

## Comparative dielectric study of monohydric alcohols with terahertz time-domain spectroscopy

Yoshiki Yomogida<sup>a,\*</sup>, Yuki Sato<sup>b</sup>, Ryusuke Nozaki<sup>a</sup>, Tomobumi Mishina<sup>b</sup>, Jun'ichiro Nakahara<sup>b</sup>

<sup>a</sup> Dielectric Laboratory, Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan

<sup>b</sup> Laboratory of Optical Science and Semiconductor Physics, Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan

### ARTICLE INFO

#### Article history:

Received 26 April 2010

Received in revised form 2 August 2010

Accepted 2 August 2010

Available online 6 August 2010

#### Keywords:

Terahertz time-domain spectroscopy

Dielectric relaxation

Hydrogen-bonded liquid

Alcohol

Low-frequency vibration

### ABSTRACT

Using terahertz (THz) time-domain spectroscopy, we have measured the complex permittivity of 14 monohydric alcohols in the frequency range 0.2–2.5 THz, at temperatures ranging from 253 to 323 K. The molecular structures of these monohydric alcohols change systematically with the position of the OH group, the number of carbon atoms, and the structure of the carbon chain. The complex permittivity in the THz region contains the following three components: (i) a high-frequency tail of dielectric relaxation processes, (ii) a broad vibration mode around 1.2 THz, and (iii) a low-frequency side of an intermolecular vibration mode located above 2.5 THz. At low temperatures, the relaxation processes shift toward a low-frequency range, while a peak of the broad vibration mode, which is independent of temperature, is clearly observed around 1.2 THz. The present comparative study shows that there is a strong correlation between this mode around 1.2 THz and the molecular structures of monohydric alcohols.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Complex permittivity measurement has long been applied in the study of numerous materials [1–3]. The advantage of this measurement is the broadness of the experimental frequency range, spanning 1  $\mu$ Hz to several THz. Below 1 MHz, the complex permittivity can be obtained easily with commercial experimental equipment. Using a network analyzer or time-domain reflectometry (TDR) [4–6], one can accurately measure the complex permittivity up to several tens of GHz. However, to measure the complex permittivity beyond this frequency, exceptional experimental equipment, such as a waveguide interferometer [7] or infrared spectroscopy [8,9], is necessary; therefore, due to the complexity, such experiments have not been performed extensively. In the 1980s, new techniques for emission and detection of terahertz (THz) waves were developed using femtosecond laser and semiconductor device technology, which lead to further research using THz waves. During this period, a new spectroscopic technique called terahertz time-domain spectroscopy (THz-TDS) was established [10,11], which allows the accurate measurement of complex permittivity above several tens of GHz.

THz-TDS has proven to be a powerful tool for the study of molecular dynamics and interactions in various materials. The study of molecular dynamics in hydrogen-bonded liquids is an

important application because of their significance in various fields such as physical chemistry, biology, and industry. In the THz region, molecular dynamics is related to the hydrogen-bonding phenomena that distinguish hydrogen-bonded liquids from simple liquids. Therefore, the observation serves as a key to explain complicated physical properties in hydrogen-bonded liquids.

Kindt and Schmuttenmaer conducted pioneering experiments on methanol, ethanol, and 1-propanol with THz-TDS in the frequency range 0.06–1.0 THz [12]. They concluded that the complex permittivity of these alcohols could be expressed only with the high-frequency tail of the dielectric relaxation processes located in the microwave range. On the other hand, Fukasawa et al. [13] reported the complex permittivity measurements on methanol in the frequency range 50 MHz–5 THz. Such a wide frequency range confirmed that the dielectric spectra of methanol in the THz region contained not only the high-frequency contribution of the dielectric relaxation processes, but also some vibration modes. In the study conducted by Kindt et al. the experimental frequency range was insufficient to entirely estimate the complex permittivity in the THz region. It is therefore necessary to reexamine the complex permittivity of monohydric alcohols in this region in detail.

In the present study, we have measured complex permittivity of 14 monohydric alcohols (Table 1) with THz-TDS in the experimental frequency range 0.2–2.5 THz. In addition, we have observed the temperature dependence of the dielectric spectra in the THz region in a temperature range of 253–323 K. Experiments on monohydric alcohols in the THz region over such a wide temperature range has not been performed till date, although this may be informative in

\* Corresponding author.

E-mail addresses: [yoshiki.yomogida@aist.go.jp](mailto:yoshiki.yomogida@aist.go.jp), [yomogidab77@yahoo.co.jp](mailto:yomogidab77@yahoo.co.jp) (Y. Yomogida).

**Table 1**  
Fourteen monohydric alcohols used in the measurement of the complex permittivity.

Number of carbon atoms	Molecular formula	Type of alcohol
1	CH <sub>3</sub> OH	Methanol
2	C <sub>2</sub> H <sub>5</sub> OH	Ethanol
3	C <sub>3</sub> H <sub>7</sub> OH	1-Propanol 2-Propanol
4	C <sub>4</sub> H <sub>9</sub> OH	1-Butanol 2-Butanol 2-Methyl-1-propanol
5	C <sub>5</sub> H <sub>11</sub> OH	1-Pentanol 2-Pentanol 3-Pentanol 2-Methyl-1-butanol 3-Methyl-1-butanol 2-Methyl-2-butanol 3-Methyl-2-butanol

understanding the behavior of the dielectric spectra in the frequency region. The objective of this study is to perform systematic experiments of monohydric alcohols in the THz region and to observe the temperature dependence of the dielectric spectra. On the basis of the systematic experimental results, we will confirm the existence of certain modes in the THz region and discuss the underlying microscopic mechanisms contributing to the dielectric spectra in this frequency region.

