nonlinear optics, initially based on the recognition of the full tensorial nature of  $\beta$ , which is reflected in the following irreducible decomposition:  $\beta = \beta_{J=1} \oplus \beta_{J=3}$ , where  $\beta_{J=1}$  and  $\beta_{J=3}$  are, respectively, the dipolar and the octupolar contributions to  $\beta$ . Nondipolar noncentrosymmetric systems, exhibiting, for example, trigonal (e.g.,  $D_{3h}$ ) or tetrahedral (e.g.,  $T_d$ ) symmetry are indeed compatible with a nonzero  $\beta$  tensor. The  $\beta$  tensor is then reduced to have only a  $\beta_{J=3}$  component, and all observable physical quantities of a dipolar nature such as the molecular permanent dipole moment  $\mu$  cancel. This precludes the use of a dipolar coupling scheme to achieve transient as well as permanent macroscopic orientation of octupolar molecules for measurements or material fabrication purposes. One recently revived approach, following the pioneering experiments of Terhune *et al.*,<sup>2</sup> enables systematic solution measurements to be made in a noncoherent regime. It has shown the giant nonlinearities associated with octupolar systems such as propeller-shaped organometallic molecules with nonresonant  $\beta$ 's of the order of  $800 \times 10^{-30}$  esu ( $\approx 3 \times 10^{-48}$  C m<sup>-3</sup> V<sup>-2</sup>).<sup>3</sup> One crucial goal is the permanent macroscopic orientation of octupolar molecules, which is a prerequisite for the practical exploitation of these systems in materials and devices. We show here an original technique that overcomes this problem, using purely optical means and based on a nonclassical holographic process with coherent mixing of two-frequency fields.<sup>4–7</sup> In the case of dipolar-type molecules, it has been shown that all-optical encoding of noncentrosymmetry can give orientation efficiencies comparable with those in the standard corona poling technique.<sup>8</sup>

The all-optical method is based on two essential properties of the time-averaged tensorial product  $\langle E^3 \rangle_t$  where  $E = E_\omega + E_{2\omega}$  is the total field that results from

the coherent superposition of two fields, namely,  $E_\omega$  at the fundamental frequency  $\omega$  and  $E_{2\omega}$  at the second-harmonic frequency.<sup>9</sup> First,  $\langle E^3 \rangle$  has a nonzero cubic average, and second, its irreducible tensor decomposition has a component with octupolar symmetry.<sup>10</sup> Coupling of the  $\langle E^3 \rangle$  field tensor with a molecule is thus permitted even in the absence of a dipole. Microscopically, the process was identified to be an orientational hole burning in the initially isotropic distribution of molecules.<sup>10</sup> Furthermore a noncentrosymmetric orientation of the molecules in a self-phase-matched structure can be achieved, resulting in a nonvanishing macroscopic second-order susceptibility  $\chi^{(2)}$ . Recently, after demonstrating the possibility of photoinducing a transient  $\chi^{(2)}$  in a solution of donor–acceptor conjugated molecules,<sup>6,11</sup> we reported what we believe is the first noncentrosymmetric transient orientation of octupolar molecules in solution, enabling us to investigate both the dynamical behavior and the symmetry properties of the induced  $\chi^{(2)}$ .<sup>10</sup>

We report here the quasi-permanent all-optical poling of a prototype octupolar guest–host system. The guest octupolar molecule is Ethyl Violet, a triphenylmethane dye, which is embedded in a standard tetramethoxysilane polymeric solgel matrix. The mechanism is discussed, and the octupolar symmetry is demonstrated by polarization analysis.

We make use of the experimental setup described previously.<sup>8</sup> The source is a Q-switched mode locked Nd<sup>3+</sup>:YAG laser delivering 25-ps pulses at 1064 nm. The coherent second-harmonic writing beam was obtained by frequency doubling with a KDP crystal. The seeding process consists of simultaneous irradiation of the sample by the two coherent copropagating beams at frequencies  $\omega$  and  $2\omega$ . The sample was at normal incidence to these two collinear writing beams. The light-induced noncentrosymmetry was probed by generation of second harmonic (SH) inside the sample. To monitor the growth dynamics of the induced  $\chi^{(2)}$  grating, we periodically stopped the seeding process for probing. For this purpose an RG630

Schott filter was inserted in front of the sample, leaving only the  $\omega$  beam incident. The SH signal was detected by a photomultiplier tube after spatial filtering. The experiment was entirely computer controlled.

