Resonance enhanced THz generation in electro-optic polymers near the absorption maximum

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The electro-optic (EO) coefficient of an organic nonlinear material exhibits a sharp resonance near the absorption maximum of the material. Due to this resonance, we experimentally observe the amplitude of the THz field generated from a 3.1-μm-thick EO polymer composite to be larger than that emitted from a 1000-μm-thick crystal of ZnTe. This comparison allows us to estimate the resonance enhanced EO coefficient of the polymer composite to be over 1250 pm/V at 800 nm. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1835550]

Terahertz applications, ranging from medical[1] and near-field imaging[2] to spectroscopy of biological and chemical agents,[3] are becoming more widespread. Efficient emitters and sensors are needed to improve the performance of all of these THz systems. Photoconductive dipole antennas, electro-optic (EO) crystals, and EO polymers can be used as THz emitters and sensors. Due to their good phase matching conditions and high electro-optic coefficients, EO polymers are promising materials to increase the spectral response as well as the signal-to-noise ratio (SNR) of THz systems.

We are studying organic guest–host polymer composites consisting of various kinds of chromophores (Fig. 1) and polymer matrices. Chromophores with extended π-electron systems and strong electron donors and acceptors exhibit large molecular hyperpolarizabilities and large dipole moments. These molecular features help to contribute to large EO coefficients in poled composites of these materials. Previously, we reported efficient EO polymers for THz applications in dicyanodihydrofurane (DCDHF) guest–host mixtures of 40% DCDHF-6-V and 60% Poly(bisphenol A carbonate-co-4,4'-(3,3,5- trimethylcyclohexylidene)diphenol carbonate) (APC).[4] We refer to this composite as DAPC. In this letter, we present resonance enhanced THz generation near the absorption maximum in another polymer composite, CFAPC, which is composed of 20% CF$_3$FTC and 80% APC, and compare it to the THz generation from DAPC and ZnTe.

We used a standard THz experimental setup described elsewhere[5] based on an amplified Ti:sapphire laser system (800 nm, <50 fs, 0.5 mJ, 1 kHz). A 1000-μm-thick ZnTe crystal and two kinds of EO poled polymer films were used as THz emitters. A 2000-μm-thick ZnTe crystal was the sensor for all the experiments described here. In a direct comparison [Fig. 2(a)], we can see that the peak-to-peak amplitude of the THz field generated from a 3.1-μm-thick film of CFAPC is 15% larger than the corresponding field from a 1000-μm-thick crystal of ZnTe. Another comparison [Fig. 2(b)] shows a 1.9-μm-thick CFAPC layer together with 3-

and 80-μm-thick DAPC samples compared to a 1000-μm-thick ZnTe crystal. The signal from the 3 μm DAPC film is much smaller than that from a CFAPC film of similar thickness. However, the THz emission from DAPC can be significantly increased by using a thicker DAPC layer [Fig. 2(b)]. These results can be understood by considering the dispersion of the EO coefficient in the EO polymer composites.

In molecular nonlinear materials, the macroscopic second order nonlinear susceptibility is directly proportional to the second order molecular polarizability. By applying time dependent perturbation theory in the two-level model (TLM) approximation,[6] the dispersion of the second order susceptibility can be expressed as $\chi^{(2)}_{333}(\lambda) \propto \lambda^2(3\lambda^2-\lambda_{ag}^2)/3(\lambda^2-\lambda_{ag}^2)^2$ where λ_{ag} is the wavelength of the transition from the ground state g to the first excited state a. A sharp resonance in the material nonlinear properties is expected at the transition wavelength λ_{ag}.

