

**Isotopic effect and amorphization of deuterated hydrogen hydrate under high pressure**Shin-ichi Machida,<sup>1,\*</sup> Hisako Hirai,<sup>1</sup> Taro Kawamura,<sup>2</sup> Yoshitaka Yamamoto,<sup>2</sup> and Takehiko Yagi<sup>3</sup><sup>1</sup>*Geodynamics Research Center, Ehime University, 2-5 Bunkyocho, Matsuyama, Ehime 790-8577, Japan*<sup>2</sup>*National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8569, Japan*<sup>3</sup>*Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha Kashiwa, Chiba 277-8581, Japan*

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High-pressure experiments of a mixture of H<sub>2</sub> and D<sub>2</sub>O were performed using a diamond-anvil cell in the pressure range of 0.5–77.0 GPa under room temperature. Raman measurements revealed that an exchange of the hydrogen atoms occurred between fluid hydrogen and liquid water before the formation of deuterated hydrogen hydrate, and that a high-pressure structure of hydrogen hydrate, a filled ice Ic structure, formed at the same pressure as H<sub>2</sub>-H<sub>2</sub>O system hydrate. Additionally, the Raman spectra of the vibron for the D<sub>2</sub>, HD and H<sub>2</sub> molecules revealed that the guest hydrogen molecules were partly extracted from the filled ice Ic structure above 20 GPa. The extraction of hydrogen molecules occurred depending on the atomic weight of the guest hydrogen molecules, and the heavier molecules were selectively released from the filled ice Ic structure. This isotopic effect in the extraction of hydrogen molecules showed differences in the stability of hydrogen hydrate depending on the species of guest molecules between D<sub>2</sub>, HD, and H<sub>2</sub>. Above 65 GPa, the filled ice Ic structure of hydrogen hydrate transformed to an amorphous phase. Formation of the amorphous phase showed the high-pressure limitation of hydrogen hydrate as a crystal structure and a new mechanism for the dissociation of gas hydrates under high pressure and room temperature.

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**I. INTRODUCTION**

Hydrogen hydrate is an inclusion compound consisting of a water-hydrogen system, with the host framework made up of hydrogen-bonded water molecules and guest hydrogen molecules trapped inside the framework.<sup>1–5</sup> Under high pressure and room temperature, two filled ice structures, filled ice II and filled ice Ic structures, are known to exist.<sup>1,2,6</sup> The filled ice II and Ic structures are formed by including the hydrogen molecules into ice II and ice Ic frameworks, respectively.<sup>1,2</sup> The filled ice II structure was synthesized at around 0.8 GPa from a mixture of water and hydrogen, and the filled ice II structure transformed to the filled ice Ic structure (FIICs) at 2.3 GPa. Previous high-pressure studies of the H<sub>2</sub>-H<sub>2</sub>O system by the present authors revealed that FIICs transformed to a high-pressure structure at 35–40 GPa.<sup>7</sup> This structural change might be induced by symmetrization of the hydrogen bond for the framework H<sub>2</sub>O molecules. In addition, this structure further transformed to a higher pressure phase at 55–60 GPa. This high-pressure phase was maintained at least up to 80.3 GPa.<sup>7</sup> Considering that many other gas hydrates decompose at lower pressure,<sup>8</sup> hydrogen hydrate shows remarkable stability under high pressure. This stability was considered to be produced by intermolecular interactions between the guest hydrogen molecules and the host water molecules.

In the Raman measurements in the H<sub>2</sub>-H<sub>2</sub>O system, the hydrogen molecules in FIICs freely rotate below 20 GPa and rotation of the hydrogen molecules is suppressed at around 20 GPa.<sup>9</sup> Above 20 GPa, the hydrogen molecules are partially extracted from FIICs and rotation of the hydrogen molecules in FIICs is recovered. These results indicate that close arrangement of FIICs, which suppressed the rotation of hydrogen molecules, was moderated by their extraction. Then, FIICs above 20 GPa became stable.<sup>9</sup> Considering that hydrogen molecules in solid hydrogen are orientationally

ordered under higher pressure such as 110 GPa,<sup>10</sup> suppression of the rotation of hydrogen molecules should be induced by the remarkable intermolecular interactions between guest hydrogen molecules and the host water molecules. However, reasons for these interactions in FIICs have not yet been clarified.

