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Investigation of inflammable liquids by terahertz spectroscopy

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We have examined a nondestructive and contactless screening method for water and inflammable liquids stored in common beverage plastic bottles by the terahertz time-domain spectroscopy. No THz transmission has been observed between 10 and 60 cm^{-1} for 45-mm-thick water in plastic bottles. Part of the THz wave, on the other hand, has been transmitted through the commercially available inflammable liquids in the same bottles. The differences in the absorption intensities and the refractive indices in the THz region, which reflect the ingredients of organic compounds, allow us to distinguish these inflammable liquids. We confirm that the screening method based on the THz transmission can be applied to classifying the commercially available inflammable liquids stored in plastic bottles and to distinguishing these inflammable liquids from water as well. © 2005 American Institute of Physics. [DOI: 10.1063/1.1999847]

During the last two decades, the femtosecond- or picosecond-laser-based methods of generating and detecting pulsed terahertz (THz) electromagnetic waves¹ has spurred advances in the THz spectroscopic studies on liquids,^{2,3} vapor,⁴ polymers,⁵ and biomolecules.^{6–9} The ultrashort laser-based THz spectroscopy, named as THz time-domain spectroscopy (THz-TDS), enables us to deduce the spectra of the refractive index as well as that of the absorption from the phase and amplitude of time-domain signals with a high signal-to-noise ratio. THz waves penetrate partly through popular packing materials such as paper,^{10,11} polymer,¹² clothes,¹³ and wood,¹⁴ allowing us to take sight-through THz spectra of objects concealed with these visually opaque packing materials and clothes. Materials have their intrinsic THz spectra in the absorption and the refractive index, usually called as “fingerprint” THz spectra, bands of which originate in intermolecular and intramolecular vibrations. For example, plastic explosives have been shown to be identified by their fingerprint THz spectra.^{11,15,16} Inspection based on the THz-TDS, therefore, can potentially be applied to screening and identification of sealed-off objects.

The development of inspection methods for hand-carried plastic bottles containing liquids has been the urgent issue on the security in subways, in airplanes, at airports and at stadiums. Inflammable liquids such as gasoline can be carried around by being stored in plastic containers. These bottled liquids have been possible threats of attacks by arsonists and terrorists, who ignite them in closed spaces full of passengers. Inflammable liquids, however, cannot presently be distinguished from water with ease when they are concealed in commonly used beverage plastic bottles. Mid-IR absorption and Raman scattering are possible methods of inspecting inflammable liquids stored in transparent bottles. These spectroscopic techniques, however, cannot be applied to opaque plastic bottles. It has been shown that several gasoline samples have many low-frequency vibrational absorption

bands from 5 to 650 cm^{-1} , which were measured by Fourier-transform far-infrared spectrometer and the THz-TDS.¹⁷ The purpose of this letter is to examine a nondestructive and contactless screening method using the THz-TDS for liquids stored in popular plastic bottles made of polyethylene (PE) and polyethylene terephthalate (PET). The transmittances and the refractive indices in the THz region are dependent on the kinds of commercially available inflammable liquids, allowing us to distinguish these liquids even in the plastic bottles. Water, which does not transmit the THz waves, can be easily distinguished from the other inflammable liquids by the criterion whether a THz wave is transmitted or not. The method of the THz screening, which employs the nonionizing radiation, can be conducted safely to human bodies as well as without any chemical reactions and changes in test objects.

We carried out the THz-TDS with a standard system (Fig. 1) using photoconductive emitter and detector antennas. A mode-locked Ti:sapphire laser (Tsunami, Spectra Physics Ltd.) with a 50 fs pulse width pumped the antennas for generating and detecting pulsed THz waves. THz transmission

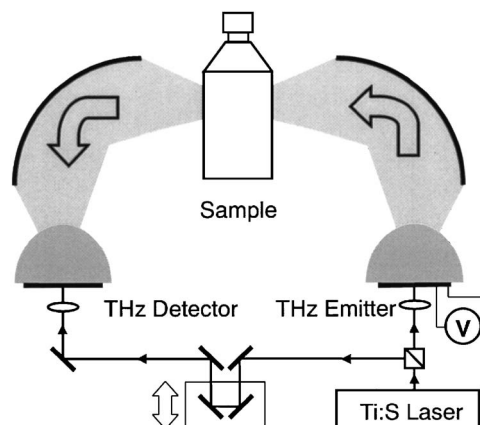


FIG. 1. Schematic diagram of the transmission measurement of the THz-TDS. A plastic bottle containing a liquid sample is placed in the path of the THz wave.

