

Dendrimer based terahertz time-domain spectroscopy and applications in molecular characterization

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ABSTRACT

Electro-optic Dendrimer is used to generate milliwatts of terahertz power by difference frequency method. A terahertz time-domain spectrometer (THz-TDS) has been designed around this source that exhibits wide broadband terahertz range, ~0.1 to 35 THz. Examples of molecular characterization are discussed for three common explosives and the vibrational states of Fullerenes. The explosives' spectra are unique for each explosive that allow detection and identification of the species. The Fullerenes C₆₀ and H₂@C₆₀ also exhibit distinctively different spectra and absorbance states indicating that the THz-TDS is suitable for probing increased number of vibrational states expected from molecular vibrations.

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1. Introduction

The electro-optic (EO) route for terahertz (THz) generation is advantageous, because, in this case the pump-THz conversion is not limited either by emission saturation or by heat dissipation. In EO route, the main mechanisms include: EO rectification (EOR), difference frequency generation (DFG), and optical parametric oscillation. Of these, EOR depends on a femto-second pulsed laser (femto-laser) where an ultra-fast laser pulse is introduced into the lattice of an electro-optically active material; the lattice acts as a rectifier to convert the very high frequency derived from the femto-laser pump to a relatively lower frequency pulse that falls in the terahertz range. This is the so-called electro-optic rectification effect. The rectification method usually uses a femto-laser at 800 nm wavelength while other wavelengths, e.g., 1064 nm may also be used. The difficulty here is that, not only the process is depended on the availability of a femto-laser, but two vital parameters of the terahertz radiation – the output power and the terahertz range – are completely dependent on the characteristics of the femto-laser. As such, only low average power has been produced and a range of a few terahertz has been possible. The output is always pulsed because of the pulsed nature of the femto-laser pulse train. Because of its low available power and low THz range (~5 THz) it is difficult to uniquely characterize many materials system. A source capable of providing higher power and wider THz range in a compact form, therefore, is important for spectroscopy applications.

2. Difference frequency generation

In contrast, difference frequency generation (DFG) (or two-photon excitation) not only eliminates the use of an expensive femto-laser, it also allows for producing both continuous wave (CW) and pulsed terahertz radiation, as well as higher output power and tunable terahertz range. Early efforts have shown that DFG can be achieved by means of commercially available diode lasers. Nobel Laureate Robert F. Curl Jr. (Chemistry, 1996) group [1] has reported generation of tunable far-IR radiation by means of two single-mode diode lasers by focusing the overlapped beam in AgGaS₂ crystal. Their scheme involved two diode-lasers with collimated output, spatially overlapped and focused into AgGaS₂ crystal. The combined pump generated 3.3 nW of far-IR radiation. Shi et al. [2] have reported terahertz generation by DFG method in GaSe crystal. These authors generated an average terahertz power of 0.43 μW corresponding to an average pump power of 895 mW. Our earlier work [3] showed that chromophore doped and poled poly(amido amine) Dendrimer can produce ~3.4 mW terahertz power when pumped by two fiber coupled diode lasers with a combined pump power of ~5.5 W. Thus the terahertz figure of merit ($P_{\text{THz}}/P_{\text{pump}}^2$) of this source is $1.124 \times 10^{-4} \text{ W}^{-1}$. This was achieved by means of the higher electro-optic coefficient of the EO Dendrimer, viz., 130 pm/V [3]. While 3.4 mW average THz power is a significant improvement over EOR or photoconduction, another important factor for terahertz applications, such as time-domain spectrometry, is the obtainable range from a given source. Both EOR and photoconductor sources span only up to a few terahertz. However, many molecular systems become indiscernible

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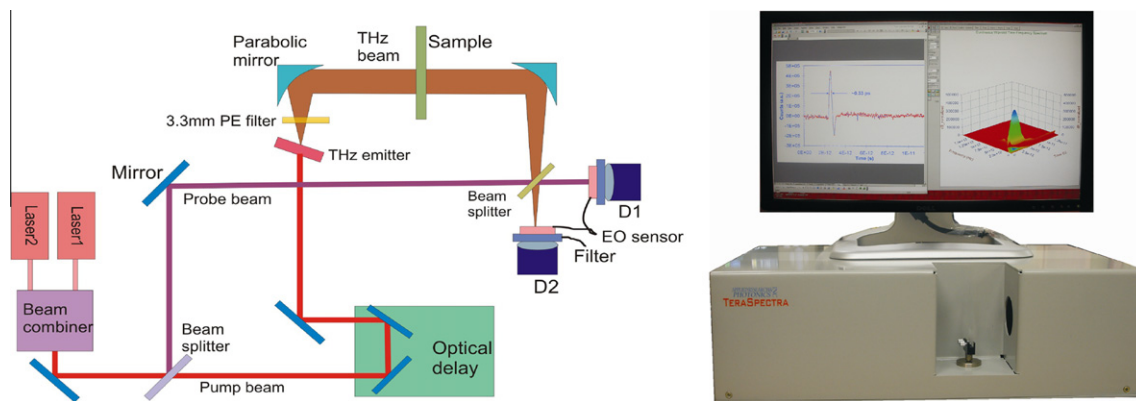


Fig. 1. Left: Layout of time-domain measurement system. Here two lasers are used with wavelengths 1064 nm and 945 nm, respectively. Consequently, a broadband terahertz spectrum is produced. Right: ARP's TeraSpectra[®] implementing the layout.

