DIELECTRIC STUDY ON GAS HYDRATES USING TERAHERTZ TIME
DOMAIN SPECTROSCOPY

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ABSTRACT
The real and imaginary dielectric constants $\varepsilon'$ and $\varepsilon''$ of SF$_6$ hydrate have been measured in the frequency range 0.3–1.0 THz and in the temperature range 50–240 K using terahertz (THz) time-domain spectroscopy (TDS) with a gas cooling cryostat. The constant $\varepsilon'$ increases with frequency and temperature. The constant $\varepsilon''$, which is mainly influenced by infrared phonon absorption, increases with frequency and temperature over the entire range considered in this study. We discuss the frequency and temperature dependence of $\varepsilon''$ using a mathematical model and obtain parameters to describe the fitted curves of $\varepsilon''$. We check our results using a mathematical model for ice.

Keywords: gas hydrates, dielectric constants, terahertz

INTRODUCTION
Gas hydrates have a curious icy structure composed of hydrogen bonds. Crystalline solid structures are stabilized under conditions of relatively high pressure and low temperature. Since their structure contains a high volume of gases, gas hydrates have attracted much attention as new materials for use in the transport and storage of natural gases. In particular, methane hydrate is abundant in many locations; it is found in sediment or permafrost regions and is expected to be a future energy resource. The structure of gas hydrates consists of many cages, which include guest gas molecules. There are several types of gas hydrates. The typical structure types are structures I, II, and H, and the type depends on the guest molecule size and temperature-pressure region.

Structures I and II have a cubic unit cell, while structure H has a hexagonal cell. In structure-II hydrates, sixteen small cages (S-cages) and eight large cages (L-cages) are present in the unit cell. Structure I is generated by molecules with sizes 0.4–0.6 nm, while structure II is formed by somewhat larger (0.6–0.7 nm) molecules that occupy only the L-cages, such as tetrahydrofuran (THF) and propane. At high pressures, some of the smallest guest molecules (0.38–0.42 nm) such as argon or nitrogen form a structure-II hydrate and occupy both the S- and L-cages. If the L-cages with structure II are fully occupied by compound A, the composition of the gas hydrate will be A•17H$_2$O [1, 2]. The stability, structure, cage occupancy, and other properties of gas hydrates have been investigated

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using Raman spectroscopy, X-ray diffraction, NMR, etc. [3-8]. The dielectric constants, which are fundamental parameters of a material, provide information on the proton disorder and water reorientation of the crystalline lattice of a hydrogen-bonded material. Although the dielectric parameters of ice have been reported in detail for a wide frequency and temperature range [9-20], there are few such studies for gas hydrates. Davidson et al. provided a systematic discussion of the reorientation and relaxation of water molecules of gas hydrates using dielectric parameters [21-23]. Williams et al. reported measurements of the dielectric parameters to determine the dipole dispersion of guest molecules [24-25]. Rick and Freeman reported a computational study of the proton disorder of structure-II hydrates using dielectric parameters [26]. These studies were conducted for frequencies below GHz frequencies, and there are few studies of gas hydrates at higher frequencies [27]. The frequency-dependent dielectric constants of the gas hydrates provide information on the hydrogen-bonded structures. Therefore, we need to study the dielectric parameters of gas hydrates over a wide frequency range.

On the other hand, to use hydrates as energy sources, it is important to study their dissociation and nucleation below freezing point. However, since their appearance and density are similar to those of ice, it is difficult to use conventional nondestructive inspection methods to distinguish the hydrates from ice [4]. However, terahertz time-domain spectroscopy may be useful. THz waves are defined as electromagnetic waves with frequencies of 0.1 to 30 THz, i.e., they lie between infrared waves and microwaves. This approximately corresponds to low-energy excitation, such as fundamental vibration modes and the thermal emission lines of simple molecules. Therefore, THz spectroscopy is expected to be a nondestructive inspection technique in physics and chemistry [13, 28-31]. Furthermore, THz-TDS facilitates the determination of both the absorption coefficients and optical constants of a sample without the need for the Kramers-Kronig relation. Hence, it is a powerful technique for determining optical properties [32]. Several fundamental THz-TDS studies on the H$_2$O molecule have been carried out, and several optical constants have been measured for ice and water [13, 33]. However, there are few studies of gas hydrates using THz technology [34]. The optical and dielectric properties of gas hydrates at THz frequencies are expected to provide meaningful information.

The present paper reports a THz-TDS study of sulfur hexafluoride (SF$_6$) hydrate over a wide temperature range (10–250 K) at atmospheric pressure. The aims are to measure the dielectric constants of a structure-II hydrate at THz frequencies and to apply a mathematical model for the dielectric constants of ice to a gas hydrate.

**MATERIALS AND METHODS**

**Sample preparation**

The procedure for preparing the gas hydrates is essentially identical to that reported previously [27, 34]. SF$_6$ hydrate was synthesized by using pressurized gas and distilled water at 275.2 K in a stainless steel cell. After stirring, the hydrates were extracted from the cell at ca. 253 K in a low-temperature chamber. The hydrate crystals were made into tablets with a diameter of 10 mm and varying thicknesses (1–2 mm) using a tablet-making apparatus (HANDTAB-Jr, Ichihashi Seiki) in the low-temperature chamber. The thickness of each sample was accurately calculated from the weight and volume. The error in the thickness is within 0.5%.