In the present study, high-pressure experiments of deuterated hydrogen hydrate, the H<sub>2</sub>-D<sub>2</sub>O system, were performed in order to detect the intermolecular interactions separately from the guest H<sub>2</sub> molecules and the host D<sub>2</sub>O molecules. X-ray-diffraction experiments and Raman measurements were performed in a pressure range of 0.5–77.0 GPa under room temperature, and the phase changes of FIICs were examined. These results were compared with those from the H<sub>2</sub>-H<sub>2</sub>O system,<sup>7,9</sup> and the isotopic effects in the structural and vibrational changes were clarified. Then, the intermolecular interactions in hydrogen hydrate with pressure were examined with regard to the isotopic effects.

**II. EXPERIMENT**

A lever-and-spring-type diamond-anvil cell (DAC) was used in the high-pressure experiments. For the pressure measurements, the ruby fluorescence method was used.<sup>11</sup> A sample was loaded by filling the cell with deuterated water and an air bubble. The cell was then placed in a glass dewar, and the air bubble replaced by liquid hydrogen under low temperatures such as 15–20 K.<sup>12</sup> After gas loading, the sample was compressed and hydrogen hydrate was formed by the reaction between deuterated water and hydrogen. A hydrogen and water composition of H<sub>2</sub>:D<sub>2</sub>O = 4:6 was prepared. The composition was estimated from the volumes of water and fluid hydrogen and the known molar volumes of the pure components.<sup>1,13</sup> Optical microscopic observations, Raman spectroscopy, and x-ray diffractometry were conducted

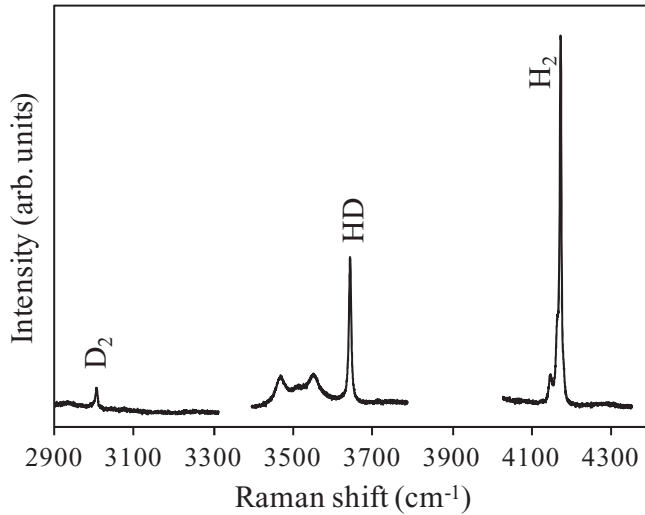


FIG. 1. Representative Raman spectra of the vibrons for the hydrogen molecules in the mixture of fluid  $H_2$  and liquid  $D_2O$  at 0.5 GPa. Spectra of the  $D_2$ , HD, and  $H_2$  vibrons are observed.

under room temperature. X-ray-diffraction experiments were performed using synchrotron radiation on a BL18C at the Photon Factory (PF) of the High Energy Accelerator Research Organization (KEK).

### III. RESULTS

Prior to the compression of samples, Raman measurements of the mixture of fluid  $H_2$  and liquid  $D_2O$  were performed. Figure 1 shows the Raman spectra for vibrons (vibrational modes) for the hydrogen molecules in fluid hydrogen at 0.5 GPa. The vibrons showed that fluid  $D_2$  and HD existed in the sample,<sup>14</sup> in addition to fluid  $H_2$ . Because the  $D_2$  and HD molecules were not loaded in the initial samples, the existence of  $D_2$  and HD molecules indicated that exchanges of hydrogen atoms occurred between the H atoms of fluid  $H_2$  and the D atoms of liquid  $D_2O$ .

