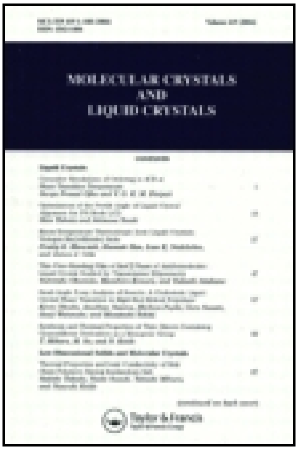

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

# Picosecond Nolinear Optics of Organic Materials

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Version of record first published: 19 Dec 2006.

To cite this article: J. C. Altman, P. J. Elizondo, G. F. Lipscomb & R. Lytel (1988): Picosecond Nolinear Optics of Organic Materials, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 157:1, 515-523

To link to this article: http://dx.doi.org/10.1080/00268948808080253

*Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.*, 1988, Vol. 157, pp. 515–523
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Printed in the United States of America

# PICOSECOND NONLINEAR OPTICS OF ORGANIC MATERIALS

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## Abstract

Organic and polymeric materials have emerged in recent years as a promising class of nonlinear optical media for device applications. Interest in polymeric materials stems primarily from the promise of large, non-resonant susceptibilities in optically clear materials, offering broadband, ultrafast response. We report measurements of the third-order nonlinear optical susceptibilities of certain side-chain polymers. Measurements were performed by the optical Kerr effect and degenerate four-wave mixing using a synchronously pumped picosecond dye-laser system operated at .580 $\mu m$. We show that the dominant contribution to the susceptibility on this time scale is electronic in origin, and compare this response with that obtained by thermally-induced degenerate four-wave mixing in an identical material.

## INTRODUCTION

Organic polymers are of great interest because of their fast response time, and flexibility in terms of engineering a material for a specific application [1]. Within rather broad limits the mechanical, thermal, electrical, and nonlinear optical properties of polymers can be tailored to a predetermined set of requirements. The tailoring process may consist of attaching molecules with desirable nonlinear optical properties to the backbone of a much larger polymer which has the required thermal and mechanical qualities. From the viewpoint of optical device applications, organic materials offer a number of benefits. These include high damage thresholds, transparency over broad ranges of wavelength, extremely large frequency bandwidth, and the ability to achieve high optical quality surfaces.

A number of experimental techniques are available to characterize the various linear and nonlinear optical properties of these materials. Some of the more common methods include linear electro-optic phase modulation, *DC* and *AC* (optical) Kerr effect phase modulation, and optical mixing (harmonic generation and four-wave mixing). The choice of method depends on the component of the nonlinear optical susceptibility under study.

We report measurements of the third order nonlinear response of a number of organic and polymeric materials, obtained via optical Kerr effect and degenerate four-wave mixing on a picosecond time scale. On this time scale the mechanisms responsible for the nonlinear response are limited primarily to the nonresonant electronic and motional Kerr effects.

Our research is a cooperative effort with Hoechst-Celanese Corporation, and we wish to acknowledge their cooperation in providing the samples used in this work.

## BACKGROUND

The optical nonlinearity is usually expressed in terms of a series expansion of the nonlinear polarization vector, $\vec{P}_{nl}$, in powers of the electric field, $\vec{E}$. On a microscopic scale the coefficients of $\vec{E}$ define the molecular polarizability and hyperpolarizabilities,

$$\vec{P}_{nl} = \alpha\vec{E} + \beta\vec{E}\vec{E} + \gamma\vec{E}\vec{E}\vec{E}. \tag{1}$$

On the macroscopic scale the coefficients are tensor elements characterizing the bulk properties of the medium,

$$\vec{P}_{NL} = \chi^{(1)}_{ij}\vec{E}_j + \chi^{(2)}_{ijk}\vec{E}_j\vec{E}_k + \chi^{(3)}_{ijkl}\vec{E}_j\vec{E}_k\vec{E}_l. \tag{2}$$

We concern ourselves here with the properties of $\chi^{(3)}_{ijkl}$, and define,

$$\vec{P}^{(3)}_{NL}(\omega_i,\vec{k}) = \chi^{(3)}_{ijkl}\vec{E}_j(\omega_j,\vec{k})\vec{E}_k(\omega_k,\vec{k})\vec{E}_l(\omega_l,\vec{k}). \tag{3}$$

Writing $\vec{E}$ as the superposition of two field components,

$$\vec{E} = \vec{E}_1 + \vec{E}_2, \quad \vec{E}_i = \vec{\mathcal{E}}_i \exp i(\omega t - \vec{k}\cdot\vec{x}) + c.c., \tag{4}$$

and performing the cube produces a number of terms having different combinations of the frequency, $\omega$. The real part of each of these corresponds to a different physical process (i.e., $\omega_i = \omega_j + \omega_k + \omega_l \equiv 3\omega$ implies third harmonic generation, $\omega_i = \pm\omega_j \pm \omega_k \pm \omega_l$ implies field mixing). Measurements were conducted utilizing both optical Kerr effect (OKE) phase modulation and degenerate four-wave mixing (DFWM) techniques. In each case the strength of the optical field intensities is found to be proportional to $[\chi^{(3)}]^2$.

