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Thermal Expansivity of Tetrahydrofuran Clathrate Hydrate with Diatomic Guest Molecules

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The guest dynamics and thermal behavior occurring in the cages of clathrate hydrates appear to be too complex to be clearly understood through various structural and spectroscopic approaches, even for the well-known structures of sI, sII, and sH. Neutron diffraction studies have recently been carried out to clarify the special role of guests in expanding the host water lattices and have contributed to revealing the influence factors on thermal expansivity. Through this letter we attempt to address three noteworthy features occurring in guest inclusion: (1) the effect of guest dimension on host water lattice expansion; (2) the effect of thermal history on host water lattice expansion; and (3) the effect of coherent/incoherent scattering cross sections on guest thermal patterns. The diatomic guests of H₂, D₂, N₂, and O₂ have been selected for study, and their size and mass dependence on the degree of lattice expansion have been examined, and four sII clathrate hydrates with tetrahydrofuran (THF) have been synthesized in order to determine their neutron powder diffraction patterns. After thermal cycling, the THF + H₂ clathrate hydrate is observed to exhibit an irreversible plastic deformation-like pattern, implying that the expanded lattices fail to recover the original state by contraction. The host-water cage dimension after degassing the guest molecules remains as it was expanded, and thus host–guest as well as guest–guest interactions will be altered if guest uptake reoccurs.

Neutron approach has been attractively used for exploring thermal, structural, and dynamic behaviors of clathrate hydrates because of its high sensitivity to the nuclei H and D, whereas X-ray scattering cannot easily detect relatively light elements such as H, C, and O.^{1–5} Particularly, the neutron diffraction patterns together with other spectroscopic data can lead to better understanding of guest occupancy and dynamics occurring in confined cages. It seemed that deuteration was inevitable to avoid a very high incoherent scattering from hydrogen (H or H₂). However, the result from the deuterated sample could lead to erroneous conclusions on the intrinsic nature of fully hydrogenous materials, especially in the case of the hydrogen molecules within the clathrate hydrate cages. In a previous work, we synthesized two different binary clathrate hydrates, tetrahydrofuran (THF) + H₂ and THF + D₂, and determined their neutron diffraction patterns, revealing discrete thermal and guest-unloading phenomena.⁶ Clathrate hydrates are known to exhibit considerably larger thermal expansivity than hexagonal ice (Ih), and several studies on this sensitive property have helped to clarify the special role of guests in expanding the host water lattices. Tse et al. suggested that the increase of anharmonicity during the interaction between the host and guest molecules is responsible for this larger thermal expansivity.⁷ Takeya et al. observed that the lattice constants of sI, sII, and sH clathrate

hydrates are strongly influenced by the physicochemical nature of the guests.^{8,9} Recently, Hester et al. reported that both sI and sII clathrate hydrates, with a few exceptions, have a common thermal expansivity, independent of entrapped guests.¹⁰

Through this letter we attempt to address three noteworthy features occurring in guest inclusion: (1) the effect of guest dimension on host expansion; (2) the effect of thermal history on host lattice; and (3) the effect of coherent/incoherent scattering cross sections on guest thermal patterns. First, we synthesized a sII clathrate hydrate (cubic, *Fd3m*) by using 5.56 mol % THF-*d*₈ (99.5 atom% D) and deuterated water (D₂O, 99.9 atom% D), in order to minimize the background signal generated by the incoherent scattering property of hydrogen (H). A stoichiometric composition of 5.56 mol % offers almost full occupation of THF molecules in 5¹²6⁴ hexakaidecahedron cages (large) with empty 5¹² dodecahedron cages (small). Pure THF clathrate hydrates were then exposed to diatomic guest gases of H₂, D₂, N₂, and O₂, which thereupon occupied 5¹² cages. During this procedure, the THF in 5¹²6⁴ cages remained intact, and thus the entrapped diatomic guests were solely responsible for the lattice modification. The neutron diffraction patterns were measured using the high-resolution powder diffractometer (HRPD) installed at the 30 MW reactor “HANARO” of the Korea Atomic Energy Research Institute (KAERI).