## 2. Experimental

THz-TDS has been developed comprehensively, and the experimental setups have been described in detail [14–17]. In the present study, a mode-locked Ti sapphire laser (Tsunami, Spectra Physics), which generates 100 fs pulses of 800 nm central wavelength, was used for emission and detection of pulsed THz waves. For emission, we produced a photoconductive (PC) antenna with electrodes, the gap distance of which was 500  $\mu\text{m}$ , fabricated on a semi-insulating gallium arsenide substrate. Modulated THz waves were generated by applying a 10 kHz alternating current bias to the PC antenna. For the detection of THz pulses, an electro-optic (EO) sampling method was employed with a (1 1 0) ZnTe crystal (1-mm thick) as an EO crystal. The wave path was enclosed in a vacuum box (<20 Pa) to reduce absorption by atmospheric water vapor. Liquid samples were put into a sample cell consisting of a pair of polypropylene windows and a spacer. The temperature of the samples was controlled to be between 253 and 323 K by a Peltier device with an accuracy of 0.2 K (except for 2-methyl-2-butanol, whose melting point is 261 K, in which measurements were obtained between 263 and 323 K). The sample thickness was controlled by the spacer (500 and 1000  $\mu\text{m}$ ). The THz pulses transmitted through an empty cell were first recorded, followed by the collection of data for the liquid samples. The complex permittivities of the samples were calculated using 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 5% for the entire frequency range.

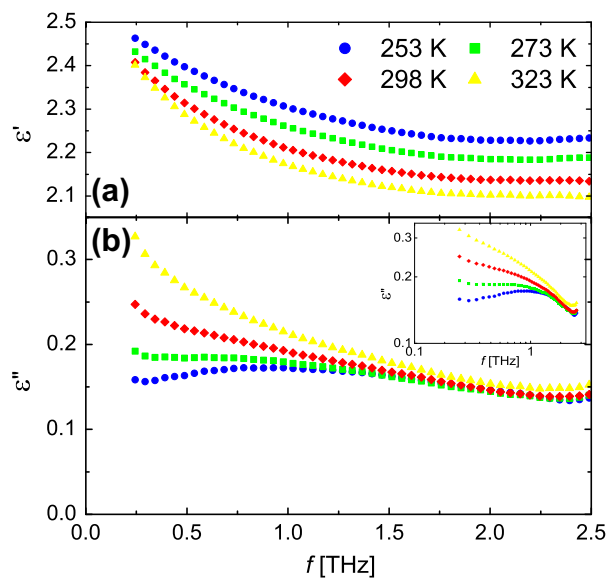
Data in the microwave range were also obtained to investigate the dielectric properties of monohydric alcohols over a wide frequency range. For the measurement within the microwave range, two different experimental setups were used to cover the frequency range 1 MHz–20 GHz: from 1 to 500 MHz, the complex permittivity measurements were performed using a network analyzer (HP4195A), and from 500 MHz to 20 GHz, TDR was used [4–6]. Details of experiments in the microwave region have been provided in our previous paper [18]. The temperature of the sample in both the experimental setups was controlled in the range 273–323 K, with an accuracy of 0.1 K.

The monohydric alcohols used in this study are listed in Table 1. 1-Pentanol was purchased from Kanto Chemical, 3-methyl-1-butanol from Kishida Chemical, 3-methyl-2-butanol from Junsei Chemical, and the other alcohols were purchased from Wako Pure Chemical Industries. These chemicals were all of analytical grade (97.0–99.9%) and were used without further purification. In case of 2-methyl-1-butanol and 3-methyl-2-butanol, the chemicals obtained were a mixture of optical isomers.

