Organic Materials for Non-linear Optics

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Third Harmonic Generation in Organic Dye Solutions

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1 INTRODUCTION

Light at the third harmonic frequency, $\nu_3 = 3\nu_L$, may be generated by the direct third-order nonlinear interaction $\nu_L + \nu_L + \nu_L \rightarrow \nu_3$ due to the third-order nonlinear susceptibility $\chi_{THG}^{(3)}$, or it may be generated by cascading the second harmonic generation, $\nu_L + \nu_L \rightarrow \nu_2$, and the frequency mixing, $\nu_2 + \nu_L \rightarrow \nu_3$. The cascading interaction is due to the second-order nonlinear optical susceptibilities $\chi_{SHG}^{(2)}$ and $\chi_{FM}^{(2)}$. Phase-matching, $\Delta k = 0$, is necessary for efficient light generation at the third harmonic frequency. Two nonlinear media in series are necessary for phase-matching both the second harmonic generation and the frequency mixing. The various generation schemes of phase-matched third harmonic light generation are summarized in Table 1.

In this paper the efficient phase-matched third harmonic generation in some organic dye solutions is studied. A picosecond Nd-phosphate glass laser is used as pump source. The third-order nonlinear susceptibilities and hyperpolarizabilities are determined. The limiting factors of the third-harmonic conversion efficiency at high pump pulse intensities are discussed. The third harmonic generation is resonantly enhanced by two-photon absorption (TPA, S_0-S_1 absorption peak between fundamental and third harmonic frequency). The phase-matching at a certain dye concentration is achieved by the anomalous dispersion of the refractive index of the dye above the S_1-absorption band.

Table 1   Schemes of phase-matched light generation at third harmo-
           nic frequency. TPA = two-photon absorption. IC = inversion
           center.

Medium	Phase-matching	Process	Resonance	Reference
Metal vapors	puffer gas	direct	TPA	1-3
Inert gases	puffer gas	direct	-	4
Organic dye				
solutions	solvent	direct	TPA	5-11
vapors	puffer gas	direct	TPA	12
Birefringent crystals				
with IC	birefringence	direct	-	13-15
without IC	birefringence	direct and cascading	-	13,14 16,17
without IC	birefringence	cascading in two crystals	-	18,19
Liquid crystals and layered materials	reciprocal lattice vector	direct	-	20,21

2 RESULTS

Determination of nonlinear susceptibilities

As long as other nonlinear optical processes and
pump pulse depletion may be neglected the third harmo-
nic energy conversion efficiency $\eta_E = W_3/W_L$ is given by[22]

$$\eta_E = \frac{\kappa}{3^{3/2}} \; |\chi_{THG}^{(3)}|^2 I_{0L}^2 \tag{1}$$

with

$$\kappa = \frac{4\pi^2 \nu_3^2 \{\exp(-3\alpha_L \ell) + \exp(-\alpha_3 \ell) - 2\exp[-(\alpha_3 + 3\alpha_L)\ell/2]\cos(\Delta k \ell)\}}{n_3 n_L^3 c_0^4 \varepsilon_0^2 [(\alpha_3 - 3\alpha_L)^2/4 + \Delta k^2]} \tag{2}$$

