Physica B 405 (2010) 2208–2212

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Comparative study of boson peak in normal and secondary alcohols with terahertz time-domain spectroscopy

Yoshiki Yomogida [a,*], Yuki Sato [b], Ryusuke Nozaki [a], Tomobumi Mishina [b], Jun'ichiro Nakahara [b]

[a] *Dielectrics Laboratory, Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan*

[b] *Laboratory of Optical Science and Semiconductor Physics, Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan*

A R T I C L E I N F O

Article history:
Received 14 October 2009
Received in revised form
10 January 2010
Accepted 2 February 2010

Keywords:
Terahertz time-domain spectroscopy
Hydrogen-bonded liquids
Boson peak

A B S T R A C T

Using terahertz (THz) time-domain spectroscopy, we measured the complex permittivity of some normal (1-propanol, 1-butanol, and 1-pentanol) and secondary alcohols (2-propanol, 2-butanol, and 2-pentanol) in the frequency ranges from 0.2 to 2.5 THz at temperatures from 253 to 323 K. For all the samples, the complex permittivity in the THz region includes the following three components: (i) a high frequency side of dielectric relaxation processes, (ii) a broad mode around 1 THz, and (iii) a low frequency side of an intermolecular vibration mode located above 2.5 THz. The mode around 1 THz is recognized as a boson peak which is related to the local structure of disordered materials. The intensity of the boson peak in secondary alcohols is higher than that in normal alcohols. On the other hand, the number of carbon atoms slightly affects the appearance of the boson peak. These observations indicate that the position of an OH group in a molecule has a profound effect on the local structures in monohydric alcohols.

1. Introduction

Terahertz (THz) time-domain spectroscopy (THz-TDS) [1,2] has been well-established with the development of THz wave emission and detection in recent years. The new experimental technique has been applied to the research of many materials and has proven to be a powerful tool for the study of molecular dynamics and interactions in these materials. The study of the boson peak is one such application [3,4] because the experimental frequency range which THz-TDS can cover corresponds to the range where the boson peak is observed. The boson peak is a universal feature of disordered materials like glasses and supercooled liquids. For various types of disordered materials, this feature has been observed in the energy range of 2–5 meV, especially from neutron and Raman scattering measurements. In specific heat measurements, the boson peak corresponds to the excess contribution found at low temperature. Despite a number of studies on the boson peak, its microscopic origin has not been understood.

Here, we performed complex permittivity measurements of two classes of monohydric alcohols: normal alcohols (1-propanol, 1-butanol, and 1-pentanol) and secondary alcohols (2-propanol, 2-butanol, and 2-pentanol). These monohydric alcohols form a network-like local structure in the liquid and glassy state through intermolecular hydrogen bonds. The network structure is affected systematically by changing the position of an OH group and the length of the carbon chain in these alcohol molecules. Because the boson peak is related to the local structure of disordered materials, normal and secondary alcohols which have different local structures are expected to show a large difference in the appearance of the boson peak. The boson peak in monohydric alcohols has been observed with various experimental techniques. Glassy methanol [5], ethanol [6], and 1-propanol [7,8] have been investigated with inelastic neutron scattering. On the other hand, no complex permittivity measurement for the study of the boson peak has been performed extensively because of the experimental difficulty in the THz region. However, the most important merit of the complex permittivity measurement is the broadness of the experimental frequency. This capability enables us to observe the boson peak and other dielectric relaxation processes simultaneously. Now that we can use the THz-TDS for the complex permittivity measurement in a new frequency range, a full comprehension of the dynamics in monohydric alcohols will be obtained.

In the present study of normal and secondary alcohols, a boson peak is observed in the dielectric loss around 1 THz. The main objective of this study is to perform systematic experiments in the THz region and to discuss the boson peak as functions of the number of carbon atoms and the position of an OH group. The systematic study can aid the understanding of the local structures and high-frequency dynamics in monohydric alcohols.

---

* Corresponding author.
E-mail address: yomogidab77@yahoo.co.jp (Y. Yomogida).

0921-4526/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2010.02.010

2. Experimental

The experimental technique of THz time-domain spectroscopy has been well developed and described in detail by others [9–13]. Our experimental setup is essentially the same as those reported by other groups. A mode-locked Ti sapphire laser (Tsunami, Spectra Physics), which generates 100 fs pulses of 800 nm wavelength, was used for the emission and detection of pulsed THz waves. For this, we produced a photoconductive antenna with electrodes, the gap distance of which is 500 μm, fabricated on a semi-insulating gallium arsenide substrate for the emission of the THz pulse. With the wide gap distance, high bias voltage, modulated at 20 kHz, was applied to the antenna. In the detection of THz pulses, an electro-optic (EO) sampling method was employed with a $\langle 1\,1\,0 \rangle$ ZnTe crystal (1 mm in thickness) as an EO crystal. The wave path was enclosed in a vacuum box (below 20 Pa) to reduce absorption by atmospheric water vapor.

Liquid samples were put into the sample cell consisting of a pair of polypropylene windows and a spacer. The temperature of liquid samples was controlled from 253 to 323 K by a Peltier device. The sample thickness was controlled by the spacer (500 and 1000 μm). The THz pulses transmitted through an empty cell were first recorded followed by collection of data for the liquid samples. The complex permittivities of the samples were calculated with the Fourier transforms of the THz waves transmitted through the samples and the empty sample cell. Typical experimental errors in both dielectric permittivity and dielectric loss were $\pm 2\%$ for the whole frequency range and $\pm 5\%$ only around 2.5 THz.