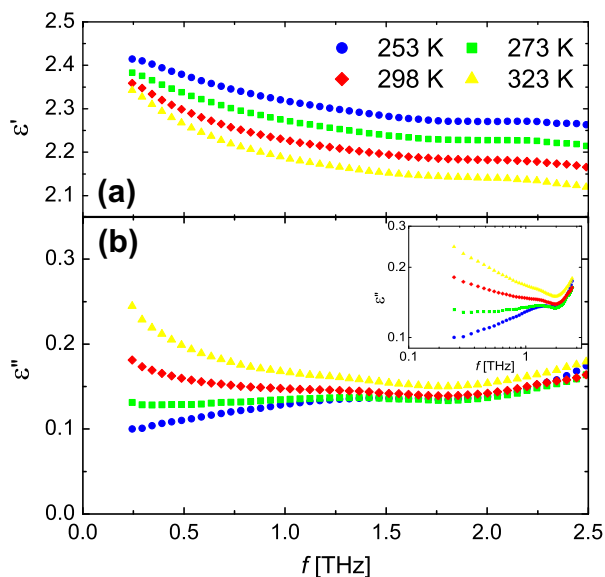
## 3. Results and discussion

### 3.1. Complex permittivity of monohydric alcohols in the THz region

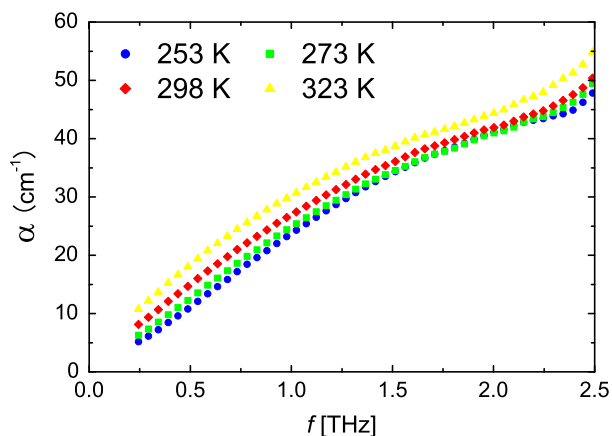
Figs. 1 and 2 demonstrate the complex permittivity of 2-methyl-1-propanol and 3-methyl-1-butanol obtained in the THz region, respectively. Previous studies reported that three Debye-type dielectric relaxation processes exist below the GHz frequency range in monohydric alcohols [19–22]. These processes contribute to  $\varepsilon^*(\omega)$  in the THz region, resulting in an increase in the dielectric permittivity  $\varepsilon'(\omega)$  and dielectric loss  $\varepsilon''(\omega)$  below 0.5 THz, as shown in Figs. 1 and 2. With decreasing temperature, these relaxation processes shift to a lower frequency range, resulting in a decrease in the values of the dielectric loss below 0.5 THz. After this shift, a clear peak can be observed around 1.2 THz. The position of this peak is almost independent of temperature. Furthermore, in some alcohols, a rise in the dielectric loss is clearly observed above 2.0 THz, which indicates the location of another mode above 2.5 THz. For the discussion of the higher frequency region, the power absorption coefficient as well as the complex permittivity has been frequently employed. Shown in Figs. 3 and 4 are the power absorption coefficients of 2-methyl-1-propanol and 3-methyl-1-butanol, respectively. The absorption curves increase with frequency and temperature. A rise in the absorption coefficient is visible in the 2.0–2.5 THz region. However, the peak position around 1.2 THz observed in the dielectric loss is indistinguishable in these figures. Therefore, we proceed in our discussion of the spectra in the THz region with the complex permittivity in the present paper. The basic characteristics of the complex permittivities of monohydric alcohols in the THz region contain three contributions: (i) a high-frequency side of the dielectric relaxation processes, (ii) a mode with peak position around 1.2 THz, and



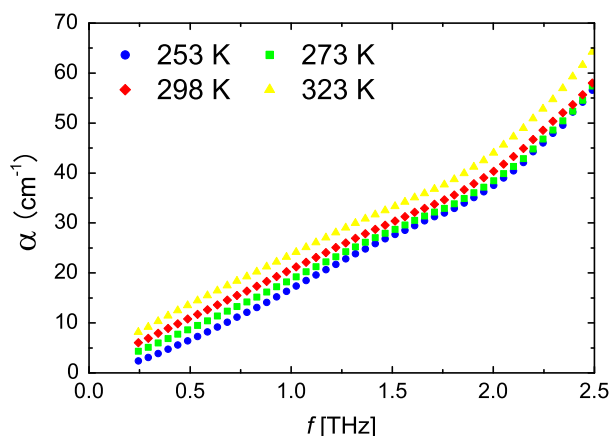
**Fig. 1.** Dielectric permittivity (a) and dielectric loss (b) of 2-methyl-1-propanol in the frequency range 0.2–2.5 THz. The inset in (b) shows the bilogarithmic plot of dielectric loss.



**Fig. 2.** Dielectric permittivity (a) and dielectric loss (b) of 3-methyl-1-butanol in the frequency range 0.2–2.5 THz. The inset in (b) shows the bilogarithmic plot of dielectric loss.



**Fig. 3.** Power absorption coefficient of 2-methyl-1-propanol in the frequency range 0.2–2.5 THz.



**Fig. 4.** Power absorption coefficient of 3-methyl-1-butanol in the frequency range 0.2–2.5 THz.

(iii) a low-frequency side of another mode located above 2.5 THz. In the following sections, these contributions are examined for the 14 alcohols.

