Capability of Terahertz-Wave Instrumentation for Non Destructive Testing of Liquids

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Abstract. Electromagnetic waves with frequencies between 0.3 and 10 terahertz (THz) ≡ 10 – 300 cm^{-1} ≡ 1 – 0.03 mm are described as THz radiation (t-ray's). They are assigned in the electromagnetic spectrum between the microwave/millimeter and the far-infrared regions. The ability to penetrate packing materials, such as paper, cardboards, plastic, glass and clothing and its non ionizing character makes THz radiation very attractive for different imaging and spectroscopic applications. Especially the security sector directed the attention to the new developments of the THz-technologies. Transmission and reflection properties of the solid explosives such as e.g. HMX and RDX were studied intensively to reveal characteristic "fingerprint" absorption spectra for further material identification during security checks. Recently, the visualization and verification of liquid explosives and flammable liquids became important. The literature reports only on few related THz spectroscopy experiments. The THz instrumentation has been experienced a fast development. Modern Time Domain Spectroscopy Systems changed from conventional open beam systems to glass fiber coupled devices. The new systems offer more flexibility and are designed also for mobile handheld application and not for laboratory use only. The THz laboratory at BAM is equipped with a glass fiber coupled Picometrix T-ray 2000 THz system and a Huber two circles goniometer system, where both sample and detector can be moved independently. Subsequently THz Time Domain Spectroscopy (TDS) experiments can be carried out either in transmission or in reflection geometry. The experimental set up allows a fast switching between transmission and reflection mode without major changes. Measurements at different incident, reflection and transmission angles between 0 ° and 90° can be performed. THz inspections of petroleum products (e.g. gasoline, kerosene, gasoil) and some non-polar liquids (e.g. benzene, toluene, and hexane) were carried out in the frequency range of 0.3 to 2 THz. The products have been studied mainly in transmission geometry at different experimental procedures. In contrast to the non-polar liquids, polar liquids could only be accessed at the reflection mode due to the high absorption in the THz range. Preliminary experiments with water, acetone, hydrogen peroxide and ethanol indicated already a blocking of the transmitting THz beam in the above described THz Spectrometer at a layer thickness of 1mm. Nevertheless, the THz-TDS results demonstrate the opportunities of non-destructive contactless inspections of polar and non-polar liquids in transmission and reflection mode. The results will be compared and complemented with conventional far infrared FTIR measurements.

1. Introduction

Electromagnetic waves with frequencies between 0.3 and 6 terahertz (THz) are described as THz radiation (t-ray's)[1]. They are assigned in the electromagnetic spectrum between the microwave/millimeter and the far-infrared regions. 1 THz (= 10^{12} Hz) corresponds to a wavelength of 300 μm or to a wave number of 33.3 cm^{-1}. THz radiation is suitable both for THz imaging and for spectroscopic material analysis. Molecular rotations in the gas phase, crystalline phonon vibrations, low-frequency vibrations and intermolecular vibrations in the solid state have been already proved by spectroscopic procedures in the THz range (Fig. 1)[2]. Based on the experimentally determined optical absorption and refraction properties, conclusions about chemical and/or morphologic composition of the examined samples are possible. In comparison to X-rays, THz radiation has a non-ionizing character. Therefore it is harmless for the human body. Common optically opaque packing materials, such as paper and plastic, and clothing (e.g. cotton) are transparent for THz radiation. Due to the mentioned characteristics and the possibility of contactless analysis, new potential applications in the safety and security sector are under development. For solid explosives, e.g. HMX and RDX as well as mixtures like C4; characteristic ‘Fingerprint’ spectra could be determined[3]. In contrast liquid explosives and flammable liquids are studied less intensive in the THz region. Only about spectral transmission properties of petroleum products and some other non-polar organic solvents in the frequency range between 0.3 to 2 THz were reported in the literature[4].

