

Wide Range Broadband Terahertz Emission From High $\chi^{(2)}$ Dendrimer

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ABSTRACT

Electro-optic dendrimer was used to generate CW terahertz radiation via difference frequency method. In case of electro-optic excitation, the pump-THz conversion is not limited either by emission saturation or by heat dissipation. Especially, the difference frequency generation (DFG) uses two-photon excitation that eliminates the use of a femto-second pulsed laser and allows for producing both continuous wave (CW) and pulsed terahertz radiation. This report outlines a wideband terahertz spectrometer that is designed around an EO dendrimer terahertz source. This source allows for a wide terahertz range and higher output power. The spectrometer (TeraSpectra) was calibrated with a polyethylene card. It was found that the TeraSpectra reproduces known absorbance peaks of polyethylene with many additional peaks not discovered before. The main origin of these additional peaks is from the fact that the TeraSpectra is sensitive to many resonances possible in a molecule.

Keywords: Electro-optic dendrimer, difference frequency generation, wideband terahertz, spectrometer calibration, polyethylene, absorbance spectroscopy.

1. INTRODUCTION

In electro-optic (EO) route, more than one mechanisms of terahertz (THz) generation are possible, of which EO rectification (EOR) is commonly used. But the terahertz output via rectification is completely dependent on the characteristics of a femto-second pulsed laser. When an ultra-fast laser pulse is introduced in to 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 in to a relatively lower frequency pulse, that falls in to the terahertz range; this is the so-called rectification effect. The difficulty here is that the process is dependent on the availability of a femto-second pulsed laser and two vital parameters of the terahertz radiation – the output power and the terahertz range – are completely dependent on the characteristics of the femto-second laser. As such, only low average power has been produced so far and a range of a few terahertz has been possible. Because of its low available THz range (~ 5 THz), many materials system cannot be effectively characterized by such THz source. A wider THz source, therefore, is important.

In this paper we describe wideband terahertz generation from an electro-optic dendrimer. The doping and poling process converts the ordinary dendrimer in to an electro-optically active material. This process produces an active material with higher electro-optic coefficient (~ 130 pm/V) that is used as the terahertz emitter. A CW terahertz time-domain spectrometer has been designed around this emitter without requiring a femto-second pulsed laser. In what follows, the electro-optic properties of dendrimer, and some details of the spectrometer calibration are described.

2. DIFFERENCE FREQUENCY AND DENDRIMER DIPOLE EXCITATION

Both difference frequency generation (DFG) [1] and two photon excitation (TPE) process eliminate the use of a femto-second pulsed laser which is the key for the other methods of terahertz generation such as optical rectification [2] and photo-conduction [3]. Fig. 1 shows the molecular structure of a dendrimer molecule having three shells around the central core (G_3). As indicated, each terminal group is capable of attaching two dopant molecules; thus the total dopant per dendrimer molecule is given by $N^{(G+2)}$, where G is the number of shells in a given dendrimer. When the dendrimer is doped with a suitable chromophore, multiple dipole moments are created because of the distribution of charge centers within a molecule. As can be reasonably assumed from the molecular structure of dendrimer, these dipoles will have a distribution of dipole moment, because, $\mu = ql \Rightarrow \mu(x) = ql(x)$, where μ is the dipole moment, q is the charge, and l is the separation. Fig. 2 shows the energy level diagram of difference frequency generation [4] and Fig. 3 shows the

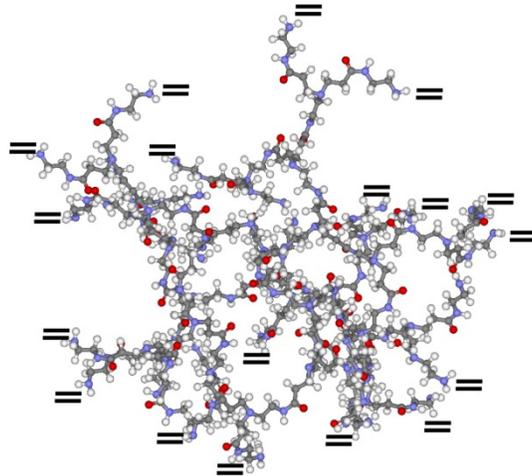


Fig. 1. Molecular structure of a dendrimer. The terminal groups each have two sites available where dopant molecules may be attached. Thus a distribution of dipoles per molecule is possible via chromophore doping.