### 3.2. Mode around 1.2 THz

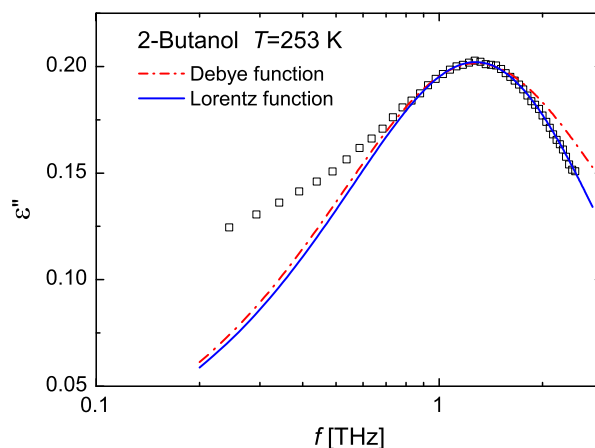
Some authors [23–26] have investigated monohydric alcohols with THz-TDS. However, the existence of a mode around 1.2 THz has been unclear due to its low intensity and the dominance of the high-frequency contribution of the dielectric relaxation processes. In this study, the mode becomes evident around 1.2 THz by lowering the temperature to 253 K. Thus, we prove that the mode with peak position around 1.2 THz is universally observed in monohydric alcohols. To our knowledge, only Fukasawa et al. [13] have previously reported a similar mode at approximately  $50\text{ cm}^{-1}$  ( $\sim 1.5\text{ THz}$ ) in the complex permittivity of methanol. They concluded that the mode was a vibration mode, although its molecular origin was not explained. We attempted to verify the type of the mode around 1.2 THz by fitting the spectra to two functions: the Debye function (Eq. (1)) and the Lorentz function (Eq. (2)). The Debye function is generally used to represent the simplest dielectric relaxation process that has a single relaxation time [27], while the Lorentz function has been introduced to fit the vibration mode of hydrogen-bonded liquids in the THz region [13,28–30].

$$\varepsilon^*(\omega) = \frac{\Delta\varepsilon}{1 + i\omega\tau} \quad (1)$$

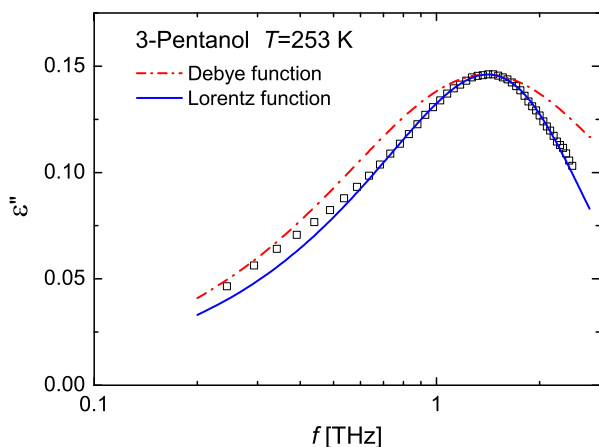
$$\varepsilon^*(\omega) = \frac{A}{\omega_0^2 - \omega^2 + i\omega\gamma_0} \quad (2)$$

Figs. 5 and 6 demonstrate the results of curve fitting with 2-butanol and 3-pentanol at 253 K, respectively. They show that the Lorentz function can represent the mode around 1.2 THz, which indicates that the mode arises from vibration dynamics. In contrast, the Debye function cannot express the narrow shape of the mode. In the case of 2-butanol (Fig. 5), there is a large deviation of the fitting for the Lorentz function at the lower frequency part of the spectrum. This deviation can be due to the large high-frequency contribution of the dielectric relaxation processes below the microwave region. The behavior of the deviation depends on the relaxation processes. The larger the amplitude of the relaxation processes, the larger is the deviation expected.

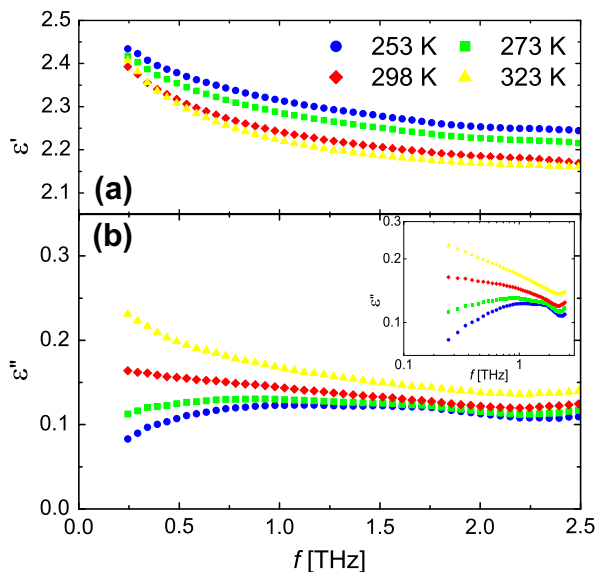
Here, we describe the shape of the peak in the dielectric loss around 1.2 THz. The peak positions are distinguishable in most of the monohydric alcohols. However, in some cases, the mode is very broad, making it difficult to distinguish the peak positions (Fig. 7).



**Fig. 5.** Dielectric loss of 2-butanol at 253 K. Open squares represent experimental data. The dashed-dotted curve and solid curve represent fitting by the Debye function and Lorentz function, respectively.



**Fig. 6.** Dielectric loss of 3-pentanol at 253 K. Open squares represent experimental data. The dashed-dotted curve and solid curve represent fitting by the Debye function and Lorentz function, respectively.



**Fig. 7.** Dielectric permittivity (a) and dielectric loss (b) of 2-methyl-1-butanol in the frequency range 0.2–2.5 THz. The inset in (b) shows the bilogarithmic plot of dielectric loss.