With increasing pressure, water and fluid hydrogen were observed to react and to form the filled ice II structure at 0.8 GPa, and the filled ice II structure transformed to FIICs at 2.3 GPa. After the formation of FIICs, no phase changes were observed under optical microscopic observation up to 46.1 GPa. Figure 2 shows representative Raman spectra of the vibrons for the  $D_2$ , HD, and  $H_2$  molecules with decreasing pressure from 46.1 GPa. The frequencies of vibrons were clearly different from those of solid  $D_2$ , HD, and  $H_2$ .<sup>14</sup> Therefore these vibrons were considered to originate from the hydrogen molecules in FIICs. Furthermore, the Raman spectra showed that all species of hydrogen molecules,  $D_2$ , HD, and  $H_2$ , were included in FIICs. The vibrons for  $D_2$ , HD, and  $H_2$  in FIICs shifted to lower frequencies with decreasing pressure. Two additional modes were observed in lower frequencies than the  $D_2$  and HD vibrons in FIICs, respectively. These modes shifted to lower frequencies with decreasing pressure and disappeared at 7.4 GPa. The additional modes were considered to be from the solid  $D_2$  and HD molecules. Furthermore, at 7.4 GPa, these solid  $D_2$  and HD were considered to be absorbed

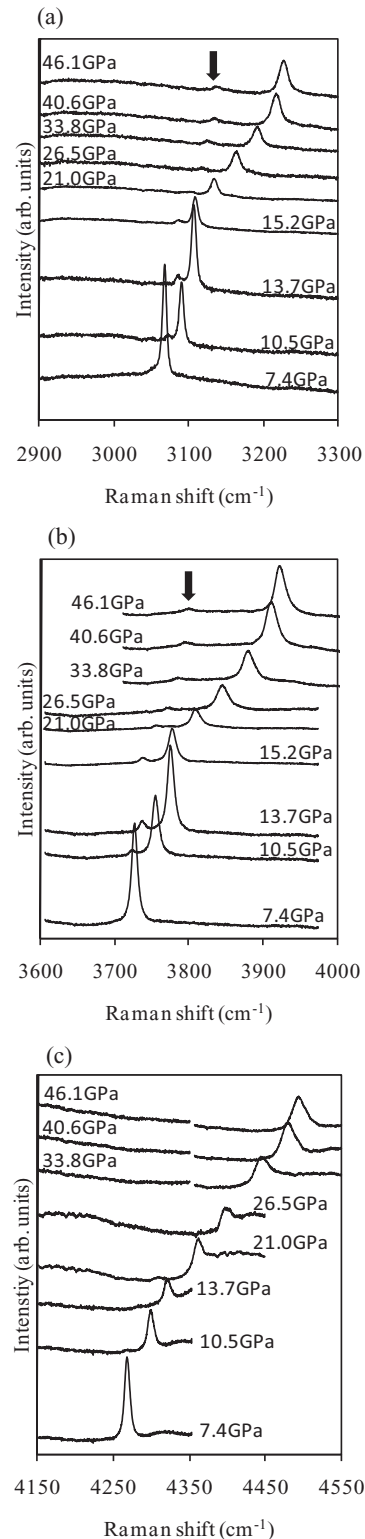


FIG. 2. Representative Raman spectra of the vibrons with decreasing pressure from 46.1 to 7.4 GPa for (a)  $D_2$ , (b) HD, and (c)  $H_2$  molecules. At 46.1 GPa, vibrons for the  $D_2$ , HD, and  $H_2$  molecules in FIICs for hydrogen hydrate were observed at around  $3230\text{ cm}^{-1}$  (a),  $3925\text{ cm}^{-1}$  (b), and  $4495\text{ cm}^{-1}$  (c), respectively. These vibrons shifted to lower frequencies with decreasing pressure. Solid arrows at around  $3140\text{ cm}^{-1}$  (a) and  $3800\text{ cm}^{-1}$  (b) at 46.1 GPa indicate the vibrons for solid  $D_2$  and HD, respectively. The vibron for solid  $H_2$  was not observed in the present Raman measurements (c).