The third order nonlinear susceptibility is a fourth rank tensor, $\chi^{(3)}_{ijkl}$, having 81 components (in future references it is to be understood that $\chi^{(3)}$ is equivalent to $\chi^{(3)}_{ijkl}$). Some tensor components are common to both experimental methods, others are not. In the special case of isotropic materials the total number of tensor components reduces to 21. Only three of these tensor components are independent ($\chi_{1122}, \chi_{1212}, \chi_{1221}$) and are related by,

$$\chi_{1111} = \chi_{1122} + \chi_{1212} + \chi_{1221} \;:\; \chi_{1111} = \chi_{2222} = \chi_{3333}\;. \tag{5}$$

Far from resonance, the Kleinman symmetry is valid and the total number of independent components reduces to only one,

$$\chi_{1122} = \chi_{1212} = \chi_{1221} = \tfrac{1}{3}\chi_{1111} \quad . \tag{6}$$

Consider the optical Kerr effect experiment with the pump beam having vertical polarization and the probe beam at 45 degrees to the pump. The measured susceptibility is given by,

$$\chi^{(3)}_{Kerr} = \chi_{1212} + \chi_{1221} = \tfrac{2}{3}\chi_{1111} \quad . \tag{7}$$

Similarly, for the DFWM experiment with all beams having vertical polarization the measured susceptibility is given by,

$$\chi^{(3)}_{DFWM} = \chi^{(3)}_{1111} . \tag{8}$$

In cases where the medium is anisotropic, the two methods can complement each other to independently measure the material properties and/or isolate a particular component of the susceptibility tensor. Where the medium is isotropic and off- resonance either method should suffice to determine the same components of $\chi^{(3)}$.

## OPTICAL KERR EFFECT

In this method (Figure 1) the pump beam induces a birefringence in the medium which permits phase modulation of the probe beam. The probe is oriented at 45 degrees to the pump so that the field components parallel and perpendicular to the pump will move through the medium at different velocities. Crossed polarizers are used to construct a polarization sensitive analyzer. The input and ouput probe intensities are then related by,

$$I_o = I_i \times sin^2(\tfrac{\Gamma}{2}) \ : \ \Gamma = \tfrac{\pi l}{\lambda} K |\vec{E}_p|^2 \quad , \tag{9}$$

where $I_i$ and $I_o$ are the input and output signal intensities, and $E_p$ is the electric field associated with the laser pump beam. The phase shift is $\Gamma$, $\lambda$ is the laser wavelength, and $l$ is the interaction length in the medium. The Kerr coefficient, $K$, and electric field, $E_p$, are usually quoted in electrostatic units while laser intensity is usually expressed in MKS units ($Watts/cm^2$), so the following conversion is needed:

$$I_p(Watts/cm^2) = (9 \times 10^4) n_0 \epsilon_0 c [E_p(statvolt/cm)]^2 \tag{10}$$

with $\epsilon_0 = 8.85 \times 10^{-12} farad/m$, $c = 3 \times 10^8 m/sec$, and $n_0$ is the linear refractive index. If the phase shift is assumed small, one can write,

$$I_o = (\frac{\pi l}{2\lambda})^2 K^2 I_i |\vec{E}_p|^4 . \tag{11}$$

The Kerr constant can be expressed in terms of the nonlinear refractive index as,

$$n_{\parallel} - n_{\perp} = \tfrac{1}{2}K|\vec{E}_p|^2 = \tfrac{2\pi}{n_0}[\tfrac{2}{3}\chi^{(3)}_{1111}]|\vec{E}_p|^2 \quad , \tag{12}$$

therefore, $K = \frac{8\pi}{3n_0}\chi^{(3)}_{1111}$ for nonresonant, isotropic media. The temporal response of the nonlinear medium is measured by delaying the probe beam relative to the pump. This results in a temporal convolution of the pump and probe beams. Using a computer controlled optical delay line the optical path length of the probe beam can be changed in increments of .2 $\mu m$, which equates to a time change of approximately .17 *femtoseconds*. Although the temporal sensitivity of the optical delay is *femtoseconds*, the experimental sensitivity is still limited by our *psec* laser pulse width.

