

Study of Tetrabutylammonium Bromide Hydrate by Two spectroscopies in THz region

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Introduction

Clathrate hydrate represented by methane hydrate, which is expected to be used as energy resource, is a compound composed of water and a guest molecule. It has a hydrogen-bonded cage structure formed by water and encloses a guest molecule. Although it looks like ice, there are many kinds of guest molecules and there are properties peculiar to hydrate. One of the features in clathrate hydrates is the self-preservation effect, which is unexpected high stability at conditions out of thermodynamic equilibrium. Ripmeester [1] suggested that the self-preservation effect is related to the interaction between guest and water molecules. As the guest molecule becomes large and the guest molecule does not fit in one cage, the guest molecule replaces a part of the host water molecule and becomes semi-clathrate hydrate having similar cage structure to clathrate hydrate. Due to having empty cages and mild formation condition under atmospheric pressure (melting temperature is above 0°C), they have a potential for using separation, storage, and transportation of gases, especially hydrogen [2]. Although various kind of guest molecules have been tested for a practical use [3] and their crystal structures have been studied by using XRD and traditional Raman, these observation techniques do not clarify intermolecular interactions that are effective for structural stability and indispensable for selecting guest molecules. Spectroscopy in THz region reveals intermolecular interaction such as lateral and translational vibration binding energy rather than intramolecular interaction. Hence, two spectroscopies in THz region, low frequency Raman spectrum and THz-Time domain spectroscopy (TDS) elucidate the interaction of guest-guest and/or guest-host molecules and influence of hydrogen bonding on the cage structure. Nevertheless, spectral study in THz region about semi-clathrate hydrate are hardly reported, though there are a few reports on Xe hydrate and THF hydrate by using low frequency Raman and THz-TDS [4–6]. Here, we measure tetrabutylammonium bromide (TBAB, C₁₆H₃₆BrN) hydrate and crystal with THz-TDS and low frequency Raman to observe absorption and Raman scattering, respectively. TBAB is a quaternary ammonium salt and well known as an ionic guest molecule. Our aim in this study is to observe directly intermolecular interaction and to discuss it by comparing the extinction coefficient and Raman spectra less than about 3 THz (100 cm⁻¹) of TBAB hydrate and crystal.

Experimental

TBAB hydrate and crystal were prepared for two spectroscopies. TBAB aqueous solution (40 wt%) was frozen at -20°C to form TBAB hydrate. Particles samples of TBAB hydrate and crystal were pressed into tablets with a diameter of 10 mm and varying thickness (0.8 - 1.5 mm) using the tablet shaper (pressure is up to 4MPa). In THz-TDS, We used a THz-TDS system incorporating an optical refrigerator [7]. THz-TDS system equipped with a p-InAs wafer as a THz emitter, a dipole-type low temperature grown GaAs (LT-GaAs) photoconductive switch as a detector, and a femtosecond pulsed laser ($\lambda = 780$ nm; repetition rate: 50 MHz; pulse width: 100 fs; power: about 24 mW). Trigger laser pulse and the radiated THz pulse simultaneously arrive at the LT-GaAs switch. The temporal photocurrent is generated. By moving delay stage, optical delay is changed, we can directly obtain both the amplitude and the phase of the radiated THz pulse. The tablet samples were set in a 10 mm aperture of a copper plate in cryostat. The copper plate with the sample was placed on the intermediate focal plane between the two sets of parabolic mirrors. The tablet samples were measured by gradually raising the temperature in the range of 150-270 K. All experiments were performed at atmospheric pressure. After the Fourier transform of the obtained data, the extinction coefficient was evaluated. On the other hands, in low frequency Raman, the powder samples were set into the aluminum block on the stage-controlled temperatures at 275 K. The spectral resolution was 3.5 cm⁻¹ and the laser was wavelength of 830 nm. Besides, the laser beam had a power about 200 mW, At the time of measurements, scan times was 200 times and exposure time was 1000 ms. To eliminate the influence in the air at the time of measurement, the data obtained by measuring the empty aluminum block was subtracted from the obtained raw data. For accuracy, all measurements were performed several times for a single sample.

Results and Discussion

Extinction coefficients and low frequency Raman spectra of TBAB hydrate and crystal are shown in Figure 1. TBAB hydrate has an absorption peak at 1.1 THz. Burnett et al. reported that TBAB crystal had infrared activity at 1.39, 1.41 THz by quantum computation, which are attributed to translatory modes involving antisymmetric movement of the four ions along each of the three crystal axis directions [8]. This is good agreement with experimentally observed peak with maximum absorption at 1.47 THz [8]. Actually, we measured TBAB crystal at the range of 0.1-1.1 THz in the same THz-TDS system and found that the absorption rose monotonically. It corresponds to tail of this peak. On the other hands, low frequency Raman revealed broad band peak at 64 cm^{-1} in TBAB hydrate and two peaks at 43, 75 cm^{-1} in TBAB crystal. The higher frequency peak may be caused by translation of the anion along with a degree of flexing and rotation of the alkyl chains [8]. The lower frequency Raman peak indicates absorption peak at 43 cm^{-1} , although clear peak was not observed in hydrate. In TBAB hydrate, both of peak are shifted to lower frequency compared to TBAB crystal. This means that the interionic distance is larger in TBAB hydrate than in TBAB crystal, since tetrabutylammonium ion is isolated by hydrogen-bonded water molecules. Whereas, hydrogen bonds may be reducing the decrease in binding energy to the increase in interionic distance.

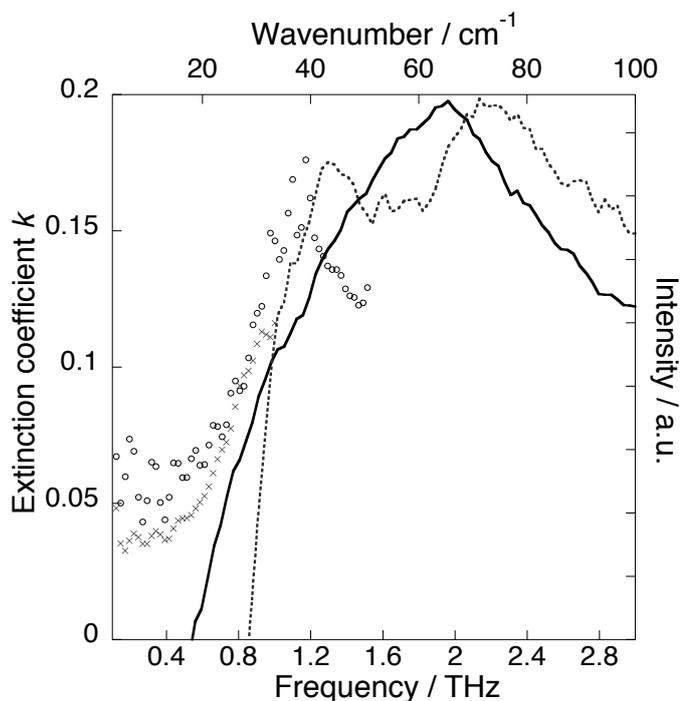


Figure 1. Extinction coefficients k and low frequency Raman spectra of TBAB hydrate and crystal in THz region. white circle: extinction coefficient for hydrate, cross mark: extinction coefficient for crystal, solid line: Raman spectrum of hydrate, dotted line: Raman spectrum of crystal.

Conclusion

THz-TDS and low frequency Raman are promising for direct observation of intermolecular interaction included hydrogen bonding, since the shift to low frequency is expected to increase the interionic distance and influence of hydration of water molecules.

Reference

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