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ABSTRACT

We have observed in cholesteric liquid crystals optical umklapp processes with which the third-harmonic generation is phase-matched. We also show that phase-matched third-harmonic generation can be used to measure both the width and the asymmetry of ultrashort pulses.

We have previously reported on the observation of optical third-harmonic generation in a cholesteric liquid crystal satisfying a certain phase-matching condition.[1] However, because of the unusual characteristics of cholesteric liquid crystals, there exist many different phase-matching conditions. In particular, some of them require simultaneous presence of fundamental waves propagating in opposite directions. In still other cases, the third harmonic emerges propagating backward with respect to the incoming fundamental. It is obvious that, in these processes, the total momentum of the interacting waves cannot be conserved but, as will be shown later, the momentum mismatch here is actually compensated by the lattice momentum, which has a unit of $(4\pi/p)\hbar$ where p is the helical pitch of the cholesteric substance. In analogy to electrons propagating in a periodic lattice, we can describe such phase-matched third-harmonic generation processes as coherent optical umklapp processes, or nonlinear Bragg reflection.[2] In this paper, we would like to report on the observation of such processes. We also show that these processes provide a technique for measurements of pulse width and pulse asymmetry.

The problem of wave propagation along the helical axis (the z-axis) in a cholesteric liquid crystal is most easily solved in a rotating coordinate system defined by $\hat{\xi} = \hat{x}\mathrm{Cos}(\frac{2\pi}{p}z) + \hat{y}\mathrm{Sin}(\frac{2\pi}{p}z)$, $\hat{\eta} = -\hat{x}\mathrm{Sin}(\frac{2\pi}{p}z) + \hat{y}(\mathrm{Cos}\ \frac{2\pi}{p}z)$ and $\hat{z}' = \hat{z}$, where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are the three orthogonal axes in the laboratory frame.[3] In the rotating coordinates, the solution of the wave equation yields two modes of propagation along $\hat{z}$ with[3]

$$(\underset{\sim}{E}_T^{(\omega)})_{\pm} = (\mathcal{E}_\xi \hat{\xi} + \mathcal{E}_\eta \hat{\eta})_{\pm}^{(\omega)} \exp[ik_{\pm}^{(\omega)} z - i\omega t]$$

$$k_{\pm}^{(\omega)} = k_o^{(\omega)} m_{\pm}^{(\omega)}$$

$$(m_{\pm}^{(\omega)})^2 = (\lambda'^2+1) \pm (4\lambda'^2+\alpha^2)^{1/2}$$

$$(\mathcal{E}_\eta/\mathcal{E}_\xi)_{\pm}^{(\omega)} \equiv i f_{\pm}^{(\omega)} = -i2m_{\pm}^{(\omega)}\lambda'/[m_{\pm}^2+\lambda'^2 - (1+\alpha)] \qquad (1)$$

where $k_o^{(\omega)} = \omega\varepsilon^{1/2}/c$, $\lambda' = 2\pi c/\omega p\varepsilon^{1/2}$, $\varepsilon = (\varepsilon_\xi+\varepsilon_\eta)/2$, $\alpha = (\varepsilon_\xi-\varepsilon_\eta)/2\varepsilon$, and ε_ξ and ε_η are the dielectric constants along $\hat{\xi}$ and $\hat{\eta}$ in the rotating coordinates. In the lab frame, the expression of the field becomes

$$\underset{\sim}{E}_{\pm}^{(\omega)} = [(\hat{x}+i\hat{y})(1+f_{\pm}^{(\omega)}) + \qquad (2)$$

$$+ (\hat{x} - i\hat{y})(1 - f_{\pm}^{(\omega)}) \exp(i4\pi z/p)](\mathcal{E}_\xi^{(\omega)}/2) \exp[i(k_{\pm}^{(\omega)} - 2\pi/p)z - i\omega t].$$

Note that, for $\lambda'^2 > \varepsilon_\xi/\varepsilon$, a negative $k_-^{(\omega)}$ corresponds to propagating waves with the Poynting vector in the $+\hat{z}$ direction, and vice versa.