α_L and α_3 are the linear absorption coefficients at ν_L
and ν_3, respectively. n_L and n_3 are the corresponding
refractive indices. ℓ is the sample length, c_0 is the
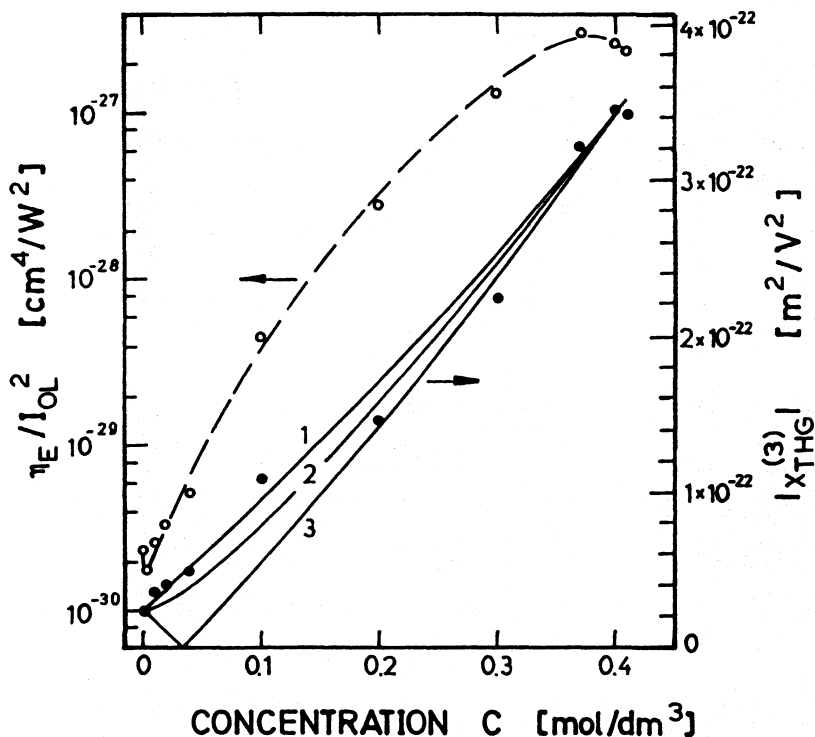vacuum light velocity, and ε_0 is the permittivity. The

Figure 1 Third harmonic energy conversion efficiency and third-order nonlinear susceptibility for methylene blue in methanol. Solid curves are calculated for $\chi_D^{(3)} > 0$ (1), imaginary (2), and < 0 (3).

wave-vector mismatch is given by $\Delta k = 6\pi\nu_L(n_3 - n_L)/c_0$. A temporal and spatial Gaussian input pulse shape is assumed [intensity $I_L = I_{0L}\exp(-t^2/t_0^2 - r^2/r_0^2)$]. An effective interaction length may be defined by

$$\ell_{eff} = \frac{\exp(-3\alpha_L\ell/2) + \exp(-\alpha_3\ell)}{[(\alpha_3 - 3\alpha_L)^2/4 + \Delta k^2]^{1/2}} \tag{3}$$

The third order susceptibility $\chi_{THG}^{(3)}$ comprises contributions from the solvent (S) and the solute (D), i.e. $\chi_{THG}^{(3)} = \chi_S^{(3)} + \chi_D^{(3)}$. $\chi_S^{(3)}$ is real since the solvent is transparent, but $\chi_D^{(3)} = \chi_D^{(3)'} - i\chi_D^{(3)''}$ is complex (resonance contributions). The nonlinear susceptibility $\chi^{(3)}$ is related to the second hyperpolarizability by

$$\chi^{(3)} = NL^{(4)}\gamma^{(3)}/\varepsilon_0 \qquad (4)$$

N is the number density of molecules and $L^{(4)} = (n^2+2)$ $\times (n^2+2)^3/81$ is the Lorentz-local field correction factor. The real and imaginary parts of $\chi_D^{(3)}$ may be resolved by measuring the third harmonic energy conversion efficiency versus dye concentration.[9] For non-phasematched third harmonic generation the cell windows and the surrounding air contribute essentially to the signal. A special experimental arrangement (sample in vacuum chamber and cell window thickness equal to an even multiple integer of the coherence length $\ell_{coh} = \pi/\Delta k$) is necessary to avoid these contributions.[22] Fig.1 shows the third harmonic conversion efficiency and the resulting third-order nonlinear susceptibility versus concentration for the dye methylene blue in methanol.[9] The S_1 absorption peak of methylene blue is at 650 nm and $\chi_D^{(3)}$ is mainly real.

Table 2 contains experimental results of $\chi^{(3)}$ and $\gamma^{(3)}$. The dye hyperpolarizabilities center around 10^{-59} cm^{4}V^{-3} ($\approx 10^{-34}$ esu). The solvents are far out of resonance. Their hyperpolarizabilities are approximately a factor of 1000 smaller (for discussion see Ref.9).

