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The Christiansen effect in terahertz time-domain spectra of coarse-grained powders

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Spectral distortions are commonly observed in terahertz transmission spectra of ground substances immersed in a transparent host medium. This effect originates from scattering due to the index contrast between the grains and diluent. A phenomenological expression quantitatively accounts for the scattering induced attenuation and the phase delay experienced by the electric field transmitted through the sample. Based on the knowledge of the refractive indices of the sample and the host material, we present a procedure to eliminate the scattering contribution from the absorption spectra. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2831910]

Over the past years, terahertz time-domain spectroscopy (TDS) has developed into a powerful tool for the investigation of a wide range of materials such as biological molecules,[1–4] compounds used in pharmaceutical applications,[5] or substances with relevance for safety and security inspections.[6] With the increasing number of terahertz spectra being published and collected in databases, issues of data reproducibility associated with particular sample preparation techniques have to be addressed. A widely adopted preparation method is based on mixing the substance under study with a material transparent in the terahertz frequency range, e.g., polyethylene (PE), and pressing the mixture to pellets. This permits to produce robust samples and to dilute strongly absorbing substances to avoid saturation of the spectra. In many cases, however, asymmetrically distorted absorption bands are observed affecting the reported line widths, peak positions, and absorption strengths.[1–3,7,8]

In this letter, we show that dispersion-induced scattering on the inhomogeneities in the sample, a behavior known as the *Christiansen effect*,[9] is responsible for these spectral distortions. Based on the knowledge of the refractive indices of sample and host medium, a recipe is presented which numerically eliminates the scattering contribution from the terahertz absorption spectrum. In contrast to conventional postprocessing tools commonly used in near-IR spectroscopy such as multiplicative scatter correction,[10] which relies on the linear regression of spectral variables versus a standard spectrum to suppress the scattering background, our approach uses the complementary information on the index of refraction, a quantity which is always obtained in a terahertz TDS measurement.

In a standard transmission terahertz TDS experiment, the dielectric function of a material is determined by measuring the electric field pulse $E_{\mathrm{sam}}(t)$ after transmission through a sample together with a reference pulse $E_{\mathrm{ref}}(t)$ that propagated through the empty spectrometer.[4] After Fourier transforming both waveforms into the frequency domain, the frequency-dependent absorption coefficient α and index of refraction n are obtained from the complex ratio

$$\frac{E_{\mathrm{sam}}(\omega)}{E_{\mathrm{ref}}(\omega)} = \exp\left[i(n-1)\frac{\omega}{c}d\right]\exp\left\{-\frac{\alpha}{2}d\right\}, \tag{1}$$

where d is the sample thickness. For the reason of simplicity, we have omitted the frequency-dependent factor used to account for Fresnel reflection losses at the sample surfaces.[4] Figure 1 shows typical plots of α and n for a polycrystalline substance (DL-phenyllactic acid), as determined from a pure and two diluted sample pellets. The pellets were prepared by pressing the powder to disks applying a pressure of about 7500 kg/cm^2 with a hydraulic press. For the measurement, the pellets were mounted in an evacuated He cryostat and cooled down to 13 K. The dashed line in Fig. 1(a) represents the saturation limit α_{max} for the spectrum of the 3 mm thick undiluted pellet (solid circles).[11] All absorption features exceeding this limit, in particular, the peaks near 1.5 and 1.7 THz and in the spectral region above 2.2 THz, cannot be

