



## Distinct hydrophobic–hydrophilic dual interactions occurring in the clathrate hydrates of 3,3-dimethyl-1-butanol with help gases

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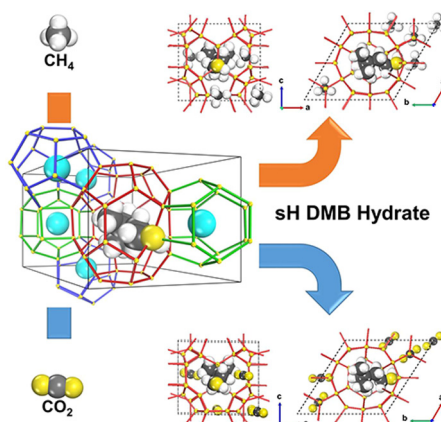
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### HIGHLIGHTS

- The complex host–guest interactions occurring on sH hydrates was investigated via experimental and DFT calculation.
- The dynamics of DMB guest molecules were significantly influenced by the type of gaseous co-guest molecules.
- The contraction and/or elongation patterns of the intermolecular hydrogen bond were examined.
- The co-guest help gases evoked a discrete torsional configuration of the DMB molecule.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

To unlock the potential of clathrate hydrate for versatile applications in energy and environmental application such as energy storage, gas separation, and novel functional materials, profound understanding of their hidden nature must be secured. In this study, we focused on the complex host–guest and heterogeneous guest–guest interactions occurring on the sH hydrates of 3,3-dimethyl-1-butanol with help gases of CH<sub>4</sub> or CO<sub>2</sub>. The density functional theory calculations and spectroscopic experimental analyses showed that the dynamics of the large 3,3-dimethyl-1-butanol guest molecule as well as the host water frameworks of sH hydrate were significantly influenced by the type of gaseous co-guest molecules via complex host–guest and/or guest–guest interactions. The flexible hydrogen-bonded water framework underwent contraction or elongation in the O:H–O hydrogen and O–H polar-covalent bonds induced by distinct occupation patterns of the co-guest help gases, and it was

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observed that, depending on the type, the co-guest help gases triggered the transformation of torsional configuration of the hydrophobic moieties of the large 3,3-dimethyl-1-butanol guest molecule while the hydrophilic part was incorporated into the host water framework.

## 1. Introduction

Locking heterogeneous binary guest molecules into the diversely assorted nano-sized polyhedral water cages of clathrate hydrate often results in unique physicochemical behaviors induced by distinct host–guest or guest–guest interactions. Although, the hydrogen-bonded water host frameworks of clathrate hydrates are, in general, stabilized by a hydrophobic guest via non-directional van der Waals forces, recent investigations revealed that particular hydrophilic guest molecules such as methanol, ethanol, and ammonia can be engaged into the lattices of clathrate hydrates and present thermodynamic promotion effect [1–4]. This reveals that the hydrophilic host–guest interaction plays a significant role, in some cases, in stabilizing the flexible host lattice of clathrate hydrates. Accordingly, to unlock their potential such as for use as an energy resource [5,6], gas storage and separation media including hydrogen [7,8] and CO<sub>2</sub> [9,10], and as novel functional materials [11–14], profound understanding of the hidden nature of the complex host–guest interactions occurring in clathrate hydrates must be secured.

What would happen to the dynamics of the water lattice of clathrate hydrates if a large organic guest molecule, which is larger than the size of the clathrate hydrate cages and has both hydrophobic and hydrophilic moieties, were injected into the cages of the clathrate hydrate? In this case, can gaseous co-guest molecules also play a specific role in the occupation behavior of the large organic guest molecule via guest–guest interactions? To answer the questions, in the present study we focused on a large monohydroxy alcohol, 3,3-dimethyl-1-butanol (DMB), as one of the longest potential guest molecules for clathrate hydrates. The monohydroxy alcohols are expected to exhibit interesting features in the formation of clathrate hydrates because the hydrophobic–hydrophilic balance shifts as the alkyl groups become longer and/or bulkier [1,3,15]. In addition, since the long alkyl chain of the large organic guest molecule could offer a large degree of conformational freedom and each conformer requires its own configurational energy to be stabilized into the cages of the clathrate hydrate [16], a variety of dramatic inclusion behaviors via host–guest or guest–guest interactions can be anticipated. In this report, we explored the distinct inclusion behavior of DMB molecule injected into the structure H (sH) type hydrate with help gases such as CH<sub>4</sub> and CO<sub>2</sub>, as shown in Fig. 1. With the aim of revealing the complex hydrophobic–hydrophilic dual interactions occurring between host water and the large monohydroxy alcohol guest system, a combinational work employing experimental and density functional theory (DFT) calculation was performed.

