Structural changes and intermolecular interactions of filled ice Ic structure for hydrogen hydrate under high pressure

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Abstract. High-pressure experiments of hydrogen hydrate were performed using a diamond anvil cell under conditions of 0.1-44.2 GPa and at room temperature. Also, high pressure Raman studies of solid hydrogen were performed in the pressure range of 0.1-43.7 GPa. X-ray diffractometry (XRD) for hydrogen hydrate revealed that a known high-pressure structure, filled ice Ic structure, of hydrogen hydrate transformed to a new high-pressure structure at approximately 35-40 GPa. A comparison of the Raman spectroscopy of a vibron for hydrogen molecules between hydrogen hydrate and solid hydrogen revealed that the extraction of hydrogen molecules from hydrogen hydrate occurred above 20 GPa. Also, the Raman spectra of a roton revealed that the rotation of hydrogen molecules in hydrogen hydrate was suppressed at around 20 GPa and that the rotation recovered under higher pressure. These results indicated that remarkable intermolecular interactions in hydrogen hydrate between neighboring hydrogen molecules and between guest hydrogen molecules and host water molecules might occur. These intermolecular interactions could produce the stability of hydrogen hydrate.

1. Introduction
Hydrogen hydrate is of great interest because it is crucial to numerous problems in planetary sciences, environmentally clean energy conversion, and fundamental chemistry and physics. At 249K and 220 MPa, structure II (sII) hydrogen clathrate hydrate crystallizes from a mixture of H2-H2O system [1]. In the sII, four hydrogen molecules forming a cluster are contained in the large cages of clathrate structure [1, 2]. As for the small cages, it was reported that two hydrogen molecule is contained in the small cages [1]. While, another study of D2 hydrate by neutron diffraction experiments reported that one hydrogen molecule is contained [2]. At any rate, the sII structure possesses high hydrogen content. Thus, the sII is attractive as a hydrogen-storage material. At room temperature, filled ice structures for hydrogen hydrate, filled ice II structure and filled ice Ic structure (FIIcS), are formed [3-5]. The filled ice II structure and the FIIcS are formed by including the hydrogen molecules in to ice II and ice Ic structure, respectively. The FIIcS also resembles the ice VII structure. Ice VII structure consists of two interpenetrating ice Ic structures, and the FIIcS is recognized as an ice VII structure in which one ice Ic structure completely replaced by hydrogen molecules (Figure. 1) [3]. The molecular ratios of hydrogen molecules to water molecules for the filled ice II structure and FIIcS are 1:6 and 1:1,
respectively. The authors of previous studies reported that the filled ice II structure was synthesized at around 0.8 GPa at room temperature. Then, the filled ice II structure was transformed to the FIIcS at 2.3 GPa [3-5]. The FIIcS was reported to be maintained to 60 GPa [4].

![Figure 1](image.png)

**Figure 1.** Structural models of (a) ice VII structure; and (b) the FIIcS illustrated from the structural analysis [3]. The blue and green spheres indicate the oxygen atoms of water molecules and form ice Ic structures. The forms of these ice Ic structures between the blue and green spheres are not different. Ice VII structure consists of two interpenetrating ice Ic structure (a). The red spheres indicate the hydrogen atoms of hydrogen molecules. The FIIcS is recognized as an ice VII structure in which one ice Ic structure replaced by hydrogen molecules (b). The hydrogen atoms of water molecules are omitted in these models.

The FIIcS of hydrogen hydrate shows a remarkable stability, although many other gas hydrates decompose lower pressure [6]. Thus, the intermolecular interactions for hydrogen hydrate may contribute to the stability. A previous high-pressure study of the filled ice structures for hydrogen hydrate in the pressure ranges of 0.2 to 8.0 GPa showed the possibility of the existence of intermolecular interactions between guest hydrogen molecules and framework water molecules affecting the stability [5]. However, the reasons for the stability of the FIIcS under higher pressure have not yet been explained. Also, phase changes in the FIIcS under high pressure have not yet been clarified. In this study, high-pressure experiments with hydrogen hydrate were carried out, and in situ x-ray diffractometry (XRD) measurements and Raman spectroscopy revealed the phase changes in the FIIcS under high pressure. Also, the Raman measurements of solid hydrogen were performed and the vibration modes for the FIIcS were compared with those for solid hydrogen. Then, the reasons for the stability were examined with regard to the intermolecular interactions.