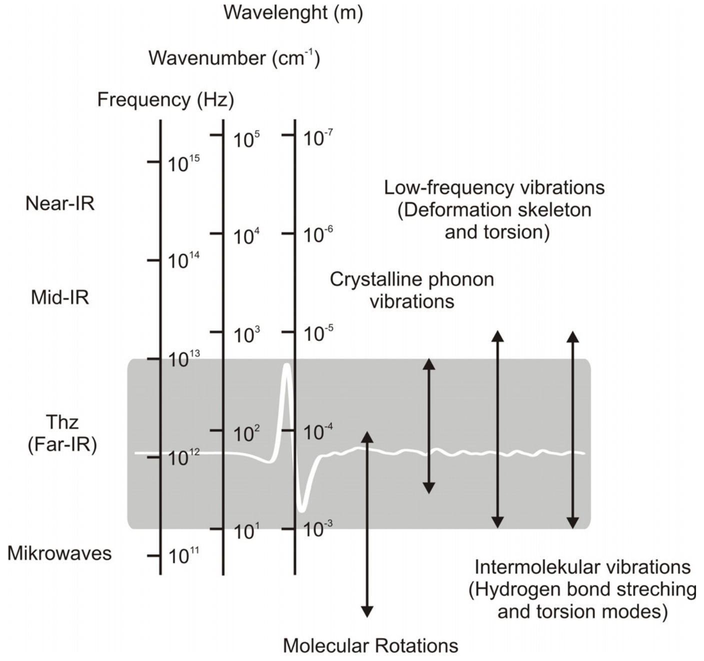


Figure 1. Characteristic absorption frequencies of chemical compounds in the THz region

Preliminary experiments with the polar liquids water and acetone expressed a complete absorption of the THz beam at a layer thickness of 1 mm in our spectrometer. In contradiction to non-polar liquids the concept of the measurement of the optical properties in the THz range in transmission mode had to be rejected. It was first sought for a more appropriated measurement principle for polar liquids. The reflection geometry was found to be a good approach because it offers also the advantage of one sided access to unknown objects, and it is therefore more oriented to practical applications in the field of security.

2. Experiments

Terahertz Time-Domain Spectroscopy (THz-TDS) System

The THz-TDS system at BAM consists of a femto second pulse laser (1) (Vitesse 800-2, Coherent Inc.), a dispersion compensator (2), fiber glass cables, a delay line (3) with an integrated beam splitter (3), a THz transmitter (4) and a THz receiver (5) (components 2–5: T-Ray 2000, Picometrix). Polyethylene (PE) lenses (6) can be optionally integrated into the THz path for collimation and focusing the THz beam. The fiber coupled THz antennas and the PE lenses are mounted onto a two circle goniometer (7) (Huber, series 402) to make angle depended measurements possible. As documented in Fig. 2, the two circle goniometer and the fiber coupling allow in contrast to conventional free beam systems fast switching between the transmission and refection mode.

The characterization of the liquids took place in different experimental setups. Spectral properties of none polar liquid, such as products of petroleum industry could be studied in transmission geometry. Non-polar liquids were measured in commercial plastic (Polystyrene, **PS**) or glass cells (optical glass, **OG** and/or quartz glass, **QS**). The cells had a wall thickness of 1.2 mm (cell window) and made transmission measurements of a layer thickness of 10 mm possible. Preliminary investigations on the transmission behavior of polar liquids were performed in a quartz glass cell, which allowed the penetration of a 1 mm thick liquid layer. The reflection measurements were realized with an incident angle of the THz pulse of 45° relative to the surface normal. All experiments were carried out at the BAM THz-TDS Spectrometer under laboratory conditions having air moisture of 20 to 30% and temperature of 25°C.