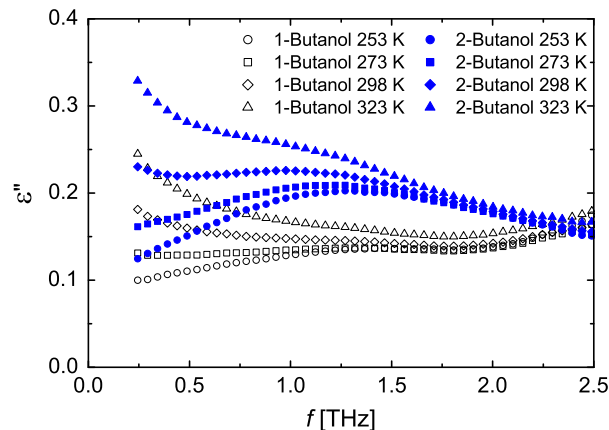
It is possible that the broad mode is a convolution of two or more modes. The details regarding the difference in the spectral shape are beyond the scope of this study; future investigations are necessary to identify the cause of this difference.

Low-frequency vibration dynamics in hydrogen-bonded liquids, emerging in the THz region, have been examined by other experimental techniques such as low-frequency Raman scattering or far-infrared spectroscopy. In water and lower monohydric alcohols, which are representatives of hydrogen-bonded liquids, some vibration dynamics in the THz region have been reported. Previous experiments on water [31,32] have observed intermolecular vibrations such as hydrogen-bond bending at  $\sim 50 \text{ cm}^{-1}$  and hydrogen-bond stretching at  $\sim 180 \text{ cm}^{-1}$ . Woods et al. investigated the low-frequency ( $< 100 \text{ cm}^{-1}$ ) intermolecular modes of methanol [33,34] with far-infrared absorption spectroscopy. They observed absorption bands at approximately  $30 \text{ cm}^{-1}$ ,  $55 \text{ cm}^{-1}$ , and  $70 \text{ cm}^{-1}$  in the experimental spectra and clarified that these bands arise from intermolecular bending, fluctuation of the methyl group in the hydrogen-bonded chain-like network, and intermolecular libration, respectively. They extended their study into water–methanol mixture systems. Addition of small amounts of water caused defor-

mation of the methanol network structure, which lead to a change in the appearance of the absorption bands. This result indicates that the vibration dynamics in the THz region is sensitive to the hydrogen-bonded network-like local structure in monohydric alcohols. A Raman scattering study of ethanol [35] detected intermolecular bending motion at  $60 \text{ cm}^{-1}$ . These vibration dynamics reported in water and lower monohydric alcohols may be candidates for the origin of the mode around 1.2 THz, in our study. However, presently, the origin of the mode around 1.2 THz cannot be determined, and we simply show the possible origin of the mode based on previous studies. Nevertheless, because the molecular dynamics emerging in the THz region are related to the formation of the hydrogen-bonded local structure, the spectra in the THz region provide an insight into the hydrogen-bonding phenomena in monohydric alcohols.

The vibration mode around 1.2 THz differs in shape and intensity according to the molecular structure of the monohydric alcohols. Fig. 8 shows the comparison between the dielectric losses of 1- and 2-butanol. The position of the OH group in 1-butanol is at the terminal carbon atom, whereas in 2-butanol it is in the middle of the carbon chain. The figure shows that the shapes of the modes are all different, and the intensity of the mode in 2-butanol is higher than that in 1-butanol. On the basis of our experimental data, it is concluded that monohydric alcohols with the OH group in the middle of the carbon chain show higher modal intensity than those with the OH group at the terminal carbon atom. Furthermore, the carbon chain structure also affects the mode around 1.2 THz, as shown in Fig. 9, which illustrates the comparison of dielectric losses between 2-pentanol and 2-methyl-2-butanol. 2-Pentanol has a straight carbon chain and an OH group at the second carbon atom, while 2-methyl-2-butanol has a branched carbon chain structure, although the position of the OH group is the same as that in 2-pentanol. The mode around 1.2 THz in 2-methyl-2-butanol is more enhanced than that in 2-pentanol. However in some cases, as shown in Fig. 10, a slight change in the carbon chain structure has a minimal influence on the mode. Fig. 10 compares the dielectric losses of 1-pentanol and 3-methyl-1-butanol. Both, 1-pentanol and 3-methyl-1-butanol have an OH group at the terminal carbon atom, while the structure of the carbon chains differs slightly. We observe that the appearances of the vibration modes around 1.2 THz are similar to each other. Further examination of the dielectric spectra of other alcohols confirms that a minor difference in the carbon chain structure barely influences the mode around 1.2 THz.