## 2. Materials and methods

### 2.1. Materials and sample preparations

CH<sub>4</sub> and CO<sub>2</sub> with purity of 99.999 and 99.998%, respectively, were purchased from SINIL Gas Inc. (Republic of Korea). Deionized water of ultrahigh purity was supplied by an ultrapure water system (HIQ, Coretech Co. (Republic of Korea)). A 3,3-dimethyl-1-butanol (C<sub>6</sub>H<sub>14</sub>O, DMB) with purity of 99% was purchased from AK Scientific, Inc. (USA).

For spectroscopic analyses, binary DMB hydrates of CH<sub>4</sub> or CO<sub>2</sub> were synthesized using frozen DMB + H<sub>2</sub>O powder. First, DMB was mixed with deionized water. Due to the poor solubility of DMB, a vortex mixer (VM-10, DAIHAN Scientific Co., Ltd. (Republic of Korea)) was employed, and the solution was mixed vigorously for at least 10 min. The DMB solution was then promptly frozen in liquid nitrogen under an atmospheric pressure condition. The frozen mixtures were then grounded finely with a 150 μm sieve in liquid nitrogen using a pestle

and mortar. The frozen powdered mixture was loaded into a high pressure vessel, which is made of 316 stainless-steel and has an internal volume of 5 ml. The vessel was closed by bolts and pressurized by CH<sub>4</sub>, or CO<sub>2</sub> up to 10 MPa using a syringe pump (500D, Teledyne Isco Inc. (USA)) to maintain constant pressure during the formation of the binary DMB hydrates. The vessel was kept in a refrigerated water–ethanol circulator (RW-2025G, Jeio Tech Co., Ltd. (Republic of Korea)) at 253 K for 5 days to complete the reaction. Finally, the binary DMB hydrates with CH<sub>4</sub> or CO<sub>2</sub> were removed from the high pressure vessel under a liquid nitrogen environment, and grounded again with a 150 μm sieve in liquid nitrogen for the spectroscopic analyses.

### 2.2. Spectroscopic analyses

The high-resolution powder diffraction (HRPD) patterns were obtained using the high-resolution powder diffraction beamline (9B) at the Pohang Accelerator Laboratory (PAL) in the Republic of Korea. During the measurement,  $\theta/2\theta$  scan mode with a fixed time of 2 s, a step size of 0.005° for  $2\theta = 0\text{--}120^\circ$ , and the beamline with a wavelength ( $\lambda$ ) of 1.5472 Å were used for each sample. The powder samples stored in liquid nitrogen were loaded to the stage of HRPD, and the measurement was performed at 77 K to minimize the possibility of sample damage. The powder diffraction patterns were analyzed by using the Checkcell program [17].

A dispersive Raman spectrometer (ARAMIS, Horiba Jobin Yvon Inc. (France)) was employed. An Ar ion laser with excitation wavelength of the 514.53 nm line was used with a typical intensity of 30 mW. The scattered light was dispersed using an 1800 grating of the spectrometer and was detected by a charge coupled device (CCD) detector with thermoelectric cooling (203 K). For the low-temperature measurement, a temperature controlled microscope stage unit (THMS600G, LINKAM Scientific Instruments Ltd. (UK)) was used. All the Raman spectra were recorded at 93 K.

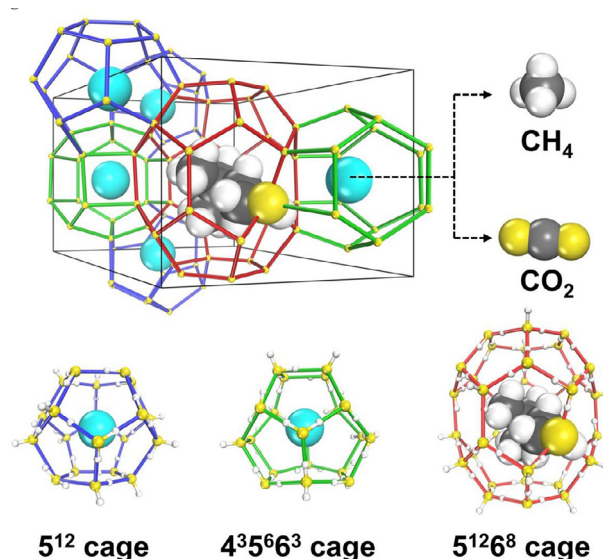


Fig. 1. A sH hydrate model system occupied by DMB molecule and help gas (CH<sub>4</sub> or CO<sub>2</sub>). In the system, one large cage (5<sup>12</sup>6<sup>8</sup>), two medium cages (4<sup>3</sup>5<sup>6</sup>6<sup>3</sup>) and three small cages (5<sup>12</sup>) were depicted by red, green, and blue colored lines (hydrogen bonds), respectively. Grey, white, yellow, and cyan spheres represent carbon, hydrogen, oxygen, and help gas, respectively.

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