

Chapter 2

High-Frequency Dielectric Response of Hydrogen-Bonded Liquids Between 0.2 and 2.5 THz

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Abstract Using terahertz (THz) time-domain spectroscopy, we measured the complex permittivity of monohydric alcohols and diols in the frequency range of 0.2–2.5 THz at temperatures from 253 to 323 K. The complex permittivities of both monohydric alcohols and diols contain the following three components: (i) a high-frequency tail of dielectric relaxation processes, (ii) a broad vibration mode around 0.5–2.0 THz, and (iii) a low-frequency side of an intermolecular stretching mode located above 2.5 THz. At low temperatures, the dielectric relaxation processes substantially shifted to a low-frequency range. On the other hand, the broad vibration mode around 0.5–2.0 THz was independent of temperature and showed a clear peak in the dielectric loss spectra. Based on the experimental results, it is considered that the broad vibration mode originates from the vibration dynamics of the OH group. The spectral shape and intensity of the broad vibration mode were strongly influenced by both the number and position of the OH groups and the structure of the carbon chain.

2.1 Terahertz Time-Domain Spectroscopy

Terahertz (THz) waves generally refer to electromagnetic waves from 0.1 to several THz. This frequency range has thus far been an unexplored gap between

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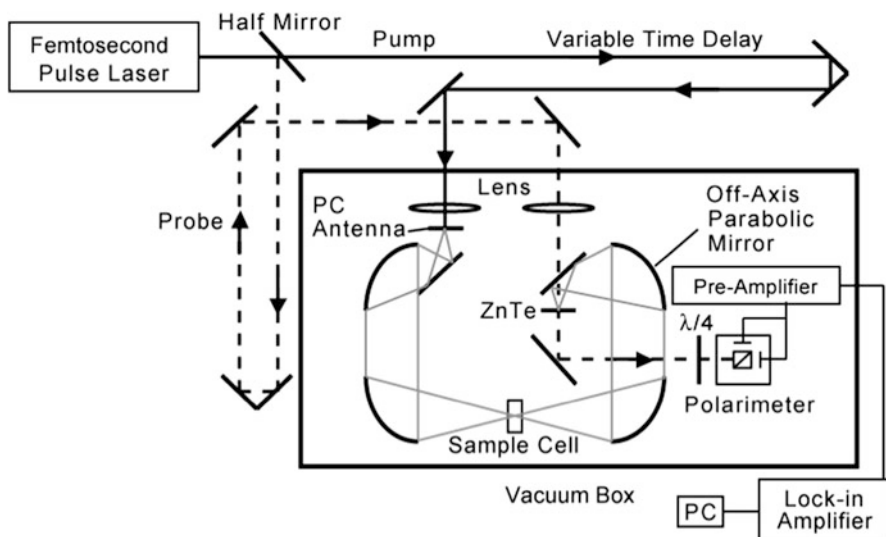


Fig. 2.1 Schematic diagram of THz-TDS

the microwave and far-infrared regions before efficient methods of THz wave emission and detection were established. In the 1980s, new techniques for the emission and detection of THz waves were developed using femtosecond lasers and semiconductor device technology, which led to further research with THz waves. In recent years, THz waves have received a great deal of attention and are actively used in various fields for applications such as screening and detection of dangerous materials, imaging techniques, and communication. In fundamental research, a new spectroscopic technique called THz time-domain spectroscopy (TDS) has been developed to measure several physical characteristics in the THz region. With THz-TDS, we can now readily obtain the complex permittivity, refractive index, and absorption coefficient in the THz region.

THz-TDS has been developed comprehensively, and detailed experimental setups have been described in previous studies (for example, see [6]). Figure 2.1 shows the schematic diagram of the experimental setups of THz-TDS used in the present study. A mode-locked Ti sapphire laser (Tsunami, Spectra Physics) that generates 100 fs pulses with a central wavelength of 800 nm was used for the emission and detection of pulsed THz waves. For the emission, a photoconductive (PC) antenna was produced (Fig. 2.2). The electrodes of the PC antenna with a gap distance of 500 μm were fabricated on a semi-insulating gallium arsenide substrate. Modulated THz pulses were obtained by applying a 10 kHz alternating current bias to the PC antenna. For the detection of the THz pulses, an electro-optic (EO) sampling method was employed using a (110) ZnTe crystal (1 mm thick) as an EO crystal. The wave path was enclosed in a vacuum box (<20 Pa) to reduce the absorption of atmospheric water vapor.

Liquid samples were placed in a sample cell consisting of a pair of polypropylene (PP) windows (with 2 mm thickness) and a spacer (Fig. 2.3). In the case of

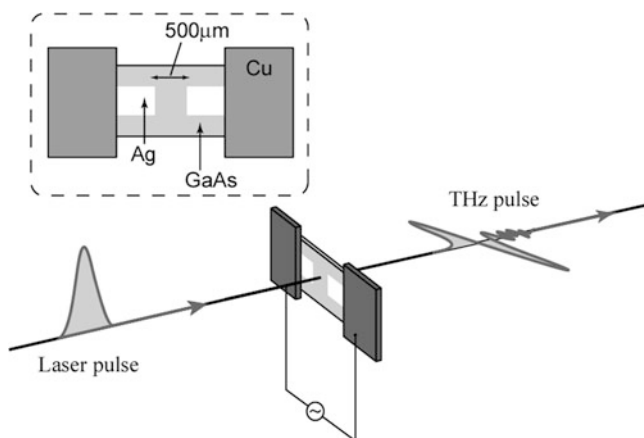


Fig. 2.2 Schematic diagram of the emission of the THz pulse. The *inset* shows a photoconductive (PC) antenna. When illuminating the laser pulse whose photon energy is higher than the band gap energy of GaAs, electrons and holes, which act as free carriers, can be generated and thus current flows between the electrode gap. The time variation of the current produces pulsed THz waves