Figure 3 shows the dispersion of the EO coefficient as predicted by the TLM of both EO polymer composites together with their measured UV-Vis absorption spectra. The
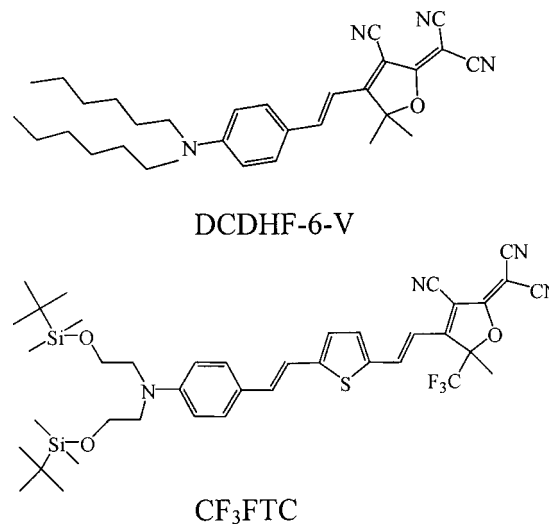
DCDHF-6-V

CF$_3$FTC

FIG. 1. Chromophores: DCDHF-6-V, CF$_3$FTC.

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FIG. 3. (Color online) Absorption spectra (arbitrary units) and the two-level model (TLM) prediction of the dispersion of the electro-optic coefficient of the CFAPC and DAPC composites. The TLM fit is applied to the 3.1-μm-thick CFAPC sample (open squares) and the 3-μm-thick DAPC sample (solid circles). The pump wavelength and TLM estimates of r_{33} at 800 nm for the CFAPC and DAPC composites are also shown.
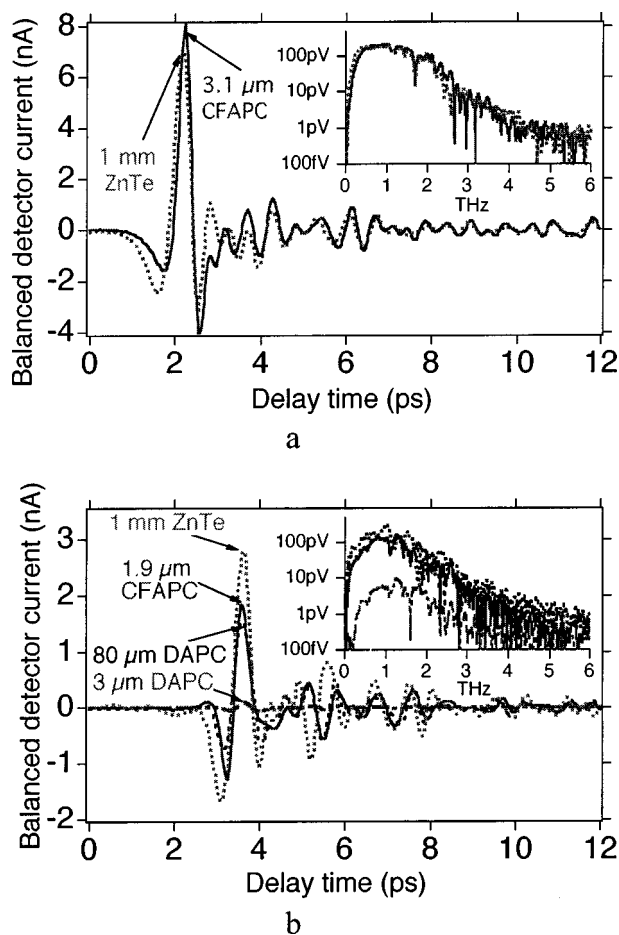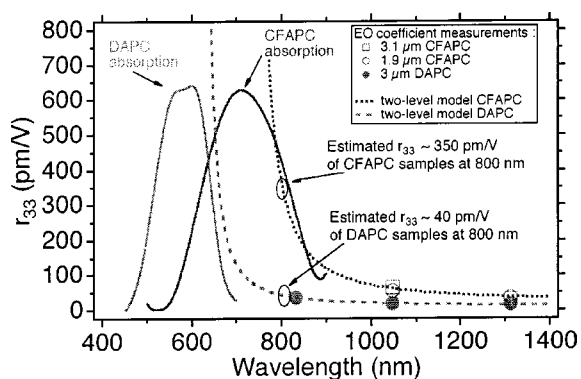
FIG. 2. (Color online) (a) Time domain THz signals generated via optical rectification in a 1000-μm-thick (110) ZnTe crystal and a 3.1-μm-thick polymer film of CFAPC. (b) Comparison of a 1000 μm ZnTe crystal, a 1.9-μm-thick film of CFAPC, and two (3- and 80-μm-thick) DAPC polymer emitters. The corresponding spectra are shown in the inset. All experiments were performed in open air and the sensor for all the experiments was a 2000-μm-thick crystal of (110) ZnTe.