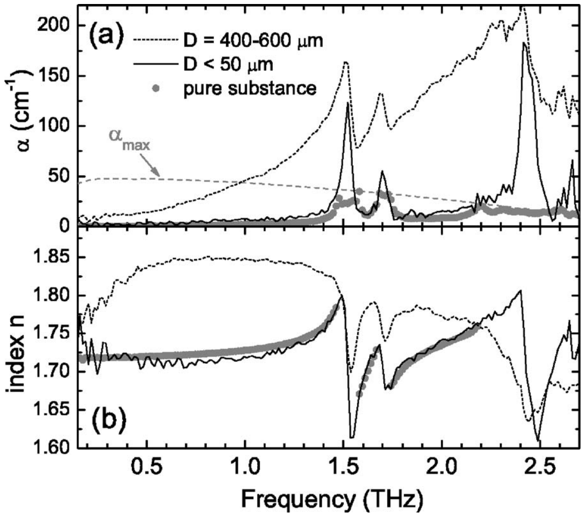

FIG. 1. Absorption coefficient (a) and refractive index (b) of DL-phenyllactic acid at 13 K. The curves correspond to measurements of a pure pellet (solid circles) and diluted samples of the ground and unground substances (estimated grain size D) mixed with PE.

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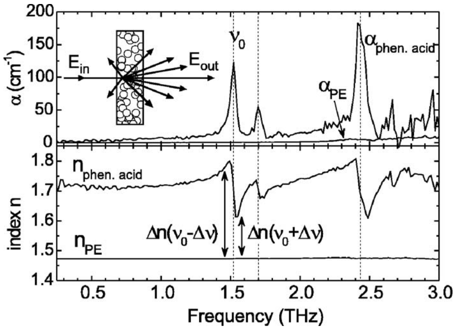

FIG. 2. Absorption coefficient and refractive index of DL-phenyllactic acid and PE. The inset illustrates light scattering by the Christiansen effect. At an absorption peak, stronger scattering occurs on the low-frequency wing due to the larger refractive index contrast.

resolved. Substantially thinner samples are required in order to obtain an unsaturated spectrum. This, however, introduces at least two complications. For one, thin pellets are often unstable and secondly, etalon reflections occur shortly after the main pulse leading to spectral artifacts. The common solution to these problems relies on diluting the substance with a transparent filling material to produce thick, nonsaturating samples.

In our example, two diluted pellets were prepared by thoroughly mixing DL-phenyllactic acid (Sigma-Aldrich) with PE powder at a mass ratio of about 1:6. For one sample, the coarse-grained substance was used as obtained (grain size distribution of 400–600 μm). For the second pellet, the substance was thoroughly ground resulting in a grain size <50 μm. The complex index of refraction $\hat{n}=n+i\kappa$ of the pure substance has been calculated from the value determined for the diluted pellets $\hat{n}_{\text{mix}}$ by $\hat{n}=(\hat{n}_{\text{mix}}d_{\text{mix}}-\hat{n}_{\text{PE}}d_{\text{PE}})/d$, where d_{mix} is the pellet thickness. d and d_{PE} correspond to the effective path lengths through the substance and through PE, which could be calculated from the masses, the mass densities (determined from pure pellets) and the pellet area A by $d=m/\rho A$ and $d_{\text{PE}}=m_{\text{PE}}/\rho_{\text{PE}}A$. Using this procedure, the absorption coefficient $\alpha=2\kappa\omega/c$ and index n of phenyllactic acid were obtained (solid and dotted lines in Fig. 1). For the ground sample, we observe nearly Lorentzian line shapes and a spectrum consistent with the pure pellet in the unsaturated regions. The spectrum of the coarse-grained sample, however, exhibits characteristic distortions consisting of asymmetrically broadened absorption peaks, a rising baseline, and a refractive index offset.

Similar band distortions have been reported from near- and midinfrared absorption spectra.[12–14] This effect, first described by Christiansen,[9] has been occasionally observed in terahertz TDS measurements,[1–3,7,8] however, was not further considered. As indicated in the inset of Fig. 2, light scattering on the suspended grains is responsible for this effect. For nonabsorbing particles, the scattering loss depends predominantly on the refractive index contrast between particles and host medium. At a frequency where both indices are equal, no scattering occurs. The sample then forms a spectral filter with bandpass characteristics (*Christiansen filter*).[15] In our case of absorbing grains immersed in a transparent matrix, the characteristic variation of n associated with each absorption maximum leads to stronger scattering on the low- than on the high-frequency wings of the peaks, as indicated by the arrows in Fig. 2, which results in asymmetrically distorted band profiles.[12]

