Detection and identification of selected alcohols using terahertz time-domain spectroscopy

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Abstract. The optical property and spectroscopy of selected kinds of alcohols are studied based on the terahertz time-domain spectroscopy (THz-TDS) in the spectral range of 0.5-2.5 THz. The B3LYP method in conjunction with the 6-31G (d) basis set was used to optimize the geometric structure of samples and simulate the alcohols spectrum. No absorption peak occurs in THz wave band based on our simulation, suggesting that the present experimental absorption peaks resulted from the intermolecular interaction.

1. Introduction
The alcohols such as 2-propanol, 1,2-propanediol and glycerol, as solvents and raw materials for synthetic resins, esters and other substances, are widely used in pharmaceutical, cosmetics, plastics, fragrances, paint and electronics industries and so on. Since the spectrometers have played a great role in chemical analysis, types of spectroscopy including raman scattering, mass spectroscopy, emission spectroscopy, chromatogram, ultraviolet absorption, infrared absorption, and nuclear magnetic resonance came into widespread in chemical area. At present much attention has been paid to the terahertz (THz) spectroscopic studies of chemical products. THz spectroscopy can serve as a potential tool in petroleum products identification, explosives and contaminations inspection, quality control, pharmaceutical analysis, medical diagnostics and security inspection or illegal drug detection [1-5].

THz time-domain spectroscopy (THz-TDS) as a new detection technology can effectively obtain amplitude, phase and structural information of the materials. Many rotational and vibrational spectra of organic molecules and related compounds lie in the THz range. In addition, THz-TDS provides absorption coefficient of a sample with high signal-to-noise ratio without using the Kramers-Kroning relation, which is ideal for the measurement of optical properties.

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In this paper, we studied the optical property and spectroscopy of selected alcohols in terms of their different kinds, based on the THz-TDS. By applying a numerical fast Fourier transform (FFT), the optical constants of selected alcohol have been calculated. Furthermore, the simulation has been carried out using the GAUSSIAN 03 software package, where the B3LYP method was used in conjunction with the 6-31G (d) basis set.

2. Experimental procedure

The THz spectrometer in the transmission mode is used to investigate the optical properties of samples. A spectra physics regenerative amplifier system produces 800 nm pulses of 100 fs duration with 1 kHz repetition rate. The source beam is split into two portions, corresponding to THz generation and probe beams, respectively. THz-TDS is based on a ZnTe emitter for THz generation and electro-optic sampling [6]. The THz radiation is detected by free-space electro-optic sampling in a \text{<110>} ZnTe crystal. Then, the signal is collected by a lock-in amplifier with phase locked to an optical chopper [7]. The path with THz radiation is enclosed and purged with dry nitrogen. THz-TDS allows us to measure both the phase and the amplitude of the THz pulses propagating through the sample and reference, respectively. The frequency-dependent refractive index and absorption coefficient are extracted from the derivation of Fresnel law. By comparison with reference and sample pulse, and use of a numerical FFT, the absorption coefficient can be calculated [8].

Figure 1 shows the different molecular structures of alcohols due to the OH group numbers, which affect the formation of hydrogen bonds in the liquid state. All these chemicals were of analytical reagent and were used without further purification. The liquid samples were put into polyethylene cells with a side thickness less than 0.5 mm, which is transparent for visible light and has a low refractive index and a low THz absorption. And the sample thickness was fixed at 0.2 cm.

3. Results and discussion

![Molecular structures of (a) 2-propanol, (b) 1,2-popanediol and (c) glycerol.](image1)

![The THz pulses of reference in free cell and the signals of alcohol.](image2)

Figure 2 displays the typical temporal profiles of THz waves. Compared with that of the reference THz pulse of free cell the amplitude of the THz wave in the time domain is attenuated...
when the THz wave passes through the alcohol samples. At the same time, the pulses of the samples relative to the reference pulse show time delays, 0.14 ps, 0.70 ps, and 0.27 ps for 2-propanol, 1,2-popanediol and glycerol, suggesting that the physical and chemical properties of the samples differ from each other [9]. In addition, the scattering of sample cause the time-domain wave broaden.

Subsequent FFT of the waveforms yields the frequency-dependent amplitude as shown in figure 3. The differences in absorption and surface reflectivity resulted in the dropped amplitude for three samples. The different frequency-domain waveform indicates that the alcohols have different properties in some aspects such as refractive index, absorption coefficient and dielectric constant.

The absorption coefficients of the alcohol in 0.5-2.5 THz were shown in figure 4. The absorption peaks were found at 0.9, 0.58 and 0.73 THz with intensity of 1143, 927 and 1096 for 2-propanol, 1,2-popanediol and glycerol, respectively, which were due to rotation and vibration of the molecule. To further reveal the origins of those characteristic spectra, the simulation has been carried out using the GAUSSIAN 03 software package. The B3LYP method was used in conjunction with the 6-31G (d) basis set. Simulated result did not show significant absorptions in THz wave band, suggesting that the present experimental absorption peaks resulted from the intermolecular interaction. The alcohols we used form a network-like local structure in the liquid through intermolecular hydrogen bonds. The hydrogen bonds often impact on the location and intensity of peak, leading to stretching vibration to move to low-frequency. And a hydrogen bond X-H···Y can be formed between a group X-H with a proton H and a proton accepted group Y. Y is usually electronegative oxygen atoms or larger electronegative atoms. This effect can average the electron density, thus reducing bond force constant, then frequency decreased. And the hydrogen bond is stronger, the more frequency reduces. In our paper, the absorption peaks can be clearly seen below 1.0 THz, so this result indicated that the low-frequency vibration of sample is sensitive to the structure in hydrogen-bonded liquids.

4. Conclusions
In summary, the different kinds of selected alcohols have been studied using the THz-TDS. The obtained results indicated that the alcohols were sensitive in the THz range, and theoretical
studies on the vibration spectra suggested that the hydrogen bond resulted in the absorption peaks of the samples. THz-TDS technology applied to alcohols analysis has a potentially significant impact on the field of chemicals, chemical products, raw materials and chemical engineering.

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