The sample was a spin-coated 1.3- $\mu\text{m}$  thin film of a silica-gel matrix doped with Ethyl Violet (10% by weight), which has octupolar symmetry and an absorption maximum peaking at 580 nm. The optical density at 532 nm was 0.5, and the film was of good optical quality. Figure 1 shows the growth of the light-induced  $\chi^{(2)}$  as a function of time. The energy in each beam was  $\sim 700 \mu\text{J}$  for the fundamental beam and  $\sim 2 \mu\text{J}$  for the SH seeding beam, with beam diameters at the sample location of 600 and 400  $\mu\text{m}$ , respectively, corresponding to fluences of 10  $\text{GW}/\text{cm}^2$  and 25  $\text{MW}/\text{cm}^2$ , respectively. Both beams were polarized vertically. The generated SH signal was analyzed parallel to excitation, i.e., vertically.

As a result of the holographic nature of the multifrequency-field process, the relative phase  $\Delta\Phi$  between the  $\omega$  and  $2\omega$  writing fields strongly influences the efficiency of the light-induced orientation process. More precisely, the induced  $\chi^{(2)}$  can be written as

$$\chi_{\text{ind}}^{(2)} = \chi_{\text{eff}}^{(2)} \cos(\Delta\Phi + \Delta kz) \exp[-(\alpha/2)z], \quad (1)$$

where  $\chi_{\text{eff}}^{(2)} \propto \|E_{\omega}^2 E_{2\omega}^*\|$ ,  $\alpha$  is the absorption coefficient at frequency  $2\omega$ ,  $\Delta k = 2k_{\omega} - k_{2\omega}$  is the spatial dispersion factor related to the wave-vector mismatch,  $k_{\omega}$  and  $k_{2\omega}$  are the wave vectors at frequencies  $\omega$  and  $2\omega$ ,  $E_{\omega}$  and  $E_{2\omega}$  are the complex field amplitudes, and  $z$  is the propagation coordinate and its origin is taken to be at the front face of the sample.

Experimentally, we controlled the relative phase  $\Delta\Phi$  between the  $\omega$  and  $2\omega$  writing beams by tilting a BK7 plate with known thickness and index dispersion between 1064 and 532 nm. We measured the dependence of the SH intensity as a function of  $\Delta\Phi$  after 30 min of preparation, as shown in the inset of Fig. 1. The experimental results show good agreement with the theoretical curve (solid curve in the inset of Fig. 1) derived from Eq. (1) after solution of the wave equation.<sup>8</sup> The fit yields a coherence length of  $\sim 6 \mu\text{m}$ , in agreement with the value derived from the absorption spectra by use of Kramers-Kronig relations.

The growth dynamics of the induced  $\chi^{(2)}$  are plotted in Fig. 1 for optimized relative phase between the seeding beams. The gradual growth of the induced  $\chi^{(2)}$  and its saturation after a few minutes' processing are similar to the behavior observed in the case of the uniaxial molecule Disperse Red One (DR1; see Fig. 2 for the molecular structure). At saturation, the induced second-order susceptibility is  $d_{33} = \chi^{(2)}/2 = 0.6 \text{ pm}/\text{V}$ . This value was determined from the SH intensity and the beams' fluences after resolution of the wave equation.<sup>8</sup> After the preparation process no significant decay of the signal was observed after tens of minutes. Unlike in the case of DR1,<sup>8</sup> for which the permanent orientation can be described in terms of a trans/cis photoisomerization process following the selective polar excitation of the molecules, the nature of the photoisomerization process remains to be clari-

fied in the case of Ethyl Violet. However, macroscopic orientation possibly occurs through breaking of the molecule-to-matrix bonds and subsequent reorganization following the orientation-selective excitation process.<sup>12</sup>

