Elimination of scattering effects in spectral measurement of granulated materials using terahertz pulsed spectroscopy

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Spectral distortions are commonly observed in terahertz spectra of granulated materials. These spurious structures in the spectroscopy are caused by scattering due to the refractive index mismatch between the particles and their surrounding medium. We find that the scattering contribution is random across sample positions and could be eliminated by summing and averaging multiple measurements over a sample area. We present experimental results of both absorbing and nonabsorbing particles in the size range $50-250$ μm and also give an empirical expression to describe the effect of grain size on the scattering-induced extinction as a function of frequency. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2840719]

The terahertz region of the electromagnetic spectrum spans the frequency range between the midinfrared and the millimeter/microwave. The relatively unexplored central part of the region ($0.3-3$ THz or $10-100$ cm^{-1}) comprises frequencies lower than those corresponding to most internal vibrations of isolated small molecules. Instead, spectra contain information on motions associated with coherent, delocalized movements of large numbers of atoms and molecules.[1] The newly developed technique of terahertz pulsed spectroscopy (TPS) has been demonstrated to be a powerful tool for studying these low-frequency vibrational modes.[2–4] A major advantage of TPS is that the transient electric field, not simply the intensity of the terahertz radiation, is measured. This coherent detection scheme not only yields terahertz spectra with excellent signal-to-noise ratio and high dynamic range but also allows both the absorption coefficient and refractive index to be obtained without the need for Kramers–Kronig dispersion relationship.[2] Owing to these advantages, TPS is being widely used in studying low-frequency vibrational modes for a wide variety of samples including chemical, biological, pharmaceutical, and security-related materials.[5–10] In most of the work reported so far, TPS measurements were performed on solid crystalline sample (powder) in the form of pellet. Therefore, it is essential to investigate the scattering of terahertz radiation by particles presented in the sample and, in particular, the practical ways to minimize the scattering effect for getting reliable terahertz spectra of granulated materials.

The propagation of terahertz pulses in random media comprising many 800-μm-diameter Teflon spheres has been studied previously,[11] and the scattering of terahertz pulses by individual spheres or cylinders has also been measured.[12] These novel studies utilized the unique capabilities of TPS for characterizing the scattered electric field with unprecedented spatial and temporal resolution, leading to further insight into the scattering phenomena.[13–15] In a recent Food and Drug Administration (FDA) study, Wu *et al.*[16] measured terahertz spectra of a number of granulated pharmaceutical materials with grain size comparable to terahertz wavelength and found that the particle scattering becomes significant at higher terahertz frequencies. Very recently, Zurk *et al.*[17] measured terahertz scattering of granular materials (polyethylene particles with two different grain sizes) and explained the observed scattering response using the dense medium theory. In this paper, we study the effect of particle scattering on TPS spectrum in the frequency range $0.3-3$ THz ($10-100$ cm^{-1}) for both absorbing and nonabsorbing particles in the size range $50-250$ μm. We find that the scattering contribution could be eliminated by either a novel procedure of summing and averaging over a mapped area or, where this is possible, a traditional procedure of proper sample preparation.

The nonabsorbing material used is the high-density polyethylene (PE) powder (Inducos $13/1$ and $13/3$, with particle sizes <80 and $50-200$ μm, respectively) (Induchem AG, Switzerland). The PE particles in these samples were further size fractionated using test sieves (Endecotts Ltd, UK) into six size categories: <53 μm, $50-75$, $75-80$, $75-106$, $106-150$, and $150-200$ μm. PE is nearly transparent with a frequency-independent index of refraction of 1.53 in terahertz region.[9] Sucrose was used as an absorbing material. Granulated sucrose (the coarse grain size up to 800 μm) was first crushed to a coarse powder using pestle and mortar, and then milled using a Specamill (Specac Ltd, UK), and finally size fractionated into five size categories: <52, $53-75$, $75-106$, $106-150$, and $150-250$ μm. For TPS measurements, the particles were contained in a specially designed powder cell with a volume of 0.53 cm^3 composed of two 3-mm-thick PE windows separated by a 3-mm-thick spacer. In all TPS measurements, the cell was filled with either 300 mg PE powder or 60 mg sucrose diluted in 260 mg PE (particle size <53 μm). The filling factor, which is defined by the ratio of the sample volume to the cell volume, was estimated to be 0.6 ± 0.04 for above powder samples.