CFAPC material has an absorption maximum near 710 nm, therefore, in the THz experiment, with the pump beam at 800 nm, we are working near the absorption maximum, causing a resonant increase of its EO coefficient. The DAPC material is much less resonantly enhanced since its absorption maximum (610 nm) is nearly 200 nm from the pump beam wavelength.

We measured the EO coefficient in our polymer composites using a polarimetric reflection technique.[7] The EO coefficient of our poled polymers is linearly dependent on the poling field. Our samples were contact poled at 120 V/μm (CFAPC) and 80 V/μm (DAPC). The poling filed was applied normal to the polymer layer. For DAPC, we measured r_{33} at three wavelengths: 831, 1047, and 1310 nm. For example, for the 3-μm-thick DAPC sample (filled circles in Fig. 3) the corresponding values of r_{33} are 36, 20, and 16 pm/V. Due to the strong material absorption of CFAPC at 710 nm, we could not measure its EO coefficient at 831 nm, but at 1047 and 1310 nm only. For the 3.1 μm CFAPC sample (open boxes in Fig. 3) these values are 66 and 32 pm/V, respectively. The TLM was fit to each set of these numbers allowing us to estimate r_{33} for the DAPC and CFAPC samples to be about 40 and 350 pm/V, respectively, at 800 nm. The measured optical density at 800 nm is 0.68 for a 1.6-μm-thick CFAPC layer (i.e., transmittance =21%).

The corresponding optical density of a 70-μm-thick DAPC layer is 0.06.

In the THz experiment, the polarization of both the pump and probe beams was horizontal, in the plane of incidence (POI). The polymer layer was oriented at an incident angle of 56°. This tilted geometry ensures the overlap of the incident pump field with the poling field direction and results in the maximum generated THz amplitude.[5] The angle between the z axis of ZnTe emitter and the horizontal pump beam polarization was 55°. The z axis of the ZnTe sensor was perpendicular to the POI, which corresponds to the optimal sensor orientation for a THz field polarized in the POI.[8] Thus, the orientation of the emitters and sensor was adjusted to be optimal for both polymers and crystals.[5,8,9]

By comparing the THz peak-to-peak amplitudes generated from the ZnTe crystal and the two CFAPC polymer emitters we see that the 3.1-μm-thick polymer layer generates a THz signal 115% of the 1000 μm ZnTe signal, but the 1.9-μm-thick layer gives only 70% of the ZnTe signal. These two experimental results are in good agreement: 115/70=3.1/1.9=1.6, indicating that the THz signal is linearly proportional to the polymer thickness.

We have two independent methods to evaluate the EO coefficients of our polymers. First, we can use the TLM to fit the polarimetric EO measurements. Second, we can compare the THz performance of EO polymer emitters with a ZnTe standard, for which $r_{41}=4$ pm/V. To compare the THz generation from a ZnTe crystal and EO polymers, the effective value of the nonlinear coefficient must be considered due to the slanted geometry of polymer emitters. The term r_{eff} can be expressed as $r_{eff}=r_{51}\cos\gamma\sin 2\beta+\sin\gamma(r_{13}\cos^2\beta+r_{33}\sin^2\beta)$ where β and γ are the propagation angles for the optical and THz beams, respectively, inside the polymer layer and $r_{51}\sim r_{13}=\frac{1}{3}r_{33}$ for our polymers. The film propagation angles are related to the incident angle α in the air by Snell's law: $\sin\alpha=n_{opt}\sin\beta=n_{THz}\sin\gamma$ where n_{opt} and n_{THz} are the refractive indices of polymer for the optical pump beam and generated THz beam, respectively. Also, the Fresnel coefficients for both the optical pump beam and the generated THz beam for the ZnTe and polymers must be considered. Table I compares the predictions of the TLM to the measured EO coefficients obtained from the THz experiments. For all these comparisons we assume a linear depen-

TABLE I. EO coefficients of polymer composites.