The present experiment conducted at a temperature of 253 K clearly shows the mode around 1.2 THz. However, the data still contain the contribution from the dielectric relaxation processes, due to which a precise estimation of the mode is difficult. By



**Fig. 8.** Comparison of dielectric losses of 1-butanol and 2-butanol.

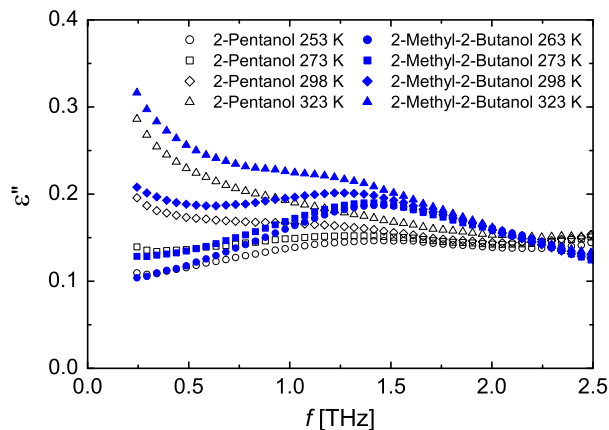


Fig. 9. Comparison of dielectric losses of 2-pentanol and 2-methyl-2-butanol.

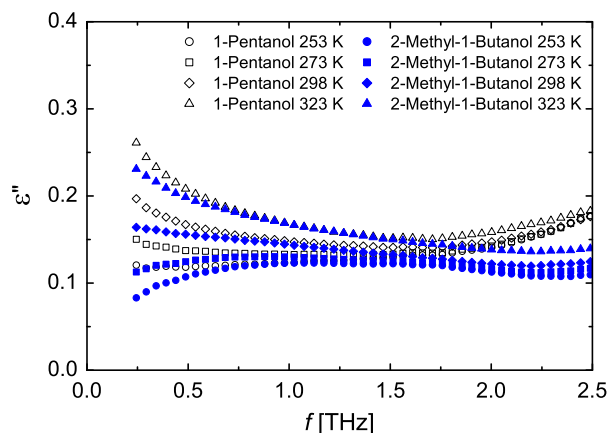


Fig. 10. Comparison of dielectric losses of 1-pentanol and 2-methyl-1-butanol.

further lowering the temperature, such a contribution may be excluded, and this may enable us to provide an accurate estimation of the mode. This future investigation will provide far more insight to the mode around 1.2 THz.

### 3.3. Complex permittivity in a wide frequency range

Fig. 11 represents the complex permittivity of normal alcohols in the frequency range 1 MHz–2.5 THz at 298 K. It shows that the contribution of the relaxation processes in the microwave region disperses toward the THz range. In the present study, it is necessary to evaluate the contribution of the high-frequency tail of the relaxation processes for a precise discussion of the spectra in the THz region. However, the lack of data between 20 GHz and 0.2 THz has limited our estimation of the relaxation processes. Hence, we attempted to estimate the dielectric relaxation processes in methanol, ethanol, 1-propanol, and 2-propanol using data of the relaxation processes from previous studies [19,20]. Fig. 12 shows the complex permittivity of 1-propanol (open diamond) along with the fitting curve results (solid line) of the three Debye-type relaxation processes using previously obtained data. By excluding the contribution of the relaxation processes from the raw data, the shape of the mode in the THz region becomes apparent (shown in closed squares). The same procedure was applied to methanol, ethanol, and 2-propanol. We compare the shapes of the mode in the THz region for methanol, ethanol, and 1-propanol shown in Fig. 13. The intensity and peak position of the mode increase slightly with the decreasing carbon number. The peak positions are at 1.26 THz for methanol, 1.05 THz for

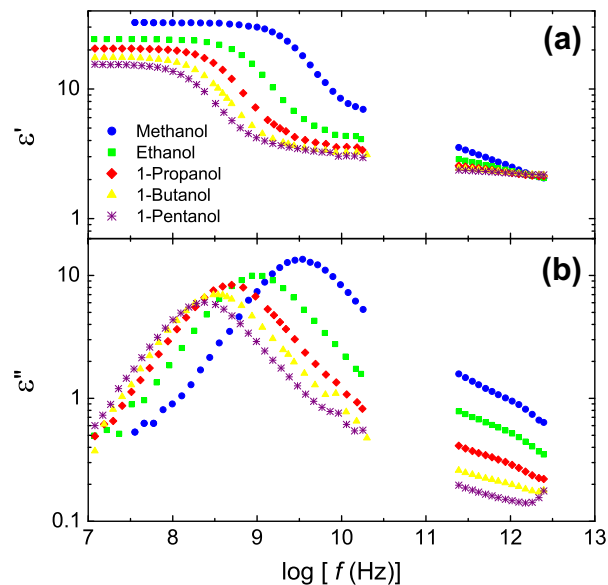


Fig. 11. Dielectric permittivity (a) and dielectric loss (b) of normal alcohols in the frequency range 1 MHz–2.5 THz at 298 K.