2. **Experiment**

A lever-and-spring type diamond anvil cell (DAC) was used in the high-pressure experiments. For the pressure measurements, a ruby fluorescence method [7] and Sm: YAG fluorescence method [8] were used. Samples were loaded by filling the cell with distilled and deionized water and air bubbles. The DAC was placed in a gas loading vessel. Then the air bubbles were replaced by supercritical hydrogen fluid at 80 to 150 MPa. After the gas loading, the sample was compressed and hydrogen hydrate was formed by the reaction between water and fluid hydrogen. Optical microscopic observations, XRD, and Raman spectroscopy were conducted at room temperature. XRD experiments were performed using synchrotron radiation on BL18C at the Photon Factory of the High Energy Accelerator Research Organization (KEK). Raman spectroscopy was performed using the 514.5 nm line of an Ar ion laser. A single monochromator and CCD-detector were used.
3. Results

Figure 2 shows the representative XRD patterns with increasing pressure. The patterns were obtained from a sample with a composition of H₂O:H₂ = 70:30. At 5.3 GPa, the typical diffraction lines of the FIIcS for hydrogen hydrate (111, 220, 311, 400, and 331) were observed. Also, the diffraction lines of ice VII were observed because of the water rich sample. The diffraction lines of hydrogen hydrate became broader and weaker, but were observed to 44.2 GPa.

Prior to conducting the high pressure Raman measurements of hydrogen hydrate, it is necessary to find out what the vibration states of hydrogen molecules in a material formed by only hydrogen molecules are. Thus, high pressure experiments of solid hydrogen were performed in the pressure range of 4.0 to 43.7 GPa, and the vibration and rotation modes, vibron and roton, respectively, were examined. Figure 3 and Figure 4 show the Raman spectra of vibron and roton of the hydrogen molecules, respectively. At 4.0 GPa, the vibron of the fluid hydrogen was observed at around 4200 cm⁻¹ (Figure 3). At around 5.2 GPa, the solidification was observed under the optical microscopy. At 6.0 GPa, the vibron for solid hydrogen was observed at around 4210 cm⁻¹. The vibron shifted to higher frequencies with pressure. However, this trend stopped at around 30 GPa. Above 35 GPa, the vibron shifted to lower frequencies. This result showed good agreement with a previous study [9]. As for the roton, three modes of hydrogen molecules for fluid hydrogen were observed at around 360 cm⁻¹, 600 cm⁻¹ and 820 cm⁻¹ at 4.0 GPa (Figure 4). No changes in the frequencies were observed between fluid hydrogen at 4.0 GPa and solid hydrogen at 6.0 GPa. The frequencies of the roton were almost unchanged with pressure, although the peaks became broader. The highest frequency mode, 820 cm⁻¹, could not be observed above 25.2 GPa, while the other modes were observed up to at least 43.7 GPa. At 35.1 GPa, a new mode appeared at around 520 cm⁻¹ and this mode shifted to higher frequencies with pressure. This mode could be assigned to the lattice mode of solid hydrogen [10].
Figure 3. Representative Raman spectra of the vibron for solid hydrogen with pressure.

Figure 4. Representative Raman spectra of the roton for solid hydrogen with pressure. Open arrows indicate the lattice mode of solid hydrogen.

Figure 5. An optical micrograph of the sample and Raman spectra of the vibron for hydrogen hydrate. The composition of the sample was H$_2$O:H$_2$ = 70:30. The black arrow in the micrograph shows the region of the sample measured.
Figure 5 shows the Raman spectra of the vibron of the FIIcS for hydrogen hydrate and the optical micrographs of the sample with composition of H$_2$O:H$_2$ = 70:30. In the optical micrographs, the differences in the refractive index were observed, and they were considered to be induced by the differences in the relative amount of the FIIcS to ice VII. The right region and left region of the sample might be the FIIcS rich region and ice VII rich region, respectively. The spectra were obtained from the FIIcS rich region. At 14.6 GPa, the vibron for the FIIcS of hydrogen hydrate was observed at around 4320 cm$^{-1}$. The vibron of hydrogen molecules in the FIIcS shifted to higher frequencies with pressure. At 20.3 GPa, a new mode appeared at 4260 cm$^{-1}$ and this mode is in good agreement with that of solid hydrogen (Figure 3). Thus, it was considered that hydrogen molecules were extracted from the FIIcS and that solid hydrogen was formed by the extracted hydrogen, because the vibron of solid hydrogen was not observed below 20.3 GPa.