Figure 1 shows the temperature dependence of the lattice parameter *a*(*T*) of the THF + H₂ clathrate hydrate. All lattice parameters were calculated from the higher peaks of (553), (620), and (862) to avoid the peak asymmetry that occurs on the low index peaks. The lattice parameter at 30 K (*a* = 17.0986 Å) was expanded by 1.249% at 270 K (*a* = 17.3104 Å), which

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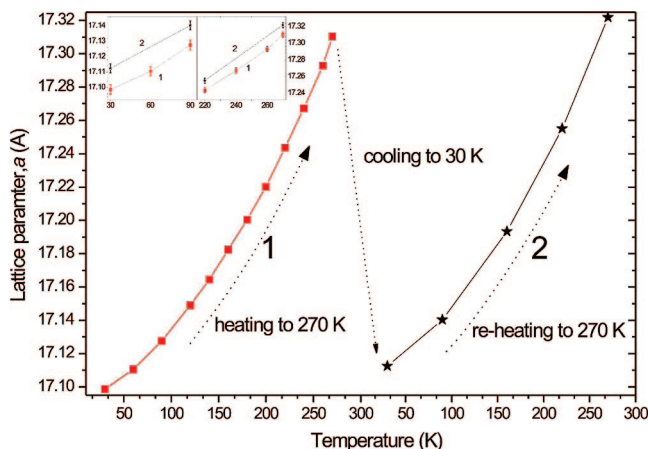


Figure 1. Lattice parameter of THF + H₂ clathrate hydrate as a function of temperature. After heating from 30 to 270 K (1), degassed THF + H₂ clathrate hydrate was measured again (2).

is equivalent to a volume expansion of 3.76%. When compared to the volume increase of the pure THF clathrate hydrate, which was expanded by 3.58% from 30 to 270 K, the THF + H₂ clathrate hydrate exhibits a slightly more expanded state at the same temperature range (Figure S1, Supporting Information). In an earlier neutron diffraction work, we could observe that the H₂ molecules in the THF + H₂ clathrate hydrate were escaping from the crystalline hydrate matrix in a temperature range of 150–250 K.⁶ Thus, it is expected that, at 270 K and 1 bar, most of the mixed THF + H₂ clathrate hydrate will be converted into pure THF clathrate hydrate, leaving most of the 5¹² cages vacant. In addition, this pure THF clathrate hydrate is known to sustain its sII structure up to 277.55 K at 1 bar.¹¹ After completion of the first heating process to 270 K, the degassed THF clathrate hydrate was again cooled to 30 K ($a = 17.1125$ Å), and the second heating process directly follows, proceeding to 270 K ($a = 17.3218$ Å). The thermal history alters the volume expansion of the pure THF as follows: 3.58% at a fresh state, 3.76% after the first heating, and 3.97% after the second heating, with consecutive expansion in a temperature range of 30–270 K.

The sI clathrate hydrate (cubic, $Pm\bar{3}n$) is known to have greater thermal expansivity than the sII clathrate hydrate, exhibiting a structure-dependent pattern.¹² For the sII THF + H₂ clathrate hydrate, the volume expansion of 3.97% after the thermal cycle is much greater than expected. Furthermore, we observed that, once the host water lattice is expanded via the thermal cycle, it tends to be unrecoverable. As such, it is likely to function as “plastic deformation” undergone beyond the elastic limit. The residual structure after dissociation, which is expected to form a partial hydrate cage or polyhedral cluster, might provoke a so-called “memory effect”. The clathrate hydrates experiencing thermal stimulation via freezing, melting, and refreezing processes are expected to restructure the host water lattices much better than can virgin hydrate crystal.^{13–15} In turn, the dominant repulsive interactions between the host water and guest molecules result in large thermal expansivity as compared to Ih, thereby weakening the water linkages.^{16,17} From the present NPD (neutron powder diffraction) measurements of the mixed THF + H₂ and nearly pure THF (degassed) clathrate hydrates, it is again noted that, once expanded, the lattice dimension cannot be recovered with suitable volume contraction of the unit cell.