The experimental setup and operating principle for TPS have been well documented.[2–4] In our experiments, we used a TPS spectra 1000 transmission spectrometer (TeraView Limited, UK). Measurements were performed in rapid scan mode at a rate of 30 scans/second, providing a useful spectral range 0.2–3.0 THz (6–100 cm^{-1}) with a spectral resolution of 40 GHz (1.3 cm^{-1}). For each sample or reference (empty powder cell) measurement, the terahertz waveform
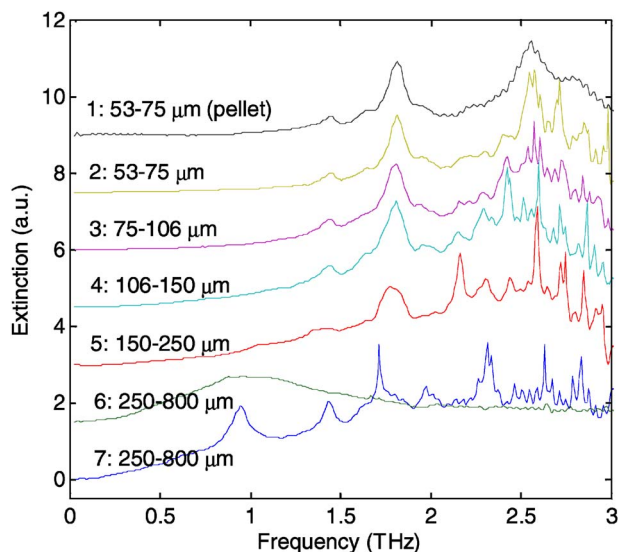
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FIG. 1. (Color online) Extinction spectra measured for absorbing sucrose samples in a powder cell. The sample composes of 60 mg sucrose and 260 mg PE powder. The PE particle size is smaller than 53 μm, and the sucrose particle sizes are $53-75$ μm [(1) and (2)], $75-105$ μm (3), $105-150$ μm (4), $150-250$ μm (5), and $250-800$ μm [(6) and (7)]. The spectra are offset vertically for clarity.

was obtained by coadding 1800 scans. Extinction spectrum (with contribution from both absorption and scattering) was then calculated as

$$\varepsilon(\nu)$$
$$= -2 \log_{10} \left| \int_{-\infty}^{\infty} E_{\mathrm{samp}}^{\mathrm{THz}}(t) e^{j2\pi\nu t} dt \middle/ \int_{-\infty}^{\infty} E_{\mathrm{ref}}^{\mathrm{THz}}(t) e^{j2\pi\nu t} dt \right|,$$

where $E_{\mathrm{samp}}^{\mathrm{THz}}(t)$ and $E_{\mathrm{ref}}^{\mathrm{THz}}(t)$ are sample and reference terahertz waveforms, respectively.

Figure 1 shows extinction spectra recorded for 60 mg granulated sucrose diluted in 260 mg PE (particle size <53 μm). A major peak at 1.81 THz (60 cm^{-1}) and a small one at 1.45 THz (48 cm^{-1}) appear in all spectra measured for sucrose particle sizes up to 250 μm. In addition, two shoulders at 1.64 and 1.95 THz (55 and 65 cm^{-1}) are also visible for samples with smaller particle sizes. These well-resolved spectral features have been reported previously by Walther *et al.*[9] and are explained as originating from intermolecular vibrational modes of the hydrogen-bonded network of the crystalline structure. It can be seen that the signal-to-noise ratio is degraded at higher frequencies owing to scattering, causing the sharp noisy features in the absorption spectra above 2 THz (66 cm^{-1}). For the same reason, these features occur at lower frequencies for larger particles where the scattering is stronger.