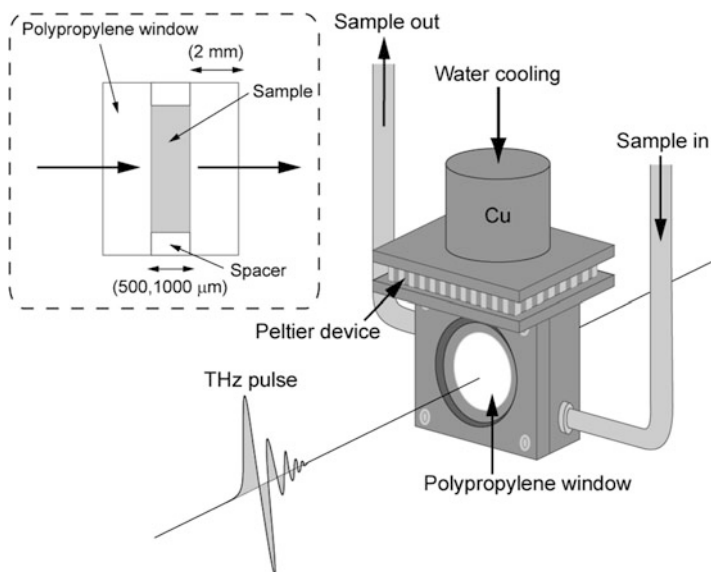


Fig. 2.3 Schematic diagram of the sample cell and temperature control system. The *inset* shows a sample cell consisting of a pair of polypropylene windows and a spacer

measurements for liquids and solutions, we needed to choose a suitable material for the window. Since absorption of THz waves in PP is not very large, PP can serve as a good choice of window for the sample cell for polar liquids. The temperature of the samples was controlled between 253 and 323 K by a Peltier device with an accuracy

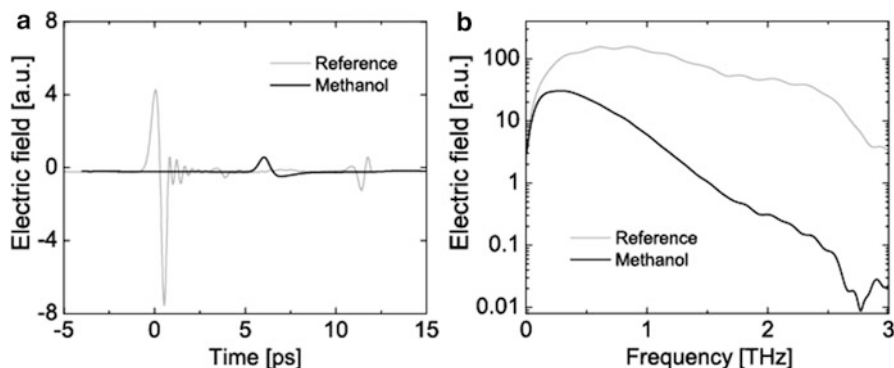


Fig. 2.4 Characteristics of the THz pulse in the time domain transmitted through an empty cell as a reference and a sample cell filled with methanol (a), and the THz wave in the frequency domain obtained by the Fourier transform (b)

of 0.2 K. The sample thickness was varied according to the intensity of the THz wave absorption by using the spacer (500 and 1,000 μm). THz pulses transmitted through an empty cell were recorded first, after which the data for the liquid sample was collected. The complex permittivities of the samples were calculated using Fourier transforms of the THz pulses transmitted through the samples and the empty sample cell. Figures 2.4a, b show the THz pulse transmitted through methanol and the empty cell in the time domain and the THz wave in the frequency domain, respectively. The figure demonstrates that the THz pulse contains electromagnetic waves in the frequency range of 0–3.0 THz. However, in the present study we employed a frequency range of 0.2–2.5 THz to ensure the reliability of the data. This experimental procedure provided information regarding both the amplitude and the phase for each frequency, which is an advantage of THz-TDS. In the present study, typical experimental errors were within 5% for the entire frequency range.

2.2 Complex Permittivity of Hydrogen-Bonded Liquids in the THz Region

THz-TDS has been shown to be a powerful experimental method for the investigation of low-frequency vibrations in various materials. The study of hydrogen-bonded liquids is one of the most important applications of THz-TDS because the vibration dynamics in the THz region are expected to be closely related to the hydrogen-bonding phenomena responsible for the unique macroscopic properties of hydrogen-bonded liquids. An understanding of the molecular dynamics of these liquids in the THz region is of significance for various fields such as physical chemistry and biology, as well as for the chemical industry.

Before THz-TDS was established, the low-frequency vibration dynamics in such liquids, emerging in the THz region, had been examined by low-frequency Raman

scattering or far-infrared absorption spectroscopy. However, the data obtained in the low-frequency range of the THz region were insufficient because of the experimental difficulties. Accordingly, an understanding of the low-frequency vibration dynamics of hydrogen-bonded liquids was still lacking. The use of THz-TDS for observing spectra has great potential for revealing the complete molecular dynamics in hydrogen-bonded liquids. In early studies with THz-TDS, some monohydric alcohols, which are representative of hydrogen-bonded liquids, were extensively studied. For example, Kindt and Schmuttenmaer [6] performed complex permittivity measurements on methanol, ethanol, and 1-propanol in the frequency range of 0.06–1.0 THz. They concluded that the complex permittivity of these monohydric alcohols could be expressed only with the high-frequency contribution of the dielectric relaxation processes located in the microwave range. Subsequently, several authors performed complex permittivity measurements of monohydric alcohols using THz-TDS and arrived at the same conclusion as Kindt et al. However, Fukasawa et al. [5] reported the spectral analysis of the complex permittivities of methanol in the frequency range of 50 MHz–5 THz using their data below 89 GHz and literature data in the far-infrared region up to 5 THz. The consideration of such a wide experimental frequency range helped to reveal that the spectra of methanol in the low-frequency side of the THz region contained not only the high-frequency contribution of the dielectric relaxation processes but also some vibration modes. The finding of Fukasawa et al. implied that the spectra for other monohydric alcohols might also contain some low-frequency vibration modes in the THz region.

In the present work, we measured the complex permittivities of several monohydric alcohols using THz-TDS in the frequency range of 0.2–2.5 THz at 253–323 K. Our data [10–13] confirmed the existence of some vibration modes in the low-frequency side of the THz region for monohydric alcohols. Furthermore, we extended our study to diols and observed vibration modes in the spectra of diols similar to those found in monohydric alcohols. In the latter text, we discuss the behavior of the spectra in the THz region and the underlying microscopic mechanisms contributing to vibration modes in this frequency range on the basis of the systematic experimental results.

