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Terahertz scattering by two phased media with optically soft scatterers

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Frequency dependent absorption by materials at distinct frequencies in the THz range is commonly used as *spectral-fingerprints* for identification and classification. For transmission measurements, the substance under study is often mixed with a transparent host material. Refractive index variations arising from the presence of impurities and inconsistencies in the sample's internal structure often cause the incident radiation to scatter. This can significantly distort the measured *spectral-fingerprints*. In this letter, we present a numerical approach to allay the scattering contribution in THz-TDS measurements, provided the sample's refractive index is known, and reveal the true absorption spectra for a given sample. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4768888]

In the last few decades, terahertz time domain spectroscopy has seen an increasing popularity in a variety of applications such as pharmaceutical material characterization, food quality control, investigation of explosive materials, and biomedical sensing. Many researchers have contributed to the development of several databases containing THz spectral *signatures* of various pure reagent-grade materials.[1,2] The availability of such databases has spurred the deployment of THz-TDS systems for real world applications. A common sample preparation technique is to mill or grind the sample material into fine powder and mix it with spectroscopic grade polyethylene powder to form rigid sample pellets. Such a preparation technique ensures a uniform sample structure with small particle sizes. However, in absence of laboratory conditions, invasive access to the sample material may not always be possible. Under such conditions, due to variations in refractive index within the sample, caused by granularity, impurities and the non-uniform internal structure, the THz radiation undergoes multiple scattering which can significantly alter/obscure the spectral fingerprints of the material.

In this letter, we present a numerical approach based on the modified Rayleigh-Gans-Debye approximation to mitigate the scattering contribution in transmission mode THz-TDS measurements of two phased media with absorbing constituents. The resulting expression describes the scattering attenuation in terms of the refractive indices of the sample constituents. The proposed technique not only eliminates the increased baseline, but also corrects the extinction spectrum for asymmetrically distorted absorption bands, often observed as consequence of multiple scattering in the sample.[3–5] The method is tested on an experimentally obtained extinction spectrum of a sample made of α-monohydrate lactose and PE powder.

The basic theory of light scattering by a single particle embedded in a non absorbing medium has been thoroughly investigated and described by various researchers.[6–8] Here, we consider a particle with refractive index n_p embedded in a homogeneous non-absorbing medium of refractive index n_m. If the relative refractive index of the embedded particle is close to unity, and its size satisfies the condition $kd|m-1| < 1$, where $m = n_p/n_m$, d is the particle diameter and k is the propagation constant of the incident radiation, then the Rayleigh-Gans-Debye (RGD) approximation for light scattering by single particle should be valid.[9] Such particles are often termed as *optically soft* scatterers. However, several researchers have reported the applicability of the RGD approximations for values of $kd|m-1|$ upto 3 with only limited disagreement ($\approx$10%).[17–19] Shimizu *et al.*[10] proposed a modification to the RGD approximation and compared the resulting scattering pattern with that calculated using exact Mie theory. Their results showed a good agreement, in the small-angle region, with the Mie theory, even for conditions beyond the validity of ordinary RGD approximation $kd|m-1| \gg 1$ (2.65 and 5.5 for their experiments). Here, we present a numerical approach based on the modified RGD approximation proposed by Shimizu *et al.*,[10] to eliminate the scattering contribution in transmission mode THz-TDS measurements.

For a two phased medium composed of the homogeneous background (n_m) and N identical particles with refractive index n_p, the transmitted intensity can be given by

$$I_t = I_0 \exp(-\alpha l), \tag{1}$$

where α represents the attenuation suffered by the radiation and l is length of the medium. Assuming the medium to be sparse, the total scattering attenuation can be obtained by multiplying the total number of scatterers (N) with the scattered intensity distribution ($I(\theta)$) of a single scatterer integrated over a sphere of radius r and divide by I_0. This can be expressed by

$$\alpha = 2\pi r^2 N \int \frac{I(\theta)}{I_0} \sin\theta d\theta. \tag{2}$$

The according to the RGD approximation, the transmitted intensity of a single sphere is given by

$$I(\theta) = \frac{(1+\cos^2\theta)k^4p^2P^2(\theta)}{2r^2}I_0, \tag{3}$$

where θ is the angle of observation, p is the polarizability of the sphere, k is the wavenumber in the surrounding medium $(k = 2\pi n_{\mathrm{m}}/\lambda)$, $P(\theta) = \left[\frac{3(\sin u \quad u\cos u)}{u^3}\right]^2$, $u = 2kam\sin(\theta/2)$, and a is the radius of the scatterer.[10] The term $P(\theta)$ is known as the form factor, and represents a correction to the Rayleigh expression which accounts for the size and the shape of the scattering particle. As the scattered intensity drops rapidly as θ increases, for transmission measurements with very small detector angle of view, the term $(1+\cos^2\theta)$ can be approximated to 2.[9,15] Using Eq. (3), and the expression for $P(\theta)$ and u, the integral in Eq. (2) can be solved by changing the variable of integration to u with the lower limit of integration given by 0 and the upper limit set to $u' = 2kam\sin(\theta'/2)$ where θ' is the detector's angle of view cutoff,