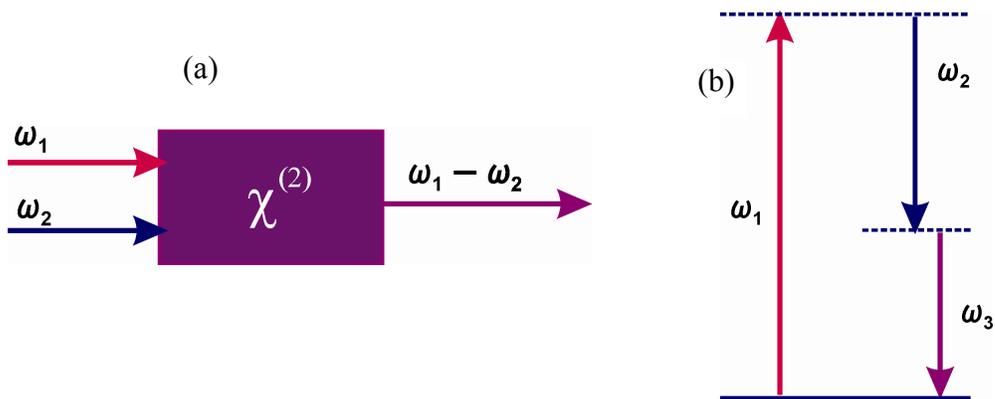


Fig. 2. (a) Interaction geometry for difference frequency generation and (b) Energy-level diagram of difference frequency generation [4].

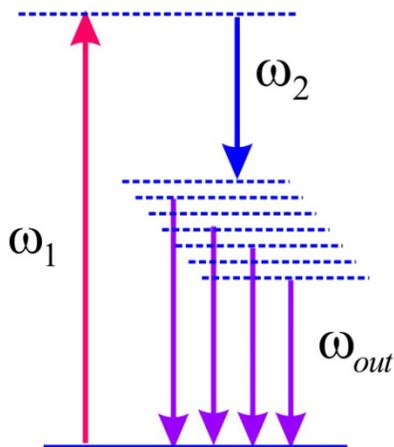


Fig. 3. Possible energy level diagram in dendrimer molecule resulting from chromophore doping and poling. A distribution of dipole moments will create multiple bands via which a broadband emission is energetically allowable.

Schematic of possible energy levels in EO dendrimer resulting from chromophore induced dipole moment distribution created by the doping and poling process. As such a broadband emission is expected.

A terahertz spectrometer was designed around the above described source; its design and functionality were described elsewhere [5]. Briefly, the beams from both input lasers are combined and the combined beam is split in to two arms of 60:40 power ratio. The 60-arm is used as the pump beam that passes through an optical delay line before being incident on the dendrimer emitter, while the 40-arm remains stationary. An interferogram is generated when the stationary beam is scanned by the terahertz beam whose intensity distribution is captured by a pair of detectors. In order to increase the dynamic reserve of the spectrometer, it is important that the ratio of the pump and stationary arms should remain fixed throughout the operation.

3. CALIBRATION VIA ABSORBANCE SPECTROSCOPY

Here we describe a calibration procedure of the terahertz spectrometer which is named “TeraSpectra.” Since the TeraSpectra is a time-domain spectrometer where the sample response resulting from the molecular interaction with terahertz radiation is recorded in time-domain (i.e., a time-delay is generated and the specimen response is plotted as a function of time); the terahertz spectrum, i.e., the observable as a function of frequency or wavenumbers, is obtained by means of Fourier transform of the time-domain signal. Thus, calibration involves reproducing known absorption peaks of standard materials to ensure measurement accuracies in this spectral region. However, TeraSpectra not only reproduces the known peaks, but also gives additional peaks – owing to its ultra-sensitivity – whose theoretical justification may or may not be known. The main origin of the additional peaks is the fact that unlike other spectrometer such as, IR, UV/Vis, Raman, etc., THz is sensitive to all kinds of resonances that may be present in a given molecule: translational, rotational, vibrational, torsional, etc. [5]. These additional peaks are thus expected, and therefore, justifies the emergence of a new spectrometer where indeed additional information is generated that are not available from its predecessors. In this section we describe measurements with an aim to compare data obtained from ARP’s TeraSpectra system with those published in contemporary literature or elsewhere. A details comparison of water spectrum is also available [6].