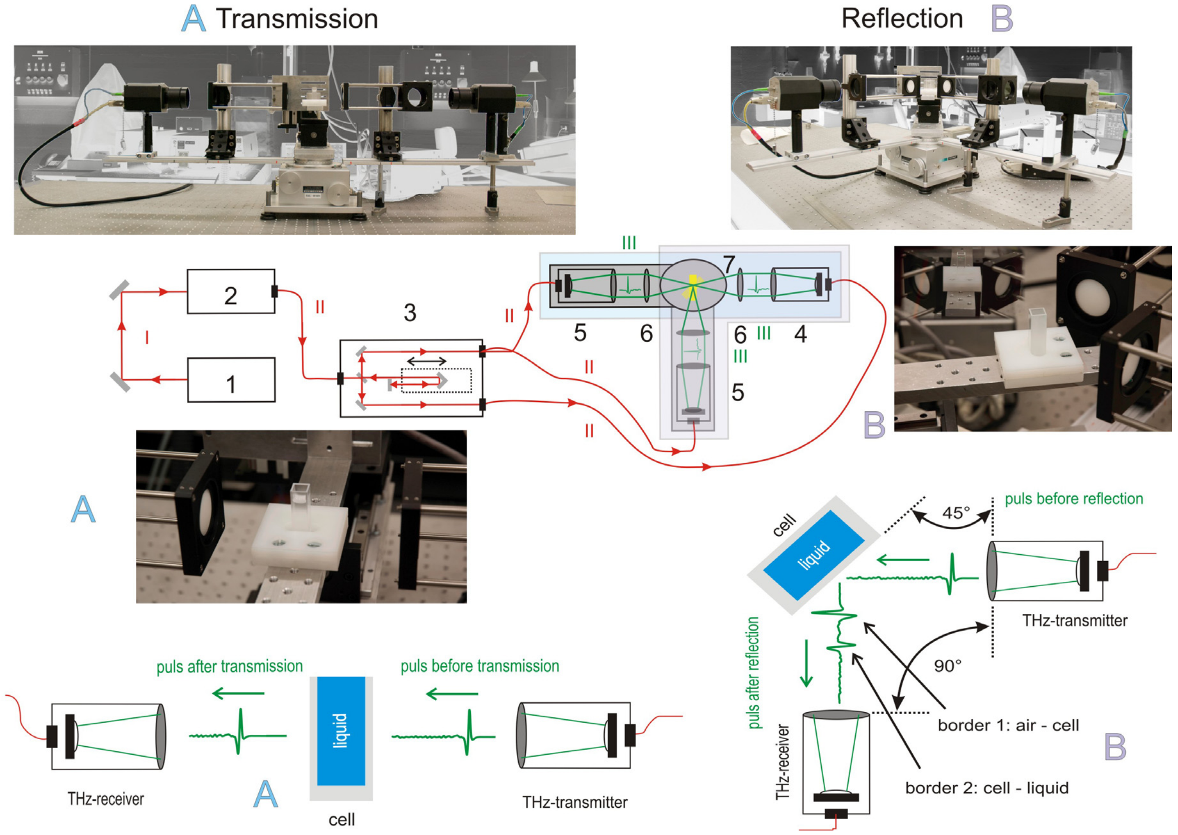


Figure 2. THz-TDS in transmission (A, left) and reflection mode (B, right), 1 = fs Laser, 2 = grading, 3 = beam splitter and delay line, 4 = THz transmitter, 5 = THz receiver, 6 = PE lenses, 7 = two circle goniometer with sample, I => free beam Laser, II => fiber coupled Laser, III => THz beam, A => transmission geometry, B => reflection geometry

Data analyses

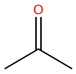
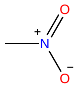
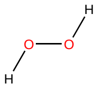
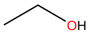
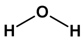
In the THz-TDS the form of the electric field is shaped as a THz pulse. The THz pulse can be detected after the interactions with the sample material as a function of the time delay. Differences of pulse maximum and minimum, integral pulse value of a certain previously fixed interval on the time delay scale or the relative time delay shift in relation to a reference time point are considered to reveal sample specific information, which can be directly used for a further simple liquid characterizations. The more detailed spectral information on the optical properties of the liquids can be obtained if the THz pulse in the time domain is Fast Fourier transformed (FFT). The resulting frequency depended amplitude and phase spectrum can distinguish the materials and facilitates the estimation of the complex refraction index or the dielectric permittivity possible respectively.