## DEGENERATE FOUR-WAVE MIXING

In this method (Figure 2) counter-propagating pump beams interact with a probe beam in the nonlinear medium, to produce a phase-conjugate signal beam which returns along the same path as the probe. The degeneracy is the result of all beams having the same frequency. The two pump beams are linearly polarized in the same direction, usually vertical or horizontal. The probe polarization is oriented parallel or perpendicular to the pump, with the direction determining the tensor components of $\chi^{(3)}$ measured. With all polarizations identical the signal intensity is given by,

$$I_s = \beta[\chi^{(3)}]^2 l^2 I_{pr} I_{p1} I_{p2}, \tag{13}$$

where $I_s$, $I_{pr}$, $I_{p1}$, $I_{p2}$ are the signal, probe, pump one, and pump two field intensities, and $\beta$ is a proportionality constant. Path lengths for the probe and two pump beams are equalized via computer controlled optical delay lines. The delay line for the probe is also used to provide the time response of the medium as in the optical Kerr effect experiment.

## COMPARISON OF OKE AND DFWM EXPERIMENTS

The optical Kerr effect and degenerate four wave mixing experiments are related in the following manner.

$$OKE \; : \; [\chi^{(3)}]^2 = \frac{I_o}{\alpha I_i I_p^2 l^2} \quad | \quad DFWM \; : \; [\chi^{(3)}]^2 = \frac{I_o}{\beta I_i I_{p1} I_{p2} l^2} \quad , \tag{14}$$

where $\alpha$ and $\beta$ are constants of proportionality. If $I_{p1} = I_{p2} = \frac{I_p}{2}$ then clearly the optical Kerr effect method yields the stronger output signal intensity by a factor of four. In addition, in the *psec* to *subpsec* regime the Kerr effect method permits a much longer interaction length. This is possible because the pump and probe signals propagate in the same direction through the nonlinear medium. In contrast, the counter-propagating pulses in the

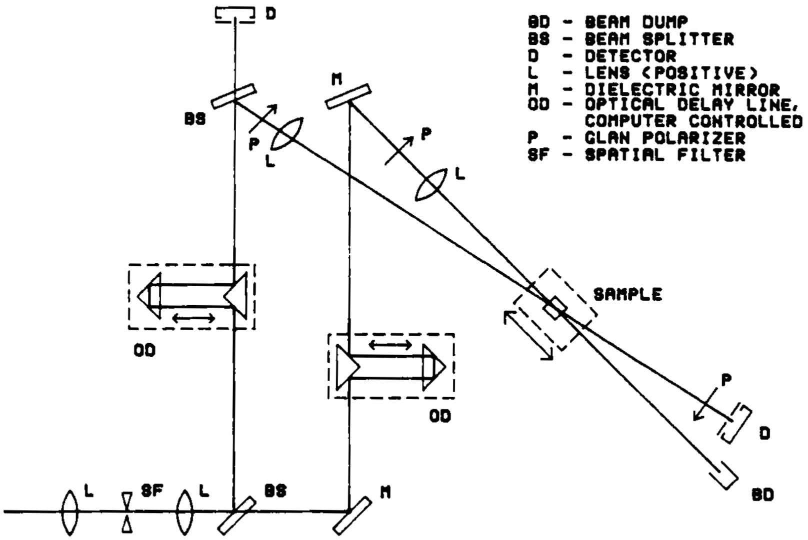

Figure 1: Optical Kerr effect experiment.

