Resonant third-order hyperpolarizabilities of large organic molecules

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Resonant degenerate four-wave mixing in a number of infrared-absorbing dyes was studied with 160-psec pulses at 1.064 μm . Hyperpolarizabilities in the range of 10^{-44} to 10^{-42} $\text{V}^{-2} \text{m}^5$ were observed. A theoretical model based on a two-band system is developed that explains the results and permits the prediction of hyperpolarizabilities from the linear spectroscopic properties.

INTRODUCTION

Third-order nonlinear optical processes have attracted considerable interest recently because of their potential applications in optical phase conjugation, optical computing, and dynamic holography and their power as a spectroscopic tool.¹ Many of the studies, however, deal with inorganic semiconductors, photorefractive materials, and atomic vapors.² The main research on organic materials in this area has centered on liquid crystals for which the nonlinearity is very large but also very slow³ and on semiconducting polymers that have a large very fast nonresonant nonlinearity.⁴ The observation of the resonant susceptibility is usually occluded by a large thermally induced refractive-index change.⁵ Frequency-domain⁶ as well as picosecond and time-resolved studies⁷ of some large dye molecules show, however, the power of using cross-polarized pump and probe beams to prevent the setting up of a thermally induced phase grating and hence measuring resonant third-order hyperpolarizabilities. Appreciable nonlinearities can be observed, with the decay time of the nonlinearity being limited by the lifetime of the excited state, that is, of the order of picoseconds to nanoseconds for the samples used in this study.

LASER-INDUCED ORIENTATION GRATINGS

In degenerate four-wave mixing (DFWM; see Fig. 1) the nonlinear interaction is generally described by laser-induced gratings. With parallel-polarized beams, the probe beam E_3 and either of the pump beams E_1 and E_2 set up a spatial modulation of the absorption and/or the refractive index, termed concentration gratings.⁸ When this configuration is used, the intensity in the medium is modulated periodically in space, but the polarization direction is uniform everywhere.

In the experiments that follow, the probe wave beam is orthogonally polarized with respect to the two pump beams. The overlapping cross-polarized waves produce a polarization direction in the medium that is periodically modulated in space but has a uniform intensity distribution. By this technique concentration (and hence thermally induced) effects are eliminated, and intrinsic nonlinearities may be studied.

The spatial dependence of the polarization direction in the medium induced by orthogonally polarized overlapping waves is complicated. The interference pattern produced by overlap at an angle θ of the wave-front maxima of two fields E_1 and E_3 is shown in Fig. 2a. E_1 is linearly polarized perpendicular to the page (z direction). E_3 is linearly polarized in the plane of the page and has a polarization component $E_3 \cos \theta$ along the x direction.

At some particular instant in time, a wave front of the backward pump is incident at the plane indicated in the diagram.

The polarization directions at points x_1 to $x_1 \pm \lambda/\sin \theta$ along this plane caused by the fields E_1 and E_3 are shown in Fig. 2b. This pattern is periodic of period $\Lambda = \lambda/\sin \theta$. The backward-pump wave E_2 thus encounters a spatially periodic polarization direction. At points $x_1 \pm n\lambda/\sin \theta$, $n = 0, 1, 2, \dots$, the polarization is always linear at an angle $\alpha = \tan^{-1} |E_1/E_3|$ to the z direction, since at these points the two waves E_1 and E_3 are in phase. Between these points, the field becomes somewhat elliptically polarized because of the phase difference between E_1 and E_3 and their differing magnitudes.

The effect on the medium is as follows: The excited-state concentration is uniform but has an orientation dependence proportional to

$$|r_{12}(\theta, \phi) \cdot \hat{\epsilon}(r)|^2, \quad (1)$$

where $r_{12}(\theta, \phi)$ is the matrix element of the dipole moment μ_{12} of a molecule with coordinates r , θ , and ϕ and $\hat{\epsilon}(r)$ is the resultant polarization vector at position r . The excited-state concentration at points $x_1 \pm n\lambda/\sin \theta$ is

$$\Delta N \propto \cos^2 \beta, \quad (2)$$

where β is the angle between $\hat{\epsilon}(r)$ and the orientation of the molecule of interest. Between these points, the molecules aligned along the polarization experience preferential excitation.