2.2.1 Monohydric Alcohols

Figure 2.5 demonstrates the complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ of a series of normal alcohols in the frequency range of 0.2–2.5 THz at 298 K. The behaviors of the data vary systematically depending on the number of carbon atoms. It was reported that some dielectric relaxation processes were observed below the THz range. For example, the complex permittivity of methanol in the GHz range could be fitted with the superposition of three Debye functions, yielding three relaxation frequencies, i.e., 3.09, 22.5, and 142 GHz at 298 K. The high-frequency tail of these dielectric relaxation processes naturally contributes to $\varepsilon^*(\omega)$ in the THz range,

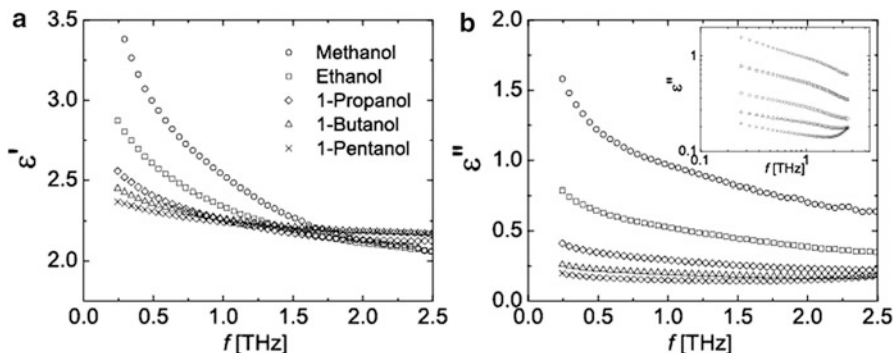


Fig. 2.5 Dielectric permittivity (a) and dielectric loss (b) of a series of normal alcohols in the frequency range of 0.2–2.5 THz at 298 K. The *inset* in Fig. 2.5b shows the bilogarithmic plot of the dielectric loss

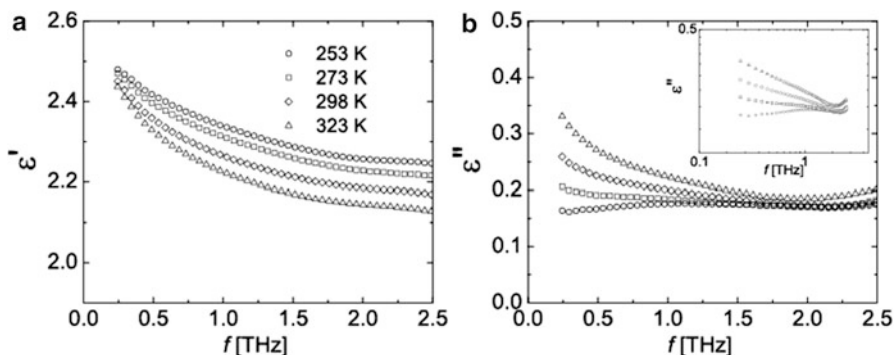


Fig. 2.6 Dielectric permittivity (a) and dielectric loss (b) of 1-butanol at temperatures ranging from 253 to 323 K. The *inset* in Fig. 2.6b shows the bilogarithmic plot of the dielectric loss

resulting in the rise in dielectric permittivity $\epsilon'(\omega)$ and dielectric loss $\epsilon''(\omega)$ below 0.5 THz as shown in Fig. 2.5. Figure 2.6 shows the temperature dependence of $\epsilon^*(\omega)$ for 1-butanol from 253 to 323 K. In this figure, the absolute values of the dielectric loss $\epsilon''(\omega)$ decrease with temperature, which is primarily because the relaxation processes shift to a low-frequency range. After the shift of the relaxation processes to a lower temperature, a broad mode around 0.5–2.0 THz can clearly be observed. The peak position of the mode is almost independent of temperature. Furthermore, in the case of 1-butanol and 1-pentanol, it is observed that the values of $\epsilon''(\omega)$ gradually increase towards a high-frequency range from 2.0 to 2.5 THz, which indicates the location of another mode above 2.5 THz.

Essentially, the complex permittivities of normal alcohols contain contributions from the following three factors: (i) a high-frequency tail of dielectric relaxation processes, (ii) a broad mode with peak position around 0.5–2.0 THz, and (iii) a low-frequency side of another mode located above 2.5 THz. In the following text, these contributions are examined for several monohydric alcohols in detail.

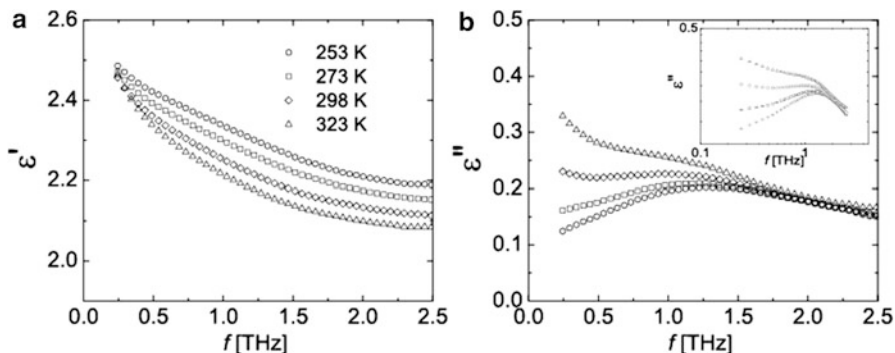


Fig. 2.7 Dielectric permittivity (a) and dielectric loss (b) of 2-butanol at temperatures ranging from 253 to 323 K. The *inset* in Fig. 2.7b shows the bilogarithmic plot of the dielectric loss

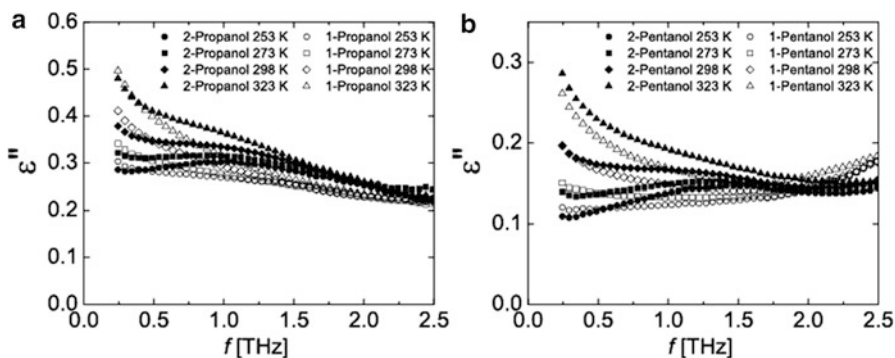


Fig. 2.8 Comparison of dielectric losses of 1- and 2-propanol (a) and 1- and 2-pentanol (b) at temperatures ranging from 253 to 323 K