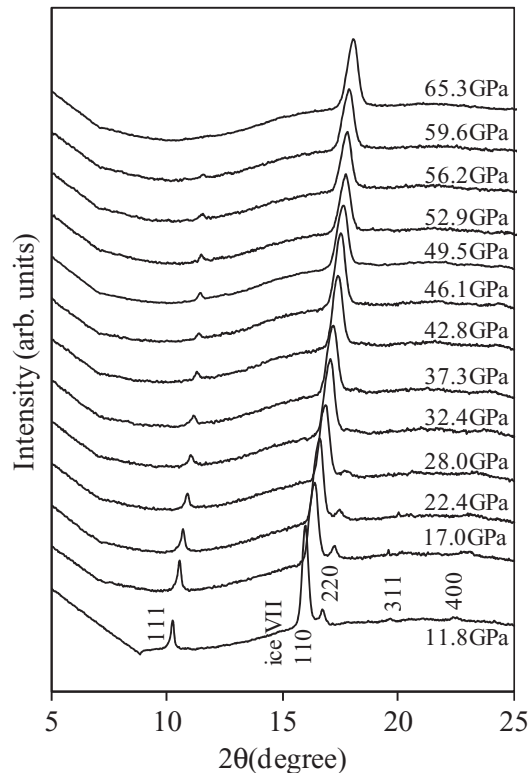


FIG. 3. Representative x-ray-diffraction patterns of hydrogen hydrate in the  $\text{H}_2\text{-D}_2\text{O}$  system from 11.8 to 65.3 GPa. The x-ray wavelength is 0.6163 Å. At 65.3 GPa, the x-ray-diffraction lines from hydrogen hydrate disappeared.

into FIICs. In contrast, the vibron of solid  $\text{H}_2$  was not observed in the present Raman measurements.

Figure 3 shows representative x-ray-diffraction patterns for  $\text{H}_2\text{-D}_2\text{O}$  hydrogen hydrate. At 11.8 GPa, typical diffraction lines of FIICs (111, 220, 311, 400), as well as ice VII (110), were observed. The diffraction lines of FIICs became broader and weaker with increasing pressure, and only two lines of FIICs (111, 220) were observed at 37.3 GPa. Above 42.8 GPa, only one line of FIICs (110) was observed. At 65.3 GPa, no diffraction lines of FIICs for hydrogen hydrate were observed. These results were clearly different from the  $\text{H}_2\text{-H}_2\text{O}$  system.<sup>7</sup> In the case of the  $\text{H}_2\text{-H}_2\text{O}$  system, the x-ray-diffraction patterns of FIICs changed above 40 GPa; a splitting of the 220 and 111 diffraction lines was observed at 40.5 and 67.9 GPa, respectively, and four diffraction lines were clearly observed up to 80.3 GPa.<sup>7</sup> Thus the disappearance of diffraction lines observed by the present x-ray-diffraction experiments in the  $\text{H}_2\text{-D}_2\text{O}$  system showed that isotopic effects existed in the phase changes of hydrogen hydrate above 40 GPa while the disappearance of diffraction lines for hydrogen hydrate indicated that a phase change occurred above 65 GPa and that the crystal structure of FIICs for hydrogen hydrate might break down.

In order to examine the phase change above 65 GPa in the  $\text{H}_2\text{-D}_2\text{O}$  system, another Raman measurement with decreasing pressure from 77.0 GPa was performed. Figures 4 and 5 show the Raman spectra of the vibron for  $\text{H}_2$  molecules and variations of the Raman frequencies for  $\text{H}_2$  vibron with pressure, respectively. The vibron of the  $\text{H}_2$  molecules in the