Efficient Phase-Matched Third Harmonic Generation

For some dyes phase-matched collinear third harmonic generation of Nd:glass laser pulses is possible at a fixed concentration C_{PM} due to the anomalous refractive index dispersion above the S_1 absorption band. High conversion efficiencies require long effective interaction lengths (small linear absorptions α_3, see Eq.3). The ℓ_{eff} values at C_{PM} are given in Table 2. Fig.2 shows the absorption cross-section spectrum of the dye PYC in hexafluoroisopropanol. The absorption minimum of this dye is at 375 nm and does not coincide with $\lambda_3 = 351.3$ nm. Nd-silicate glass lasers may be frequency tuned near to the absorption minimum.[23]

The third harmonic conversion efficiency η_E versus pump pulse peak intensity is plotted in Fig.3 for the
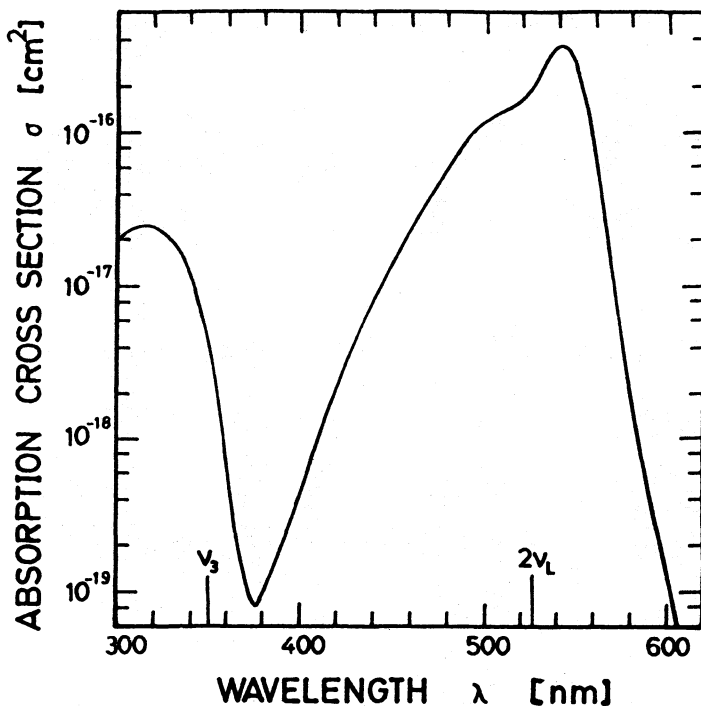
<u>Figure 2</u>   Absorption cross-section spectrum of 0.0825
             molar PYC in HFIP.

dye PYC in hexafluoroisopropanol. At high pump pulse in-
tensities the conversion efficiency saturates. n_E-values
at $I_{0L} = 2 \times 10^{11}$ W/cm² are listed in Table 2.

<u>Limitation Of Conversion Efficiency</u>

    At high pump pulse intensities the two-photon ab-
sorption dynamics (two-photon absorption, excited-state
absorption, amplified spontaneous emission, refractive
index changes) and the self-phase modulation reduce the
third harmonic conversion efficiency.[11] Some dependences
of the conversion efficiency on material parameters are
summarized in Table 3.[1,2,11]

Table 2 Dye and solvent parameters and THG results

| Dye	Solvent	C [mol/dm³]	ℓ_{eff} [μm]	$\lvert\chi^{(3)}_{THG}\rvert$ [m²V⁻²]	$\lvert\gamma^{(3)}_{THG}\rvert$ [cm⁴V⁻³]	n_E [a]
Rhodamine 6G	ME	0.3 [b]	2.8	8×10^{-22}	1.4×10^{-59}	
Fuchsin	ME	0.25 [b]	7.9	5.1×10^{-22}	1.2×10^{-59}	
Methylene blue	ME	0.37 [c]	13	3.2×10^{-22}	4×10^{-60}	
Safranine T	HFIP	0.33 [c]	48	1.7×10^{-22}	3.3×10^{-60}	1×10^{-4}
PYC	HFIP	0.0825 [c]	113	2×10^{-22}	1.7×10^{-59}	2×10^{-4}
HMICI	HFIP	0.08 [c]	160	2.48×10^{-22}	2×10^{-59}	4×10^{-4}
-	ME	24.73 [b]	2.7	2.4×10^{-23}	6×10^{-63}	1×10^{-7}
-	HFIP	9.46 [b]	5.1	1.4×10^{-23}	1×10^{-62}	1.3×10^{-7}