The appearance of the broad mode around 0.5–2.0 THz differs considerably in shape and intensity depending on the molecular structure of the monohydric alcohols. First, we focus on the position of the OH group in a molecule. Figure 2.7 shows the temperature dependence of the complex permittivity of 2-butanol as an example of secondary alcohols. The position of the OH group in 2-butanol is in the middle of the carbon chain, whereas the OH group in 1-butanol is at the terminal carbon atom. In the case of 1-butanol, the peak magnitude around 0.5–2.0 THz is very small making it appear simply as a kink in the dielectric loss curve (Fig. 2.6b). In contrast, in Fig. 2.7, the intensity of the mode is significantly enhanced and its peak position can be clearly recognized, demonstrating that the peak position is independent of temperature in secondary alcohols as well. Figures 2.8a, b show the comparison of dielectric losses of 1- and 2-propanol, and 1- and 2-pentanol, respectively. These figures confirm that the intensity of the mode around 0.5–2.0 THz for the secondary alcohols is higher than that of the normal alcohols. In other words, it is concluded that the position of the OH group in a molecule significantly influences the broad mode.

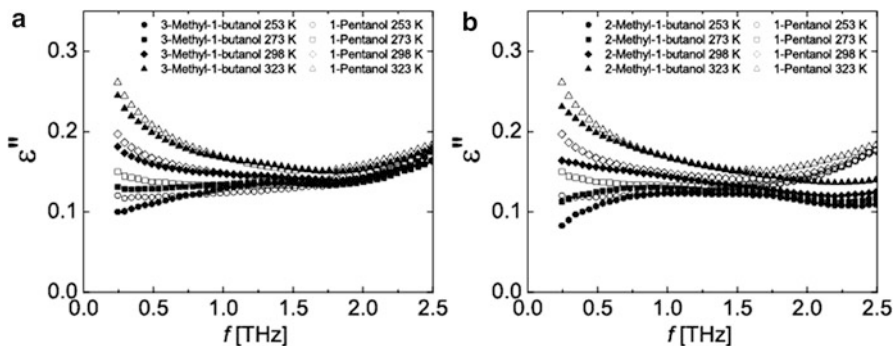


Fig. 2.9 Comparison of dielectric losses of 3-methyl-1-butanol and 1-pentanol (a) and 2-methyl-1-butanol and 1-pentanol (b) at temperatures ranging from 253 to 323 K

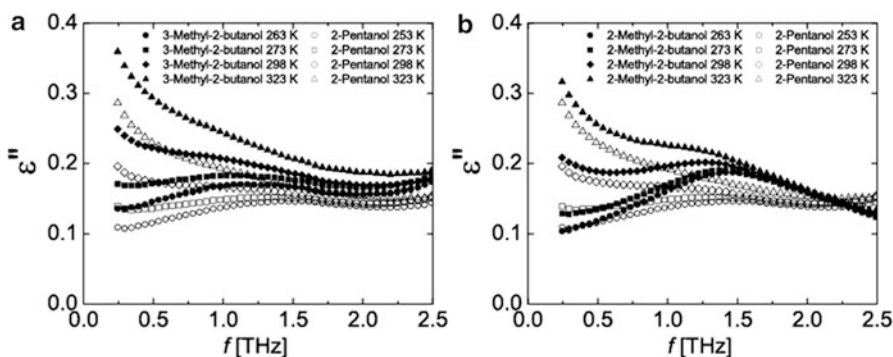


Fig. 2.10 Comparison of dielectric losses of 3-methyl-2-butanol and 2-pentanol (a) and 2-methyl-2-butanol and 2-pentanol (b) at temperatures ranging from 253 to 323 K

In contrast, the influence of the carbon chain structure on the broad mode is different according to circumstances. First, we compared the dielectric losses between 1-pentanol and 3-methyl-butanol (Fig. 2.9a) and 1-pentanol and 2-methyl-1-butanol (Fig. 2.9b). 1-pentanol has a straight carbon chain and an OH group at the terminal carbon atom, whereas 3-methyl-1-butanol and 2-methyl-1-butanol have branched carbon chain structures, although the position of the OH group is the same as that in 1-pentanol. In Fig. 2.9a, the spectra of 1-pentanol and 3-methyl-1-butanol show complete consistency throughout the frequency range. Further, in the comparison between 1-pentanol and 2-methyl-1-butanol (Fig. 2.9b), the appearance of the mode around 0.5–2.0 THz is similar for both materials, although a large deviation is observed in the dielectric loss spectra above 2.0 THz. As described above, the molecular structure dependence of the broad mode could not be observed in Fig. 2.9a, b. Contrastingly, in the case of the comparison of 2-pentanol, 3-methyl-2-butanol, and 2-methyl-2-butanol in Fig. 2.10a, b, the broad mode is found to

change according to the carbon chain structure. All these molecules have an OH group located at the second carbon atom in the carbon chain. 2-Pentanol has a straight carbon chain, whereas the others have branched carbon chain structures. In Fig. 2.10a, although the overall spectral shapes of 2-pentanol and 3-methyl-2-butanol are similar, the intensity of the spectra for 3-methyl-2-butanol is higher than that for 2-pentanol. Moreover, in Fig. 2.10b, 2-methyl-2-butanol clearly has a higher intensity of the broad mode around 0.5–2.0 THz and the spectral shape of 2-methyl-2-butanol is completely different from that of 2-pentanol. Thus in these comparisons, we can observe a significant influence of the carbon chain structure on the broad mode around 0.5–2.0 THz.

As has been observed, both the position of the OH group and the carbon chain structure could affect the broad mode around 0.5–2.0 THz. Here, we add a brief note on the shape of the broad mode. The peak positions in the dielectric loss spectra 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 (for example, in Fig. 2.9b). Further investigations are now in progress to identify the cause of the difference in the spectral shape.