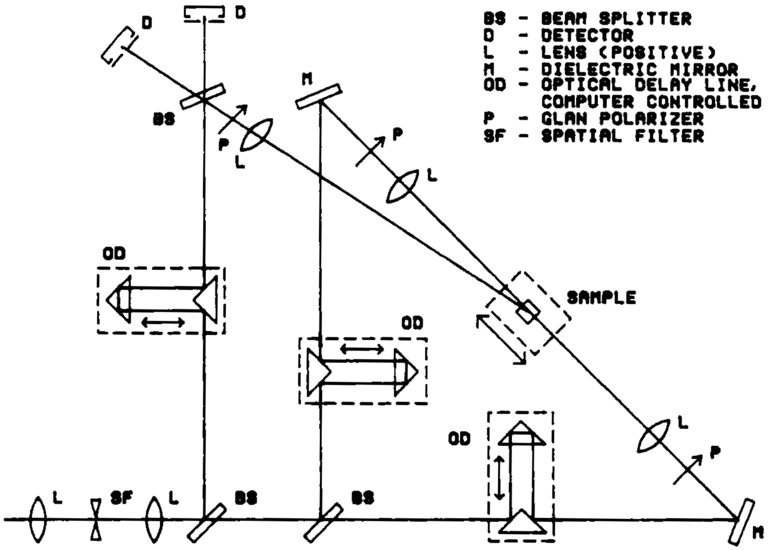

Figure 2: Degenerate four-wave mixing experiment.

| Mechanism | Temporal Response (sec) |
|---|---|
| Thermal | $10^{-1}$ |
| Electrostriction | $10^{-9}$ |
| Molecular Orientation (Kerr effect) | $10^{-12}$ |
| Molecular Redistribution | $10^{-13}$ |
| Electronic | $10^{-15}$ |

Table 1: Temporal response mechanisms.

DFWM experiment limit the interaction length to the laser pulse width. For a 1.5 *psec* FWHM pulse and a medium 1 *cm* thick, the Kerr effect interaction length is 1 *cm* while the DFWM length is about .05 *cm*. The OKE output intensity is almost 80 times greater than that for DFWM. Therefore, when off- resonance isotropic materials are being studied, the OKE technique can yield greater signal strength with less experimental effort than DFWM.

## TEMPORAL RESPONSE MECHANISMS

The nonlinear optical susceptibility is composed of a number of physical processes, which contribute independently to the observed change in the optical properties of a material. Table 1 lists these processes and their corresponding response times [4]. The dynamic range of temporal response covers many orders of magnitude, with thermal being the slowest and electronic the fastest. The time dependency of these various mechanisms can be experimentally exploited to permit measurements of a specific process. By varying the duration of the pump and probe signals it is possible to isolate the individual contributions to $\chi^{(3)}$. As an example consider the picosecond response of nitrobenzene shown in Figure 3. The sharp peak represents the fast electronic contribution, while the long exponentially decaying tail is due to the slower motional contribution. The motional response has been reported [2] to be of order 32 *psec*. If one observes a similar response from carbon disulfide (Figure 3) there is a marked difference. There is almost no tail at all because the motional contribution is much faster in $CS_2$ due to its smaller molecular size. If the $CS_2$ plot is expanded to show greater detail as in Figure 4, a small shoulder can be seen on the trailing edge of the pulse. A motional response slightly longer than our pulse width of 1.5 *psec* is indicated. This is agrees with recent subpicosecond measurements of $CS_2$ [3] reporting a motional response time of order 1.6 *psec*.

## EXPERIMENTAL RESULTS

Measurements were made on a number of organic and polymer materials, with the results shown in Table 2 below. Typical pulse width was 1.5 *psec*

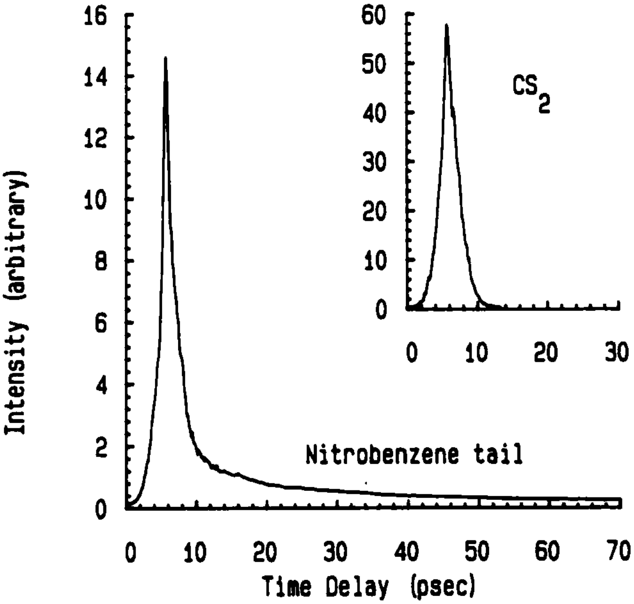

Figure 3: Temporal response mechanisms in Nitrobenzene and $CS_2$.

