Terahertz wave detection by the Stark effect in nonlinear optical polymers

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We report on terahertz (THz) wave detection by the Stark effect in nonlinear optical (NLO) polymers, which is a type of NLO effect in a resonant condition. We compare THz wave detection by the Stark effect in NLO polymers with that by the EO sampling technique using ZnTe crystals. The differences in the optical geometry and the detection bandwidth between both techniques are also discussed. One of the advantages of THz wave detection by the Stark effect is the wide bandwidth accompanied by gapless in the THz frequency region. Utilizing the Stark effect in NLO polymers provides us with a wide variety of applications for electromagnetic wave detection.

The generation and detection of THz waves is attracting a lot of interest for applications in THz wave science and technology. Research into the generation and detection of THz pulses includes fields such as THz time domain spectroscopy (TDS) and THz pulse imaging for various material systems. Generation and detection of THz pulses can be performed using femtosecond laser pulses and the electric field of THz pulses in the near field can be detected using photoconductive switches and the electro-optic (EO) effect. The EO sampling technique is commonly used and is an important option for THz pulse detection. The EO effect induced by the electric field of THz pulses is used to produce optical birefringence in EO crystals in the vicinity of the THz pulse beam, and a synchronized femtosecond optical pulse is used as the probe pulse. The THz pulse and optical probe pulse co-propagate in the EO crystal, and the electric field of the THz pulse is encoded by monitoring the change in the polarization state of the probe pulse with an optical delay. Among EO materials, ZnTe crystal delivers an excellent performance at a wavelength of around 800 nm from a mode-locked Ti:sapphire laser and second-harmonic generation of a mode-locked 1.55 μm femtosecond laser. However, the bandwidth of EO sampling is affected and limited by the dielectric properties at optical wavelengths and the THz frequency region as well as the duration of the probe pulse.

In this paper, we report on THz wave detection by the Stark effect in nonlinear optical (NLO) polymers. The Stark effect being a kind of nonlinear optical effect under resonant conditions. The concept behind this new technique originates from Stark spectroscopy with π-conjugated molecules and polymers, which measures the change in the absorption spectrum under the application of an AC and/or DC voltage (electric field) to elucidate the electronic and vibrational structures of these materials as well as imaginary and real parts of second- or third-order nonlinear susceptibility. We are able to detect an electric field by utilizing the change in the absorption spectrum even if the electric field has a THz frequency. There are a few previous studies related to THz pulses and the Stark effect or electro-absorption effect. Upon the irradiation of CdSe/CdS colloidal quantum dots by THz pulses, the changes in the dynamics and spectrum of the THz-induced luminescence are characterized. Femtosecond optical switching in semiconductor quantum dots has been observed by the THz electro-absorption effect. However, direct probing of the THz waveform by the Stark effect, and its advantages, have not been reported. In this paper, we compare THz wave detection by the Stark effect in NLO polymers with detection by the EO sampling technique using ZnTe crystals. The differences in the optical geometry and the bandwidth between both techniques are also discussed. Finally, we mention a wide variety of applications of this technique as well as the particular advantages of the dielectric properties of NLO polymers.