If we allow waves to propagate in both $+\hat{z}$ and $-\hat{z}$ directions, then collinear phase matching of third-harmonic generation results when $[\pm k_{\pm}^{(\omega)} \pm k_{\pm}^{(\omega)} \pm k_{\pm}^{(\omega)}] - [\pm k_{\pm}^{(3\omega)}] = 0$ for any combination of signs in the expression.[1] This can be achieved by adjusting the helical pitch by external means such as changing the temperature of the sample. Although we have observed most of these different phase matching conditions, we shall consider only two special cases here. They correspond

to

$$k_{-}^{(\omega)} + k_{-}^{(\omega)} + k_{-}^{(\omega)} = \overline{k_{-}^{(3\omega)}} \tag{3}$$

and

$$k_{+}^{(\omega)} + k_{+}^{(\omega)} + \overline{k_{-}^{(\omega)}} = k_{+}^{(3\omega)} \tag{4}$$

where $\overline{k}$ indicates waves with energy propagating in the $-\hat{z}$ direction. For both cases, we can often neglect α in the expression for $k_{\pm}$, so that $k_{\pm} \cong k_o \pm 2\pi/p$. The two phase matching conditions, Eqs. (3) and (4), then reduce to the forms $3k_o^{(\omega)} \cong -k_o^{(3\omega)} + 2(4\pi/p)$ and $k_o^{(\omega)} + k_o^{(\omega)} + (-k_o^{(\omega)}) \cong k_o^{(3\omega)} - (4\pi/p)$ respectively. Since the cholesteric structure has a period of $p/2$ along z, the unit lattice momentum is given by $\hbar(4\pi/p)$. Therefore, it is seen that the momentum mismatches in the above cases of third-harmonic generation are actually compensated by lattice momentum.

We can also treat the problem in analogy to the problem of electron propagation in a one-dimensional periodic lattice. We can put Eq. (2) in the form of a Bloch function

$$\underset{\sim}{E}_{\pm}^{(\omega)} = \underset{\sim}{u}(z) \exp[iq_{\pm}^{(\omega)} z - i\omega t]$$

as required by the Bloch theorem, where $\underset{\sim}{u}(z)$ is a periodic function of z, and $q_{\pm}^{(\omega)} \equiv (k_{\pm}^{(\omega)} - 2\pi/p) + n_{\pm}(4\pi/p)$ (with $n_{\pm}$ being integers) are limited to the first Brillouin zone ($-2\pi/p \leq q_{\pm}^{(\omega)} \leq 2\pi/p$).[4] In this formulation, Eqs. (3) and (4) become respectively

$$q_-^{(\omega)} + q_-^{(\omega)} + q_-^{(\omega)} = -q_-^{(3\omega)} + 4\pi/p \quad \text{and}$$

$q_+^{(\omega)} + q_+^{(\omega)} + (-q_-^{(\omega)}) = q_+^{(3\omega)} + n(4\pi/p)$ with n = 0, -1, or -2. These third-harmonic generation processes can therefore be called coherent optical umklapp processes, in analogy to electron scattering in a lattice.

The experimental setup and procedures were basically the same as before.[1] A mode-locked Nd-glass laser provided the fundamental pumping beam. To observe the phase-matching condition in Eq. (3), we used a sample 130 μm thick, composed of 30% (by weight) cholesteryl oleyl carbonate, 35% cholesteryl nonanoate, and 30% cholesteryl chloride.[5] The dielectric constants $\varepsilon(\omega)$ and $\varepsilon(3\omega)$ measured by the prism method in the isotropic phase at T = 55°C were 2.18 and 2.30 ± .01 respectively, and the birefringence factor α deduced from optical rotation measurements was 0.027 ± .002 in the vicinity of the phase-matching pitch. Using Eqs. (1) and (3), we then predicted that phase matching should appear at a pitch value p = 473 ± 3 μm. This corresponds to a sample temperature of 38.0 ± 1°C as obtained from the measured temperature dependence of the pitch.[6] With the sample temperature controlled to within ± 0.02°C, the uncertainty in the predicted temperature is mainly due to uncertainty in the pitch measurements.