Material	Thickness	r_{33}(pm/V) at 800 nm	
		THz experiment	TLM
DAPC [a]	80 ± 5 μm	45 ± 5	44 ± 5
DAPC	80 ± 5 μm	22 ± 5	35 ± 5
DAPC	3.0 ± 0.2 μm	39 ± 5	42 ± 5
CFAPC	3.1 ± 0.1 μm	1250 ± 100	360 ± 50
CFAPC	1.9 ± 0.1 μm	1240 ± 100	330 ± 50

[a]Reference 5.

dence of the generated THz amplitude with polymer thickness and EO coefficient. Absorption of the pump beam was not taken into consideration when making the comparisons in Table I. Since we observe a linear dependence of the generated THz field as a function of the CFAPC film thickness in the range of $1-3$ μm, this approximation is reasonable for these thin films.

Previously,[5] we demonstrated that a highly poled DAPC material ($r_{33}\sim50$ pm/V at 785 nm) gives the same peak-to-peak THz amplitude as a 1000 μm ZnTe emitter. This result corresponds to the first line in Table I. In general, we can see that the TLM demonstrates good agreement with the experimental THz results for DAPC in a wide range of film thicknesses, which means that our initial assumption about the linear dependence of the THz amplitude with thickness and EO coefficient of the emitter is valid. However, for the CFAPC composite, the TLM significantly underestimates the EO coefficients determined by the THz measurements. This indicates that the TLM may be too simple of an approach near resonance. Incorporation of an inhomogeneously broadened dispersion model[10,11] is not expected to alter these results significantly.

In our experiment the observed signal-to-noise ratio (SNR) was only a few hundred (Fig. 2 inset). There are two reasons for such a low SNR. First, in order to prevent damage to the polymer films, the pump power was limited to 25 mW, with a spot size of 1 mm. The strong absorption of the CFAPC composite at 800 nm causes bleaching of the polymer layer, when illuminated for several minutes, even at this low pump power. For this reason, the CFAPC traces in Fig. 2 were obtained by averaging ten fast scans (lock-in time constant =30 ms) where each scan was taken on a different spot of the polymer film. For a consistent comparison, the traces corresponding to ZnTe and DAPC samples were obtained by the same method, although these kinds of emitters required much less caution. By using a CFAPC sample with a larger poled area, the SNR can be improved by averaging more scans. Second, the SNR is low also due to the low repetition rate of the amplified laser system used in this experiment (1 kHz).

The issue of optical damage caused by absorption is certainly an impediment to application development for the

CFAPC material at 800 nm. However, we believe that widely available and affordable THz systems for commercial applications may need to operate at $1.06-1.55$ μm, where more compact and potentially cheaper ultra fast fiber lasers operate.[12] In this wavelength range, recently developed NLO polymers[13] which are improved modifications of CF_3FTC show great promise since their EO coefficients are still very large (>55 pm/V @ 1300 nm) but the chromophores experience virtually no linear absorption. In addition, they retain 90% of their initial nonlinearity when stored at $85\,^\circ$C for more than 600 h. Our near term goal is to develop efficient THz emitters and sensors suitable for use with $1.0-1.55$ μm compact, ultrafast fiber lasers.

In summary, we have demonstrated resonance enhanced THz generation near the absorption maximum in an EO polymer composite. At a wavelength close to the absorption maximum of the nonlinear material, the EO coefficient increases dramatically giving rise to enhanced THz field generation. The THz field generated from a 3-μm-thick EO polymer film is shown to be equivalent to that generated from a 1000-μm-thick ZnTe reference. From this comparison, the near resonant EO coefficient of this CFAPC sample is about 1250 pm/V.

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