More important in view of the particular symmetry of Ethyl Violet is the symmetry analysis of the radiated SH signal. Figure 2 shows a polar plot of the vertically polarized signal amplitude. This amplitude is derived from the square root of the signal intensity. The plot shown in Fig. 2 was obtained from a vertically polarized  $\omega$ -reading beam as a function of the in-plane rotation of the sample. The cases of both the uniaxial molecule DR1 and the octupolar molecule Ethyl Vio-

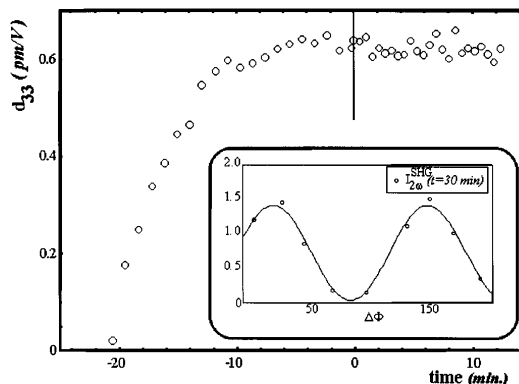


Fig. 1. Experimental growth (negative times) and free evolution (positive times) of the induced  $d_{33}$ . The inset shows the experimental dependence of the SH signal intensity (in arbitrary units) on the relative phase  $\Delta\Phi$  of the  $\omega$  and  $2\omega$  writing beams. The origin of  $\Delta\Phi$  was arbitrarily taken for normal incidence of the writing beams on the BK7 plate. The signal intensity was recorded after a 30-min preparation of the sample. Growth and decay dynamics are measured with  $\Delta\Phi = 25^\circ$ , corresponding to a maximum signal. The solid curve in the inset shows the theoretical fit.

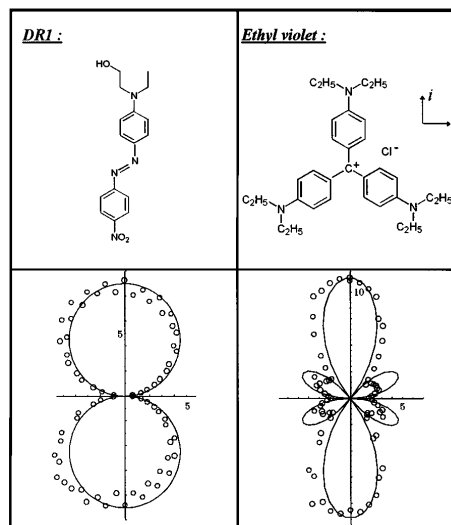


Fig. 2. Molecular structure and polar representation of the vertically polarized SH signal amplitude as a function of the in-plane rotation of the sample. The cases of both the uniaxial molecule DR1 and the octupolar molecule Ethyl Violet are shown. Solid curves correspond to the expected theoretical dependences.

let are shown for comparison. The vertical direction corresponds in both cases to the seeding polarization axis. These two systems exhibit drastically different features. Indeed, as shown below, analysis of the radiated SH signal provides a unique insight into the tensorial nature of the induced second-order susceptibility and thus reveals the nature of the light-molecule interaction.

The macroscopic polarizabilities of an assembly of noninteracting molecules are obtained from the corresponding microscopic ones after averaging over all possible orientations. In the case of frequency doubling, the second-order susceptibility  $\chi^{(2)}$  is related after statistical averaging to the hyperpolarizability  $\beta$  of the molecules according to

$$\chi_{\Delta\Delta\Delta}^{(2)} = \int_{\Omega} N(\Omega)\beta_{\Delta\Delta\Delta}(\Omega)d\Omega, \quad (2)$$

where  $N(\Omega)$  is the density of molecules oriented in a direction  $\Omega$  and where  $\Delta$  is a given direction in the  $(x, y)$  plane of the film.  $\beta_{\Delta\Delta\Delta}(\Omega) = (\Delta \cdot \mathbf{i})(\Delta \cdot \mathbf{j})(\Delta \cdot \mathbf{k})\beta_{ijk}$ , with the implicit repeated index summation convention. The projection factors depend on the Euler angles  $(\theta, \varphi, \psi)$  between the laboratory and molecular reference frames.  $d\Omega$  is the normalized element of the solid angle. For the sake of clarity, local field effects are not explicitly mentioned and may be considered included in the  $\beta$  expression.