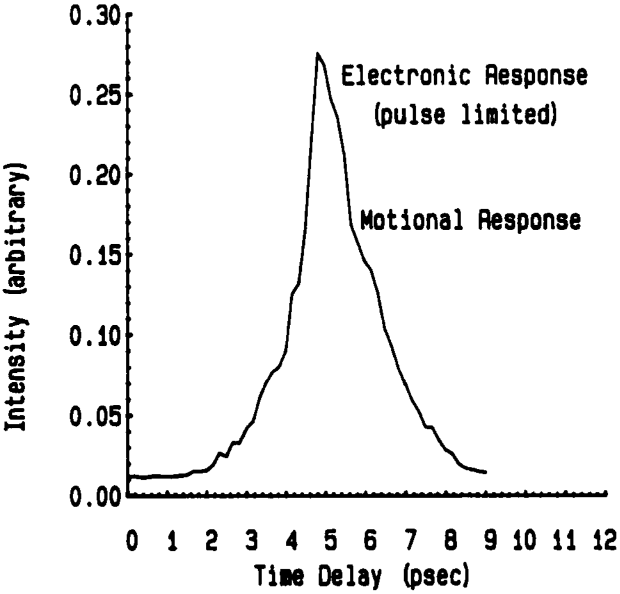

Figure 4: Carbon disulfide response time.

| Material | Normalized Response | Phase | Method |
|---|---|---|---|
| Nitrobenzene | .5 ± .3 | liquid | OKE |
| Vanillin | 1.4 ± .9 | solid | DFWM |
| MNA | .6 ± .4 | solid | DFWM |
| PC6S | 1.2 ± .8 | liquid | OKE |
| PMMA* | .01 ± .006 | solid | OKE |
| Chloroform* | .11 ± .8 | liquid | OKE |
| Trichloropropanol* | .5 ± .3 | liquid | OKE |
| * solvent or host for another material. | | | |

Table 2: Experimental results normalized to $CS_2$.

FWHM at a wavelength of .580 $\mu m$. All values of the susceptibility are normalized to those of $CS_2$. The $CS_2$ normalization data was repeated periodically to insure reproducibility. A normalization procedure was used to eliminate the need to determine such parameters as beam spot size and interaction length, or to determine system losses. Response times of the Vanillin, PC6S, and MNA samples were less than or equal to our laser pulsewidth.

The PC6S sample is a bi-phenyl, side-chain liquid crystal polymer in solution with trichloropropanol. This material is a proprietary product of the Hoechst-Celanese Corporation and a general description of its structure has been described in the literature [5]. We have previously reported measurements of this material on a nanosecond time scale, at a wavelength of .532 $\mu m$ [6]. Those results indicated a $\chi^{(3)}$ of 36 times $CS_2$, about 30 times larger than the current picosecond measurement. It is apparent that in this material the slower response mechanism dominates the nonlinear susceptibility. The magnitude of the optical nonlinearities for the materials reported here are only of the order of $CS_2$ or smaller, with the largest response seen in the Vanillin and PC6S. Our uncertainty was estimated to be roughly 66%, and was the result of 20% to 30% energy fluctuations in the laser beam from shot to shot. Improvements currently underway should reduce uncertainty in future measurements to $\leq 20\%$.

A viable $\chi^{(3)}$ material would need to be at least $10^2 \rightarrow 10^4$ times larger than $CS_2$ on the *psec* to *subpsec* time scale. This is necessary to reduce the laser input power requirements, as well as the associated problem of heat dissipation in the organic material. Larger electronic responses have been reported in polydiacetaline (PTS) [7] and phenylenebenzobisthiazole (PBT) [8]. The $\chi^{(3)}$ for PTS was reported to be as large as 80 times $CS_2$. Although we do not report any outstanding materials here, progress is clearly being made toward the $10^4$ times $CS_2$ goal in PTS, and we expect to receive much better materials in the near future.

## DEVICE APPLICATIONS

Some potential applications of third order materials are in optical switching, tunable optical filters, and all-optical computing. The advantages of constructing optical devices lies in their potential ultrafast response times. Subpicosecond switching can only be achieved through optical means. Electronic devices are near their theoretical limits, with the fastest device (high electron mobility transistor) projected to operate at about 10 *psec*. In contrast, the non-resonant electronic response time of organic materials is considerably faster ($10^{-3}$ *psec*). Most device structures are based upon the intensity dependent phase shift a light pulse experiences in traversing a nonlinear medium. It is advantageous therefore to construct devices having as long an interaction region as possible, leading to a nonlinear guided wave architecture. However, in some applications the physical constraints on guided wave designs can make device construction diffcult. Major improvements in $\chi^{(3)}$ will eventually permit the design and fabrication of non-guided wave, all-optical devices, such as etalons, based on organic materials.

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