The laser beam normally incident on the sample along $\hat{z}$ was left circularly polarized ($\hat{x} + i\hat{y}$). It fed very efficiently into the $k_-^{(\omega)}$ mode since in the present case this mode is nearly left circularly polarized in the lab frame as seen from Eq. (2). To detect the phase-matched third-harmonic generation in the backward direction, we used a

glass beam splitter to couple out part of the third-harmonic output. The results of third-harmonic intensity (normalized against the third harmonic generated from a phase-matched solution of fuchsin dye in hexafluroacetone sesquihydrate)[7] as a function of temperature are shown in Fig. 1. There indeed exists a peak at the predicted phase-matching temperature. However, the width of the peak is several times broader than that of the theoretical phase-matching curve for a monochromatic input laser beam. This broadening can be explained by assuming that the mode-locked laser pulses we used had a 7.5 psec pulse-width (full width at half maxima) and a linear frequency chirping of 20 Å/psec. As a further confirmation of the theoretical predictions, we found in the same temperature range no phase-matching peak for third-harmonic generation in the forward direction and no peak for backward third-harmonic generation with the fundamental right circularly polarized. We also found that the phase-matched third-harmonic output was nearly left circularly polarized as predicted by the theory. From the relative intensity of third-harmonic outputs from the liquid crystal and from the dye solution, we obtained a ratio of nonlinear susceptibilities $|\chi^{NL}_{LQ}/\chi^{NL}_{Dye}| \sim 0.003$.

To observe the phase-matching condition of Eq. (4), we used a mixture of 30% cholesteryl oleyl carbonate, 30% cholesteryl nonanoate, and 40% cholesteryl chloride.[8] Measurements on the sample gave $\varepsilon^{(\omega)} = 2.19 \pm .01$, $\varepsilon^{(3\omega)} = 2.31 \pm .01$, and $\alpha = 0.030 \pm .002$, from which we predicted a phase-matching pitch $p = 688 \pm 4\mu m$ and the corresponding phase-matching temperature $T = 29.9 \pm 0.5°C$. For the phase-matched third-harmonic generation, the laser beam was again circularly polarized in order to feed efficiently into the $k_+^{(\omega)}$ mode. A front surface

mirror in contact with the back of the sample provided the other fundamental beam traveling backward in the $k_-^{(\omega)}$ mode. The third-harmonic output was again coupled out by a beam splitter, and the results are shown in Fig. 2. The major peak appears again at the predicted phase-matching temperature, and its width is also primarily due to frequency chirping of the mode-locked pulses. From the relative intensity measurements, we calculated a ratio of nonlinear susceptibilities $|\chi_{LQ}^{NL}/\chi_{dye}^{NL}| \sim 0.04$. Fig. 2 also shows a minor peak at T = 31.2°C. This peak actually came from third-harmonic generation under another phase-matching condition $\bar{k}_-^{(\omega)} + \bar{k}_-^{(\omega)} + k_+^{(\omega)} = k_-^{(3\omega)}$ which was also predicted by our calculation.

Phase-matched third-harmonic generation has been used for pulsewidth measurements.[9] In principle, it can also be used to measure pulse asymmetry, if phase-matching requires two fundamental photons in one mode and one in the other mode, since then the correlation function $G(\tau) = \int_{-\infty}^{\infty} |E(t)|^4 \; |E(t+\tau)|^2 dt \neq G(-\tau)$. This is the case for the phase-matching condition in Eq. (4). To demonstrate the technique, we split the laser beam into two beams with proper polarizations. The two beams, after traveling about the same optical path, met each other at the sample from opposite sides. A variable optical delay in one arm allowed continuous variation of the relative arrival time τ of the two pulses. Our results are shown in Fig. 3. The curve shows an average pulsewidth of about 7.5 psec and a slight pulse asymmetry in the sense that the trailing edge of the pulse was steeper than the leading edge.[10] Since the observed asymmetry is weak, we have made no attempt on any more quantitative description. Here the resolution of

the curve was limited by the sample thickness which was 130 μm. For better resolution and signal-to-noise ratio, we should probably use crystals such as calcite[11] as the nonlinear medium for phase-matched third-harmonic generation in such measurements.