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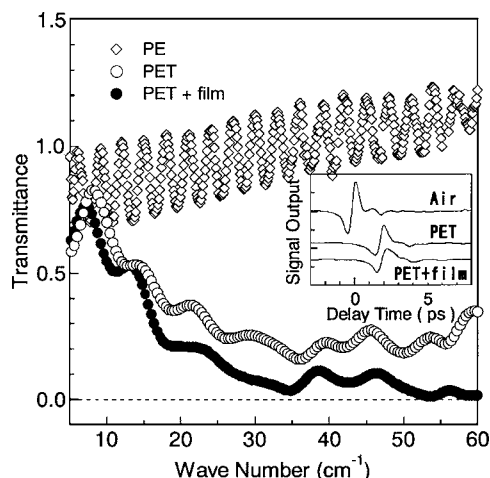


FIG. 2. THz transmittance of the plastic bottles. Inset: temporal behavior of the THz pulse transmitted through air, the PET bottles with and without a plastic label.

measurements were conducted for a liquid sample stored in a plastic bottle in the path of the THz wave. Commercially available inflammable liquid samples, i.e., gasoline (flash point (fp): $\sim -40^\circ\text{C}$), benzene (fp: $\sim -40^\circ\text{C}$), kerosene (fp: $\sim 40^\circ\text{C}$), and gas oil (fp: $\sim 50^\circ\text{C}$) were measured. Pure organic solvents of *n*-alkanes (C_6H_{14} and C_8H_{18}) and toluene were also measured for comparison. The PE cylindrical bottles and the PET square bottles were 1 and 0.5 mm in plastic thickness, and 45 and 60 mm in path length, respectively. The PET bottles examined in the experiments are generally used as beverage bottles. Accurate THz measurements for the refractive index were conducted for liquid samples in a stainless-steel cell (25 mm in path length for liquid samples except for toluene and 10 mm in path length for toluene) with silicon windows (3 mm in thickness).

Figure 2 shows the THz transmittance spectra of the empty PE and PET bottles. The periodic modulations of the spectra are due to the multiple reflections of the THz waves inside the plastic walls of the bottle. The transmittance of the PE bottle in the THz region is larger than that of the PET bottle although the wall of the former is thicker than that of the latter. The increase of polar groups in polymers has been suggested to increase the absorption intensity in the THz region.⁵ Ketone, which has the polar keto group ($>\text{C}=\text{O}$) binding two hydrocarbon radicals, has been predicted to have resonance absorption between 0.3 and 3 THz in solid state.¹⁸ The polar carbonyl groups in the PET chains are, therefore, considered to contribute to the increase in the THz absorption, leading to the low transmittance in the THz region. The THz radiation between 5 and 60 cm^{-1} is, nonetheless, transmitted through the PET bottle sufficiently to conduct the inspection of concealed liquids. The inset of Fig. 2 represents the influence of the plastic label on the temporal behavior of the THz pulses. The transmission through the colored and optically opaque plastic label film over the PET bottle reduces the peak intensity of the THz pulse, resulting in the low transmittance in Fig. 2. A considerable portion of the THz pulse can, however, be transmitted through both label and PET bottle. This result shows the feasibility of the THz inspection through the PET bottle irrespective of the opaque plastic label over it. The transmittance larger than unity is observed in the transmittance spectra of the PE bottle. It probably results from the tighter focusing of the transmitted

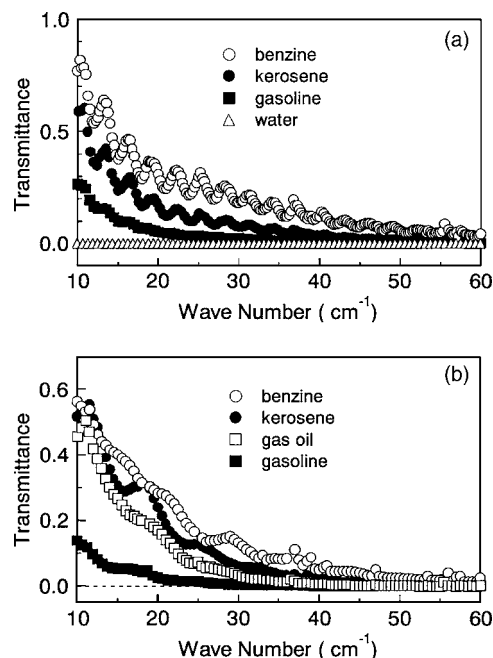


FIG. 3. THz transmittance of the liquids stored in the PE bottle (a) and the PET bottle (b).

THz wave at the detector antenna than the reference THz wave due to the lens effect of the “cylindrical” bottle.