a: $I_{OL} = 2\times10^{11}$ W/cm². b: not phase-matchable. c: phase-matched concentration C_{PM}. ME = methanol. HFIP = hexafluoroisopropanol. PYC = 1,3,1',3'-tetramethyl-2,2'-dioxopyrimido-6,6'-carbocyanine hydrogen sulphate. HMICI = 1,3,3,1',3',3'-hexamethylindocarbocyanine iodide. $\chi^{(3)}$(esu)=$(9\times10^{8}/4\pi)\chi^{(3)}$(SI). $\gamma^{(3)}$(esu)=$8.088\times10^{24}\gamma^{(3)}$(SI).

3 CONCLUSIONS

The highest conversion efficiency obtained was 4×10^{-4}. Efficiencies n_E up to the percent region are expected for dyes with extremely low α_3 values and moderate excited state absorption cross-sections.

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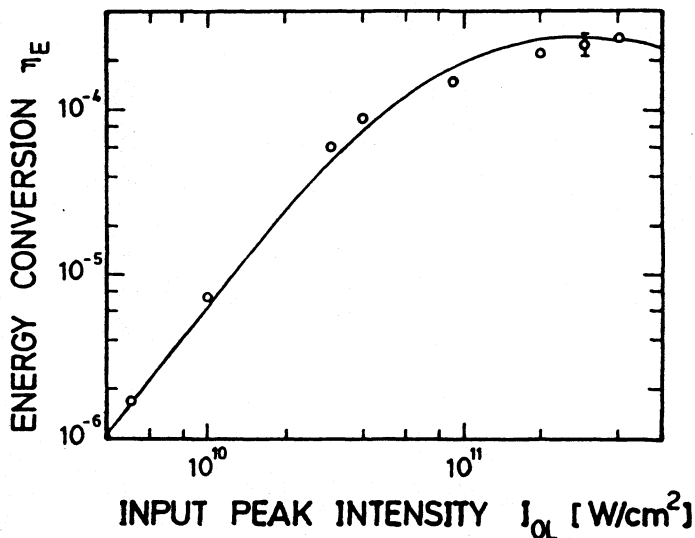
Figure 3 Third harmonic energy conversion efficiency of 0.0825 molar PYC in HFIP. Sample length 0.1 mm.

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Table 3 Limitation dependences of third harmonic generation[11]

Linear absorption, α_L	$\eta_E \propto |\chi_{THG}^{(3)}|^2 I_{OL}^2 \alpha_L^{-2}$
Linear absorption, α_3	$\eta_E \propto |\chi_{THG}^{(3)}|^2 I_{OL}^2 \alpha_3^{-2}$
TPA of $2\nu_L$, $\sigma_{LL}^{(2)}$	$\eta_E \propto |\chi_{THG}^{(3)}|^2 (\sigma_{LL}^{(2)})^{-2}$

Excited state absorption, σ_{ex}

without ground state depletion

$(\alpha_{ex} = N_{ex}\sigma_{ex} \propto \sigma_{ex}\sigma_{LL}^{(2)} I_{OL}^2)$ $\eta_E \propto |\chi_{THG}^{(3)}|^2 (\sigma_{ex}\sigma_{LL}^{(2)} I_{OL})^{-2}$

with ground state depletion

$(\alpha_{ex} = N_D \sigma_{ex})$. $\eta_E \propto |\chi_{THG}^{(3)}|^2 I_{OL}^2 \sigma_{ex}^{-2}$

Refractive index dispersion

$(D = \partial n_3/\partial\nu - \partial n_L/\partial\nu)$ $\eta_E \propto |\chi_{THG}^{(3)}|^2 I_{OL}^2 D^{-2}$

Refractive index change due to

excited state population, Δn Change of C_{PM}

Nonlinear refractive index, n_2 Change of C_{PM}

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