In the transmission geometry THz pulses of air, the empty cells and cells filled with sample liquids were measured in the time domain. In all tree cases the detected signal consists of one pulse (Fig. 2, A left bottom). In comparison to the reference pulse (air), the sample pulse (empty cell or cell without liquid) is shifted by a certain amount of delay time (Δt) and a shows a smaller value of amplitude. For further analyses the amplitude spectrum was calculated from the detected THz pulse by using FFT.

The reflection geometry measurements show for both, the full and empty cell configuration a characteristic pulse pattern in the time domain (Fig. 2, B right bottom). Two pulses could be detected. The first one originates from the reflection on the air-window material surface. The second one is related to the window material-filling surface reflection of the filled cell. The changes of the amplitudes of the pulses are due to the differences of the indexes of refraction of the different materials at the boundary layers and can be deduced from the complex Fresnel's equations. At the chosen reflection measurement setup the second pulse amplitude is not only influenced by the transmission and reflection amplitude ratios t_{ij}^{k} and r_{ij}^{k} (i = material i, j = material j and k = polarization direction) but also additionally reduced by the absorption of the material of the front cell window which is double passed by the THz pulse. All values, contributing to the absorption of the second pulse are influenced by the indecent angle and by the material of the cell window. The relative distances between the pulses on the time scale depend only on the angle of incidence, the complex refraction index of the window material and its thickness. The transformation of the pulses to the frequency domain is sometimes problematic. Parts of the first and the second pulse can interfere each other, this goes along with a reduction of spectral information. Therefore the reflection measurements are only discussed in the time domain at the first approach.

Liquids

Table 1. Liquids used in the experiments characterized with formula, structure and properties[6]. The warning symbols indicate the danger of the liquids.

Name	Formula	Structure	Properties	Warning Symbol
non-polar liquids				
Liquid grill lighter	-	-	Hydrocarbon mixture, chain lengths: C9 – C10, Distributor: Eucasan	Xn
Lighter gasoline	-	-	Hydrocarbon mixture, chain lengths: C7 – C12), Distributor: Centralin	F Xn N
polar liquids				
Acetone	C_3H_6O		Colorless liquid, BP: -95, MP: 56, FP: -20, M_r: 58.08, n_D^{20}: 1.3588	F Xi
Nitro methane	CH_3NO_2		Colorless liquid, MP: -29, BP: 101, FP: 35.6, M_r: 61.04, n_D^{20}: 1.3806	Xn
hydrogen peroxide	H_2O_2		Colorless liquid, MP: 0.41, BP: 150.2, M_r: 34.02, n_D^{22}: 1.414	C O
Ethanol	C_5H_6O		Colorless liquid, MP: -114.5, BP: 78.32, FP: 12, M_r: 46.07, n_D^{20}: 1.3638	F
reference liquid				
Water	H_2O		Colorless liquid, MP: 0, BP: 100, M_r: 18.02, n_D^{20}: 1.3330	-

Legend: MP = melting point / °C, BP = boiling point / °C, FP = flash point / °C, M_r = molar mass / $g\cdot mol^{-1}$, n_D^x = index of refraction at x °C, C = corrosive, F = flammable, N = environmental dangerously, O = fire promoting, Xi/Xn = irritating.

Non-polar flammable liquids are used as fuels (e.g. gasoline, gasoil, kerosene) and/or for heating and current generation. Commercially available liquid grill lighter and lighter gasoline act as examples for easy accessible flammable liquids and were studied in transmission mode.

The polar liquids acetone, nitro methane, ethanol and hydrogen peroxide were examined in the reflection geometry mode. Nitro methane is used as additive to fuel, acetone and ethanol are solvents in synthetic organic chemistry. Hydrogen peroxide is a substitute for poisonous chlorine; witch is used as bleach or for disinfection. An overview of examined dangerous liquids with their physical and chemical characteristics as well as the referring to their dangers is given in Tab. 1. Distilled water is used as a not dangers liquid for comparative studies.

