Sensing of phase transition in medium with terahertz pulsed spectroscopy

Kirill I Zaytsev, Irina N Fokina, Aleksey K Fedorov and Stanislav O Yurchenko
Bauman Moscow State Technical University, 2nd Baumanskaya str., 5, Moscow, 105005, Russia
E-mail: kirzay@gmail.com

Abstract. Phase state identification and phase transition registration in condensed matter are significant applications of terahertz spectroscopy. A set of fundamental and applied problems are associated with the phase state problem. Our report is devoted to the experimental analysis of the spectral characteristics of water and water solution during the phase transition from the solid state to the liquid state via the method of terahertz pulsed spectroscopy. In this work transformation of the sample spectral characteristics during the phase transition were observed and discussed. Possible application of terahertz pulsed spectroscopy as an effective instrument for phase transition sensing was considered.

1. Introduction and background
There are many fundamental and applied problems associated with the study of medium phase transitions which could be solved by the use of terahertz (THz) pulsed spectroscopy. For example, one of them is an important problem of technological non-destructive evaluation during a process of vacuum molding of the polymer composite materials. There are a lot of polymer vacuum molding technologies [1],[2]. All of them involve fabrication of a polymer composite using polymer phase transition under the change of any internal or external environment conditions, for example: changes of the medium chemical compound, changes of the polymer temperature, etc. In order to reduce the wastes of materials in the vacuum molding technologies, several tasks of the polymer molding process control need to be solved. It includes the polymer medium homogeneity control, control of the package filling completeness, control of the phase transition process in polymer medium during the composite manufacturing, etc. Note, during the vacuum molding process, polymer is located in a vacuum package which is transparent for THz rays and opaque for visual and infrared radiation, thus visual and infrared light could not be used for solving control task. This paper shows that the THz pulsed spectroscopy system could sense the phase transitions in media, and since the molding package is transparent for the THz radiation, all of the listed control problems could be successfully solved with THz pulsed spectroscopy.

The region between 0.1 and 10.0 THz is commonly referred to THz region [3]. THz rays are non-ionizing in nature, and are able to penetrate a certain depth into a large number of dielectric materials. THz spectral absorption lines of media are associated with the presence of molecular low-energy rotational and vibrational degrees of freedom. Absorption is caused by changes in energy levels of molecule movements induced by THz rays. The more complex the medium molecule is the more powerful THz absorption line is.
Because of all these properties there are a lot of potential applications of THz technologies, including spectroscopy of biological tissue [4],[5], medical diagnostics [6]-[9], detection of concealed weapons, explosives and drugs [10],[11], nondestructive evaluation of constructional materials [12], art inspection [13], gas sensing [14],[15] etc. Since absorption of THz light in various media is caused by the changes in molecule energy levels associated with different molecule rotational and vibrational states, and the spectrum of possible molecule states transforms significantly during the medium phase transition, THz spectral characteristics of medium also undergo great transformations during the phase transition. This fact provides the ability to use THz spectra for studying and controlling processes of phase transitions in media. This property of THz spectra is beneficial in different fundamental and applied aspects of THz science. And it could be used for technological non-destructive evaluation of constructional materials, in particular for control the vacuum molding process, mentioned above, during manufacturing of polymer composite materials.

This work shows the ability for studying the processes of phase transition in a medium via the instrument of THz pulsed spectroscopy using the ice-water transition as an example.

Recently much attention is paid to the investigation of chemical, physical and biological properties of water [17]-[21] and aqueous solution in THz range of the electromagnetic spectrum. Water molecule is strongly polar and has many rotational and vibrational degrees of freedom, thus the THz absorption spectrum of water is very complex. In gas state water molecule has symmetric and asymmetric stretches and bending of the covalent bonds. In liquid state the motion and the structure of water are more complex because of the long-range interaction between molecules due to the hydrogen bonding [22]. Note, the absorption of water is much higher in THz range in contrast to microwave and optical ranges of the electromagnetic spectrum [23]. Paper [24] is dedicated to determination of the liquid water complex dielectric permittivity model in the THz range. It was shown, that the THz complex dielectric permittivity of water could be accurately described with the double Debye model. Moreover, information about microscopic mechanisms, leading to water anomalous properties, is contained in the temperature dependence of its THz absorption spectrum. Ronne et al. [25] determined the optical constants of liquid water as a function of temperature in the discrete temperature scale between 271.1 and 366.7 K and in the frequency range from 0.1 to 2.0 THz.