3.1. POLYETHYLENE CARD

A standard polyethylene card was used for measurements. It was found that the spectrum obtained from TeraSpectra reproduced absorbance peaks known from other methods [7]. In addition, many peaks not visible from other methods were also discovered. The experimental setup is shown in Fig. 4. Following procedure was used:

- a) The TeraSpectra was stabilized overnight.
- b) A time-domain signal (THz pulse) was generated for the empty spectrometer (Fig. 5).
- c) The PE card was positioned for maximum transmission (Fig. 4); no further change in any settings.
- d) THz pulse was recorded for the PE card (Fig. 6).
- e) Fourier transform was performed.
- f) Absorbance spectrum was analyzed for matching peaks.



Fig. 4. A polyethylene card mounted on the xyz-stage; positioned for maximum transmission. The setup is located at the Materials Research Institute, The Pennsylvania State University, University Park, PA 16802.

The Fourier transform absorbance spectrum of the PE card is shown in Fig. 7 and reported spectra of polyethylene are shown in Fig. 8. Table 1 shows the absorbance peaks extracted from both the terahertz and reported spectra. It is seen that the TeraSpectra reproduces the known peaks reasonably well in the lower frequency region while the higher frequency region the reproducibility is within the experimental error limits.

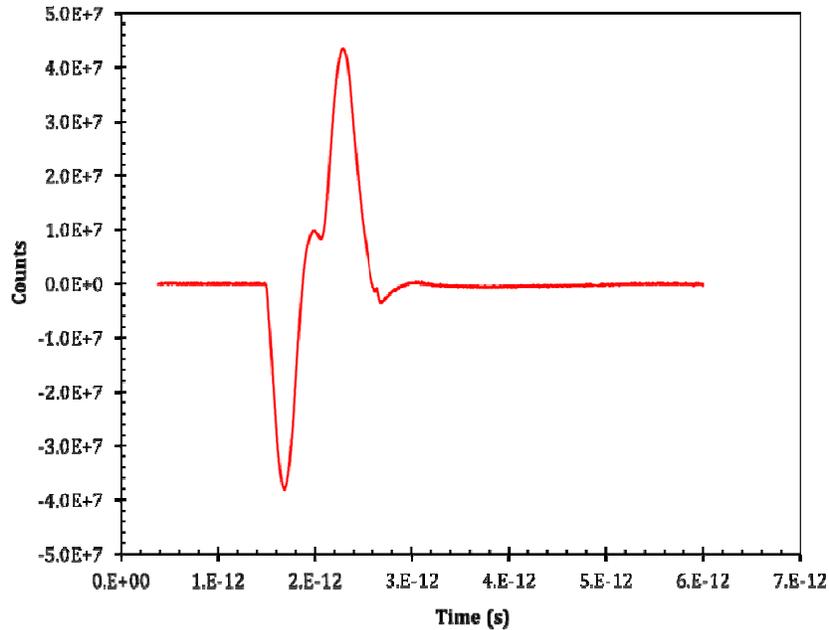


Fig. 5. Time-domain signal of the empty spectrometer

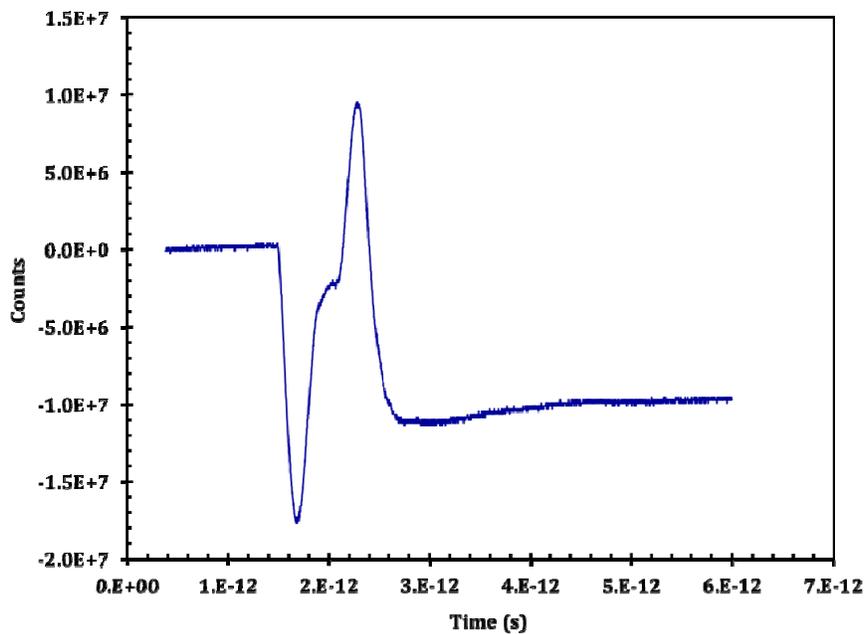


Fig. 6. Time-domain signal of the PE card. The signal was acquired from the setup shown in Fig. 4.