Figure 1 shows a schematic for the detection of THz waves by the Stark effect and the NLO polymer used in this study. The glass transition temperature (Tg) of the NLO polymer is 148 °C. The NLO polymer backbone is a copolymer of methyl-methacrylate and cycloalkane-methacrylate, and the NLO chromophore as the side chain moiety comprises a tricyanofuran derivative as the acceptor unit, thiényl-divinylene as the π-electron bridge and amino-benzene with a benzyloxy group as the donor unit, and is a chromophore with one of the highest first hyperpolarizabilities (β). The cycloalkane-methacrylate part in the polymer backbone increases Tg, which leads to improved thermal stability of polar orientations in NLO polymers. The NLO polymer contains 30 wt% of chromophores. The NLO polymer was poled under an appropriate poling electric field and the resulting EO coefficient, r33, was 57 pm V−1 at 1.31 μm. The thickness of the poled NLO polymer film was 1 μm, and the poled film was transferred onto a cyclo-olefin polymer (Zeonex 480R) substrate with a thickness of 1 mm; Zeonex 480R is very transparent over a wide THz frequency range. Because we use the first-order Stark effect in NLO chromophores for THz wave detection, polar orientations are required otherwise the first-order Stark effect disappears under the averaged orientation. The Stark shift as shown in Fig. 1 is proportional to (μee − μgg) · E, where μee and μgg represent the excited state dipole moment, the ground state dipole moment and the electric field. E corresponds to ETHz for THz wave detection. The first hyperpolarizability β(−ω; ω, 0) under the two-level model is expressed as
Here, $\Delta \mu = \mu_{ee} - \mu_{gg}$, $\mu_{ee}$ is the transition dipole moment between the ground state and excited state and $\omega_{eg}$ is the angular frequency between the ground state and excited state. Thus, a high-$\beta$ chromophore has a large value of $\Delta \mu = \mu_{ee} - \mu_{gg}$, which exists in the numerator in the expression, and therefore shows a large Stark shift. Furthermore, the first hyperpolarizability $\beta_0$ in the low-frequency limit under the two-level model \(21\) is expressed as

$$
\beta(-\omega; \omega; 0) = \frac{\mu_{eg}^2 \Delta \mu}{2\hbar^2} \left\{ \frac{1}{(\omega_{eg} - \omega - i\Gamma_{eg})(\omega_{eg} - \omega + i\Gamma_{eg})} + \frac{1}{(\omega_{eg} - \omega - i\Gamma_{eg})(\omega_{eg} + \omega + i\Gamma_{eg})} + \frac{1}{(\omega_{eg} + \omega + i\Gamma_{eg})(\omega_{eg} + \omega + i\Gamma_{eg})} + \frac{1}{(\omega_{eg} + \omega + i\Gamma_{eg})(\omega_{eg} - \omega + i\Gamma_{eg})} + \frac{1}{(\omega_{eg} + \omega + i\Gamma_{eg})(\omega_{eg} + \omega - i\Gamma_{eg})} \right\}.
$$

(1)

Fig. 1. (Color online) Schematic illustration of THz wave detection by the Stark effect and the nonlinear optical polymer used in this study.
1.75, 1.62 and 1.61, respectively. The frequency dispersion of the refractive index is reasonable considering the relationship between the extinction coefficient and the refractive index.

Figure 4(a) shows the spectrum of the absorption coefficient $\alpha$ (in cm$^{-1}$) of the NLO polymer depicted in Fig. 1 in the 0.1–20.0 THz region. The method of sample preparation for the measurements has been described elsewhere. The NLO polymer has a broad and featureless absorption, and $\alpha$ is smaller than 60, 100 and 180 cm$^{-1}$ at 0.1–5.0, 0.1–10.0 and 0.1–20.0 THz, respectively; $\alpha$ is very small at 0.1–1.0 THz. Compared with the EO polymers with a poly-methyl-methacrylate backbone that were previously investigated, the absorption coefficient $\alpha$ of the NLO polymer is smaller, and the absorption bands are broader and featureless. Since the polymer backbone of the NLO depicted in Fig. 1 is a copolymer of methyl-methacrylate and cycloalkane-methacrylate, the portion of cycloalkane-methacrylate in the polymer backbone may reduce the absorption. It is known that cycloalkane polymers such as ZEONEX have very small absorption over a wide THz region. Figure 4(b) shows the spectrum of the refractive index $n_{THz}$ in the 0.1–7.0 THz.