Presumably because of symmetry of molecular arrangement in cholesteric liquid crystals, we have observed no phase-matching peak of second-harmonic generation at any predicted phase-matching temperature. We realize that coherent, optical, umklapp processes arise in cholesteric liquid crystals because their helical structure provides a periodicity of the order of optical wavelengths. The same processes would also occur in crystals with periodic layers (one-dimensional superlattice) of appropriate thickness.[12]

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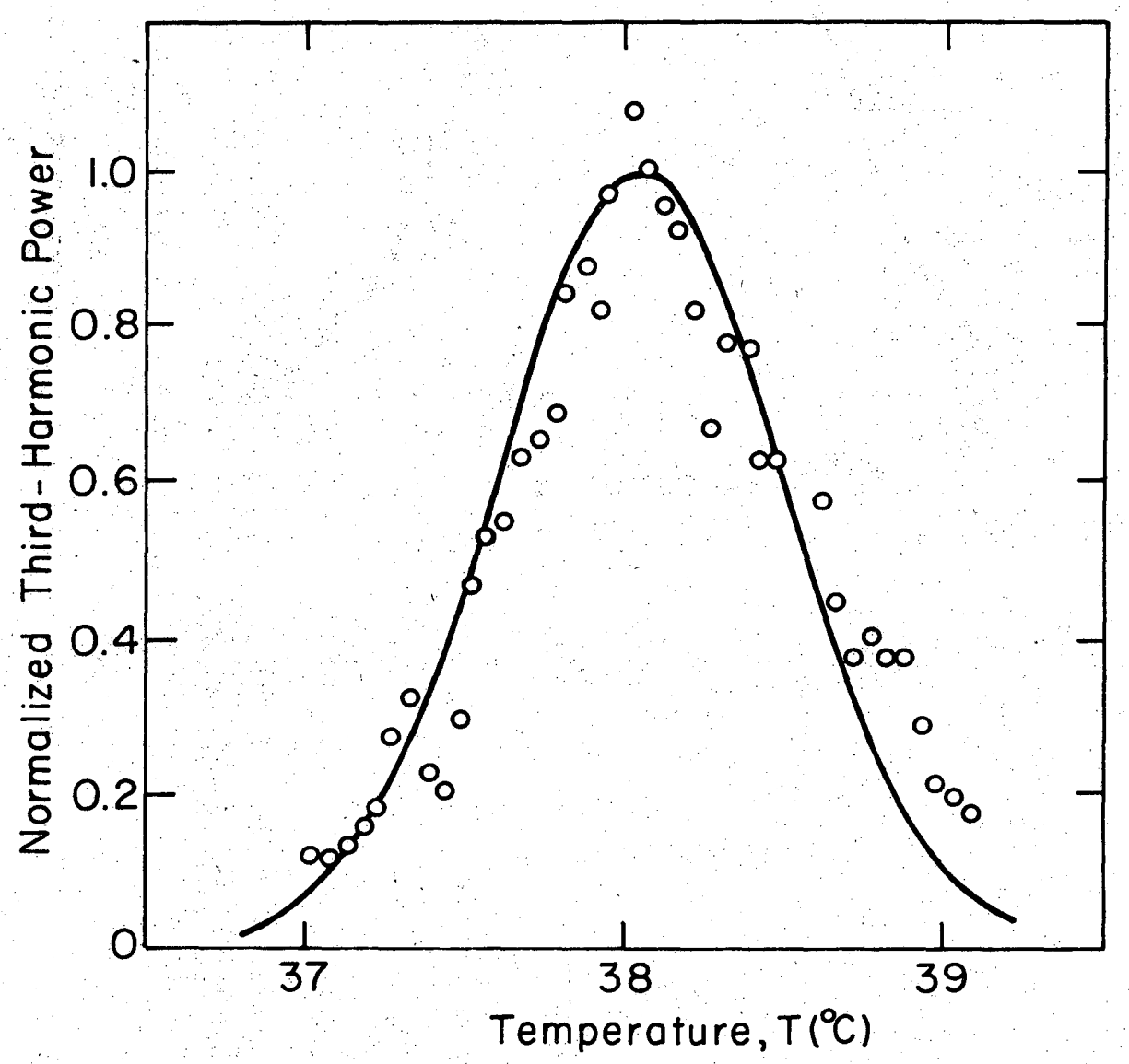
FIGURE CAPTIONS

Fig. 1. Normalized third-harmonic power generated in the backward direction as a function of temperature in a mixture of 35:35:30 by weight of cholesteryl oleyl carbonate, cholesteryl nonanoate, and cholesteryl chloride. The phase-matching peak appears at the temperature predicted by Eq. (3). The circles are the experimental data and have about a 20% uncertainty. The solid line is a theoretical phase-matching curve, assuming the laser pulses had a pulsewidth of 7.5 psec and a linear frequency chirping of 20 Å/psec.