Thus far, we have largely focused on the lattice constant variation caused by H₂ inclusion/exclusion, partly because of

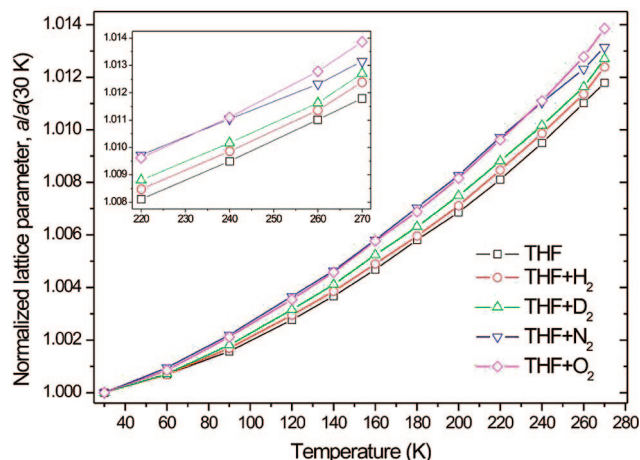


Figure 2. Normalized lattice parameters of the THF, THF + H₂, D₂, N₂, and O₂ clathrate hydrates.

the recent attention that has been directed toward this phenomenon, but three other diatomic gases of D₂, N₂, and O₂ that also form the sII with THF were tested to assess whether there is a specific correlation between guest and lattice dimensions. The inclusion of guest molecules with diameters of H₂ \approx 2.3, D₂ \approx 2.3, N₂ \approx 4.1, and O₂ \approx 4.2 Å in sII small cages lead to lattice expansions of 1.24, 1.27, 1.31, and 1.39%, respectively, which is equivalent to volume expansions of 3.76, 3.86, 3.99, and 4.21%, respectively, in a temperature range of 30–270 K (Figure 2). On the other hand, the corresponding expansions of pure THF hydrate with no guests in sII-S were found to be 1.18% and 3.58%, respectively, in the same temperature range.

The anharmonic term representing the guest vibrational energy plays a key role in increasing the thermal expansion of clathrate hydrates. Although a larger guest size exhibits lower anharmonicity, which reduces thermal expansivity, rotational motion of an aspherical guest molecule can contribute to anharmonic term free energy.¹⁸ However, it is likely that the thermal expansion of clathrate hydrates is to some extent dependent on the guest volume as well as guest mass. As shown in Figure 2, even though hydrogen and deuterium molecules have almost the same guest dimension, they show different thermal expansions. A similar pattern is found in nitrogen and oxygen molecules in THF clathrate hydrates. It is also clearly seen from Figure 2 that the expansion difference between H₂ and D₂ is larger than that between N₂ and O₂, which appears to be attributable to the large mass ratio (1:2) between H₂ and D₂. Another factor that should be taken into account when evaluating the cause of the lattice expansion is the internal pressure by kinetic motion of guest molecules stimulated by mass-dependent thermal energy. We expect that many other variables may be involved in the host–water lattice distortion in terms of short- and long-range interactions.

To reveal whether the thermal expansivity is still governed by the guest volume and mass dependency even after the gaseous guest molecule has been degassed, it is necessary to predict the degassing temperature for each gaseous guest molecule. Thus we also evaluated whether the temperature-dependent neutron diffraction pattern caused by degassing is related to the coherent/incoherent scattering cross section. A more precise description of this feature will contribute to better understanding of both guest-dependent thermal motion and structural dimension. In the case of the binary THF clathrate hydrates, the gaseous guest dissociation causes contrast variation of neutron diffraction patterns, directly affecting the coherent