In order to verify the type of the broad mode around 0.5–2.0 THz, we applied the fitting procedure to the data with the Debye function (Eq. 2.1) and the Lorentz function (Eq. 2.2). The Debye function is generally used to represent the simplest dielectric relaxation process that has a single relaxation time, whereas the Lorentz function has been introduced to fit the vibration mode of hydrogen-bonded liquids in the THz region

$$\varepsilon^*(\omega) = \frac{\Delta\varepsilon}{1 + i\omega\tau}, \quad (2.1)$$

$$\varepsilon^*(\omega) = \frac{A}{\omega_0^2 - \omega^2 + i\omega\gamma_0}. \quad (2.2)$$

In Fig. 2.11, the results of curve fitting are demonstrated for 2-butanol and 3-pentanol at 253 K. They show that the Lorentz function can represent the mode around 0.5–2.0 THz. In contrast, the Debye function cannot express the narrow shape of the mode. This fitting examination clarifies that the broad mode around 0.5–2.0 THz originates from vibration dynamics. Previous studies have investigated the low-frequency vibration dynamics in some monohydric alcohols and water, and have shown the existence of several vibration modes below 2.0 THz in the experimental spectra and in the results of molecular dynamics simulation. Woods and Wiedemann [8,9] observed absorption bands at ~ 0.90 , 1.65, and 2.1 THz in the infrared absorption spectra. They concluded that these bands arose from intermolecular bending, fluctuation of the methyl group in the hydrogen-bonded chain-like network, and intermolecular libration with the aid of a first-principles molecular dynamics simulation. A Raman scattering study (see [4]) of ethanol detected intermolecular bending motion at 60 cm^{-1} . In the case of water (see [1]), intermolecular hydrogen-bond bending motion was observed at 50 cm^{-1} .

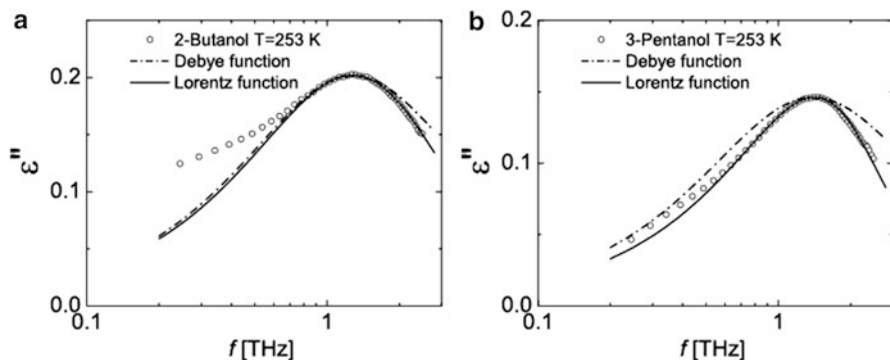


Fig. 2.11 Dielectric loss of 2-butanol (a) and 3-pentanol (b) at 253 K. *Open circles* represent experimental data. The *dashed-dotted curve* and *solid curve* represent fitting by the Debye function and Lorentz function, respectively

In summary, the results of these previous studies indicate that the spectra in the low-frequency side of the THz region reflect molecular dynamics of the intermolecular hydrogen-bond or the hydrogen-bonded network structure. One of these vibration dynamics or a combination of the dynamics can be candidates for the origin of the broad vibration mode around 0.5–2.0 THz.

For the discussion of the low-frequency vibration dynamics, the power absorption coefficient as well as the complex permittivity have been employed. The absorption coefficient α is related to the complex permittivity through the following equation:

$$\alpha = \frac{4\pi}{\lambda} \sqrt{\frac{1}{2} \left(\sqrt{\varepsilon'^2 + \varepsilon''^2} - \varepsilon' \right)}. \quad (2.3)$$

Here, λ indicates the wavelength. Figure 2.12a and b display the absorption coefficients of normal alcohols and secondary alcohols in the frequency range of 0.2–2.5 THz at 298 K. In this form, the absorption curves increase with frequency and the contribution of the dielectric relaxation processes below the THz region is completely suppressed. The broad vibration mode observed in the dielectric loss around 0.5–2.0 THz can be recognized as a bulge in the absorption coefficient. Figure 2.12b also contains the absorption coefficient of *n*-hexane, which is a hydrocarbon with the chemical formula C_6H_{14} . The absorption coefficient α of hexane shows a broad mode around 2.0 THz, indicating that the vibration dynamics of the hydrocarbon can contribute to α in the frequency range. However, its intensity is quite small when compared to that of monohydric alcohols. These results suggest that the broad vibration mode observed in monohydric alcohols mainly reflects the molecular dynamics of the OH group, namely, the intermolecular hydrogen bond. In addition, the absorption increases with an increase in the density of the OH group. The relation between the absorption coefficients and the density of the OH group are displayed for a series of monohydric alcohols in Fig. 2.13. There is a

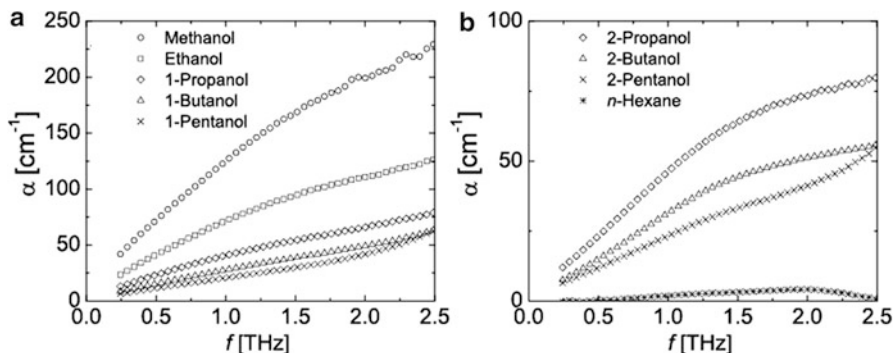
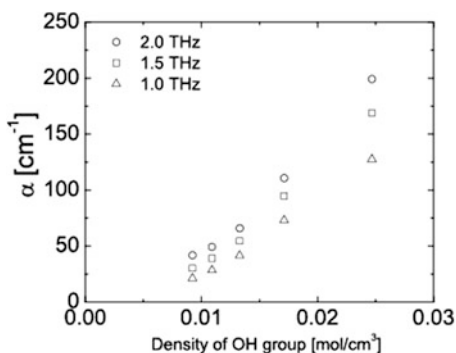


Fig. 2.12 Absorption coefficient of normal alcohols (a) and secondary alcohols (b) in the frequency range of 0.5–2.0 THz at 298 K. Figure 2.12b contains the absorption coefficient of *n*-hexane at 298 K

Fig. 2.13 The values of the absorption coefficient at 1.0, 1.5, and 2.0 THz for normal alcohols, plotted against the density of the OH group



nearly proportional relationship between the values of the absorption coefficient and the density, again confirming that the molecular dynamics of the OH group is the primary factor responsible for the broad vibration mode.