Fig. 2. Normalized third-harmonic power around the phase-matching temperature predicted by Eq. (4) for a mixture of 30:30:40 by weight of cholesteryl oleyl carbonate, cholesteryl nonanoate, and cholesteryl chloride. The circles are experimental points with an uncertainty of 20%. The dashed curve is a smooth fit to the data.

Fig. 3. Normalized third-harmonic power vs relative time delay of the two fundamental laser pulses propagating in opposite directions in the mixture of Fig. 2 at the phase-matching temperature 29.9°C. The circles are experimental points with an uncertainty of 20%. The dashed curve is a smooth fit to the data.



XBL 7012-7411

Fig. 1

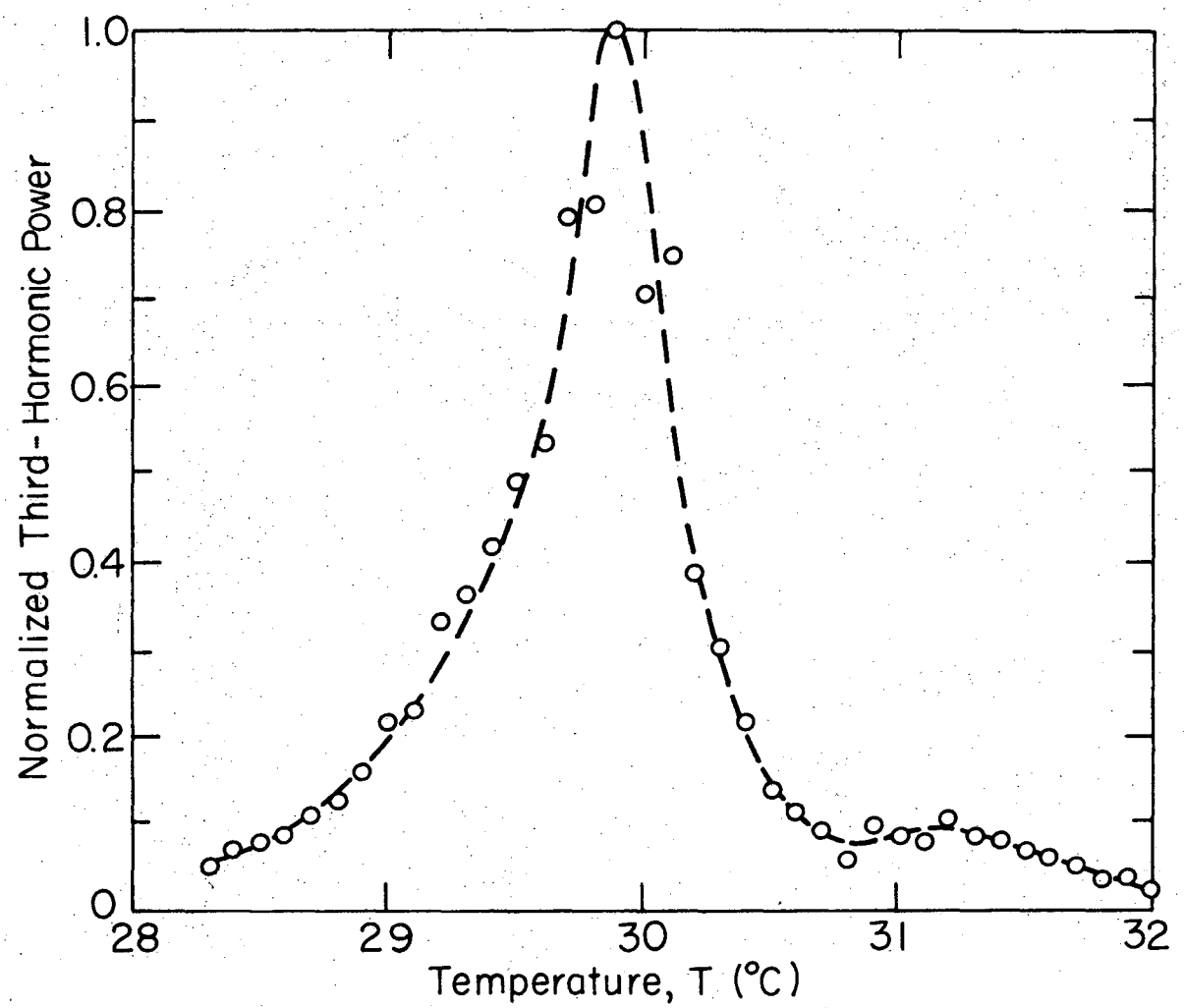

Normalized Third-Harmonic Power
1.0
0.8
0.6
0.4
0.2
0
28
29
30
31
32
Temperature, T (°C)
XBL 7012-7409