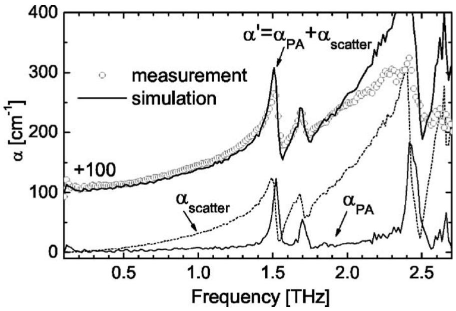

FIG. 3. Absorption coefficient of the finely ground phenyllactic acid (PA) sample (lower solid line) and calculated scattering loss (dashed line). Their sum (upper solid line) is plotted with the spectrum of the unground sample (open circles), both vertically offset for better clarity.

Raman provided a theoretical description based on electromagnetic wave propagation through an inhomogeneous medium.[16] He modeled the sample by a succession of thin layers of thickness Δ, each consisting of laterally arranged cells with refractive indices of either n_1 or n_2. Due to the associated phase retardations and subsequent interference, the intensity of an electromagnetic wave of frequency ω gets attenuated after propagating through a sample of thickness d by a fraction $I_{\text{out}}/I_{\text{in}}=\exp\{-[K\omega/c(n_1-n_2)]^2 d\Delta\}$, where c is the speed of light and K is a numerical factor determined by the shape, concentration, and distribution of the cells.[16] In order to account for the Christiansen effect in our spectra, we can therefore introduce a corresponding term in Eq. (1), which then becomes

$$\frac{E_{\text{sam}}}{E_{\text{ref}}}=\exp\left[i\left\{(n-1)\frac{\omega}{c}d+\phi\right\}\right]\exp\left(-\frac{\alpha}{2}d\right)\times\exp\left[-K^2\frac{\omega^2}{2c^2}(n-n_{\text{PE}})^2 d\Delta\right], \tag{2}$$

where n and n_{PE} are the refractive indices of the grains and the host medium (PE). Note that an additional frequency-dependent phase ϕ has also been introduced to account for the scattering-induced contribution to the refractive index, as we will discuss later.

According to Eq. (2), the Christiansen effect contributes to α', the absorption coefficient determined in an experiment by a scattering term

$$\alpha'=\alpha+\alpha_{\text{scatter}}=\alpha+K^2\frac{\omega^2}{c^2}(n-n_{\text{PE}})^2\Delta. \tag{3}$$

In Fig. 3, the absorption coefficient of the finely ground sample is plotted together with this scattering background, calculated from the measured refractive indices in Fig. 2. The absorption determined from the coarse-grained sample is also shown in Fig. 3 (open circles) together with the simulated spectrum consisting of the sum of absorption and scattering contributions. The unknown parameters K and Δ in the scattering term have been adjusted to best fit the measurement. The asymmetric peak profiles and the rising background absorption are reproduced by the simulation. The discrepancy above 2 THz can be attributed to the fact that the measured spectrum is slightly saturated in that regime.

In order to account for the offset of the refractive index, an additional phase ϕ was introduced in Eq. (2), leading to an effective index of

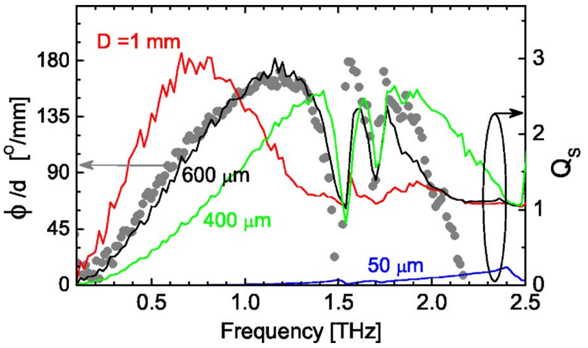

FIG. 4. (Color online) Accumulated scattering phase per path length of the unground sample (solid circles). The solid curves are calculated Mie-scattering efficiencies for spherical particles of DL-phenyllactic acid with diameters *D*.