Data in the microwave range were also obtained to study dielectric properties of alcohols in a wide frequency range. For the measurement of the microwave range, two different experimental setups were used in order to cover the frequency ranges between 1 MHz and 20 GHz. From 1 to 500 MHz, the complex permittivity measurements were performed with a network analyzer (HP4195A). The complex permittivity was obtained from reflection measurements with the sample cell located at the end of a coaxial line. The coaxial sample cell (10 mm length) was composed of an outer conductor with an inner diameter of 3.5 mm and a center conductor with an outer diameter of 2 mm. From 500 MHz to 20 GHz, the complex permittivity was obtained by time-domain reflectometry [14]. A flat-end capacitor cell using a 2 mm semi-rigid coaxial waveguide was used in this measurement. The temperature of the sample cells in both experimental setups was controlled at 298 K.

The normal alcohols used were 1-propanol, 1-butanol, and 1-pentanol, and secondary alcohols were 2-propanol, 2-butanol, and 2-pentanol. These chemicals were obtained from Wako Pure Chemical Industries and were used without further purification.

3. Results and discussion

3.1. A dielectric loss peak around 1 THz

Figs. 1 and 2 represent the complex permittivities $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ of 1- and 2-propanol in the frequency range between 0.2 and 2.5 THz at temperatures from 253 to 323 K. It has been reported that there exists three dielectric relaxation processes [15–19] below the GHz frequency range in monohydric alcohols around room temperature. These processes contribute to $\varepsilon^*(\omega)$ in the THz range, resulting in the rise of dielectric permittivity and dielectric loss below 1 THz as shown in Figs. 1 and 2. With decreasing temperature, the relaxation processes shift to a lower frequency range, thus decreasing the dielectric loss $\varepsilon''(\omega)$ below 1 THz. At low temperatures, after the shift of the dielectric relaxation processes, a peak can be clearly seen around 1 THz, which is indicated by arrows in the insets of Figs. 1 and 2. The peak positions in both normal and secondary alcohols are almost independent of temperature.

The complex permittivities for a series of normal and secondary alcohols at 253 K, respectively are shown in Figs. 3 and 4. The intensity of the peak around 1 THz for the secondary alcohols (Fig. 4) is higher than that of the normal alcohols (Fig. 3). In normal alcohols, the peak magnitude is so small that it appears just as a kink in the dielectric loss. On the other hand, in the case

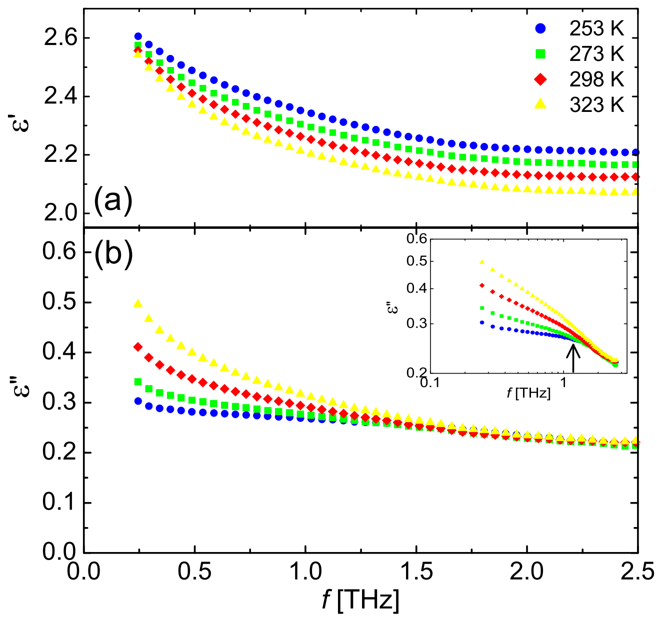

Fig. 1. Dielectric permittivity (a) and dielectric loss (b) of 1-propanol in frequency range between 0.2 and 2.5 THz at 253–323 K. Inset in (b) shows bilogarithmic plot of dielectric loss.

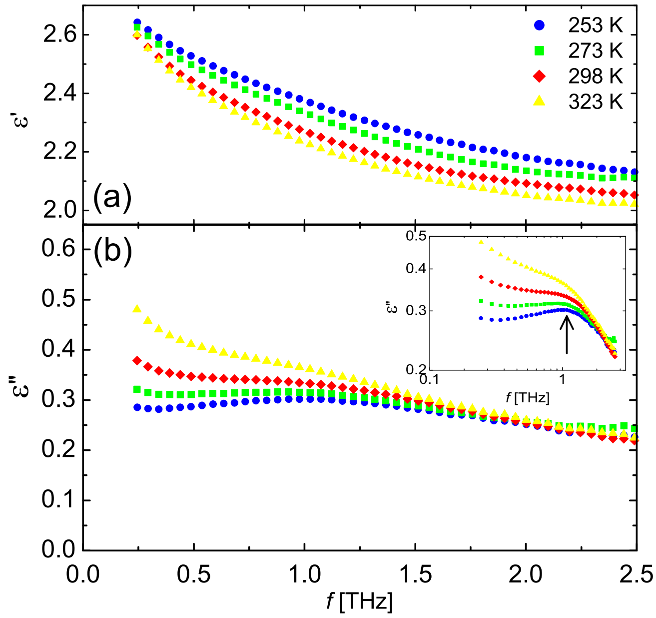

Fig. 2. Dielectric permittivity (a) and dielectric loss (b) of 2-propanol in frequency range between 0.2 and 2.5 THz at 253–323 K. Inset in (b) shows bilogarithmic plot of dielectric loss.