3. Results

Non-polar liquids in transmission mode

Representative measurements of non-polar flammable mixtures of hydrocarbon liquids, lighter gasoline (carbon chain length C7 – C12) and liquid grill lighter (carbon chain length C9 – C10) within polystyrene (PS) cells in transmission geometry mode are shown in Fig. 1. Both hydrocarbon mixtures could be clearly differentiated from water, because the water absorbs the THz-beam totally at a beam path length of 10 mm in our system.

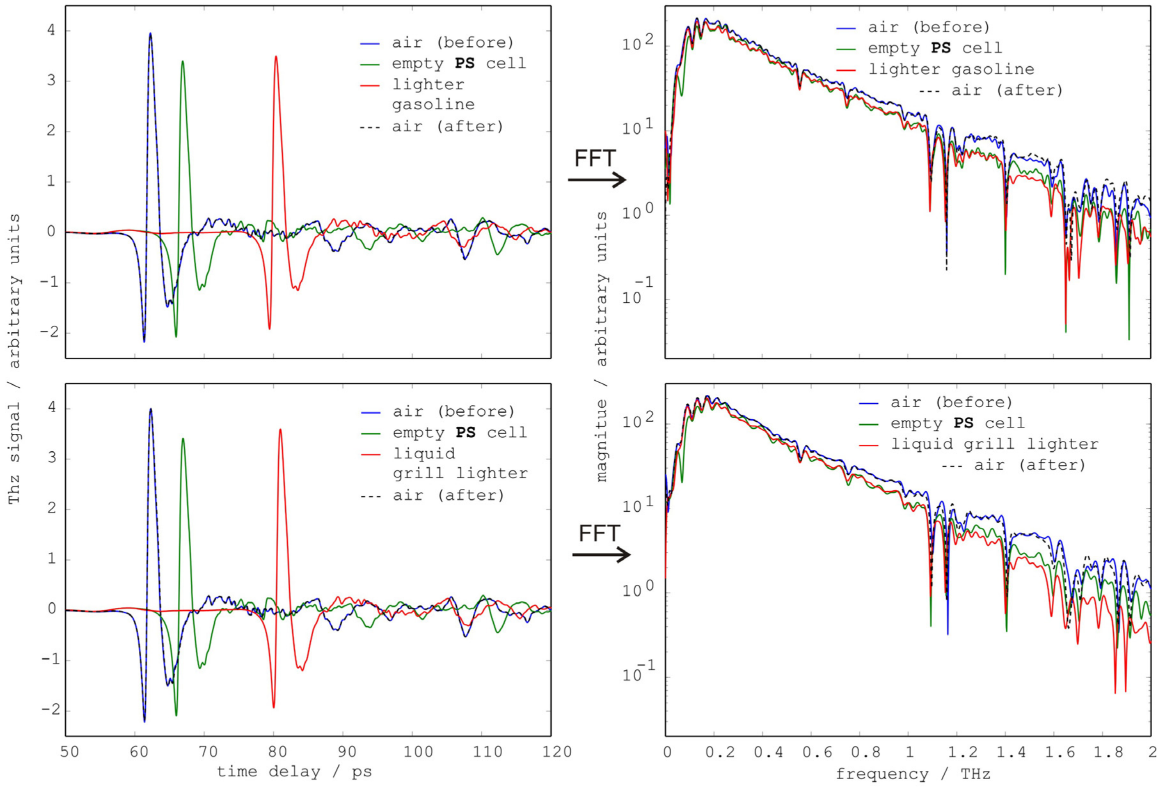


Figure 3. THz signals in dependence of the time delay (*left*) and the FFT of the time signals into the frequency domain (*right*) of lighter gasoline (*top*) and liquid grill lighter (*bottom*) filled in polystyrene (PS) cells.