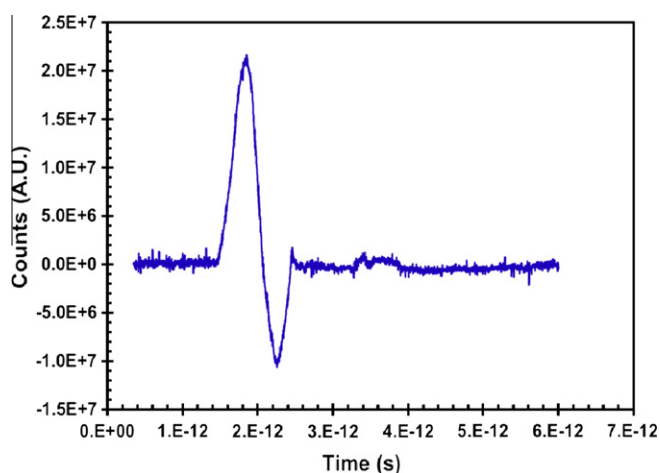


Fig. 2. Representative time-domain temporal signal (aka THz Pulse or interferogram) of the empty spectrometer.

within the first few terahertz, while over a longer range almost all molecules will exhibit discernible behavior. DFG enjoys particular advantage in this regard. Because the resulting terahertz frequencies are given by the difference of the pump laser frequencies, $\nu_{\text{THz}} \propto \nu_1 - \nu_2$, one can choose appropriate pump frequencies to obtain desired output terahertz bandwidth [3]. In practice, however, both ν_1 and ν_2 are not single frequency lasers because the diode lasers always have a bandwidth distribution around their main peaks; as such when a stationary beam of the generated terahertz is scanned by a moving beam derived from the same source, a wide frequency distribution will result. This is the so called electro-optic sampling or probing and the basis of the so called pump-probe method.

3. Terahertz time-domain spectrometer

Fig. 1 illustrates the functional diagram of a terahertz time-domain spectrometer¹ (THz-TDS) where the EO Dendrimer is used as the terahertz emitter as well as the sensor. Here we used two diode lasers at 1064 nm and 945 nm, respectively; consequently, a

¹ Although the term “spectrophotometer” has been used traditionally based on the fact that most spectrometer functions based on the measurements of light of one kind or another, however, the terahertz spectrometer deploys a different mode of measurements, viz., the time-domain measurements based on electro-optic sampling. Therefore, most authors in this area including this one choose to use the term “terahertz time-domain spectrometer (THz-TDS).”

range of ~ 35 THz is expected. A compact layout is achieved by arranging the components in the manner shown in Fig. 1. An interferogram is generated when the stationary beam is scanned by the terahertz beam whose intensity distribution is captured by the detector pair. Fig. 2 exhibits the time-domain pulse generated for the setup without any sample in. A self-calibrating algorithm is implemented such that the effect of atmospheric moisture is minimized. That is, a sample must be placed in the spectrometer for it to be measured; otherwise, the spectrometer will reproduce the same (empty) characteristic spectrum. A slightly different algorithm called Fourier transform of unevenly sampled data (aka Lomb periodogram, Fig. 3) [4] was deployed to analyze the experimental data. This algorithm essentially defines a transform by suppressing spectral leakage. Fig. 3 exhibits that the spectrum spans up to ~ 35 THz. In practical measurements this “empty” spectrum will serve as the background but when the sample is placed on a substrate (e.g., glass slide), then the blank substrate spectrum will serve as the background.

4. Principle of THz spectroscopy

When THz radiation interacts with molecules, it may stimulate many resonances such as molecular vibrations, phonons and/or other resonances in the system (in general molecular “events”), resulting in the THz photons being affected by characteristic amounts determined by a specific interaction or event (see Fig. 4). The change in energy and/or frequency yields information about the molecular nature of the interaction. Infrared and Raman spectroscopy yields similar information but not capable of detecting many resonant states as can be detected with THz because terahertz photons are sensitive to the vibrational states of the entire molecule as opposed to just a bond or charge state. Molecular simulation, especially molecular dynamics, reveals that there are numerous vibrational and conformational states possible when a molecule is not at its lowest energy state. As most material remains at its lowest energy state under normal and steady state conditions, THz perturbation will stimulate possible available states in the low frequency regions.

In common techniques such as Raman or IR spectroscopy, typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and passed through a monochromator. Wavelengths close to the laser line, due to elastic Rayleigh scattering, are filtered out while the rest of the collected light is dispersed onto a detector. Modern Raman instruments employ notch or edge filters for laser rejection and spectrographs (either axial transmissive (AT), Czerny–Turner (CT) monochromator) or FT (Fourier transform spectroscopy based), and CCD

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