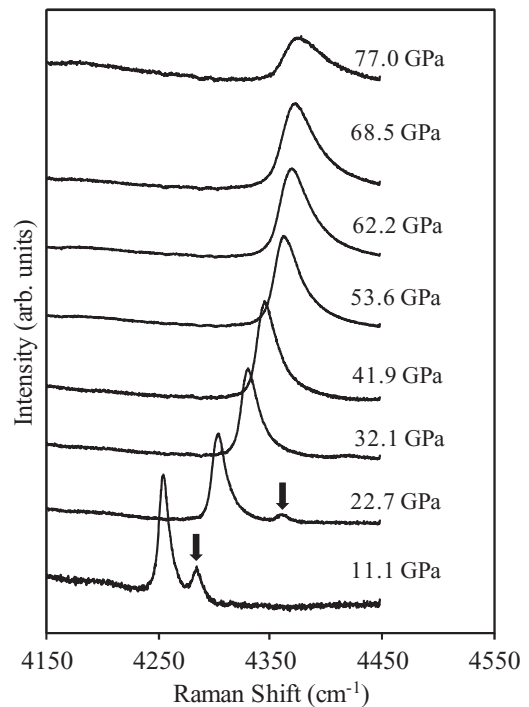


FIG. 4. Representative Raman spectra of the vibron for  $\text{H}_2$  molecules in the  $\text{H}_2\text{-D}_2\text{O}$  system with decreasing pressure from 77.0 to 11.1 GPa. The vibron spectra were considered to originate from the  $\text{H}_2$  molecules in the amorphous phase for hydrogen hydrate. Solid arrows indicate the Raman spectra for  $\text{H}_2$  vibron from nonamorphized FIICs.

new phase was observed at around  $4370\text{ cm}^{-1}$  at 77.0 GPa, and the vibron shifted to lower frequencies with decreasing pressure. At around 40 GPa, the Raman frequency of the vibron became around  $4340\text{ cm}^{-1}$ , and this vibron was observed at lower frequencies, by  $120\text{ cm}^{-1}$ , than that in FIICs (Fig. 2). The Raman spectra of the vibron from 77.0 GPa continued to be observable at lower frequencies than FIICs down to 11.1 GPa, indicating that the observed phase change from FIICs to the new phase above 65 GPa was not reversible. At 22.7 GPa, an additional peak was observed at around  $4360\text{ cm}^{-1}$  (Fig. 4). The Raman frequency of this peak corresponded to that for FIICs. Thus the additional mode was considered to be the vibron for the unreacted FIICs.

#### IV. DISCUSSION

In the Raman measurements, an exchange of hydrogen atoms occurred between fluid  $\text{H}_2$  and liquid  $\text{D}_2\text{O}$  before the formation of hydrogen hydrate. The filled ice II structure and FIICs were formed at 0.8 and 2.3 GPa, respectively, and the transition pressures of the filled ice structures for hydrogen hydrate in the  $\text{H}_2\text{-D}_2\text{O}$  system were the same as in the  $\text{H}_2\text{-H}_2\text{O}$  system. Thus there was no isotopic effect in the transition pressures of the filled ice structures. However, some isotopic effects were observed under higher pressures in the Raman measurements and x-ray-diffraction experiments.

In the Raman measurements, vibrons of solid  $\text{D}_2$  and HD were observed (Fig. 2), in addition to the vibrons for the