$$n' = n + n_{\text{scatter}} = n + \phi\frac{c}{\omega d}. \tag{4}$$

In our particular example, the additional phase per path length, as determined from the index difference between the ground and unground samples through $\phi/d=(n'-n)\omega/c$, is plotted in Fig. 4 (solid circles). Since a phase accumulation due to scattering does not occur in the simple picture of wave propagation through dispersive cells, a refined model needs to incorporate the effect of light scattering on dielectric particles as treated most generally by Mie theory.[17] In the Mie approach, a spectral scattering efficiency $Q_s=\sigma_s/\pi r^2$ can be calculated for a spherical particle, where σ_s corresponds to its frequency dependent scattering cross section and πr^2 to the geometric cross section.[17] Figure 4 shows spectral scattering efficiencies calculated for spherical DL-phenyllactic acid particles of different diameters *D* embedded in PE. The n and α required for the calculation of σ_s have been taken from our measurement (Fig. 2). The calculated curves show the typical spectral characteristics of Mie scattering on a dielectric sphere:[17] a rising scattering efficiency $\sim 1/\lambda^4$ in the limit of $\lambda \gg D$ (Raleigh scattering) with a maximum due to interference of the incident with the forward-scattered waves. At high frequencies ($\lambda \ll D$) Q_s approaches 1 which corresponds to geometric scattering ($\sigma_s=\pi r^2$). The features at 1.5 and 1.7 THz are due to the resonances in the dielectric function of DL-phenyllactic acid (PA). Note that the measured additional phase follows remarkably well the calculated scattering efficiency for a spherical particle of 600 μm diameter.

Based on our model, we propose a recipe to eliminate the scattering contribution from the data to unravel the true absorption spectrum. Figure 5 shows α and n of polycrystalline fructose at 10 K determined from a pellet prepared by mixing the unground grains with PE (from Ref. 7). Using the refractive index of fructose and of PE, the scattering contribution has been calculated according to Eq. (3) and was subtracted from the absorption spectrum. The only unknown parameters in this calculation were K and Δ, which have been adjusted so that the background absorption between the peaks in the corrected spectrum is close to 0. By this simple procedure, the scattering contribution to the absorption spectrum is fully eliminated, resulting in nearly Lorentzian line shapes. We note that our approach is not limited to terahertz TDS but is universally applicable provided that the frequency-dependent index is an independently measured quantity.

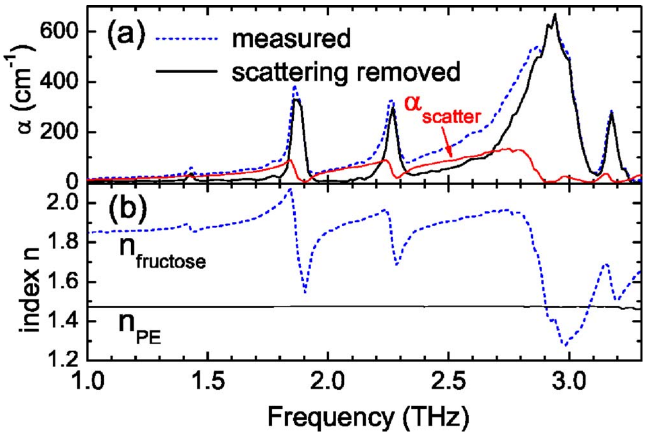

FIG. 5. (Color online) Absorption coefficient (a) and refractive index (b) of fructose measured for a diluted sample at 10 K (dashed lines). Using the indices of fructose and PE, the scattering contribution to the absorption coefficient is calculated and removed from the spectrum.

In conclusion we investigated the influence of the Christiansen effect on terahertz time-domain spectra. Based on the knowledge of the refractive index, which is directly measured in terahertz TDS, a numerical procedure is introduced to eliminate the scattering contribution from the absorption spectra.

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