2. Results
This work shows the results of the “ice-water” phase transition studying via the method of THz pulsed spectroscopy. The THz reflectivity transformation during the samples of pure water and 5% water sugar solution defrosting are presented and discussed.

The main idea of the terahertz pulsed spectroscopy (TPS) can be described as follows. Short pulses of THz radiation with a wideband spectrum (from 0.1 THz to at least 3.5 THz) are utilized to measure THz optical properties of media. The electrical field of the THz pulse $E_{THz}(t)$ is detected with high time resolution up to 50.0 fs after transmission or reflection of the pulse from sample surface. It is possible to analyze complex amplitude transmission or reflection coefficients of a sample in a wide frequency range via the procedure of the fast Fourier transformation, applied to the detected time-domain signal.

For our purposes we have used a TPS system fully described in paper [26]. It was complemented by the thermostat module as it is shown in the figure 1. TPS system utilizes ultra-short optical pulses for both generation of THz radiation in a LT – GaAs photoconductive antenna and detection of THz pulses in a ZnTe electrooptical detector. The used TPS system is able to detect THz spectral characteristics of a sample in a frequency range from 0.1 to 3.0 THz in reflection and transmission modes with a repetition rate up to 400.0 Hz. Such a high repetition rate could be achieved due to the usage of the ultra-fast delay stage in the TPS system. Averaging of 10 signals was applied during the measurements to provide satisfactory signal-to-noise ratio (SNR) and dynamic range [27] (DNR) in the TPS time domain data. Therefore the sample spectrum characteristics were registered with the frequency rate 40.0 Hz during the experiment.
Two signals need to be obtained for reconstruction of the sample THz reflectivity: $E_r(t)$ is the signal reflected from the reference surface with a very high and homogeneous reflectivity in a wide spectral range, and $E_s(t)$ is the sample signal reflected from the sample surface. The reference signal needs to be detected once (before the experiment), and the sample signal needs to be detected on each step of the sample temperature variation. A planar gold mirror was used to obtain the reference signal. As the signals were detected, the sample reflectivity reconstruction could be accomplished according to the following equation:

$$\tilde{R}(v_t) = \frac{\tilde{E}_s(v_t)}{\tilde{E}_r(v_t)}$$  \hspace{1cm} (1)

where $\tilde{E}_r(v_t)$ and $\tilde{E}_s(v_t)$ are the Fourier spectra of the reference and the sample signals, respectively. Note, equation (1) should be applied to every sample signal obtained on each step of the sample temperature variation; therefore the temporal dependence of the sample reflectivity during the phase transition would be obtained.

The samples were studied with TPS system in the reflection mode during the samples defrosting. Since THz beam was focused on the air-medium interface with a high aperture lens, the THz spot diameter close to $1.22 \cdot \lambda$ was achieved. Temperature of the samples was controlled with a thermostat built of thermocouple and Peltier element. The sample was connected with the Peltier element via the metal plate and the thermopaste. The temperature of the samples varied continuously within the interval between $-10$ and $+20$ $^\circ$C and then in steps of $5^\circ$C with the accuracy.
of the temperature keeping equal to \( \pm 0.1 \) °C. The samples reflectivity was measured both at the different stationary samples temperatures and during the continuous changes of the temperature.

The recorded time dependences of the THz amplitude reflectivity variations during the phase transition in the media are presented in the figure 2a (water sample) and figure 2b (5% sugar aqueous solution sample). In order to notice the clear differences and rather high contrast between solid and liquid states reflectivity one could consider figure 3, which contains the results of samples reflectivity determination at the discrete stationary temperatures: \(-5\), \(+5\), \(+10\), \(+15\) and \(+20\) °C.

![Figure 2](image1.png)

**Figure 2.** Time dependence of the sample reflectivity modulus during the phase transition in the medium: (a) corresponds to the water sample, (b) corresponds to the water sugar solution sample.

![Figure 3](image2.png)

**Figure 3.** Amplitude reflectivity modulus at the different discrete sample temperatures: (a) corresponds to the water sample, (b) corresponds to the 5% water sugar solution sample.