Fig. 2. (Color online) (a) Schematic illustration of the optical setup for THz wave detection. (b) Schematic illustration of the unit for THz wave detection by the Stark effect. (c) Schematic illustration of the unit for THz wave detection by electro-optic sampling. In (a), the direction of polarization of the excitation laser is along the $a$-axis of the $c$-cut DAST crystal for THz wave generation.
region. $n_{THz}$ is between 1.75 and 1.55 over a wide THz frequency region and tends to decrease as the frequency increases. Accordingly, $n_{THz}$ in NLO polymers has small frequency dispersion and the refractive index in the THz frequency region is almost the same as that in the optical frequency region, which is highly advantageous for velocity matching between these frequency regions, resulting in practical advantages in many optical devices used in these frequency regions.20,24)

Figure 5(a) shows the temporal waveform of a THz electric field generated by DAST, which was detected using the NLO polymer with the optical geometry shown in Figs. 2(a) and 2(b). The p-polarized THz pulses and p-polarized probe pulses impinge on the NLO polymer sample, and the angle of incidence on the NLO polymer sample for both THz pulses and probe pulses was 60°, which was optimized by changing the angle of incidence. The THz pulses generated by DAST under an excitation of around at 8.0 mW were detected. The
temporal waveform has an initial sharp peak and contains the detailed structures. The inset shows the dependence on pump power of the peak-to-peak value of the temporal waveform detected by the NLO samples, indicating a linear relationship with pump power. This means that the amplitude of the detected temporal waveform has a linear dependence on the generated THz wave electric field because the generated THz wave electric field is linearly dependent on pump power. Negligible signals were observed when the NLO polymer sample was impinged by s-polarized THz pulses and s-polarized probe pulses at an angle of incidence of 60° or under normal incidence. The dependence on pump power, polarization and angle of incidence means that the temporal waveform detected using the NLO polymer sample is due to the first-order Stark effect. Note that no optical components such as a quarter-wave plate or Wollaston prism are present in Fig. 2(b).

Figure 5(b) shows the corresponding power spectrum calculated from the data in Fig. 5(a). We find a broadband THz wave of around 6 THz when the NLO polymer sample was detected under our experimental conditions. The large dip at 1.1 THz originates from the absorption by the lattice vibrations of DAST, and the large dip at 1.7 THz is attributable to the strong absorption of water vapor in the air. Broad dips around at 3.1 and 5.1 THz are attributable to absorption by DAST, although the broad dip at around 3.1 THz is modified by the absorption lines of water vapor in air. The dips at 4.2 and 4.5 THz are also attributable to the strong absorption lines of water vapor in the air. All these dips are observed repeatedly. We thus observed temporal waveforms that have a sharp initial peak and the detailed structures and the corresponding broadband power spectrum due to the Stark effect in the NLO polymers.

Figure 6(a) shows the temporal waveform detected by the EO sampling technique with a 100-μm-thick ZnTe crystal using the optical geometry in Fig. 2(c). We observed a similar level of signal intensity using EO sampling with 100-μm-thick ZnTe crystal as with the using Stark effect of a 1-μm-thick NLO polymer. The overall view of the temporal waveform contains dull structures compared with that in Fig. 5(a). Figure 6(b) shows the corresponding power spectrum. We find THz wave detection at up to around 4 THz under our experimental conditions and a sharper decrease in the intensity at more than 2.5 THz. The broad dip at 3.1 THz is unclear, and the dips at 4.2 and 4.5 THz and the broad dip at 5.1 THz were not observed. A sharper decrease of the intensity at more than 2.5 THz can be explained by the absorption loss and the frequency dispersion of the coherent length (l_c) that is defined by 

\[ l_c = \frac{\pi c}{\omega_{THz} n_{THz} - \lambda_{opt} (dn_{opt}/d\lambda) - n_{THz}} \]