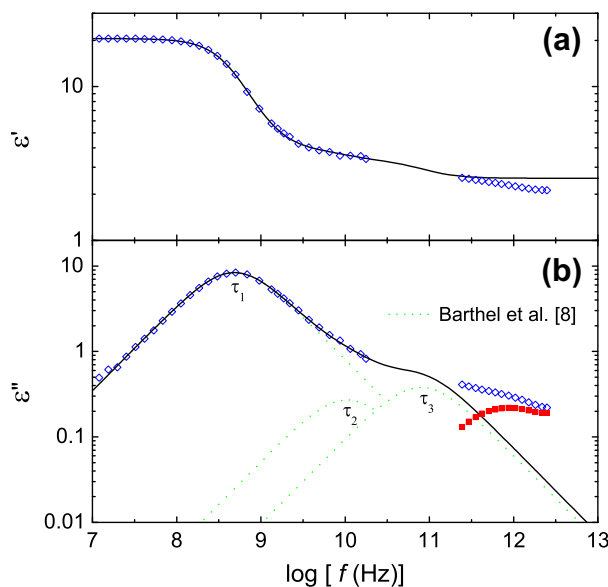
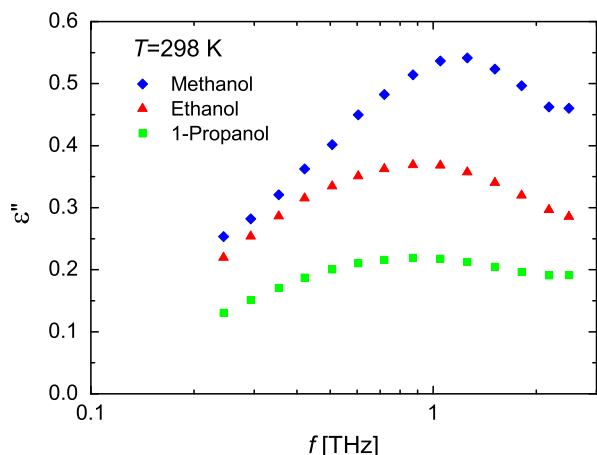


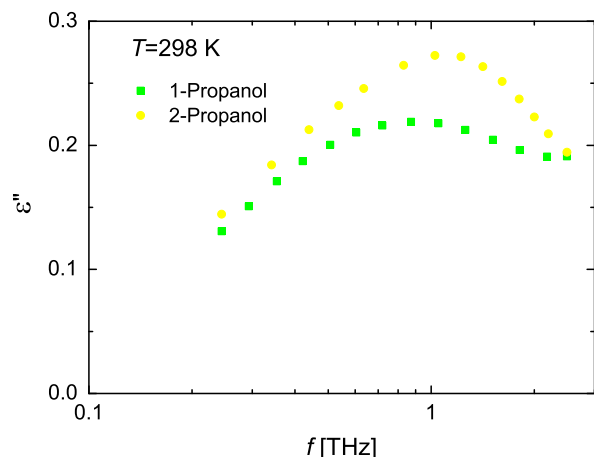
Fig. 12. Dielectric permittivity (a) and dielectric loss (b) of 1-propanol at 298 K. Open squares represent experimental data. Solid curve represents fitting results of superposition of three Debye functions, showing contributions of each relaxation process [20].

ethanol, and 0.87 THz for 1-propanol. Because the spectral shapes are broad, it might be possible to decompose the mode into several modes. In the present situation, we cannot decide whether the mode is expressed with only one Lorentz function in these alcohols. Fig. 14 shows that the peak of 2-propanol has a larger intensity and a higher peak position (i.e., at 1.03 THz) than that of 1-propanol. This result confirms that monohydric alcohols with the OH group at the middle position of the carbon chain show higher modal intensity around 1.2 THz than those with the OH group at the terminal carbon atom.

Here we append a note on the mode located above 2.5 THz. As in the case of the vibration mode at above 2.5 THz, low-frequency Raman scattering and far-infrared spectroscopy [35–37] have indicated that there exists an intermolecular stretching mode above 2.0 THz in monohydric alcohols. It is reasonable to suppose that the rise of the dielectric loss above 2.0 THz is the low-frequency



**Fig. 13.** Dielectric losses of methanol, ethanol, and 1-propanol at 298 K after excluding the contribution of dielectric relaxation processes [19,20] from raw data.



**Fig. 14.** Dielectric losses of 1-propanol and 2-propanol at 298 K after excluding the contribution of dielectric relaxation processes [19] from raw data.

side of this mode. Vij et al. [37] reported that the intermolecular stretching mode of methanol, ethanol, and 1-propanol appeared at  $130\text{ cm}^{-1}$ ,  $110\text{ cm}^{-1}$ , and  $145\text{ cm}^{-1}$  (3.90 THz, 3.30 THz, and 4.35 THz), respectively. In the present study, we cannot observe the entire mode due to the limitation of the frequency range, and therefore cannot discuss the details of the mode using our data alone. Nevertheless, by observing the rise in the dielectric loss towards 2.5 THz, it becomes apparent that the intermolecular stretching mode is strongly influenced by the molecular structure of the monohydric alcohols. Our data show that the OH group and carbon chain structure have an influence on the vibration dynamics above 2.0 THz.

#### 4. Conclusions

We have measured the complex permittivity of 14 monohydric alcohols with THz-TDS. The complex permittivities investigated contain three contributions: (i) a high-frequency side of the dielec-

tric relaxation processes, (ii) a broad vibration mode around 1.2 THz, and (iii) a low-frequency side of an intermolecular vibration mode located above 2.5 THz. At low temperatures, the dielectric relaxation processes shift to a low-frequency range. On the other hand, the broad vibration mode is independent of temperature, which shows a clear peak around 1.2 THz in most of the alcohols. The appearance of the broad vibration mode is strongly influenced by the position of the OH group and the structure of the carbon chain.