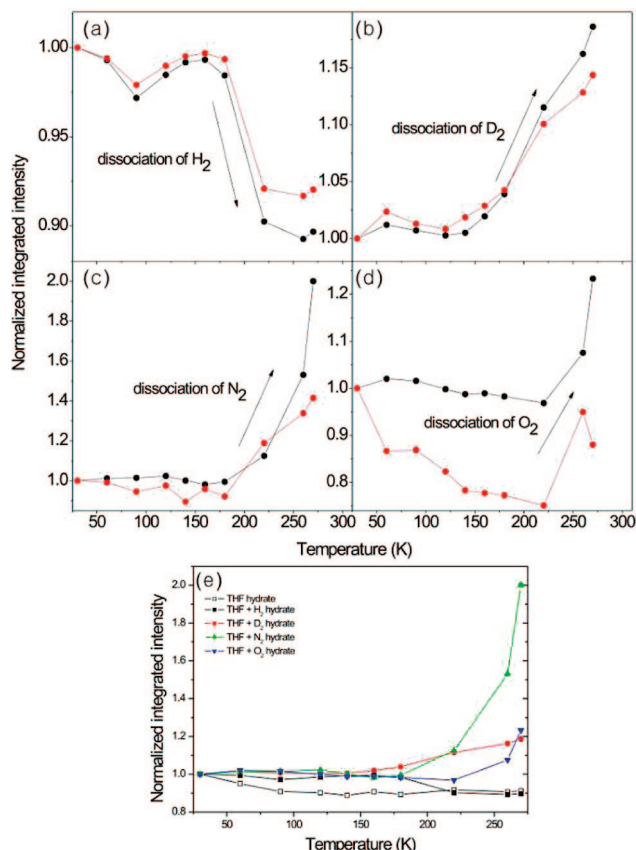


Figure 3. Specific integrated peak intensities of the (a) THF + H₂ (Choi, et al.⁶), (b) THF + D₂ (Choi, et al.⁶), (c) THF + N₂, and (d) THF + O₂ from neutron powder diffraction patterns (black: (111), red: (331)). (e) Temperature dependence of integrated intensity of (111) with various guest molecules.

(peak) or incoherent (background) scattering term. According to the coherent/incoherent scattering length of H₂, D₂, N₂, and O₂, the existence or nonexistence of guest molecules in 5¹² cages tends to provoke a significant change in the peak intensity/background level. The normalized integrated intensities of pure THF/binary THF clathrate hydrates are shown in Figure 3a–e. The THF + H₂ clathrate hydrate presents discrete thermal patterns with a degree of dissociation of H₂ with temperature (Figure S2), due to a considerably larger incoherent scattering cross section than those of other diatomic gases.¹⁹ In addition, unique on/off-like gas dissociation patterns were observed from the coherent scattering contributed parts. As shown in Figure 3, at approximately 150 K for H₂ and D₂ and roughly 200 K for N₂ and O₂, substantial changes of peak intensity occurred, which indicates the degassing process from 5¹² cages. Furthermore, depending on the coherent scattering cross section (σ_c) of the guest molecules (H₂ \approx 1.8, D₂ \approx 5.6, N₂ \approx 11, O₂ \approx 4.2 b),^{20–22} the relative integrated intensities of the thermal peak patterns exhibit a negative (H₂) and positive (D₂, N₂, and O₂) tendency, as shown in Figure 3e. Those different features result from the negative coherent scattering length of H₂, whereas other gases have the positive ones. However, the thermal expansivity before and after the degassing process, as shown in Figures 2 and S3, is not significantly changed. Thus, the tendency of thermal expansion appears to be “memorized” from previous history.

Thus far, we explored the thermal behavior of sII clathrate hydrates with diatomic guests and observed that the expanded lattices failed to recover their original state by contraction. The host–water cage dimension after degassing the guest molecules remains expanded, which will alter the host–guest as well as guest–guest interactions if guest uptake reoccurs. Accordingly, it is anticipated that the resulting guest occupancy and thermodynamic stability will be substantially changed after thermal history. Nevertheless, more experiments using various types of guests via several thermal cycles are needed to reveal further details. The present approach, which can be applied to tune the cage dimension, could potentially be useful for application to gas storage.

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Supporting Information Available: Sample preparation and experimental procedure details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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