$$\alpha = \frac{4\pi Nk^2p^2}{d^2m^2}\frac{9}{2}\left[\frac{-1}{u'^2} + \frac{\sin 2u'}{u'^3} + \frac{\cos 2u'}{2u'^4} - \frac{1}{2u'^4}\right], \tag{4}$$

where d is the diameter of the particle. For a spectrometer with a detector aperture size of 10 mm, the maximum value of u' for a particle of diameter $100\mu m$ and for frequencies upto 6 THz is found to be $\approx$1. For values of u' upto 1, the last term $F(u') = \left[\frac{1}{u'^2} + \frac{\sin 2u'}{u'^3} + \frac{\cos 2u'}{2u'^4} - \frac{1}{2u'^4}\right]$ of Eq. (4) can be approximated as a quadratic given by $1 - 0.025u' - 0.18u'^2$.

The polarizability p for a sphere of radius a and refractive index n_{p} in a background medium n_{m} is given be the Clausius-Mossotti relation,

$$p = 4\pi a^3\left[\frac{m^2-1}{m^2+2}\right], \tag{5}$$

and given the condition that $|m-1| \ll 1$, the above equation can be approximated as

$$p = \frac{8}{3}\pi a^3(m-1). \tag{6}$$

Substituting the above equation for p and $m = n_{\mathrm{p}}/n_{\mathrm{m}}$ in Eq. (4) we get

$$\alpha = 12\pi^2k^2dV\frac{(n_{\mathrm{p}}-n_{\mathrm{m}})^2}{n_{\mathrm{p}}^2}[1 - 0.025u' - 0.18u'^2], \tag{7}$$

where V represents the volume fraction of the scattering particles in the medium.

The above equation provides a detailed description of the scattering attenuation characteristics of a two phased composite medium. It can be seen that the scattering attenuation is directly proportional to the propagation length l and the volume fraction of the scatterers. Similarly, an increment in the refractive index mismatch between the components of the medium will also cause the attenuation to increase. The size of the scatterer is related to the total scattering attenuation via the term $F(u') = [1 - 0.025u' - 0.18u'^2]$, which in turn depends on u' or the measuring system's detector's angle of view. In our measurement setup and generally in all THz photoconductive antenna (PCA) detector based setups, a hyper-hemispherical silicon lens is mounted on the aperture to further focus the incoming THz beam to almost a single point on the detector. Such transmission spectrometers have a very small detector angle of view and therefore the value of u' is very small and $F(u') \approx 1$, the scattering attenuation is found to be linearly dependent on the scatterer size d,

$$\alpha = 12\pi^2k^2dV\frac{(n_{\mathrm{p}}-n_{\mathrm{m}})^2}{n_{\mathrm{p}}^2}. \tag{8}$$

One of the conditions of the RGD approximation is that the scatterers of the medium are well separated and act as independent Rayleigh scatterers. The condition of being well separated corresponds to cases where the inter-particle distances are much greater than the particle dimensions, hence the sparse volume concentration. When the volume density increases, the inter-particle effects become stronger and they can not be neglected for the calculation of the transmitted intensity. Many authors have addressed the problem of accounting the inter-particle interferences by incorporating an additional structure factor (S) to the expression of the total scattering attenuation given by Eq. (2).[11–15] Dunlap *et al.*[15] reported that a structure factor accounting for the inter-particle interferences must be a function of the volume fraction, scatterer shape, and size distribution. Under the assumption of spherical particles with uniform particle size distribution, the structure factor $S(V,d,\ldots)$ reduces to an additional constant factor S to the expression of the total attenuation. Under such conditions, the total scattering attenuation for transmission through a dense two phased medium can be given by

$$\alpha = 12S\pi^2\left[\frac{\omega}{c}\right]^2dV\frac{n_{\mathrm{m}}^2}{n_{\mathrm{p}}^2}(n_{\mathrm{p}}-n_{\mathrm{m}})^2[1 - 0.025u - 0.18u^2], \tag{9}$$

and for the case of high resolution transmission measurement,

$$\alpha = 12S\pi^2\left[\frac{\omega}{c}\right]^2dV\left(\frac{n_{\mathrm{m}}}{n_{\mathrm{p}}}\right)^2(n_{\mathrm{p}}-n_{\mathrm{m}})^2, \tag{10}$$

where k is substituted with $(2\pi n_{\mathrm{m}}/\lambda)$, ω is the angular frequency, and c is the speed of incident radiation. While Dunlap *et al.* applied a similar approach to study the temperature dependence of the refractive index and the effect of fillers on the thermal expansion properties of the polymer composites using ordinary RGD approximation, unlike the proposed method, their results are valid for composite materials with constituents satisfying the condition $kd(m-1) \ll 1$ and therefore are applicable to a limited number of materials.