Orientation gratings have been studied extensively in semiconductors.^{8,9} They arise through anisotropic-state filling where carriers are preferentially excited to energy states of a particular k direction. Although the intensity throughout the interaction region of the medium is uniform, the orientation of the excited states is periodic in space.

Fig. 1. Schematic illustrations of the DFWM geometry.

Fig. 2. a, Interference pattern created by overlap of pump wave E_1 and probe wave E_3 in the medium. b, Variation of the electric-field amplitudes and resultant polarization in the medium along the grating plane.

In liquids and liquid solutions two different processes can give rise to orientation gratings: alignment of the molecules along the field direction or distortion of the molecule's electron cloud by the field, both of which lead to a transient refractive-index grating in the material.

The first of these occurs in liquids composed of anisotropic molecules whose optical polarizabilities along different axes are unequal. In the absence of a field, the molecules of the liquid are randomly oriented, and its refractive index is isotropic. The periodic polarization field induces dipole moments that exert torques causing the molecule to be rotated into alignment with the field. Consequently, the refractive index becomes periodically modulated in space. The orientation time of the molecules may be estimated by using the Debye equation¹⁰

$$\tau_0 = \frac{4\pi\eta a^3}{kT}, \quad (3)$$

where η is the viscosity of the liquid, a is the radius of the molecular volume, and k and T are Boltzmann's constant and the temperature, respectively. In CS_2 this molecular Kerr effect forms the predominant contribution to its nonlinear index of refraction.¹⁰

In all materials, an electronic contribution to the nonlinear index of refraction can occur from an optically induced distortion of the electronic-cloud distribution. This effect is generally considerably smaller in magnitude than the molecular orientational Kerr effect. However, it can be magnified in organic systems containing long conjugated chains where delocalization of the π -electron cloud along the chain is possible. The effect is essentially instantaneous, with a time constant of $\sim 10^{-15}$ sec.

EXPERIMENTS

The experimental arrangement has been described in detail elsewhere.⁷ All the beams were derived from a single 160-psec laser pulse at $\lambda = 1.064 \mu\text{m}$. The samples were contained in $l = 2$ -mm-thick quartz cuvettes.

Each of the dyes investigated is listed in Fig. 3 together with the solvent and the spectral position of the absorption maximum. It was decided to work in liquid solutions, as problems with laser-induced damage are avoided. Of the

SAMPLE	CHEMICAL STRUCTURE	ABSORPTION MAX. (μm)
β -Carotene/Ethanol		0.48
Nigrosine/Water		0.56
DTTC/Methanol		0.74
DNTPC/Methanol		0.98
BDN/Toluene		1.03
A9860/1,2-dichloroethane		1.06
IR5/1,2-dichloroethane		1.08
S501/1,2-dichloroethane		1.47

Fig. 3. Chemical structural formulas, solvents, and absorption maxima of the samples used.

Fig. 4. a, DFWM signal peak reflectivity as a function of incident pump intensity; b, DFWM signal intensity as a function of the backward pump delay for a solution of S501 in 1,2 dichloroethane.

molecules chosen, only β -carotene has been shown to have a large nonresonant electronic nonlinearity that has been explained in terms of π -electron delocalization along its conjugated chain.¹¹ Nigrosine is a short-chain substitute of the

conducting polymer polyaniline and, as such, promises to have a large nonresonant susceptibility.¹² Figure 4 shows the measured intensity dependence of the phase-conjugate reflectivity, R_{PC} , with varying incident pump-pulse intensity for the dye S501. A square dependence is found. The decay of the nonlinear excitation was probed by temporally delaying the second pump pulse E_2 . The decay in the case of S501 was found to be faster than the pulse width of the laser, in accordance with a measured excited-state lifetime of 17 psec (Ref. 13) for this sample.

