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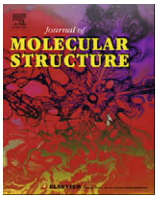

Comparative dielectric study of pentanol isomers with terahertz time-domain spectroscopy

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ABSTRACT

Using terahertz (THz) time-domain spectroscopy, we have measured the complex permittivity of seven pentanol isomers (1-pentanol, 2-pentanol, 3-pentanol, 2-methly-1-butanol, 3-methyl-1-butanol, 2-methyl-2-butanol, and 3-methyl-2-butanol) in the frequency range of 0.2–2.5 THz at temperatures from 253 to 323 K. For all samples, the complex permittivity contains the following three components: (i) a high-frequency side of dielectric relaxation processes, (ii) a broad vibration mode around 1.5 THz, and (iii) a low-frequency side of an intermolecular stretching mode located above 2.5 THz. At low temperatures, the relaxation process moves to a low-frequency range and a peak of the broad vibration mode, which is independent of temperature, is clearly observed around 1.5 THz. Spectra in the THz region change sensitively according to the molecular structure of the pentanol isomers. We have also observed the complex permittivity in the microwave range of 1 MHz–20 GHz. The behavior of the dielectric relaxation processes below GHz region much depend on the isomers. Our experimental data demonstrate that the molecular structures of the pentanol isomers influence all the molecular dynamics ranging from dielectric relaxation phenomena, which are due to reorientational motion of the molecules, to vibration dynamics within the hydrogen-bonded network structure.

1. Introduction

"THz waves" is a generic term used to refer to electromagnetic waves of $0.1–10 \times 10^{12}$ Hz in frequency. Before efficient methods of THz wave emission and detection were established, the THz region was not studied extensively. However, emission and detection techniques for THz waves have been developed with a femtosecond laser and semiconductor device technology in recent years. THz waves are now attracting attention in fundamental and applied research. In the former, THz time-domain spectroscopy (THz-TDS) has been established [1,2], enabling us to accurately measure complex permittivity in the THz region.

The new experimental technique 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 one of the most important applications because of their significance in various fields such as physical chemistry, biology, and industry. In the THz region, molecular dynamics are expected to be related to the hydrogen-bonding phenomena that distinguish hydrogen-bonded liquids from simple liquids. Observation will therefore serve as a key to explaining complicated physical properties in hydrogen-bonded liquids.

In the present study, we have performed complex permittivity measurements of pentanol isomers (1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-2-butanol, and 3-methyl-2-butanol) with THz-TDS. These structural isomers differ in the position of the OH group and the structure of the carbon chain, which affects the formation of hydrogen bonds in the liquid state. The objective of this study is to perform systematic experiments with pentanol isomers in the THz region. On basis of the experimental results, we will discuss the underlying microscopic mechanisms contributing to dielectric spectra in this frequency range.

2. Experimental

The experimental technique of THz-TDS has been well developed and described in detail by others [3–5]. A mode-locked Ti sapphire laser (Tsunami, Spectra Physics), which generates femtosecond pulses with the wavelength of 800 nm, was used for the emission and detection of pulsed THz waves. For the emission, we produced a photoconductive antenna with electrodes, the gap distance of which is 500 μm, fabricated on a semi-insulating

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gallium arsenide substrate. In the detection of THz pulses, an electro-optic (EO) sampling method was employed with a <1 1 0> 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 sample was controlled from 253 to 323 K by a Peltier device. (Except for 2-methyl-2-butanol, whose melting point is 261 K, measurements for this sample were made from 263 to 323 K.) 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 pentanol isomers 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 5% for the whole frequency range.

Data in the microwave range were also obtained to study dielectric properties of pentanol isomers 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). From 500 MHz to 20 GHz, the complex permittivity was obtained by time domain reflectometry [6–8]. Concerning the experimental details in the microwave region, we refer the reader to our previous paper [9]. The temperature of the sample in both experimental setups was controlled at 273–323 K.

The molecular structures of pentanol isomers used in this study are indicated in Fig. 1. 1-Pentanol was purchased from Kanto Chemical, 3-methyl-1-butanol was purchased from Kishida Chemical, 3-methyl-2-butanol was purchased from Junsei Chemical, and other alcohols were purchased from Wako Pure Chemical Industries. All these chemicals were of analytical grade (97.0–98.5%) and were used without further purification. In the case of 2-methyl-1-butanol and 3-methyl-2-butanol, the chemicals obtained were a mixture of the optical isomers.

