

# Terahertz Characterization Of Hydrogen Bonded Materials

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**Abstract**—Terahertz time-domain spectroscopy of hydrogen bonded materials was carried out to investigate the dielectric and optical properties of materials in the THz frequency range. The complex dielectric constant (i.e.,  $\epsilon'$  and  $\epsilon''$ ) of H<sub>2</sub>O ice, D<sub>2</sub>O ice, propane hydrate, SF<sub>6</sub> hydrate and CH<sub>4</sub> hydrate was measured at frequencies in the range 0.4–1.2 THz and temperatures in the range 20–240 K.

We discuss the frequency and temperature dependence of  $\epsilon'$  and  $\epsilon''$  using a mathematical model to obtain specific parameters. These results show that it is possible to analyze the dielectric constants of gas hydrates using a mathematical model of ice.

## I. INTRODUCTION

TERAHERTZ time-domain spectroscopy (THz-TDS) can be used to determine the absorption coefficients and dielectric constants of samples without requiring the use of the Kramers–Kronig relation; hence, it is a powerful technique for determining dielectric properties [1–4]. Here, we report a THz-TDS study of hydrogen-bonded materials over a wide temperature range (20–240 K) at atmospheric pressure. The absorption coefficient, index of refraction, and dielectric constants of various materials were measured in the THz region using THz-TDS. The optical properties can be a particularly useful parameter for material characterization. For hydrogen-bonded materials, these properties provide information on the polarization of water molecules and the proton flow through crystalline structures. Furthermore, the state of the molecular dipoles of icy materials contributes to the dielectric properties in the THz region. Therefore, in this study, we examined ice and several gas hydrates.

Gas hydrates have a curious icy structure formed by hydrogen bonds, whereas the crystalline solid structures are stable under relatively high pressures and low temperatures. Since their structure contains a high volume of gas, gas hydrates have attracted a great deal of attention as new materials for use in the transport and storage of natural gases. In particular, methane hydrate is abundant in many locations (i.e., sediment or permafrost regions) and is a potential future energy resource. The structure of gas hydrates consists of many cages that contain guest gas molecules. Typically, gas hydrate structures are classified as either type I, II or H, depending on the size of the guest molecule, the temperature and the pressure. Types I and II have cubic unit cells, whereas type II has a hexagonal unit cell. In type-II hydrates, a unit cell contains 16 small cages (S-cages) and eight large cages (L-cages). Type I hydrates are typically generated by molecules that are 0.4–0.6 nm in size, whereas type-II hydrates are formed by somewhat larger (0.6–0.7 nm) molecules that occupy only the L-cages, such as sulfur hexafluoride (SF<sub>6</sub>), tetrahydrofuran (THF), and propane. At high pressures, some smaller guest molecules (0.38–0.42 nm), such as argon or nitrogen, form a type-II hydrate, and

occupy both the S- and L-cages. If the L-cages are fully occupied by compound A, the composition of the gas hydrate will be A•17H<sub>2</sub>O [5–12].

## II. RESULTS

The procedure used to prepare the gas hydrates was as described in Ref. [13]. The samples were measured using a THz-TDS system equipped with a dipole-type low-temperature-grown GaAs (LT-GaAs) photoconductive switch as the emitter and detector, and with a fiber laser ( $\lambda = 780$  nm; repetition rate: 82 MHz; pulse width: 100 fs; IMRA, Ann Arbor, Michigan, U.S.A.) femtosecond pulsed source. A gas-cooled cryostat (PASCAL, Osaka, Japan) was used for the low-temperature measurements. The temperature of the sample enclosure in the cryostat was maintained in the range 20–240 K using compressed helium gas.

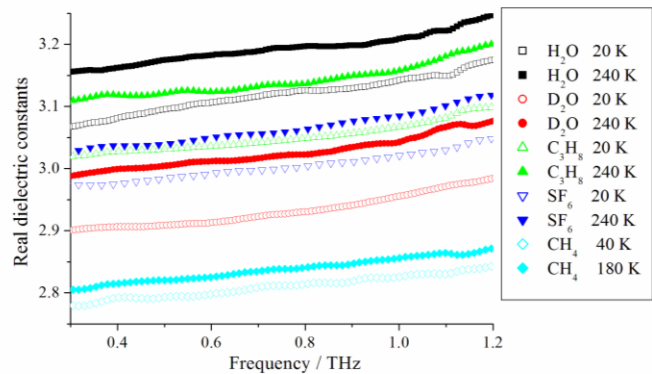


Figure 1 The frequency dependence of the real part of the dielectric constant  $\epsilon'$  of H<sub>2</sub>O ice, D<sub>2</sub>O ice, C<sub>3</sub>H<sub>8</sub> hydrate SF<sub>6</sub> hydrate and CH<sub>4</sub> hydrate at two temperatures.  $\epsilon'$  increased with both frequency and temperature. In the THz region, all samples exhibited similar behavior.