The liquids exhibit no significant differences in the time domain, within the consideration of errors, neither the shifts of the time delay nor the changes of the maximum amplitude size. Significant differences between air and the empty PS cell in the frequency domain could be observed. Above 0.5 THz a stronger drop of the magnitude is observed for the empty cell, which increases at higher frequencies. After cell filling, changes in the amplitude could be observed beyond 1.2 THz for the liquid grill lighter (Fig. 1 *top right*) and at frequencies higher than 1.5 THz for the lighter gasoline (Fig. 1 *bottom right*). The beam transmitted 10 mm of the liquid material in both cases.

The amplitude processes in the lower frequency range are behaving similar to the empty cells. The evaluation of the frequency domain is strongly disturbed by the presence of the rotational lines of the naturally in air existing water vapour[6].

Polar liquids in reflection mode

Representative measurements of polar liquid explosives in reflection geometry mode are shown in Fig. 4. Acetone (red), nitro methane (blue), ethanol (green) and water (yellow) were investigated in two cells made of different glass types (OG = optical glass, Fig. 4, *top left* and QS = quartz glass, Fig. 4, *bottom left*) in the reflection geometry mode. Significant differences in the behaviour of the empty cells could be observed in the time delay values and in the amplitude maxima (dotted black curves). The amplitude maxima ratio for OG:QS is 1:0.64 for the first pulse and 1:1.69 for the second pulse. The time delay difference (time delay second pulse – time delay first pulse) for the OG cell is 20.98 ps, the corresponding value for the QS-cell is about 5 ps shorter (15.76 ps). This is due to the different index of refraction of the glasses because the incident angle and the geometries for both cells were not changed during the experiments. This behaviour is also present after the cells were filled with liquids, a change in the amplitude maximum is only observes in the second pulses for each glass type. All first pulses overlap each other.