When the average particle size increases above 250 μm, we observed anomalous spectral features, and we also found that the spectra vary significantly depending on the part of the sample measured. This indicates that the sample can no longer be considered as uniform, with the highly absorbing sucrose particles separated by regions of PE with high transmittance. Furthermore, in the TPS spectra 1000 instrument, the terahertz beam is focused at the sample position to a spot of diameter $\sim$800 μm at 1 THz; thus, only a limited number of sucrose particles are present in the terahertz beam path. As a result, individual scattering events of reflection and refraction become significant and can be directly detected in time
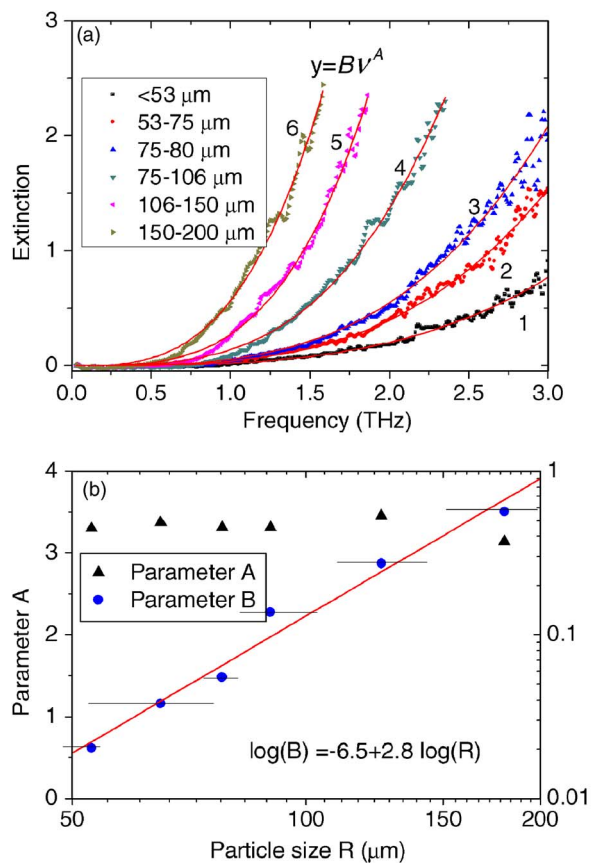

FIG. 2. (Color online) (a) Extinction spectra measured for 300 mg nonabsorbing polyethylene particles in a powder cell. Point, experimental results; Solid line, best-fit results obtained using the formula given in the inset. (b) Parameters A (triangle) and B (solid cycle) plotted as a function of particle size. Solid line represents the best-fit results for parameter B and the best-fit equation is given in the inset. Note that both parameter B and the particle size are in logarithm scale.

domain. After using a deconvolution procedure to remove instrumental system response from the recorded raw terahertz waveform, these individual scattering events were indeed observed in the terahertz waveform corresponding to the terahertz spectrum with artifacts (curves 6 and 7 of Fig. 1). The deconvolution is performed first by dividing, in the frequency domain, the raw terahertz waveform reflected from a sample by a reference waveform recorded from a mirror. A numerical bandpass filter is then applied to remove high- and low-frequency noise. The normalized terahertz spectrum is finally inverse Furier transformed to get the terahertz pulse waveform.

In order to further understand the effect of the grain size on the scattering-induced extinction, we measured the extinction spectra of nonabsorbing PE powders using terahertz pulsed spectroscopy. As shown in Fig. 2, the extinction increases with frequency in the range $0.5-3.0$ THz. We found that the observed extinction spectra can be modeled using $\varepsilon(\nu) = B\nu^A$, where parameter A was found to have a best-fit value of 3.3 ± 0.2 for all particle sizes studied, indicating that the scattering-induced extinction increases as the 3.3 power of the frequency. Parameter B, on the other hand, was found to increase as the third power of the particle size [see the curve of Fig. 2(b) and the equation given in the inset]. Theoretical calculations[18] indicate that for particles of these sizes, the extinction is proportional to the sixth power of the particle size. However, the particle number density decreases
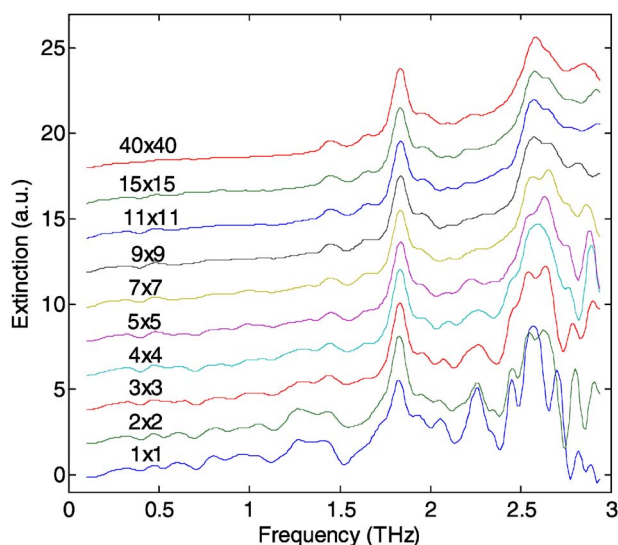
FIG. 3. (Color online) Extinction spectra measured for granulated sucrose samples with particle size up to 800 μm. The number above each curve is the pixel number used in averaging (over a squared area), and the spectra are offset vertically for clarity.