Here, we describe the mode located above 2.5 THz. Previous studies with low-frequency Raman scattering and far-infrared spectroscopy have indicated that there exists an intermolecular stretching mode above 2.5 THz in monohydric alcohols. For example, Vij et al. [7] reported that the intermolecular stretching mode of methanol, ethanol, and 1-propanol appeared at 130, 110, and 145 cm^{-1} (3.90, 3.30, and 4.35 THz), respectively. In the present data, we cannot observe the entire mode due to the limitation of the experimental frequency range. Nevertheless, it is reasonable to suppose that the rise of the dielectric loss above 2.0 THz is the low-frequency side of the intermolecular stretching mode. Besides, we could mention that the mode is influenced by the molecular structure of the monohydric alcohols. In the present study, the behavior of the intermolecular stretching mode is observed to be unrelated to the broad vibration mode around 0.5–2.0 THz.

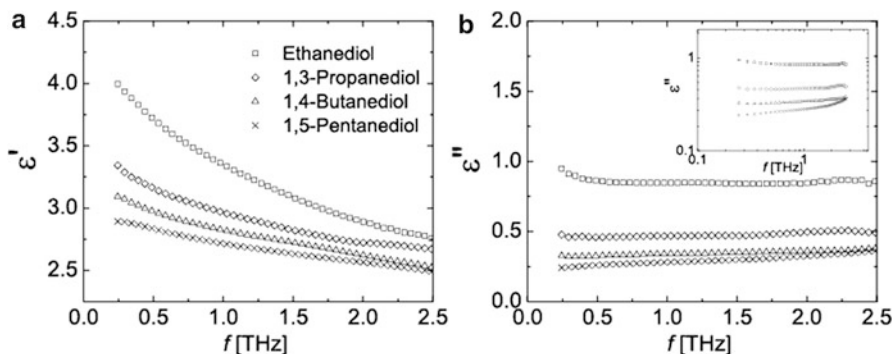


Fig. 2.14 Dielectric permittivity (a) and dielectric loss (b) of a series of diols in the frequency range of 0.2–2.5 THz at 298 K. The *inset* in (b) shows the bilogarithmic plot of the dielectric loss

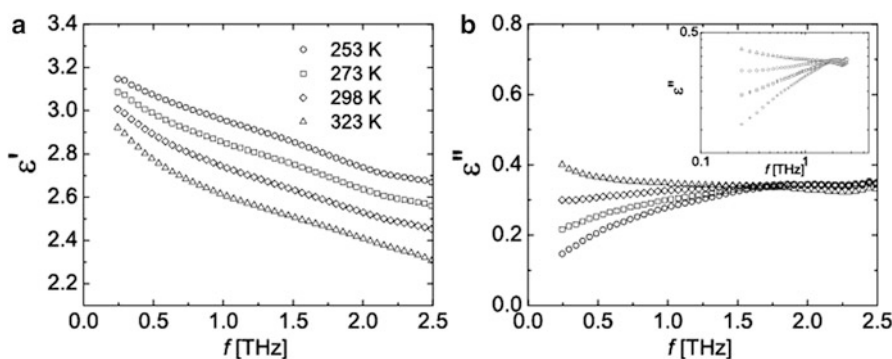


Fig. 2.15 Dielectric permittivity (a) and dielectric loss (b) of 1,3-butanediol at temperatures ranging from 253 to 323 K. The *inset* in (b) shows the bilogarithmic plot of the dielectric loss

2.2.2 Diols

In this section, we examine the influence of the number of OH groups in a molecule on the broad mode 0.5–2.0 THz. We measured the complex permittivity of some diols that have two OH groups in a molecule. Figure 2.14 demonstrates the complex permittivity $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ of a series of diols in the frequency range of 0.2–2.5 THz at 298 K. The values of the dielectric permittivity $\epsilon'(\omega)$ decrease monotonically with frequency. On the other hand, the values of the dielectric losses $\epsilon''(\omega)$ are almost constant in this frequency range at 298 K. Figures 2.15 shows $\epsilon^*(\omega)$ of 1,3-butanediol at temperatures of 253–323 K. The values of the dielectric permittivity $\epsilon'(\omega)$ increase with the decreasing temperature. In the dielectric loss (Fig. 2.13b), the low-frequency side below 1.0 THz decreases with temperature. This is clearly due to the shift of the relaxation processes to a low-frequency range, as is the case of monohydric alcohols. At lower temperatures, a broad mode around 0.5–2.0 THz can be observed and its peak position seems to be independent

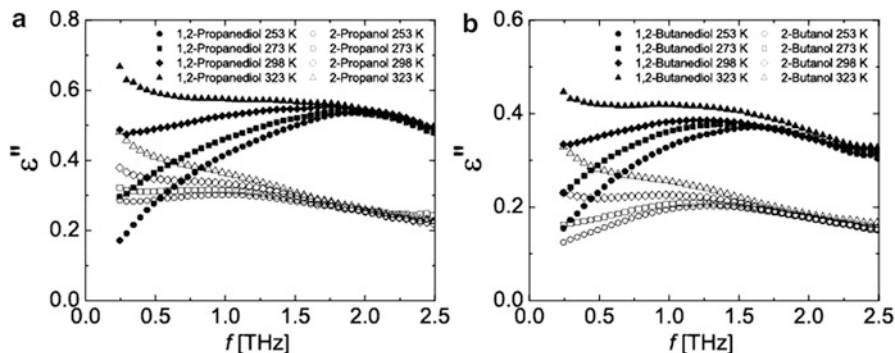


Fig. 2.16 Comparison of dielectric losses of 1,2-propanediol and 2-propanol (a) and 1,2-butanediol and 2-butanol (b) at temperatures ranging from 253 to 323 K

of temperature. From the appearance of the spectra, the broad mode in diols is found to have the same molecular origin as in monohydric alcohols. Even then, subtle differences are found in the behavior of the mode for monohydric alcohols and diols. Figures 2.16a and b show the comparison of dielectric losses between 1,2-propanediol and 2-propanol and 1,2-butanediol and 2-butanol, respectively. These figures indicate that the peak around 0.5–2.0 THz in diols has a larger intensity than that in monohydric alcohols, which again confirms that the broad mode arises from the molecular dynamics of the OH group. In addition, these figures clearly indicate that the mode around 0.5–2.0 THz in diols is much broader than that in monohydric alcohols and that diols have a higher peak position than that of monohydric alcohols. It may not be possible to express the broad mode in diols with only one Lorentz function. It is possible that the broad mode is a convolution of two or more modes. However, further investigation is necessary to identify the cause of the difference in the spectral shape between monohydric alcohols and diols.