In complete accordance with the theoretical conception [28],[29], spectral characteristics of the samples were transformed during the phase transition. Therefore, in both our experiments phase transition was registered. There are several strong lines in the spectral reflectivity curves (figures 2,3), especially at the frequencies above \(1.6\) THz. These lines are caused by the fluctuations of the water vapor content along the THz beam path during our experiment. To prevent the appearance of this lines in future works one should vent the THz beam path with nitrogen. Reflectivity of the second sample is higher than \(1.0\) arb. units at low frequencies. This is due to the low signal-to-noise ratio of the TDS system in defined frequency range.
The TDS system utilized in the present work could be used for detection of medium phase transitions with the temporal resolution higher than 0.1 sec. The temporal resolution of the considered method is limited both by the repetition rate of the THz spectrum registration, and by the size of the spot of THz beam focused on the surface of the sample. Phase transition of the medium does not occur simultaneously at every point of the medium-air interface. The transition starts from several active points of the sample surface and runs as a wave in the medium-air interface. Since this wave runs through the THz beam spot for a finite time, the THz pulsed spectrometer obtained the average THz reflectivity of the liquid and the solid state regions of the sample surface which are on the THz beam path. The velocity of the phase transition wave depends on a large numbers of factors, including the degree of the sample overcooling, but it is constant for the fixed experiment conditions. Possible ways of raising the temporal resolution of the phase transition sensing is reduction of the THz spot size and raising of the TDS system repetition rate. Modern THz pulsed spectrometers could reach 500.0 Hz repetition rate of the spectrum registration. Being equipped with a high aperture optical system focusing the THz beam on the sample surface, modern TDS system could provide temporal resolution higher than 0.01 s.

Conclusions
The ability of the THz pulsed spectroscopy usage for studying of the medium phase transitions have been discussed. The results of the water sample and the water solution of sugar sample studying during the medium phase transition were obtained. The dependence of the samples reflectivity versus the experiment time was shown. High contrast between the reflectivity of the samples in the liquid and the solid states was observed. The ability of THz pulsed spectroscopy usage for non-destructive sensing of the polymer phase transition during the process of the polymer composite material vacuum molding was suggested.

Acknowledgments
This work was partially supported by grants of the Ministry of Education and Science of Russian Federation (№ 14.B37.21.0898, № 14.B37.21.1282) and of the Russian Foundation for Basic Research (RFBR 12-08-31104; RFBR 12-08-33112). A.K.F. is an RQC Fellow.

References
[1] van Rijswijk K, Bersee H E N, Beukers A, Picken S J, van Geenen A A 2006 Optimisation of anionic polyamide-6 for vacuum infusion of thermoplastic composites: Influence of polymerisation temperature on matrix properties Polymer Testing 25(3) 392-404
[2] Goren A, Atas C 2008 Manufacturing of polymer matrix composites using vacuum assisted resin infusion molding Archives of Materials Science and Engineering 34(2) 117-120
[3] Lee Y-S 2009 Principles of Terahertz Science and Technology (Springer, New York, NY)
[4] Nazarov M M, Shkurinov A P, Kuleshov E A, Tuchin V V 2008 Terahertz time-domain spectroscopy of biological tissues Quantum Electronics 38(7) 647-654
[5] Pickwell E, Cole B E, Fitzgerald A J, Wallace V P, Pepper M 2004 Simulation of terahertz pulse propagation in biological systems Appl. Phys. Lett. 84(12) 2190 – 2192
[6] Wallace V P, Woodward R M, Fitzgerald A J, Pickwell E, Pye R J, Arnone D D 2003 Terahertz-pulsed imaging of cancers Proc. SPIE 4949 353 – 359
[7] Zaytsev K I, Karasik V E, Koroleva S A, Fokina I N 2012 Study the ability of terahertz imaging systems application for medical diagnosis “Herald of Bauman Moscow State Technical University. Series: “Instrumentation” 4 114 – 127
[8] Fitzgerald A J, Wallace V P, Jimenez-Linan M, Bobrow L, Pye R J, Purushotham A D, Arnone D D 2006 Terahertz Pulsed Imaging of Human Breast Tumors Radiology 239(2) 533–540
[9] Yu C, Fan S, Sun Y, Pickwell-MacPherson E 2012 The potential of terahertz imaging for cancer diagnosis: A review of investigations to date Quantum Imaging in Medicine and Surgery
2(1) 33 – 45

[10] Murrill S R, Franck C C, Espinola R L, Petkie D T, De Lucia F C, Jacobs E L 2011 Enhanced terahertz imaging system performance analysis and design tool for concealed weapon identification Proc. SPIE 8188 81880J-1 – 81880J-15