The absorption coefficient of ZnTe is about 100 cm⁻¹ between 3.0 and
4.0 THz. This means that the loss is about 4.4 dB for 100-μm-thick ZnTe between 3.0 and 4.0 THz. Moreover, the absorption coefficient α increases strongly and sharply from 4.3 THz toward 5.3 THz, which is the resonance frequency of the transverse optical phonon mode of ZnTe crystal. This indicates that the temporal waveform modified by ZnTe itself as the detection material is observed for frequency components at more than 3.0 THz. The l_c of ZnTe at 800 nm decreases sharply at higher frequencies and l_c is less than 100 μm at 4 THz, which also results in the temporal waveform being modified by ZnTe itself (as the detection material) for higher-frequency components. The normalized amplitude of the detector response function of 100-μm-thick ZnTe is almost negligible above 4 THz due to the absorption loss and frequency dispersion of l_c, which is consistent with our data shown in Fig. 6(b).

For THz wave detection by the Stark effect in a NLO polymer we use a very thin film compared with that for THz wave detection by EO sampling of ZnTe. As shown in Fig. 4(a), α of the NLO polymer is very small between 0.1 and 1.0 THz and is smaller than 180 cm⁻¹ in the wide 0.1–20.0 THz region. The absorption loss is less than 0.08 dB for 1-μm-thick film, which is almost negligible. In addition, we do not need to consider the frequency dispersion of l_c, because the NLO polymer is very thin: n_THz in the NLO polymer has a small frequency dispersion, and the refractive index in the THz frequency region is almost the same as in the optical frequency region, which means that l_c is much longer than 1 μm. Accordingly, we consider that the temporal waveform obtained from the Stark effect in the NLO polymer precisely reproduces the intrinsic temporal waveform without any modification by the NLO polymer itself as the detection material, which is a far preferable characteristic for THz wave detection.

THz wave detection using the Stark effect in a NLO polymer may be better for broadband and gapless THz detection using shorter probes and excitation pulses because there are no restrictions on either absorption loss or frequency dispersion of the coherent length.

Numerous improvements are expected in detection efficiency. The first involves the search for NLO chromophores with a large Stark effect. We need a high-β chromophore that has a large value of Δμ. In addition, we need to consider the relationship between the wavelength of the probe beam and the maximum absorption wavelength of the chromophore. As clearly shown in Fig. 1, these two wavelengths should not be coincident, and the wavelength of the probe beam should preferably be located at a wavelength which has a large slope in the absorption line shape. The slope of the absorption line shape can be modified by the molecular design, the possibility of which we showed previously. Moreover, the local environments of the chromophores in the polymer matrix

![Graphs showing temporal waveform and power spectrum](image_url)
should also be taken into account for adjusting the absorption line shape. Thus, the control of homogeneous and inhomogeneous broadening of the absorption band, which is related to the damping constant in Eq. (1), is important. The second is increasing the value of the molecular order parameter, which is accomplished by optimizing poling conditions. The third is the poling direction. If we perform in-plane poling, Stark effect measurements using the most effective component at an angle of incidence of 0°, where the power density of the THz wave is maximized at the focal point, are possible.

Finally, we would like to emphasize the variety of uses for THz wave detection by the Stark effect in NLO polymers. This technique could be applied to electromagnetic wave detection, not only for a wideband THz wave but also for mid-infrared light or millimeter waves. A thin NLO polymer film in conjunction with a couple of dipole, bowtie or patch antennae is most promising for efficient THz wave detection by the Stark effect, because the antenna can convert and concentrate the free THz wave to its localized field in the gap,29) and the probe optical beam in the gap is modulated by the Stark effect, because the antenna can convert and concentrate the free THz wave to its localized field in the gap. Combination with photonic crystal structures or surface plasmon polaritons is also possible,30,31) which may drastically increase the efficiency of THz wave detection by the Stark effect in NLO polymers. Because NLO polymers can receive THz waves and probe beams as very thin films or a surface thin film, that is they are a planar detection medium, many extensions as well as imaging applications are expected. This is in contrast to EO sampling with a bulk detection medium. Utilizing the Stark effect in NLO polymers will open up numerous possibilities for electromagnetic wave detection.

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