**THz-TDS measurement**

The tablet samples were measured using a THz-TDS system equipped with a dipole-type low-temperature-grown GaAs (LT-GaAs) photoconductive switch as an emitter and detector, and a Ti:sapphire laser (Mai-Tai, Spectra-Physics; $\lambda = $ 780 nm; repetition rate: 82 MHz; pulse width: 100 fs) as a femtosecond pulsed laser source (Figure 1). The femtosecond laser pulse is first separated into a “pump pulse” and a “trigger pulse.” The THz pulse is generated at the surface of $p$-InAs by the pump-pulse illumination and collimated onto the sample kept in the cryostat using a set of off-axis parabolic mirrors. It is then collimated again onto the LT-GaAs detector using another set of off-axis parabolic mirrors. Since the temporal photocurrent is generated only when the trigger laser pulse and the radiated THz pulse arrive simultaneously at the LT-GaAs switch, we can directly obtain both the amplitude and the phase of the radiated THz pulse by changing the optical delay and measuring the corresponding change in the photocurrent.
Figure 1. Illustration of a THz-TDS system. The femtosecond pulses are split into pump pulses which generate THz pulse and trigger pulses which gate the detector and measure THz electric field. The sample is held on sample-rod in cryostat system between two parabolic mirrors.

Gas-cooling cryostat
We used a gas-cooling cryostat manufactured by PASCAL for the low-temperature measurements. Using compressed He gas, we maintained the temperature of the sample room in the cryostat in the range 10–240 K. The sample room was placed on the intermediate focal plane between the two sets of parabolic mirrors; it has quartz windows for transmitting THz waves. The gas hydrate tablets were held on top of the sample rod and kept at the center between the windows. During the initial sample setting, the sample rod was cooled by liquid nitrogen. The temperature distribution of the sample room was kept uniform by the circulation of cooling gas. For accuracy, all the THz-TDS measurements were performed several times and then averaged for each sample.

Calculation of complex dielectric parameters
The real and imaginary part of the complex refractive indices $n(\omega)$ and $k(\omega)$ of the samples can be directly calculated from the following equations:

$$E_{\text{sam}}(\omega) = \rho(\omega) \exp[-i\phi(\omega)]$$  \hspace{1cm} (1)

$$n(\omega) = \frac{c\phi(\omega)}{\omega L} + 1$$  \hspace{1cm} (2)

$$k(\omega) = \frac{c}{\omega L} \ln \left( \frac{4n(\omega)}{\rho(\omega)[n(\omega) + 1]^2} \right)$$  \hspace{1cm} (3)

where $\omega$ is the frequency, $E_{\text{sam}}(\omega)$ is the fast Fourier transform (FFT) spectrum of the THz pulse propagated through the hydrates, $E_{\text{ref}}(\omega)$ is the reference FFT spectrum, $\rho(\omega)$ is the transmission, $\phi(\omega)$ is the phase shift, $c$ is the light speed, and $L$ is the thickness of the sample [32].

Using these estimated complex refractive indices, we can obtain the real $\varepsilon'$ and imaginary $\varepsilon''$ dielectric constants of the samples as follows:

$$\varepsilon'(\omega) = [n(\omega)]^2 - [k(\omega)]^2$$  \hspace{1cm} (4)

$$\varepsilon''(\omega) = 2n(\omega)k(\omega)$$  \hspace{1cm} (5)

RESULTS AND DISCUSSION
Frequency and temperature dependence of real dielectric constants

Figure 2 shows our results for the frequency dependence of the real dielectric constant $\varepsilon'$ of SF$_6$ hydrate in the range 0.3–1.0 THz at 100.6, 199.9, and 239.9 K. As the frequency increases from 0.3 THz to 1.0 THz, $\varepsilon'$ increases from 3.02 to 3.09 at 199.9 K. These values are similar to but slightly lower than those for ice under the same conditions [13]. As for the hydrogen-bonded crystal of the water molecules, a lattice vibration significantly contributes to the amplitude of $\varepsilon'$ in the THz frequency range [13]. Hence, on the basis of a comparison of $\varepsilon'$ values, the states of the hydrogen-bonding matrices of ice and gas hydrate, including the non-dipolar molecules, are observed to be similar. The difference in the polarizability and the molecular density between ice and the gas hydrate is likely to contribute to a slight difference
in these $\varepsilon'$ values.

According to previous studies, the $\varepsilon'$ values for ice are constant from 0.1 MHz to 1 THz and show complex behavior beyond 1 THz. The maximum occurs at a few THz [17-19]. The frequency range of our measurements corresponds to the above range, so we expect that a local maximum for the $\varepsilon'$ of gas hydrate exists at a few THz, similar to the local maximum for ice [19].

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**Figure 3** Temperature dependence of real dielectric constant $\varepsilon'$ at 0.50, 0.75, and 1 THz.