For our measurements, two sample pellets were prepared by thoroughly mixing α-lactose monohydrate (Sigma-Aldrich) with two PE powders (with different granularity both supplied by Inducos) with a mass ratio of about 1:2.

The grain size of the samples was determined using scanning electron images (SEM) of the powders. From these images, a spherical shape was assumed for all the particles and an average particle diameter of 60 μm and 360 μm, respectively, for PE powders and μm, for the α-lactose monohydrate powder was measured. These dimensions were found to be well within the ranges provided by the supplier. Using a standard setup, we performed transmission mode THz-TDS of the above described sample. The optical parameters of the sample can be determined from Fourier transforms of the measurement of the sample transmitted electric field E_t and the reference electric field measured in absence of the sample E_{ref} as

$$\frac{E_t(\omega)}{E_{ref}(\omega)} = \frac{4n_s(\omega)}{(n_s(\omega)+1)^2}\exp\left[i(n_s-1)\frac{\omega}{c}l_s\right]\exp\left[-\alpha_s\frac{l_s}{2}\right], \tag{11}$$

where n_s represents the refractive index of the sample, α_s represents the total attenuation or extinction coefficient of the sample, and l_s represents the thickness of the sample.

The extinction coefficient contains contributions from both absorption and scattering.[16] Using Eq. (10) to represent the total scattering attenuation α, the extinction coefficient can be expressed as

$$\alpha_s = \alpha_{abs} + 12S\pi^2\left[\frac{\omega}{c}\right]^2 dV\left(\frac{n_m}{n_p}\right)^2(n_p - n_m)^2, \tag{12}$$

where α_{abs} represents the absorption coefficient of the sample, n_p represents the refractive index of α-lactose monohydrate, and n_m represents the refractive index of PE. To calculate the refractive index of pure lactose, we use the method suggested by Franz *et al.*,[20] $n_p = (n_s - n_m V_m)/V_p$, where V_m and V_p represent the volume fractions of the host medium (PE) and the embedded particles (lactose), respectively. It must be noted that $V_m + V_m = 1$. The volume fraction of the host medium (PE), V_m, can be calculated as the ratio of the mass of PE (in grams) and the density of PE ($0.926 - 0.940\text{g/cm}^3$ as specified by the supplier Inducose). Hence, with the knowledge of the measured sample refractive index and the host medium, the unknown refractive index n_p can be calculated. The extracted parameters for both the samples are plotted in Fig. 1. It must be noted that the condition required for the validity of the modified RGD approximation proposed by Shimizu *et al.*[10] is met, even for the maximum value of n_p ($\approx$1.7 at 0.53 THz) as $|n_p/n_m - 1| = |1.7/1.46 - 1| = 0.165 \ll 1$.

According to Eq. (12), the true absorption spectra of the given samples can be obtained by simple subtracting total scattering attenuation α from the measured extinction α_s. The unknown parameters S, V, and d are adjusted to best fit the measurements. The results are plotted in Fig. 2.

In conclusion, we present a method to numerically mitigate the scattering contribution in THz-TDS measurements for a two phased composite media. The final expression of the scattering attenuation given by Eq. (10), look very similar to the one derived by Franz *et al.*,[20] who argued the applicability of Raman's theoretical model for describing the Christiansen effect.[21] Similar to the technique proposed by Franz *et al.*,[20] the proposed method not only eliminates the scattering baseline but also corrects for the asymmetrical band distortions by using the knowledge of the refractive index, which is directly measured in THz-TDS. However, it must be noted that unlike the model of Franz *et al.*[20] the proposed model does not assumes a layered structure for modeling an inhomogeneous sample with a random structure, instead it relies on widely accepted RGD approximation of the Mie's theoretical description of single particle scattering.[6] The technique was tested on two samples of α-lactose monohydrate and PE powder (with different granularities). As can be seen in Fig. 2, the method reasonably eliminates the scattering contribution for the measured extinction, using the THz-TDS measurements of sample's refractive index, to reveal the scattering mitigated absorption spectra for a given sample.