The third-order nonlinear susceptibility was calculated from¹⁴

$$|\chi_{xyyx}^{(3)}| = \frac{4c^2\epsilon_0\sqrt{R_{PC}}n^2\alpha}{3\omega IT(1-T)}, \quad (4)$$

with sample transmission T , absorption coefficient $\alpha = \ln(T)/l$, refractive index n , and laser frequency ω .

In the case of low absorption, $T \rightarrow 1$, Eq. (4) can be reduced to

$$|\chi_{xyyx}^{(3)}| = \frac{4c^2\epsilon_0\sqrt{R_{PC}}n^2}{3\omega l}. \quad (5)$$

Table 1 gives a list of experimental parameters for each sample and the measured nonlinear susceptibilities.

For molecular systems the parameter describing the nonlinear response on a molecular scale is the hyperpolarizability. The third-order hyperpolarizability is related to $\chi^{(3)}$ by

$$\gamma_{xyyx} = \frac{\chi_{xyyx}^{(3)}}{L_L^4 N_0}, \quad (6)$$

where L_L is the Lorentz field factor accounting for the microscopic applied electric field and N_0 is the number density of dye molecules, related to the concentration c by $N_0 = N_A c$, with N_A being Avogadro's number. For the calculations the formula for spherical molecules $L_L = (\epsilon(\omega) + 2)/3$ was used, which is sufficiently accurate to describe the studied molecules within the experimental errors. The conversion factor from SI to electrostatic units is

$$\gamma_{esu} = \gamma_{SI} \times 7.16 \times 10^{13}. \quad (7)$$

Table 1 also lists the measured third-order hyperpolarizabilities. They clearly decrease with increasing detuning of the absorption maximum from the laser frequency, therefore pointing to a resonantly enhanced nonlinearity. In what follows a theory is developed that seeks to explain the results at a more fundamental level.

Table 1. Solution Parameters and Measured Third-Order Nonlinearity for the Samples Used

Dye	T	n	R	$\chi_{xyyx}^{(3)}$ (m ² /V ²)	L_L^4	N_0 (m ⁻³)	γ_{xyyx} (V ⁻² m ⁵)
β -Carotene	1.0	1.3	<0.0010	$<0.2 \times 10^{-20}$	0.726	2×10^{23}	$<1 \times 10^{-44}$
Nigrosine	0.38	1.33	0.0056	2.62×10^{-20}	0.726	4.2×10^{23}	7.2×10^{-44}
DTTC	1.0	1.3	0.0054	0.8×10^{-20}	0.726	2.5×10^{23}	4.9×10^{-44}
DNTPC	0.94	1.3	0.0074	1.02×10^{-20}	0.726	4.3×10^{22}	3.27×10^{-43}
BDN	0.53	1.49	0.011	1.7×10^{-20}	1.23	1.6×10^{22}	8.6×10^{-43}
A9860	0.65	1.45	0.023	1.75×10^{-20}	1.1	5.8×10^{21}	2.7×10^{-42}
IR5	0.55	1.45	0.021	2.13×10^{-20}	1.1	1×10^{22}	1.9×10^{-42}
S501	0.67	1.55	0.27	1.25×10^{-19}	1.65	5×10^{21}	1.27×10^{-42}

THEORY

The simplest but rather successful description of absorbing organic molecules is using a two-level (band) system. A precise treatment of the nonlinear interactions occurring must start with a density-matrix formulation and must take time ordering into account. A detailed treatment of this will be published by us elsewhere. In this paper we begin with the expression derived by Gower¹⁴ from time-ordered perturbation theory. This yields a third-order polarization induced in the medium of the form

$$P^{(3)} = \frac{-2iN_0}{(2h)^3} |\mu_{12}|^4 \epsilon_1 \epsilon_2 \epsilon_3^* \left(\frac{1}{\phi_1} + \frac{1}{\phi_2} \right) \left[\frac{1}{(\Delta\omega - i\phi_{12})} - \frac{1}{(\Delta\omega + i\phi_{21})} \right] \frac{\exp[i(\omega t + k_3 z)]}{(\Delta\omega + i\phi_{12})} + \text{c.c.}, \quad (8)$$

where ϵ_i is the electric-field amplitude of beam E_i , $\Delta\omega$ is the detuning from resonance, and all other terms are as explained below or above.