In this study, we prove the existence of the broad vibration mode around 1.2 THz in monohydric alcohols. A further direction of our study will be to extend the experimental frequency range or temperature range to discuss the mode more comprehensively. Addition of new data to the current results will aid in the full understanding of the vibration dynamics in the THz region.

#### References

- [1] N.G. McCrum, B.E. Read, G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Dover Publications, New York, 1991.
- [2] F. Kremer, A. Schönhal, *Broadband Dielectric Spectroscopy*, Springer, Berlin, 2003.
- [3] K.C. Kao, *Dielectric Phenomena in Solids*, Academic Press, California, 2004.
- [4] R.H. Cole, J.G. Berberian, S. Mashimo, G. Chryssikos, A. Burns, E. Tombari, *J. Appl. Phys.* 66 (1989) 793.
- [5] R. Nozaki, T.K. Bose, *IEEE Trans. Instrum. Measure.* 39 (1990) 945.
- [6] Y. Feldman, A. Andrianov, E. Polygalov, I. Ermolina, G. Romanychev, Y. Zuev, B. Milgotin, *Rev. Sci. Instrum.* 67 (1996) 3208.
- [7] J. Barthel, K. Bachhuber, R. Buchner, H. Hetzenauer, M. Kleebauer, *Ber. Bunsenges. Phys. Chem.* 95 (1991) 853.
- [8] U. Schneider, P. Lunkenheimer, R. Brand, A. Loidl, *J. Non-Cryst. Solids* 235–237 (1998) 173.
- [9] P. Lunkenheimer, A. Loidl, *Chem. Phys.* 284 (2002) 205.
- [10] M.C. Nuss, J. Orenstein, *Millimeter and Submillimeter Wave Spectroscopy of Solids*, Springer, Berlin, 1998.
- [11] M.C. Beard, G.M. Turner, C.A. Schmittenmaer, *J. Phys. Chem. B* 106 (2002) 7146.
- [12] J.T. Kindt, C.A. Schmittenmaer, *J. Phys. Chem.* 100 (1996) 10373.
- [13] T. Fukasawa, T. Sato, J. Watanabe, Y. Hama, W. Kunz, R. Buchner, *Phys. Rev. Lett.* 95 197802 (2005).
- [14] L. Thrane, R.H. Jacobsen, P.U. Jepsen, S.R. Keiding, *Chem. Phys. Lett.* 240 (1995) 330.
- [15] C. Rønne, P. Åstrand, S.R. Keiding, *Phys. Rev. Lett.* 82 (1999) 2888.
- [16] K. Yamamoto, M. Tani, M. Hangyo, *J. Phys. Chem. B* 111 (2007) 4854.
- [17] M. Koeberg, C. Wu, D. Kim, M. Bonn, *Chem. Phys. Lett.* 439 (2007) 60.
- [18] Y. Yomogida, R. Nozaki, *J. Mol. Liq.* 149 (2009) 101.
- [19] J. Barthel, K. Bachhuber, R. Buchner, H. Hetzenauer, *Chem. Phys. Lett.* 165 (1990) 369.
- [20] R. Buchner, J. Barthel, *J. Mol. Liq.* 52 (1992) 131.
- [21] T. Sato, R. Buchner, *J. Chem. Phys.* 118 (2003) 4606.
- [22] T. Sato, R. Buchner, *J. Phys. Chem. A* 108 (2004) 5007.
- [23] M.L.T. Asaki, A. Redondo, T.A. Zawodzinski, A.J. Taylor, *J. Chem. Phys.* 116 (2002) 8469.
- [24] H. Kitahara, T. Yagi, K. Mano, M. Wada Takeda, S. Kojima, S. Nishizawa, *J. Korean Phys. Soc.* 46 (2005) 82.
- [25] P.Uhd. Jepsen, U. Möller, H. Merbold, *Opt. Express* 15 (2007) 14717.
- [26] P.Uhd. Jepsen, J.K. Jensen, U. Möller, *Opt. Express* 16 (2008) 9318.
- [27] P. Debye, *Polar Molecules*, Dover Publications, New York, 1929.
- [28] W.J. Ellison, *J. Phys. Chem. Ref. Data* 36 (2007) 1.
- [29] S. Schrödle, B. Fischer, H. Helm, R. Buchner, *J. Phys. Chem. Lett.* 111 (2007) 2043.
- [30] H. Yada, M. Nagai, K. Tanaka, *Chem. Phys. Lett.* 473 (2009) 279.
- [31] G.E. Walrafen, Y.C. Chu, G.J. Piermarini, *J. Phys. Chem.* 100 (1996) 10363.
- [32] Y. Amo, Y. Tominaga, *Physica A* 276 (2000) 401.
- [33] K.N. Woods, H. Wiedemann, *J. Chem. Phys.* 123 (2005) 134506.
- [34] K.N. Woods, H. Wiedemann, *J. Chem. Phys.* 123 (2005) 134507.
- [35] K. Egashira, N. Nishi, *J. Phys. Chem. B* 102 (1998) 4054.
- [36] J.K. Vij, C.J. Reid, *Chem. Phys. Lett.* 92 (1982) 528.
- [37] J.K. Vij, C.J. Reid, M.W. Evans, *Mol. Phys.* 50 (1983) 935.