[11] Federici J F, Schultkin B, Huang F, Gary D, Barat R, Oliveira F, Zimdars D 2005 THz imaging and sensing for security applications – explosives, weapons and drugs Semicond. Sci. Technol. 20(7) S266 – S280

[12] Stoik C D, Bohn M J, Blackshire J L 2008 Nondestructive evaluation of aircraft composites using transmissive terahertz time domain spectroscopy Opt. Express 16(21) 17039 – 17051

[13] Abraham E, Younus A, Delagnes J C, Mounaix P 2010 Non-invasive investigation of art paintings by terahertz imaging Appl. Phys. A 100(3) 585 – 590

[14] Jacobsen R H, Mittleman D M, Nuss M C 1996 Chemical recognition of gases and gas mixtures with terahertz waves Opt. Lett. 21(24) 2011 – 2013

[15] Mittleman D M, Jacobsen R H, Neelamani R, Baraniuk R G, Nuss M C 1998 Gas Sensing Using Terahertz Time-domain Spectroscopy Appl. Phys. B 67(3) 379 – 390

[16] Mittleman D M, Nuss M C, Colvin V L 1997 Terahertz spectroscopy of water in inverse micelles Chem. Phys. Lett. 275(3-4) 332 – 338

[17] Globus T, Bykhovski A, Khromova T, Gelmont B, Tamm L K, Salay L C 2007 Low-terahertz spectroscopy of liquid water Proc. SPIE 6772 67720S-1 – 67720S-11.

[18] Bunkin N F, Yurchenko S O, Suyazov N V, Shkirin A V 2012 Structure of the nanobubble clusters of dissolved air in liquid media J. Biol. Phys. 38(1) 121 – 152

[19] Gorshunov B P, Zhukova E S, Torgashev V I, Lebedev V V, Shakurov G S, Kremer R K, Pestrijakov E V, Thomas V G, Fursenko D A, Dressel B 2013 Quantum Behavior of Water Molecules Confined to Nanocavities in Gemstones J. Phys. Chem. Lett. 4(12) 2015 – 2020

[20] Aliev I N, Yurchenko S O 2010 Evolution of perturbations of a charged interface between immiscible inviscid fluids in the interelectrode gap Fluid Dynamics 45(5) 817-826

[21] Bunkin N F, Yurchenko S O, Suyazov N V, Shkirin A V 2012 Structure of the nanobubble clusters of dissolved air in liquid media J. Biol. Phys. 38(1) 121-152

[22] Siegel P H 2004 THz Technology in Biology and Medicine IEEE Trans. Microwave Theory Tech. 52(10) 2438 – 2448

[23] Xu J, Plaxco K W, Allen S J 2006 Absorption spectra of liquid water and aqueous buffers between 0.3 and 3.72 THz J. Chem. Phys. 124(3) 036101-1 – 036101-3

[24] Pickwell E, Cole B E, Fitzgerald A J, Pepper M, Wallace V P 2004 Simulation of terahertz pulse propagation in biological systems Appl. Phys. Lett. 84(12) 2190 – 2192

[25] Ronne C, Thrane L, Astrand P O, Wallqvist A, Mikkelsen K V, Keiding S R 1997 Investigation of the temperature dependence of dielectric relaxation in liquid water by THz reflection spectroscopy and molecular dynamics simulation J. Chem. Phys. 107(14) 5319–5331

[26] Zaitsev K I, Karasik V E, Fokin I N, Aleckhnovich V I 2013 Invariant embedding technique for medium permittivity profile reconstruction using terahertz time-domain spectroscopy Opt. Eng. 52(6) 068203-1 – 068203-10

[27] Nattaly M, Dudley R 2009 Methodologies for determining the dynamic ranges and signal-to-noise ratios of terahertz time-domain spectrometers Opt. Lett. 34(8) 1213 – 1215

[28] Lee D C, Chapman D 1986 Infrared spectroscopic studies of biomembranes and model membranes Bioscience Reports 6(3) 235 – 256

[29] Lima Jr J A, Freire P T C, Melo F E A, Filho J M, Fischer J, Havenith R W A, Broer R, Bordallo H N 2013 Using Raman spectroscopy to understand the origin of the phase transition observed in the crystalline sulfur based amino acid l-methionine Vibrational Spectroscopy 65 132 – 141