2.3 Complex Permittivity in a Wide Frequency Range

Figure 2.17 shows the complex permittivity of normal alcohols in the frequency range of 1 MHz–2.5 THz at 298 K. As mentioned above, the contribution of the dielectric relaxation processes below the GHz region disperses toward the THz region. Figures 2.18 and 2.19 display the temperature dependence of the complex permittivities of monohydric alcohols and diols from 273 to 323 K. These figures clearly show that the dominant dielectric relaxation process dramatically moves to low-frequency regions with decreasing temperature. With decreasing temperature, the existence of the broad mode around 0.5–2.0 THz becomes apparent, enabling us to discuss the mode qualitatively. However, the data still contain the contribution from the dielectric relaxation processes and a quantitative estimation of the mode is difficult. Thus, it is quite necessary to obtain information regarding dielectric relaxation processes below the THz region. In the present study, because of a lack of

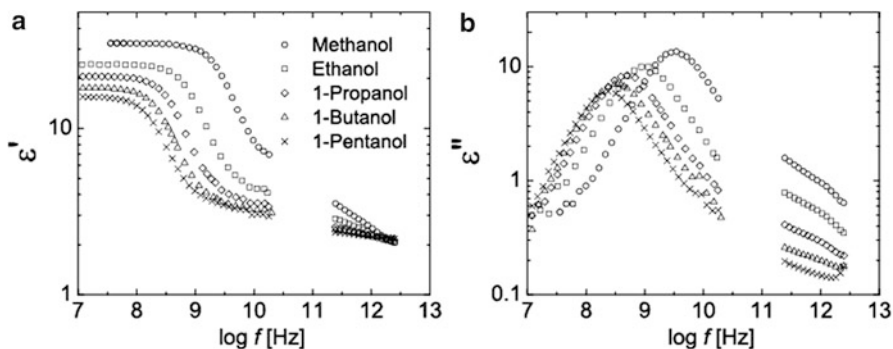


Fig. 2.17 Dielectric permittivity (a) and dielectric loss (b) of normal alcohols in the frequency range 1 MHz–2.5 THz at 298 K. Data in the microwave range were obtained with two different experimental setups. From 1 to 500 MHz, the complex permittivity measurements were performed using a network analyzer (HP4195A). From 500 MHz to 20 GHz, time-domain reflectometry was used

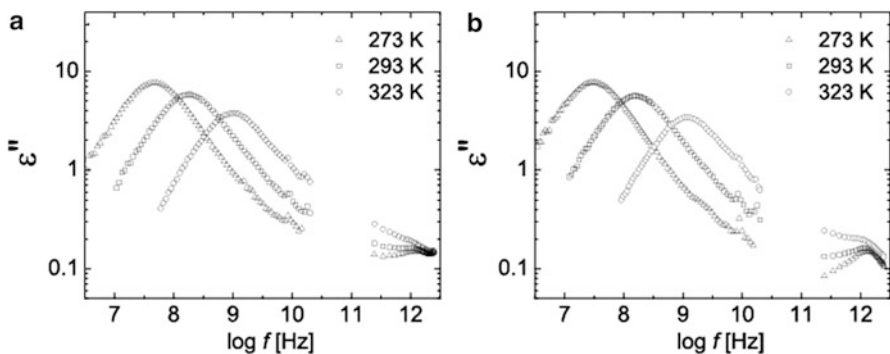


Fig. 2.18 Dielectric loss of 2-pentanol (a) and 3-pentanol (b) in the frequency range between 1 MHz and 2.5 THz at 273–323 K

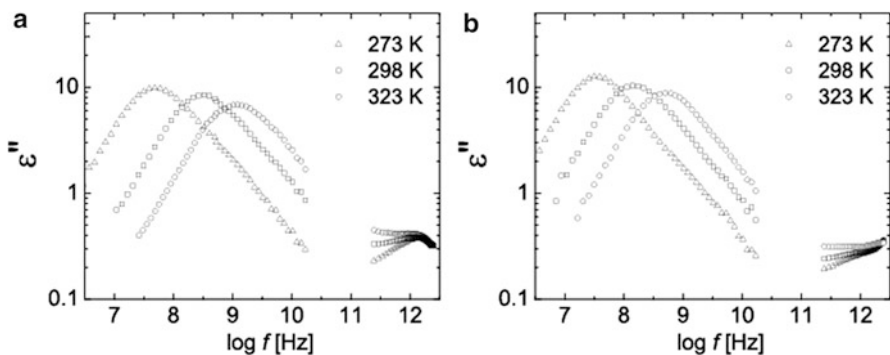


Fig. 2.19 Dielectric loss of 1,3-butanediol (a) and 1,5-pentanediol (b) in the frequency range between 1 MHz and 2.5 THz at 273–323 K

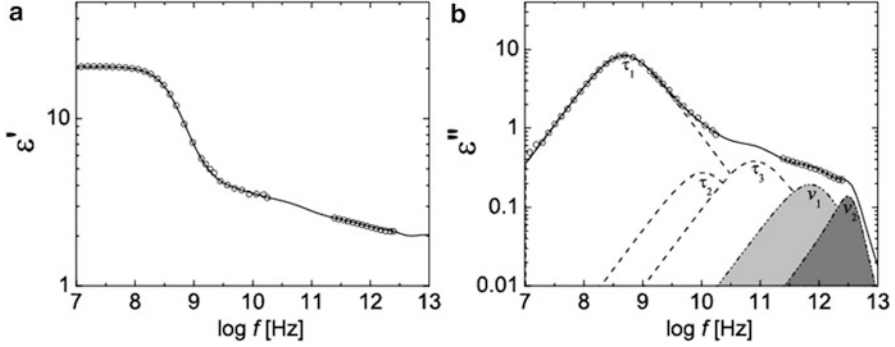
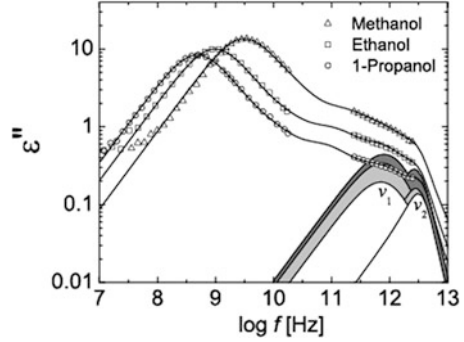