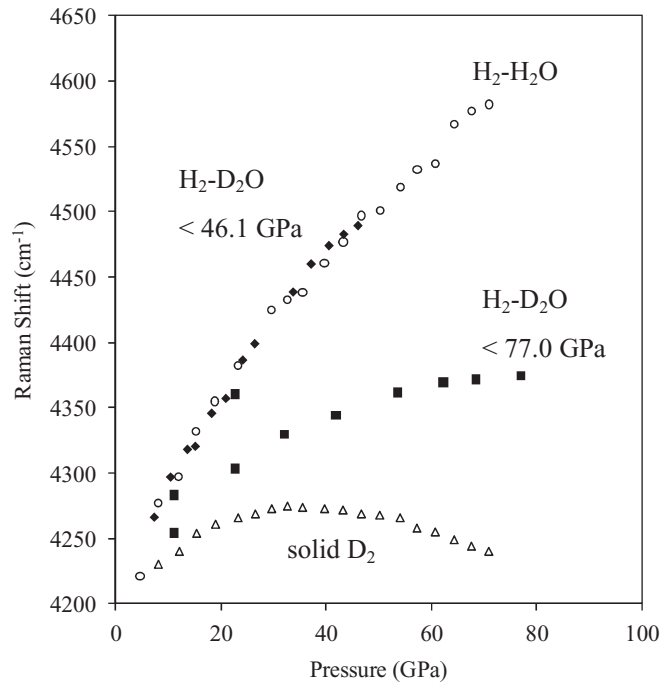


FIG. 5. Variations of the Raman shift of the vibron for the  $\text{H}_2$  molecules with pressure. Black rhombuses and squares indicate the  $\text{H}_2$  vibrons in the  $\text{H}_2\text{-D}_2\text{O}$  samples from 46.1 GPa and 77.0 GPa, respectively, observed in the present experiments. Open circles and triangles indicate the  $\text{H}_2$  vibrons in FIICs for the  $\text{H}_2\text{-H}_2\text{O}$  sample (Ref. 9) and solid hydrogen (Refs. 10 and 14), respectively. The frequencies of the vibron for  $\text{H}_2$  molecules in the  $\text{H}_2\text{-D}_2\text{O}$  system were different depending on the maximum pressure of the experiments.

$\text{D}_2$ , HD, and  $\text{H}_2$  molecules in FIICs. These solid  $\text{D}_2$  and HD were considered to be formed by the extracted hydrogen molecules from FIICs. In the  $\text{H}_2\text{-H}_2\text{O}$  system, the extraction of guest  $\text{H}_2$  molecules actually occurred above 20 GPa.<sup>9</sup> We considered this extraction of hydrogen molecules to be a stabilization mechanism of FIICs for hydrogen hydrate. In hydrogen hydrate, FIICs assumes a very close arrangement with molecules under high pressure, such as 20 GPa. Consequently, the rotation of the hydrogen molecules in FIICs is suppressed by this close arrangement. The instability of FIICs that this close arrangement induces is moderated by the extraction of hydrogen molecules from FIICs, in which case rotation of the hydrogen molecules in FIICs recovers.<sup>9</sup> As for the  $\text{H}_2\text{-D}_2\text{O}$  system, stabilization by extraction of hydrogen molecules was also observed in the present Raman measurements. The  $\text{D}_2$  and HD molecules were extracted from FIICs in experiments in which the pressure increased. With decreasing pressure, the extracted  $\text{D}_2$  and HD molecules were absorbed into FIICs. The extraction and absorption of  $\text{D}_2$  and HD molecules for FIICs were consistent with the results of the  $\text{H}_2\text{-H}_2\text{O}$  system. On the other hand, because no solid  $\text{H}_2$  vibron was observed in the  $\text{H}_2\text{-D}_2\text{O}$  system experiments,  $\text{H}_2$  molecules were not released from FIICs. Therefore it was clarified that the extraction of hydrogen molecules from FIICs depends on atomic weight and heavier molecules are selectively released from FIICs. In other words, the remaining lighter  $\text{H}_2$  molecules in FIICs produced the stability of hydrogen hydrate. The present Raman results showed differences in the stability of FIICs depending on the

species of guest molecules between  $\text{D}_2$ , HD, and  $\text{H}_2$ . This isotopic effect was considered to be induced by the difference in the intermolecular interactions between guest and host. In previous studies, it was reported that hydrogen molecules in FIICs for hydrogen hydrate interact with the host framework water molecules and that the vibrational states of hydrogen and water molecules change.<sup>1,9</sup> The hydrogen molecules in  $\text{D}_2$ , HD, and  $\text{H}_2$  molecules have different vibrational states, vibron and roton.<sup>14,15</sup> The  $\text{D}_2$ , HD, and  $\text{H}_2$  molecules in FIICs for hydrogen hydrate were also considered to produce different vibrational interactions with the host framework. These different intermolecular interactions between guest molecules ( $\text{D}_2$ , HD, and  $\text{H}_2$ ) and host molecules might induce the isotopic effects in the high-pressure behaviors of deuterated hydrogen hydrate.