This expression was originally derived for the third-order polarization giving rise to DFWM in narrow-band, two-level systems near resonance.

In such narrow-band systems as atomic sodium vapor, the energy-level populations decay radiatively at a rate $\phi_{1,2} = \Gamma_{1,2} = 1/\tau_{\text{rad}}$, and the total number of molecules contributes to the nonlinear polarization.

This is not the case in organic systems, in which the nonradiative decay rates $1/\tau_{\text{nonrad}}$ are appreciable and often orders of magnitude greater than $1/\tau_{\text{rad}}$. The effect of τ_{nonrad} is accounted for in the term

$$\phi_{1,2} = \Gamma_{1,2} + \gamma_{1,2}^c. \quad (9)$$

In the organic molecules

$$\Gamma_{1,2} = 1/\tau_{\text{rad}}, \quad \gamma_{1,2}^c = 1/\tau_{\text{nonrad}},$$

so the term $(1/\phi_1 + 1/\phi_2)$ in Eq. (8) becomes

$$1/(\Gamma_1 + \gamma_1^c) + 1/(\Gamma_2 + \gamma_2^c) = 2\tau_F \\ = 2\phi_F \tau_{\text{rad}}, \quad (10)$$

where ϕ_F is the fluorescence quantum yield. This implies that only molecules that decay radiatively contribute to nonlinear polarization. In most of the investigated inorganic molecules, the fluorescence quantum yield is as low as $\sim 10^{-4}$, such that the nonlinear polarization is considerably reduced. Consequently, organic molecules with high-fluorescence quantum yields are suited to efficient DFWM.

It should be mentioned that the induced nonlinearity de-

cays with the coherence dephasing rate $\phi_{12} = 1/T_2 = 10^{14} \text{ sec}^{-1}$. As the excited-state population decays as $K_{\text{rad}} = 1/\tau_{\text{rad}} = 10^8 \text{ sec}^{-1}$, the maximum repetition rate is limited by τ_{rad} and not by T_2 . Damage from high power absorption in the nonlinear material may, however, ultimately limit the repetition rate.

A further factor to be considered is that in liquid solutions the transition dipole moments of the solute molecules are randomly oriented. A simple geometrical calculation shows that the third-order hyperpolarizability components γ_{xxxx} and γ_{xyyx} in isotropic media are related by

$$\gamma_{xyyx} = \gamma_{xxxx}/3. \quad (11)$$

We can now write

$$P^{(3)}(r, t) = \frac{3}{4} \epsilon_0 (L_L^4 N_0 \gamma_{xyyx} \times 3) \frac{\epsilon_1 \epsilon_2 \epsilon_3^*}{8} \exp[i(\omega t + k_3 z)] + \text{c.c.} \quad (12)$$

$$= -\frac{2iN_0}{8h^3} \frac{|\mu_{12}|^4}{(\Delta\omega + i/T_2)} \phi_F 2\tau_{\text{rad}} \\ \times \left[\frac{1}{(\Delta\omega - iT_2)} - \frac{1}{(\Delta\omega + iT_2)} \right] \\ \times \epsilon_1 \epsilon_2 \epsilon_3^* \exp[i(\omega t + k_3 z)] + \text{c.c.} \quad (13)$$

Substituting¹⁵

$$|\mu_{12}|^2 = \frac{3\epsilon_0 \hbar c}{2\omega_0^3 \tau_{\text{rad}} n^3} \quad (14)$$

for the transition dipole moment and equating Eqs. (12) and (13) gives

$$|\gamma_{xyyx}| = \frac{8\epsilon_0 c^6 \phi_F}{\hbar L_L^4 \omega_0^6 n^6 \tau_{\text{rad}} T_2} \frac{1}{[\Delta\omega^2 + (1/T_2)^2]^{3/2}}. \quad (15)$$

The relevant parameters are listed in Table 2. The values of γ_{xyyx} predicted by the Eq. (15) are compared with measured values from Table 1.