Fig. 2.20 Dielectric permittivity (a) and dielectric loss (b) of 1-propanol at 298 K. Open circle represent experimental data. The solid curve represents the fitting results of Eq. (2.4), showing the contributions of the three Debye-type dielectric relaxation processes τ_1 , τ_2 , and τ_3 (dashed curves) [2] and the two damped harmonic oscillator modes ν_1 and ν_2 (dashed-dot curves)

Fig. 2.21 Dielectric losses of methanol, ethanol, and 1-propanol at 298 K with fitted curves of two damped harmonic oscillator modes. The shaded areas show vibration modes (ν_1 and ν_2) for methanol (gray), ethanol (light gray), and 1-propanol (white)



data between 20 GHz and 0.2 THz, we were not able to estimate the broad mode precisely. Hence, we employed the parameters for dielectric relaxation processes in methanol, ethanol, 1-propanol, and 2-propanol obtained from previous studies [2,3]. Figure 2.20 shows the complex permittivity of 1-propanol along with the fitting results of the two damped harmonic oscillators with the literature data on the three Debye-type dielectric relaxation processes. In this case, our data are described by the following equation:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{k=1}^3 \frac{\Delta\varepsilon_k}{1 + i\omega\tau_k} + \sum_{l=1}^2 \frac{A_l}{\omega_l^2 - \omega^2 + i\omega\gamma_l}. \quad (2.4)$$

The same fitting procedure was applied to methanol and ethanol as shown in Fig. 2.21. The parameters obtained from the fitting results are listed in Table 2.1. Within the fitting errors, the peak frequencies of the vibration mode ν_1 and the damping factor γ_1 increase slightly with an increase in the number of carbon atoms N_C . Parameter A_1 linearly decreases with an increase in the N_C . The peak

Table 2.1 Fitting parameters of the two vibration modes for methanol, ethanol, and 1-propanol at 298 K. Parentheses show fitting errors

	Mode ($i = 1, 2$)	$A_i/(2\pi)^2$ (THz ²)	$\omega_i/2\pi$ (THz)	$\gamma_i/2\pi$ (THz)
Methanol	ν_1	2.36 (0.42)	1.73 (0.12)	1.96 (0.27)
	ν_2	2.53 (0.98)	3.56 (0.24)	2.21 (0.45)
Ethanol	ν_1	1.79 (0.13)	1.74 (0.12)	2.39 (0.24)
	ν_2	1.90 (0.50)	3.46 (0.21)	1.94 (0.24)
1-Propanol	ν_1	1.08 (0.14)	1.76 (0.10)	2.55 (0.20)
	ν_2	1.53 (0.16)	3.56 (0.20)	1.99 (0.12)

positions of ν_1 , shown in Figs. 2.17 and 2.18, around 1.2 THz are lower than the center frequencies listed in Table 2.1 (~ 1.7 THz). This discrepancy between the two values is caused by the large damping factor γ_1 , which is comparable to the center frequency values. As for the intermolecular stretching mode ν_2 , the estimated center frequencies listed in Table 2.1 are almost independent of the materials. However, in the previous studies on Raman scattering [7], the intermolecular stretching modes of methanol, ethanol, and 1-propanol appeared at 130, 110, and 145 cm^{-1} , respectively. This result implies that the position of the intermolecular stretching mode depends on the material. Since the experimental frequency range was insufficient to completely cover the mode ν_2 , the fitting errors for ν_2 are large, as indicated in parentheses in Table 2.1. Clearly, we need to expand the frequency range above 2.5 THz for a precise discussion of this mode.

With literature data for the dielectric relaxation processes below the THz region, our data on only methanol, ethanol, and 1-propanol at 298 K could be described by Eq. (2.1). The fitting results provide us with the quantitative information on the broad vibration mode around 0.5–2.0 THz, enabling us to discuss the mode more comprehensively. Thus, it is imperative to obtain the data in a wide frequency range for other materials at various temperatures.

2.4 Summary

In the present study, we measured the complex permittivity of several monohydric alcohols and diols with THz-TDS. The results of our study showed that the complex permittivities studied in this work invariably contain the following three contributions: (i) a high-frequency side of the dielectric relaxation processes, (ii) a broad vibration mode around 0.5–2.0 THz, and (iii) a low-frequency side of an intermolecular stretching mode located above 2.5 THz. By decreasing the temperature down to 253 K, the dielectric relaxation processes move abruptly to a lower frequency range. However, the broad vibration mode around 0.5–2.0 THz is independent of temperature and its peaks are clearly observed for almost all samples at lower temperatures. The shape of the broad mode varies sensitively depending

on the molecular structure such as the position of the OH group, the structure of the carbon chain, and the number of OH groups. Since the intensity of the broad mode has correlation with the density of the OH group, the mode is considered to originate from the molecular dynamics of the OH group. Combined with the results of previous studies, the molecular dynamics of the intermolecular hydrogen bond or the hydrogen-bonded network structure can be a possible origin of the broad mode around 0.5–2.0 THz.

In the case of monohydric alcohols and diols, some dielectric relaxation processes in the microwave region largely contribute to the spectra in the THz region. Consequently, we need to estimate the contributions to the THz spectra for the precise analysis of the vibration mode in the THz region. In the present study, we could obtain data for dielectric relaxation processes only on methanol, ethanol, and 1-propanol at 298 K from previous reports in the literature. With these data, we succeeded in estimating the complex permittivity in the THz region by the superposition of two damped harmonic oscillators. From the fitting results, we could obtain some fitting parameters as given in Table 2.1 and discuss the behavior of the mode in minute detail. Thus, it is indispensable to measure the experimental spectra in a wide frequency range for quantitative discussion of the vibration mode in the THz region. Moreover, the broadband measurement is important for not only decoupling the modes but also for observing the relation of various molecular dynamics inherent in liquids. Now that THz-TDS, which can cover the THz frequency range, has become available, we can finally investigate the complete molecular dynamics in the liquid state. In particular, hydrogen-bonded liquids form a complicated cluster structure through intermolecular hydrogen bonds and consequently contain a wide variety of molecular dynamics. Thus, the addition of the data from THz-TDS to the traditional experimental results will aid in the complete understanding of the molecular dynamics in hydrogen-bonded liquids.

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