3. Results and discussion

3.1. Complex permittivity in the THz region

Fig. 2(a)–(g) show the complex permittivities $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ of all the pentanol isomers studied. Some dielectric relaxation processes below the GHz frequency region in monohydric alcohols have been reported [10–14]. These processes contribute to $\varepsilon'(\omega)$ in the THz region, resulting in the rise in dielectric permittivity $\varepsilon'(\omega)$ and dielectric loss $\varepsilon''(\omega)$ below 0.5 THz in Fig. 2(a)–(g). With decreasing temperature, these relaxation processes shift to a lower frequency range, leading to the decrease in dielectric loss values below 0.5 THz. After this shift, a peak can be clearly seen around 1.5 THz; the peak position is almost independent of temperature. Furthermore, above 2.0 THz, a rise in the dielectric loss is observed for almost all pentanol isomers, which indicates the location of another mode above 2.5 THz. To sum up the basic characteristics of the complex permittivities of pentanol isomers in the THz region, they contain three contributions: (i) a high-frequency side of dielectric relaxation processes, (ii) a mode with peak position around 1.5 THz, and (iii) a low-frequency side of another mode located above 2.5 THz. We will examine these contributions more closely in the following sections.

3.2. Peak in the dielectric loss around 1.5 THz

Let us begin our discussion by considering a peak observed in the dielectric loss $\varepsilon''(\omega)$ around 1.5 THz. In the present study, by lowering the temperature down to 253 K, the mode with peak position around 1.5 THz is clearly observed in pentanol isomers. This mode shows a broad vibration feature as demonstrated in Fig. 3 with the fitting results of two functions: Debye function [Eq. (1)] and Lorentz function [Eq. (2)]. The Debye function [15] is used to represent the simplest dielectric relaxation process which has one relaxation time. On the other hand, the Lorentz function has been introduced to fit the vibration mode of hydrogen-bonded liquids in the THz region [14,16,17].

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

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

In Fig. 3, the Lorentz function can represent the mode around 1.5 THz, which indicates that the mode arises from vibration dynamics, while the Debye function cannot express the narrow shape of the mode.

Studies on molecular dynamics of hydrogen-bonded liquids in the THz region have been conducted with other experimental and theoretical techniques. In water and lower alcohols, which are representatives of hydrogen-bonded liquids, some vibration dynamics were reported to be observed in the THz region. Previous

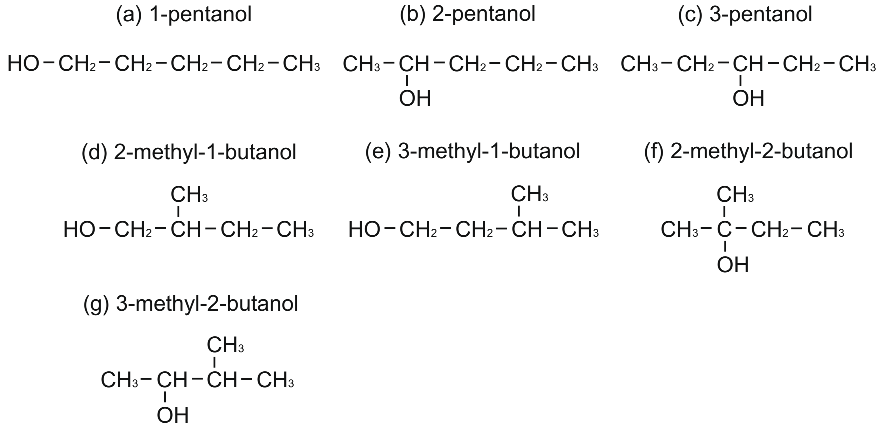
(a) 1-pentanol
(b) 2-pentanol
(c) 3-pentanol
(d) 2-methyl-1-butanol
(e) 3-methyl-1-butanol
(f) 2-methyl-2-butanol
(g) 3-methyl-2-butanol

Fig. 1. Molecular structure of (a) 1-pentanol, (b) 2-pentanol, (c) 3-pentanol, (d) 2-methyl-1-butanol, (e) 3-methyl-1-butanol, (f) 2-methyl-2-butanol, and (g) 3-methyl-2-butanol.