Ethyl Violet exhibits  $D_{3h}$  symmetry, which leads to the following expression for the  $\beta$  tensor<sup>13</sup>:  $\beta(-2\omega; \omega, \omega) = \beta_{iii}(i \otimes i \otimes i - i \otimes j \otimes j - j \otimes i \otimes j)$ .

A general treatment is given in Refs. 10 and 11. In the present case the preparation process preserves the symmetry along the vertical axis (axis  $x$  in the laboratory frame), so the angular distribution  $N(\Omega)$  will not depend on the azimuthal angle  $\varphi$ . Thus  $N(\Omega) = N(\theta, \psi)$  can be expanded in spherical harmonics<sup>14</sup>:

$$N(\Omega) = N(\theta, \psi) = \sum_{l=0}^{\infty} \sum_{m=0}^l A_{lm} Y_{lm}(\theta, \psi). \quad (3)$$

Equations (2) and (3) permit the calculation of the macroscopic component of the induced susceptibility  $\chi^{(2)}$  for a given writing polarization direction  $\Delta$ , deviating by an angle  $\delta$  from the vertical direction  $x$ , leading to

$$\chi_{\Delta\Delta\Delta}^{(2)} \propto \left( \frac{5}{14} \sqrt{4\pi/7} A_{30} + \frac{4}{7} \sqrt{2\pi/105} A_{32} \right) \times \left( \cos^3 \delta - \frac{3}{5} \cos \delta \right). \quad (4)$$

In the case of a uniaxial molecule,  $\beta$  is reduced to a single coefficient, namely,  $\beta(-2\omega; \omega, \omega) = \beta_{iii}(i \otimes i \otimes i)$ , so  $N(\Omega)$  is simply a function of the tilt angle  $\theta$ :  $N(\Omega) = N(\theta)$ . The expected dependence for  $\chi_{\Delta\Delta\Delta}^{(2)}$  is then

$$\chi_{\Delta\Delta\Delta}^{(2)} \propto \left( \sqrt{4\pi/7} A_{30} \right) (\cos^3 \delta) + \frac{3}{5} \left( \sqrt{4\pi/3} A_{10} - \sqrt{4\pi/7} A_{30} \right) (\cos \delta). \quad (5)$$

It can be seen from Fig. 2 that in the case of DR1 the contribution of  $\cos^3 \delta$  appears experimentally to be negligible, so the dependence on  $\cos \delta$  is sufficient to describe the symmetries of the induced  $\chi^{(2)}$ .

The best-fitting curves (solid curves) in Fig. 2 are derived from relation (4) for the octupolar Ethyl Violet molecule and from relation (5) for the uniaxial DR1 molecule.

In conclusion, we have demonstrated quasi-permanent light-induced second-order susceptibility  $\chi^{(2)}$  in a polymeric solgel matrix doped with the octupolar Ethyl Violet molecule. It can be interpreted in terms of the holographic recording of an interference pattern induced by the coherent interference of dual-frequency fields. The possibility of patterning a long-lived second-order susceptibility by all-optical means opens up a new avenue for the breaking of centrosymmetry in organic media, especially in the case of molecules without a permanent dipole. Indeed, in such cases, polar orientation is impossible by conventional electric poling techniques. Furthermore, optical poling is a simple technique giving exactly the micropatterning of the induced order required for phase matching without any need for the complicated technology required for periodic electrode shaping. The octupolar symmetry of the induced  $\chi^{(2)}$  has also been confirmed. The combination of octupolar molecules and all-optical poling opens new directions for the design of devices for frequency conversion.

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