As shown in Fig. 1, the THz-TDS measurements show that  $\epsilon'$  increased with increasing frequency. Numerical calculations indicated a local maximum in  $\epsilon'$  at a few THz. The polarizability  $\alpha$  obtained from  $\epsilon'$  exhibited a linear increase as a function of temperature squared ( $T^2$ ). The imaginary part of the dielectric constant  $\epsilon''$ , which is mainly influenced by infrared phonon absorption, increased with the frequency and temperature over the entire range considered in this study. A mathematical model was created to describe the frequency and temperature dependence of  $\epsilon'$ . For the gas hydrates, the observed behavior of  $\epsilon'$ ,  $\epsilon''$ , and the polarizability  $\alpha$  was similar to that of ice (see Fig. 1), which allows us to analyze the dielectric constants of gas hydrates using a mathematical model for ice [14], and makes it possible to discuss the polarization and optical properties of gas hydrates using THz-TDS analysis. This technique can also be used to obtain a parameter that is closely related to the physics of the lattice structure that provides

information on the polarizability, relaxation time, and the structure of hydrogen bonds.

The structure of methane hydrate (a type-I hydrate) differs from that of ice and type-II hydrates. Although the dielectric constants of ice and type-II hydrates ( $C_3H_8$  and  $SF_6$  hydrates) were in the range 3.0–3.2, that of methane hydrate was somewhat smaller (see Fig. 1.). This probably results from the difference in the structures, because the dielectric constant is determined mainly by the lattice dynamics in this frequency range. The dielectric response in the THz region can be described as overlaying the dispersion of the Debye relaxation and infrared absorption spectra. At visible wavelengths, the dielectric constants of ice and gas hydrates are similar [15], hence the difference based on the infrared dispersion is small. The difference in the THz region is expected to be due to differences in the Debye relaxation.

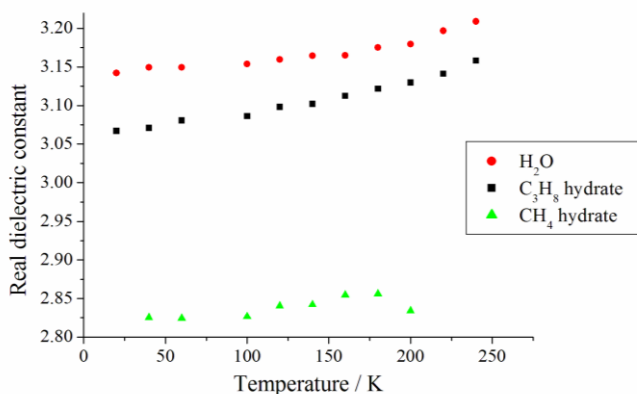


Figure 2 The temperature dependence of the real part of the dielectric constant  $\epsilon'$  of  $H_2O$  ice,  $C_3H_8$  hydrate and  $CH_4$  hydrate at 1.0 THz. All samples exhibited similar behavior at THz frequencies. For the  $CH_4$  hydrate at 200 K,  $\epsilon'$  was small because the dissociation temperature for  $CH_4$  hydrate is 193 K.

Figure 2 shows the temperature dependence of the real part of the dielectric constant of  $H_2O$  ice,  $C_3H_8$  hydrate and  $CH_4$  hydrate at 1.0 THz. For the  $CH_4$  hydrate, we find that  $\epsilon'$  was significantly smaller than for ice and the  $C_3H_8$  hydrate; however, the gradient of the temperature dependence below 180 K was similar. It follows that the temperature dependencies of the dielectric constants of ice, type-I hydrates and type-II hydrates are similar.

### III. SUMMARY

We measured the temperature and frequency dependence of the complex dielectric constants of hydrogen-bonded materials in the THz range over a wide range of temperatures (i.e., 20–240 K), using THz-TDS with a gas-cooled cryostat.

For all the samples, the real part of the dielectric constant  $\epsilon'$  increased with frequency and temperature in the THz region. For all samples, a local maximum in  $\epsilon'$  was found at a few THz, which was calculated using the Sellmeier equation. The temperature and frequency dependence of the imaginary part of the dielectric constant  $\epsilon''$  was well described by the mathematical model for ice in the GHz range. Ice exhibits increasing absorption with frequency at THz frequencies due to

the low-frequency tail of the infrared absorption band. This behavior was also observed for gas hydrates.

We showed that the dielectric constant of gas hydrates in the THz frequency range can be analyzed using a method similar to that used for ice. The complex dielectric constants in the THz range contribute to the infrared polarization and phonon absorption of water molecules in the hydrogen-bonding matrices. Therefore, THz-TDS is a particularly useful tool for structural studies of gas hydrates.

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