Figure 3 shows the temperature dependence of the real dielectric constant $\varepsilon'$ at 0.50, 0.75, and 1 THz. As the temperature increases from 50 to 240 K, $\varepsilon'$ increases from 3.00 to 3.03 at 500 GHz and from 3.02 to 3.08 at 1 THz. The rate of increase of $\varepsilon'$ with temperature ($d\varepsilon'/dT$) clearly increases beyond 0.75 THz.

**Frequency and temperature dependence of imaginary dielectric constant**

**Figure 4** Imaginary dielectric constant $\varepsilon''$ of SF$_6$ hydrate at four temperatures plotted double logarithmically versus frequency. The reported values for ice are shown as white squares. The solid lines are fitted curves obtained from Eq. (6).

Figure 4 shows the frequency dependence of the imaginary dielectric constants $\varepsilon''$ of SF$_6$ hydrate in the range 0.3–1.2 THz at 100.6, 199.9, and 239.9 K, together with the reported values for ice [13]. As frequency and temperature increase, $\varepsilon''$ increases over the range considered in this study. Our $\varepsilon''$ values approximately agree with those reported by Zhang et al for ice at the same temperature [13]. For ice, the frequency range below 1 THz is the low-frequency tail of the infrared-absorption band, so $\varepsilon''$ is dominated by the contribution from molecular reorientation. Moreover, the influence of Debye relaxation extends to this frequency range, and thus, a simple model for the frequency dependence of $\varepsilon''$ is the sum of two components. One term is contributed by the Debye relaxation and decreases with increasing frequency. The other term increases with increasing frequency since it is the low-frequency tail of the infrared absorption band at a high frequency [11, 13, 27]. From previous studies, the equation for $\varepsilon''$ in this frequency range is

$$\varepsilon'' = \frac{A}{\omega} + B\omega^C$$  \hspace{1cm} (6)

where the coefficients $A$, $B$, and $C$ are temperature-dependent empirical constants. Applying this formula to our results, we obtain the constants $A$, $B$, and $C$, which give the fitted curves at each temperature, as shown in Figure 4.
As the temperature increases, parameters \( A \) and \( B \) increase but parameter \( C \) decreases (Table 1). This behavior is consistent with that of ice in the GHz range.

### Table 1. Empirical coefficients \( A, B, \) and \( C \) obtained via least squares.

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>( A / \text{THz} )</th>
<th>( B / \text{THz}^{-1} )</th>
<th>( C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3</td>
<td>0.00137</td>
<td>0.0474</td>
<td>2.364</td>
</tr>
<tr>
<td>100.6</td>
<td>0.00172</td>
<td>0.0574</td>
<td>2.246</td>
</tr>
<tr>
<td>200</td>
<td>0.00289</td>
<td>0.0675</td>
<td>2.081</td>
</tr>
<tr>
<td>240</td>
<td>0.00477</td>
<td>0.0765</td>
<td>1.894</td>
</tr>
</tbody>
</table>

CONCLUSIONS

We measured the temperature and frequency dependence of the complex dielectric constants of SF\(_6\) hydrate in the THz range over a wide temperature range (50 to 240 K) using THz-TDS with a gas-cooling cryostat. The real dielectric constant \( \varepsilon' \) increases with frequency in the range 0.3–1.0 THz. The value of \( \varepsilon' \) increases with temperature between 50 and 240 K in all the frequency ranges considered in this study.

We check the temperature and frequency dependence of the imaginary dielectric constant \( \varepsilon'' \), using a mathematical model for ice in the GHz range. Ice exhibits increasing absorption with frequency in the THz range because of the low-frequency tail of the infrared absorption band. This behavior is also observed in SF\(_6\) hydrate. The parameters \( A, B, \) and \( C \) describing the frequency dependence of \( \varepsilon'' \) are treated as a function of temperature. Their temperature dependence differs from that of ice, so further study of these parameters is necessary.

Finally, we have shown that the dielectric constants of gas hydrate in the THz range can be analyzed using methods for ice. The complex dependence of \( \varepsilon'' \), we have to consider the approximation of these formulas in terms of the following factors. For ice, phenomena such as Debye relaxation, the excitations of acoustic phonons, and infrared phonon absorption have been reported in detail using various methods [10, 11, 19, 27]. For gas hydrates, there have been few reports for this frequency range. In addition, the structures of gas hydrates are different from those of ice. To investigate the dielectric parameters physically and chemically, we need more information on gas hydrates in this frequency range.

Further, we have to consider the contribution of guest molecules to the polarizability and the properties of the hydrogen bond of the gas hydrate. The hydration number of SF\(_6\) hydrate is 17, and the SF\(_6\) molecule is nonpolar. We therefore ignored the contribution of guest molecules. In the future, we will carry out a more detailed dielectric study of gas hydrates, including the influence of guest molecules. Nonetheless, since our results in this study show good agreement between the experimental data and the theoretical description, our analysis is reasonably accurate for the investigation of the dielectric behavior of the gas hydrate in the THz frequency range.

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dielectric constants in the THz range contribute to the infrared polarization and phonon absorption of the water molecules on the hydrogen-bonding matrices, so we suggest that THz-TDS is useful for structural studies of gas hydrates.

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