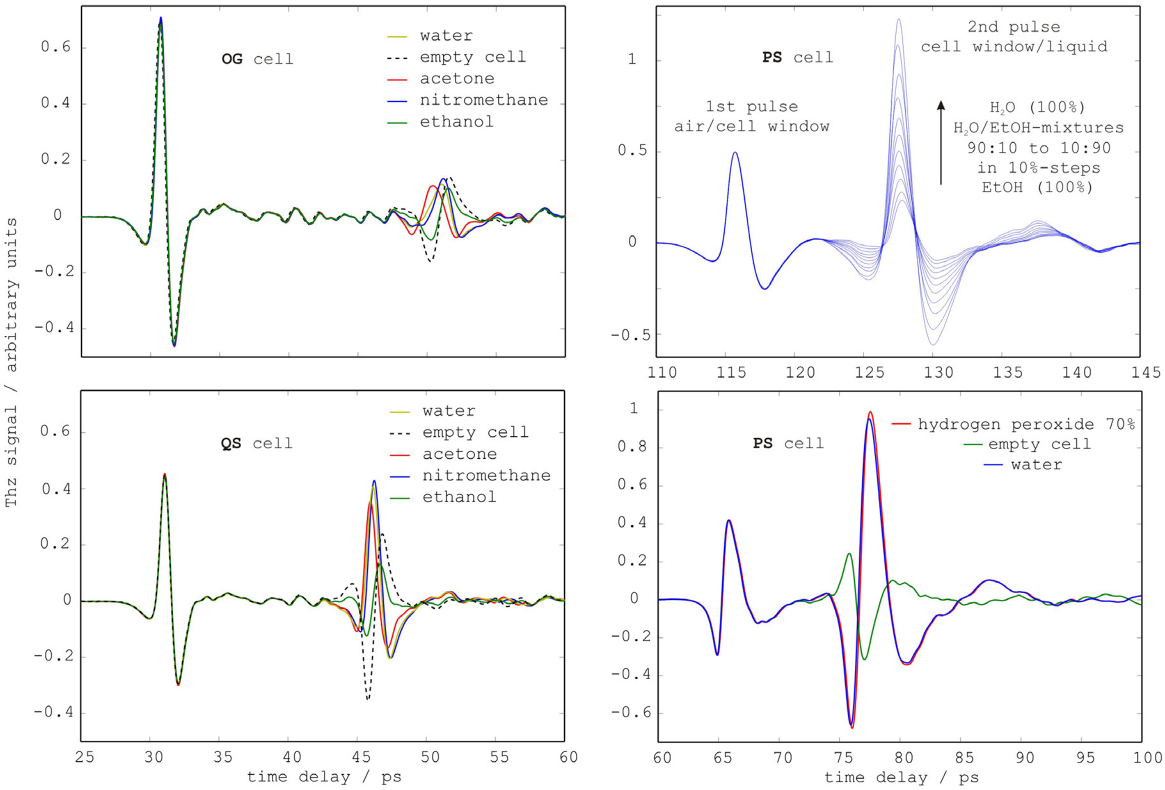


Figure 4. Detected THz signal in dependence of the time delay in reflection geometry mode: *top left* OG and *bottom left* QS cell (red = acetone, blue nitro methane, green ethanol, yellow water and black empty cell). *top right* water, ethanol and nine water/ethanol mixtures (10% to 90% water content) in PS cells, *bottom right* water (blue), hydrogen peroxide (red) both in PS cells and a empty PS cell (green).

The amplitude maximum of the reflected second pulses changes from lower to higher values if the cells are filled with acetone, water and nitro methane. This behaviour is independent of the glass materials and influenced by the refraction index of the filler.

Ethanol expressed a different behaviour in both cells and switches the phase as well. Ethanol, water and nine ethanol/water mixtures with ethanol concentration changed in 10% steps were investigated in PS cells (Fig. 4, *top left*). Each first pulse, originated from the air/PS window interface, is superimposed on the other, in a similar way like observed at the glass cells. The pulse maximum of the second pulse (PS window/liquid interface) differs significantly in the mixtures. The smallest value belongs to ethanol, the highest to water. After calibration, the concentration of an unknown solution can be determined. Similar results were observed by Jepsen *et al.*[7] characterising alcohol solutions in bottles. Water and hydrogen peroxide were also inspected in PS cells (Fig. 4, *bottom right*). As observed before, the local position of the first PS interface determines the time position of the first reflected pulses. The reflected pulses of the material liquid interface show for the inspected incident angle of 45° only very weak amplitude differences between water (blue) and hydrogen peroxide (red).

Nevertheless, THz-TDS in transmission and reflection geometry mode is suitable to characterize liquids. Non-polar flammable liquids, for example hydrocarbon mixtures and polar liquid explosives like nitro methane could be differentiated from harmless water.

4. Conclusions

The THz-TDS is suitable for the characterization of liquids by application of the corresponding transmission and reflection mode. The examined liquid explosives and flammable liquids could be differentiated from water on the basis of their transmission and reflection properties. Polar liquids could be separated from non-polar liquids.

Non-polar liquids were initially examined in transmission mode with glass or plastic cells. The detected pulse could be transformed to the frequency domain between 0.1 and 2 THz via FFT and subsequently characterized in regards to different amplitude spectrums.

In contrast, polar liquids are absorbing the THz pulse at a layer thickness of 1 mm completely in the chosen experimental setup. Out of this reason transmission measurements in conventional liquid cells (layer thickness of 10 mm) could not be preformed. Polar liquids should be preferentially examined in the reflection mode.

The reflection mode is also oriented on many daily used practical applications, were the object allows access to its surface from only one side. Unknown liquids can be analysed directly in closed glass, ceramic or plastic containers), independent of their form and shape with a focused THz beam. The reflection, the electric field of the first THz pulses is an indicator for the container material and can be used as a reference signal for further evaluation of the second reflected THz pulses. The amplitude of the second pulse differs for different liquids if identical container material is used. In the reflection mode the interference of both pulses signals make reliable analyses of the complex optical properties such as refraction index and absorption in the frequency domain difficult. The frequency resolution of the calculated spectrum is restricted by the time difference between the two pulses (time separation).

5. Acknowledgement

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