Figure 3 represents the THz transmittance spectra ($=|E_{b+\nu}(\tilde{\nu})|^2/|E_b(\tilde{\nu})|^2$) of the liquids stored in the PE and PET bottles where $E_b(\tilde{\nu})$ and $E_{b+\nu}(\tilde{\nu})$ are complex THz fields transmitted through an empty bottle and a liquid-containing bottle at a frequency $\tilde{\nu}$, respectively. Water is highly absorptive in the THz region, resulting in no THz transmission for 45-mm-thick water as shown in Fig. 3(a). The inflammable liquids, on the other hand, partly transmit the THz waves, the transmittance of which is dependent on the species of the liquids. This obvious difference in the THz transmittance allows us to distinguish water from the other liquids very easily. The difference in the THz transmittance spectra for various liquids also implies the possibility of classification of the inflammable liquids by the THz-TDS. The inflammable liquids with 6 cm thickness in the PET bottles also partly transmit the THz wave [Fig. 3(b)], indicating that this screening method can be applied to liquids stored in the PET bottle. The periodic modulations on the transmittance spectra in Fig. 3 are due to the multiple reflections as in Fig. 2. Figure 4 represents the THz absorption spectra of the inflammable liquids, which are obtained from the transmittance spectra in Fig. 3(b). Absorption intensity increases in the order of benzene, kerosene, gas oil, and gasoline. These liquids consist of different kinds of hydrocarbon ingredients, leading to the different intensities of the THz absorption. The principal ingredient of benzene, kerosene, and gas oil is paraffin (carbon number: 6–24), the absorption of which is very low in the THz region (absorption coefficient: $0.12\text{--}0.14\text{ cm}^{-1}$ at 35 cm^{-1}). Gasoline contains appreciable quantities of aromatic hydrocarbons such as toluene, ethylbenzene, and xylene as the main ingredients ($\sim 25\%$ in total), moderately absorbing the THz wave (absorption coefficient: $0.87\text{--}1.48\text{ cm}^{-1}$ at 35 cm^{-1}) owing to the high polarizability of electrons in the aromatic π orbitals.² Therefore benzene, kerosene, and gas oil, which contain very small quantities of

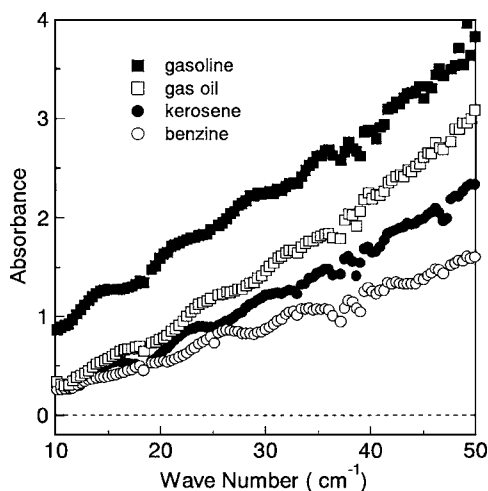


FIG. 4. THz absorption spectra of inflammable liquids in the PET bottles.

aromatic hydrocarbons, show the low THz absorption intensity relative to that of gasoline.

Figure 5 shows the refractive indices of the inflammable liquids measured by using the stainless steel sample cells with the silicon windows. The refractive indices are distributed from 1.37 to 1.50 with the highest value for toluene and the lowest value for $n\text{-C}_6\text{H}_{14}$. The refractive indices of respective inflammable liquids are separated by more than 0.01 with each other. The difference of 0.01 in the refractive index corresponds to the delay of the main THz pulse by as much as 2 ps after transmitting through a 60-mm-thick medium (the same thickness of the PET bottles in this study). The delay time of a THz pulse after transmitted through a 60-mm-thick medium with the refractive index of 1.45, for ex-

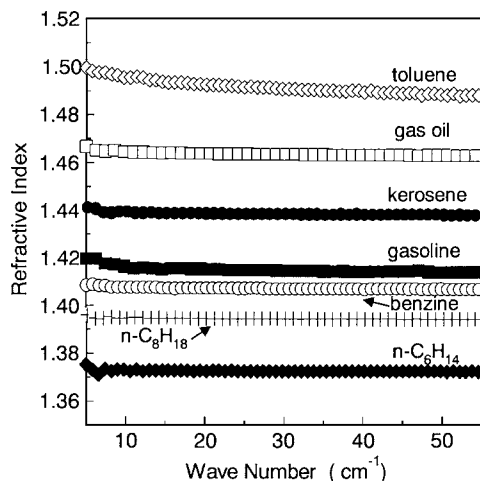


FIG. 5. Refractive indices of the inflammable liquids and pure hydrocarbon solvents.

ample, is 90 ps relative to the reference THz pulse. The time deviation of 2 from 90 ps can be easily detected in the THz-TDS. The difference in the refractive indices larger than 0.01 in Fig. 5, therefore, implies that the screening of these liquids can be conducted by detecting an arrival time of a THz pulse in combination with precise measurement of the sample thickness by such as laser interferometers.

In the present work, we have examined the feasibility of application of the THz-TDS to the nondestructive and contactless screening of liquids stored in the PE and PET bottles. These plastic bottles transmit sufficient amounts of THz waves to inspect concealed liquids in the bottles. Water and the commercially available inflammable liquids in the bottles can be easily distinguished by the criterion whether a THz wave is transmitted or not. The differences in the transmittances and the refractive indices in the THz region imply that the THz-TDS can be used for screening and discrimination of the inflammable liquids.

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