Fig. 2

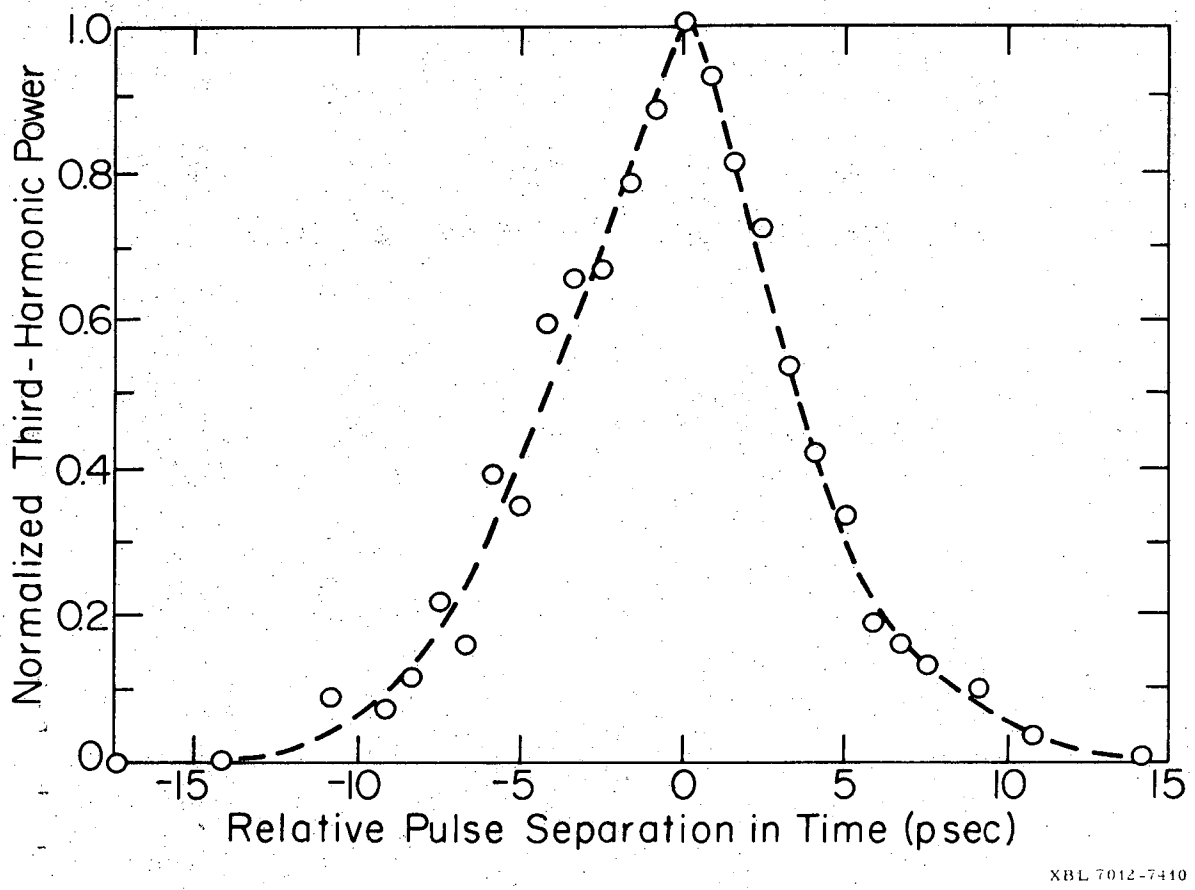

Normalized Third-Harmonic Power
1.0
0.8
0.6
0.4
0.2
0
-15
-10
-5
0
5
10
15
Relative Pulse Separation in Time (psec)
XBL 7012-7410

Fig. 3

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