as the third power of the particle size because the PE mass in the cell is constant (300 mg). This explains our experimental observations that the overall extinction increases as the third power of the particle size in the range 50–250 μm.

These results highlight the need of a proper sample preparation in order to obtain reliable terahertz spectrum of granulated samples. In many real terahertz spectroscopic applications, scattering effects can be minimized by (1) using finely milled samples ensuring that powders are well mixed for even distribution of absorbing particles and (2) compressing loose powders to form compact pellets, thus reducing the refractive index mismatch between the absorbing particle and its surrounding medium. One such example is shown in curve 1 of Fig. 1, where the high-quality terahertz absorption spectrum of granulated sucrose has been obtained by using a pellet sample comprising of fine sucrose and PE particle.

In some specific terahertz spectroscopic applications, it may not be always possible to prepare fine particle samples (for example, explosive material is difficult to be milled). Here we propose an alternative procedure to obtain a reliable terahertz spectrum of the granulated sample with large particle sizes. For demonstration purpose, we used a highly scattering material, i.e., the raw granulated sucrose with the coarse grain size up to 800 μm. Instead of single point measurement, we used a TPI imaga 1000 (Teraview Ltd, UK)[6] to map the sample over an area of 10×10 mm^2 (pixel number, 50×50; step size, 200 μm; overall measurement time, 2 min). Figure 3 shows the obtained terahertz spectra of the granulated sucrose sample. It is clear that the terahertz spectrum obtained using single point measurement is noise and subject to spectral artifacts related to the terahertz scattering. However, by averaging over a large area, reliable terahertz spectrum of granulated sucrose has been obtained. The underlying mechanism of this averaging procedure is that the scattering contribution is random (scattering events are not in phase and vary across sample positions) and thus will be averaged out, while the sample contribution will be enhanced by the averaging process.

It should be pointed out that in this work, we used a highly scattering system, that is, a terahertz beam focused

into a loosely packed powder consisting of large particles, to highlight the scattering effects. In fact, terahertz spectroscopy has the advantage over many other optical techniques (in which particle size below 1 μm may be required[19]) because it utilizes much longer wavelengths and is therefore less prone to scattering by microsized particles. Nevertheless, with the increasing widely spread applications[3–11] and the ever-increasing bandwidth of the TPS systems,[3,20] the effects of scattering on TPS measurements must be taken into account, particularly for granulated materials with sizes comparable to the wavelengths of the terahertz radiation.

In conclusion, we have studied the effect of particle size on scattering in transmission at terahertz frequencies. For nonabsorbing PE particles, the scattering-induced extinction increases as the 3.3 ± 0.2 power of the frequency in the range 0.3–3.0 THz (10–100 cm^{-1}) and as the third power of the particle size in the range 50–200 μm. For absorbing sucrose particles, the absorption features dominate the extinction spectrum for particle sizes up to 150 μm. However, spectral artifacts are observed when the sucrose particle size approaches the terahertz wavelength. Therefore, for reliable terahertz spectroscopic measurements, it is important to consider scattering effects and, wherever possible, to minimize such effects by using finely milled powder and compressed powder into the form of pellet. Alternatively, good quality terahertz spectrum can also be obtained by averaging multiple measurements over a large sample area.

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