Values for τ_{rad} were calculated from absorption and fluorescence spectra by using the Strickler-Berg expression¹⁶

$$\tau_{\text{rad}} = 8\pi c n^2 \frac{\int E(\lambda) \lambda^4 d\lambda}{\int E(\lambda) \lambda d\lambda} \int \frac{\sigma(\lambda)}{\lambda} d\lambda, \quad (16)$$

with $E(\lambda)$ being the fluorescence spectrum and σ the absorption cross section. Values for T_2 were estimated from the inverse linewidth of the absorption spectra ($T_2 \sim 1/\Delta\nu_a$) and agree to within 1 order of magnitude with direct femtosecond measurements.¹⁷

Agreement between experiment and theory is remarkably

Table 2. Parameters Used in Calculation of the Third-Order Hyperpolarizabilities of the Dye Samples and Third-Order Hyperpolarizabilities Calculated Using Eq. (15)

Dye	ω (sec ⁻¹)	$\Delta\omega$ (sec ⁻¹)	τ_{rad} (nsec)	τ_f (psec)	T_2 (fsec)	ϕ_f	γ_{xyyx} (V ⁻² m ⁵)
Nigrosine	3.34×10^{15}	1.57×10^{15}	3	—	40	1.0×10^{-4}	3.25×10^{-44}
DTTC	2.5×10^{15}	7.34×10^{14}	12	2000	18.7	1.67×10^{-1}	9.5×10^{-43}
DNTPC	1.89×10^{15}	1.2×10^{14}	54	—	7.6	1.0×10^{-4}	1.16×10^{-43}
BDN	1.81×10^{15}	0.41×10^{14}	56	5600	14.8	1.0×10^{-1}	2.7×10^{-43}
A9860	1.76×10^{15}	—	28	7.0	18.1	2.5×10^{-4}	4.9×10^{-42}
IR5	1.73×10^{15}	—	37	2.7	18.5	7.3×10^{-5}	1.26×10^{-42}
S501	1.26×10^{15}	—	90	17	15.3	1.89×10^{-4}	2.56×10^{-42}

good, considering the number of variables to be measured experimentally with errors ranging from 5 to 20%. In addition, the derivation of the expression for γ is based on a quantum-mechanical approach, and there are no adjustable parameters. Of significance is the fact that the theoretical values of γ for dyes whose absorption maxima fall to the long-wavelength side of $1.064\ \mu\text{m}$ agree well with experimentally measured values if $\Delta\omega$ is taken to be zero. This indicates simply that, on the time scale of the total interactions taking place within T_2 , the dye absorption appears inhomogeneously broadened.

CONCLUSIONS

We have measured the third-order hyperpolarizabilities of a range of infrared-absorbing dye molecules. A theoretical model was developed that describes the nonlinear interaction by using a two-level system. The agreement between theory and experiments is remarkably good, such that a prediction of third-order nonlinearities from the theory is possible to better than 25% from absorption, fluorescence, and quantum yield data only.

The results, both experimental and theoretical, suggest that near-infrared-absorbing organic materials, because of their large nonlinear optical susceptibilities and fast response and decay times, should be strong candidates as materials for all-optical signal-processing devices at wavelengths between 1.0 and $1.6\ \mu\text{m}$. Incorporation of these molecules into thin-film structures such as Langmuir-Blodgett multilayers would enhance the susceptibilities further, thus rendering them more compatible with semiconductor lasers and more practical as materials for such devices.

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