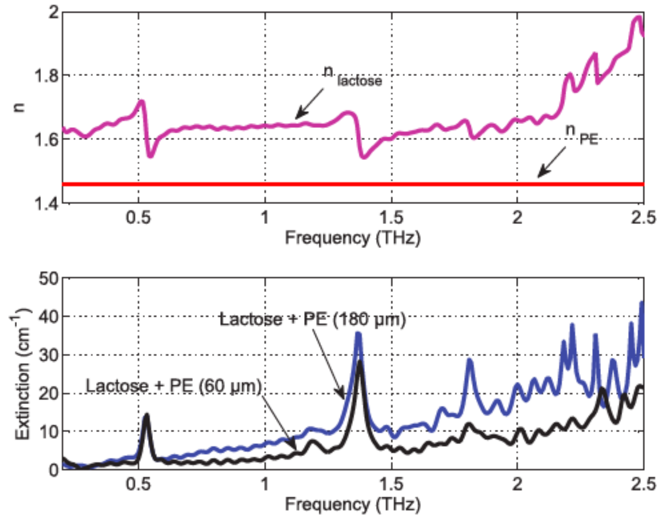

FIG. 1. Extinction coefficient and refractive index of the alpha lactose monohydrate and PE sample.

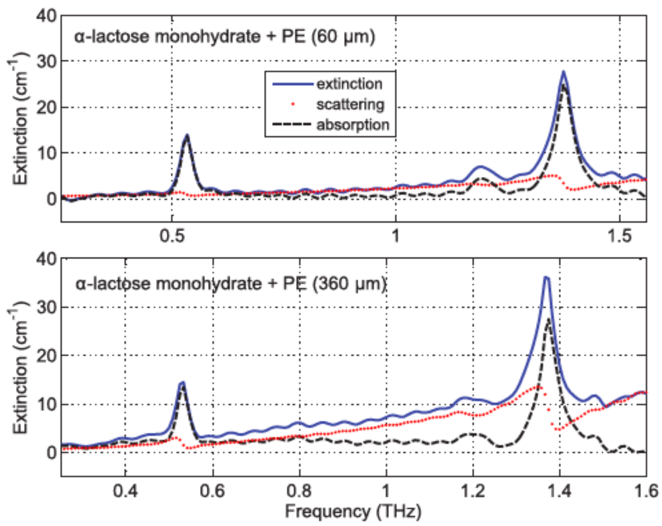

FIG. 2. Measured extinction spectrum (solid line), estimated scattering (dotted line), and scattering mitigated spectrum (dashed line) for alpha lactose monohydrate and PE samples.

[1]See http://www.riken.jp/THzdatabase/ for THz database, Tera Photonics Laboratory, RIKEN Sendai.
[2]See http://www.thzdb.org for Terahertz database.
[3]B. M. Fischer, M. Walther, and P. U. Jepsen, Phys. Med. Biol. **47**, 3807 (2002).
[4]M. Walther, B. M. Fischer, and P. U. Jepsen, Chem. Phys. **288**, 261 (2003).
[5]M. Kaushik, B. Ng, B. M. Fischer, and D. Abbott, IEEE Photon. Technol. Lett. **24**, 155 157 (2012).
[6]G. Mie, Ann. Phys. **330**, 377 (1908).
[7]A. Ishimaru, *Wave Propagation and Scattering in Random Medium* (Aca demic, New York, 1978).
[8]H. C. Hulst and H. C. van de Hulst, *Light Scattering by Small Particles* (Courier Dover, 1957).
[9]M. Elimelech, J. Gregory, X. Jia, and R. A. Williams, *Particle Deposition and Aggregation: Measurement, Modelling and Simulation* (Elsevier, 1995).
[10]K. Shimizu, J. Opt. Soc. Am. **73**, 504 507 (1983).
[11]G. Frdric, J. Quant. Spectrosc. Radiat. Transfer **110**, 240 246 (2009).
[12]J. Holoubek, Proc. SPIE **3726**, 438 (1999).
[13]C. Belanger, P. Cielo, B. D. Favis, and W. I. Patterson, Polym. Eng. Sci. **30**, 1090 1097 (1990).
[14]J. B. Hayter and J. Penfold, Mol. Phys. **42**, 109 118 (1981).
[15]P. N. Dunlap and S. E. Howe, Polym. Compos. **12**, 39 47 (1991).
[16]Y. C. Shen, P. F. Taday, and M. Pepper, Appl. Phy. Lett. **92**, 051103 (2008).
[17]T. Farias, U. O. Koylu, and M. Carvalho, Appl. Opt. **35**, 6560 6567 (1996).
[18]G. Wang and C. Sorensen, Appl. Opt. **41**, 4645 4651 (2002).
[19]C. M. Sorensen, Aerosol Sci. Technol. **35**, 648 687 (2001).
[20]M. Franz, B. M. Fischer, and M. Walther, Appl. Phy. Lett. **92**, 021107 (2008).
[21]C. Raman, Proc. Math. Sci. **29**, 381 390 (1949).