Figure 6 shows the representative Raman spectra of the roton for hydrogen hydrate with composition of the H$_2$O:H$_2$ = 70:30. The two modes of the roton were observed. Until 20.3 GPa, the modes of the roton were clearly observed. At 23.1 GPa, the intensity of the roton decreased. But at 27.2 GPa, the intensity of the roton became stronger again. In the case of solid hydrogen, roton of the hydrogen molecules clearly observed to 43.7 GPa shown at Figure 4. Thus, the decreasing of the intensity of the roton for the FIIcS was considered to be an intrinsic behavior. And, this result might indicate that the rotation of the hydrogen molecules in the FIIcS was suppressed at around 23 GPa.

4. Discussion
In the present XRD study, the diffraction lines of hydrogen hydrate were observed up to 44.2 GPa. This result suggested that hydrogen hydrate survived at least up to 44.2 GPa. Then, we attempted to analyze the FIIcS and check the indexing of hydrogen hydrate. When the indexing of the FIIcS was performed below 33.1 GPa, the deviations between the calculated and observed d-values were small such as less than 0.39 %. However, above 38.4 GPa, the deviations became larger, and the deviation grew to 1.68 % at 44.2 GPa. These results indicated that the indexing as the FIIcS was not appropriate above 38.4 GPa and that the FIIcS might transformed to a new high-pressure structure at around 38.4 GPa. In the previous study by the present authors, the structural changes of the FIIcS were reported to occur at around 35-40 and 55-60 GPa in the samples with a composition of H$_2$O:H$_2$ = 40:60 [11]. The present result showed that the water rich sample of the FIIcS with the composition of the H$_2$O:H$_2$ =
70:30 also transformed to the new structure at 35-40 GPa, although the new diffraction lines did not observed in this sample. At around 40 GPa, the intermolecular distance of host water molecules consisting the framework attained the critical distance of symmetrization of the hydrogen molecules [11]. Therefore, the structural change of the FIIcS was considered to be induced by the symmetrization of hydrogen bond for the framework water molecules. The symmetrization of hydrogen molecules could imply that water molecules dissociate to form an ionic crystal from hydrogen atoms and oxygen atoms. Thus, the structure of hydrogen hydrate might become stiffer after the symmetrization. This stiffness was considered to contribute to the stability of hydrogen hydrate.

Raman spectra of the roton for hydrogen hydrate showed that the intensity for the roton of the FIIcS decreased at around 23 GPa and that it increased again above 27.2 GPa. In the case of solid hydrogen, the roton of hydrogen molecules was clearly observed until 43.7 GPa (Figure 4). These results indicated that the rotation of the hydrogen molecules in the FIIcS suppressed at 23 GPa. And then, the rotation was considered to recover above 27 GPa. Because no structural changes were observed in these pressure ranges by the XRD experiments, this suppression of the rotation of hydrogen molecules in the FIIcS might occur without structural changes. In the previous study by the present authors, it was reported that the intensity of the roton decreased at 19.9 GPa, but it increased again at 23.2 GPa [12]. Although the pressure of weakening intensity did not agree, the change in the behaviour was similar between the previous and present studies. The compositions of the previous and present samples are H2O:H2 = 50:50 and H2O:H2 = 70:30, respectively, thus the differences in the pressure of weakening intensity could be induced by the difference of the compositions. The suppression of the rotation of hydrogen molecules might imply that hydrogen molecules were partly ordered. And then, the intermolecular interactions between neighboring hydrogen molecules and between guest hydrogen molecules and host water molecules might increase. These intermolecular interactions could produce the stability of the FIIcS. Actually, in the case of methane hydrate, the intermolecular interactions produced by the orientational ordering of the guest hydrogen molecules were considered to contribute to the stability of methane hydrate [13]. The hydrogen molecules in hydrogen hydrate, however, could not be fully ordered because of the quantum effect of hydrogen molecule, and thus the FIIcS might become unstable above 20 GPa. This instability might be relieved by the extraction of hydrogen molecules from the FIIcS (Figure 5). The extraction also induced the recovery of the rotation for the hydrogen molecules in the FIIcS above 27.2 GPa.

The present finding of the structural changes of the FIIcS for hydrogen hydrate leads to new developments in gas hydrates science. And, the detection of the intermolecular interactions which produced the stability of the FIIcS will help for a general understanding on gas hydrates stability.

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