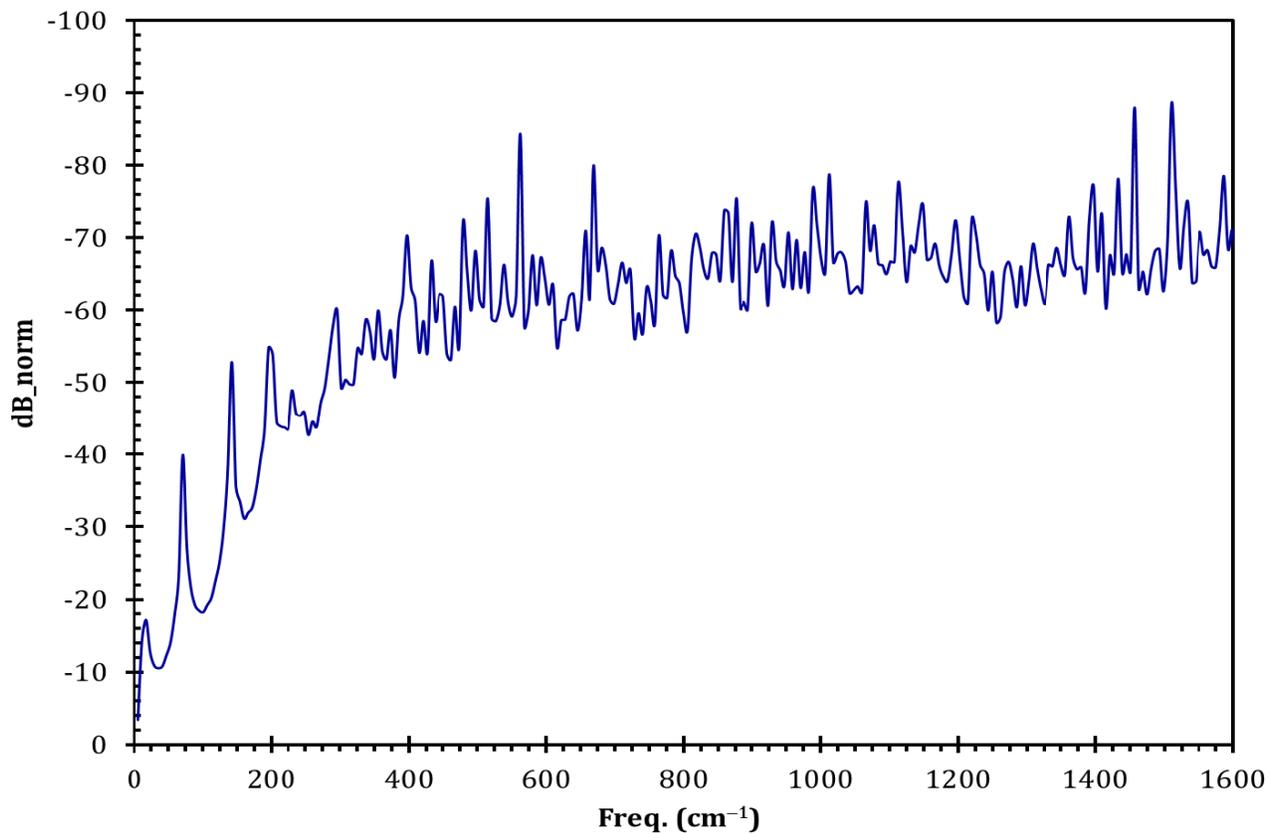


Fig. 7. Fourier transform absorbance spectrum of a PE card corresponding to Fig. 6. For samples those will be prepared on the PE card, this spectrum will serve as the background.

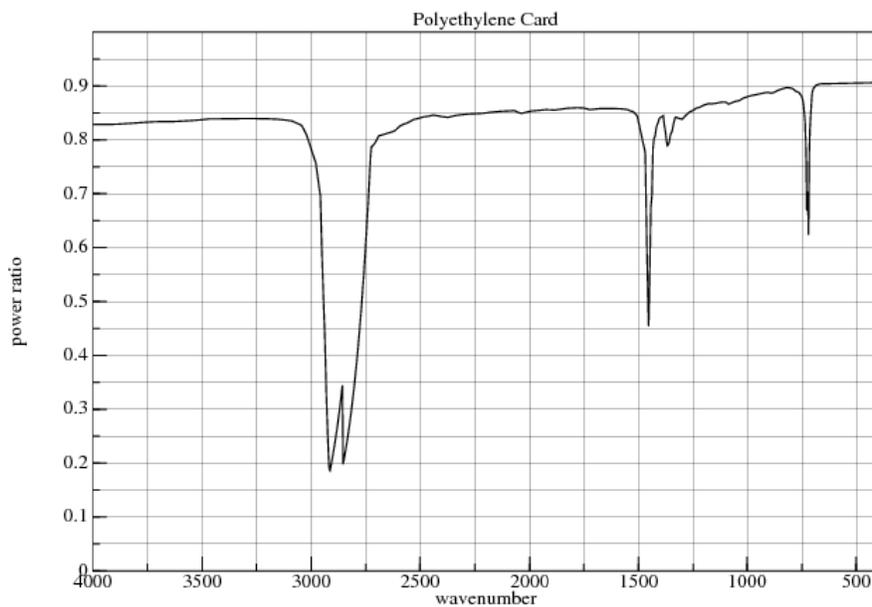


Fig. 8. Polyethylene spectrum adapted from FreeSnell: <http://people.csail.mit.edu/jaffer/FreeSnell/polyethylene.html>

Table 1. Comparison

Source	Reported (1/cm)	TeraSpectra (1/cm)
Sigma-Aldrich [7]	70.8	71
FreeSnell [6]	723.3	722.5
	749.5	746.2
	1466.02	1457, 1469
	1492.23	1486.4, 1510

4. SUMMARY

Wideband CW terahertz radiation has been generated from an electro-optic dendrimer without requiring a femto-second pulsed laser. A spectrometer has been designed around this source. A standard polyethylene card was used to calibrate the spectrometer. Calibration involves reproducing known absorption peaks of standard materials to ensure measurement accuracies in this spectral region. However, TeraSpectra not only reproduced the known peaks, but also yielded additional peaks owing to its ultra-sensitivity. The theoretical justification of these additional absorbance peaks may or may not be known *a priori*. The additional peaks arise because of the fact that unlike other spectrometer such as, IR, UV/Vis, Raman, etc., THz is sensitive to all kinds of resonances that may be present in a given molecule, viz., translational, rotational, vibrational, torsional, etc. [5]. The additional peaks are thus expected, and therefore, justifies the emergence of a new spectrometer that indeed yields additional information that are not available from its predecessors. Because too many peaks are placed on a single plot (Fig. 7), the plot looks rather busy. It was found that in lots of places the peaks are clearly defined while in some places they are not. For clear visualization, the x-axis may be enlarged and the plot may be divided in to several segments. In view of Table 1, it is seen that the TeraSpectra reproduces the known peaks reasonably well in the lower frequency region while in the higher frequency region the reproducibility is within the experimental error limits.

5. REFERENCES

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