The vibrational states of the  $\text{H}_2$  molecules in hydrogen hydrate for the  $\text{H}_2\text{-D}_2\text{O}$  system showed that the frequencies of the vibron for  $\text{H}_2$  molecules in the  $\text{H}_2\text{-D}_2\text{O}$  system were different depending on the maximum pressure of the experiments (Fig. 5). In the case of the decreasing pressure experiment from 46.1 GPa, the Raman frequencies of the vibron for the hydrogen molecules showed agreement with those in FIICs of hydrogen hydrate. This result indicates that FIICs of hydrogen hydrate was maintained up to at least 46.1 GPa. On the other hand, the Raman spectrum of the vibron at 77.0 GPa appeared at a lower frequency than that from FIICs.<sup>9</sup> Also, this Raman frequency was different from that for solid hydrogen.<sup>10,14</sup> These results clearly show that the hydrogen molecules in the  $\text{H}_2\text{-D}_2\text{O}$  system assumed different vibrational states from FIICs and solid hydrogen. The present x-ray-diffraction experiments showed that no diffraction lines of hydrogen hydrate were observed at 65.3 GPa, indicating that the crystal structure of hydrogen hydrate might break down. Since the frequencies of the  $\text{H}_2$  vibron in hydrogen hydrate were different from those of solid hydrogen, the phase change observed in the x-ray-diffraction experiments was not induced by the decomposition of FIICs into solid hydrogen and ice. Therefore this phase change was considered to form an amorphous phase above 65 GPa. The formation of the amorphous phase for hydrogen hydrate could explain why the phase change above 65 GPa was not reversible.

In general, the crystal structures of gas hydrates decomposed into ice and a solid crystal from the guest molecules when the crystal structures of gas hydrates became unstable to dissociate under high pressure. On the other hand, decomposition of hydrogen hydrate was not observed in the present  $\text{H}_2\text{-D}_2\text{O}$  system, but amorphization was observed. These differences in behavior under high pressure between hydrogen hydrate and other gas hydrates are considered to relate to the dissociation pressure of gas hydrates. In the case of argon hydrate and krypton hydrate, the dissociation pressures are lower than hydrogen hydrate, e.g., below 6.5 GPa. The reconstruction of the ice VII structure is considered to have easily occurred, and thus decomposition of hydrates into ice and guest materials also occurs. Meanwhile, the crystal structure of hydrogen hydrate shows remarkable stability above 60 GPa, and symmetrization of the hydrogen bond for the host water molecules occurs at around 35–40 GPa. After symmetrization of the hydrogen bond, the water molecules dissociate to form an ionic material from hydrogen and oxygen atoms, and thus

the host framework becomes stiffer. The stabilized framework was considered to inhibit the reconstruction of ice VII structure under high pressure. This might cause the crystal structure of hydrogen hydrate to break down and form an amorphous phase instead of decomposing when the FIICs of hydrogen hydrate cannot be kept under high pressure.

The Raman frequencies of the vibron for hydrogen molecules in the amorphous phase in the H<sub>2</sub>-D<sub>2</sub>O system decreased continuously to 11.1 GPa with decreasing pressure (Fig. 5). This result indicates that no phase transition from the amorphous phase might occur to 11.1 GPa, a result which was clearly different from the amorphization of ice. In the case of ice, two different amorphous phases for H<sub>2</sub>O molecules are formed under low temperature. It has been reported that changes in pressure and temperature cause the transitions between two amorphous phases and also amorphous phases to crystal structure phases to occur.<sup>16</sup> In the present H<sub>2</sub>-D<sub>2</sub>O system, the amorphous phase formed above 65 GPa was kept until 11.1 GPa, and the amorphous phase of hydrogen hydrate showed stability under wide pressure ranges under room temperature. This result indicated that hydrogen molecules in the host framework might inhibit the transition. Thus it was considered that no transition from the amorphous phase for hydrogen hydrate to another amorphous phase or FIICs occurred, and that the decomposition to ice VII and solid hydrogen also did not occur. The present results suggest a

different mechanism for the dissociation of gas hydrates under high pressure. Also, we suggest the high-pressure limitation of hydrogen hydrate as a crystal structure in the H<sub>2</sub>-D<sub>2</sub>O system. In the case of the H<sub>2</sub>-H<sub>2</sub>O system, the crystal structure of hydrogen hydrate was maintained up to at least 80.3 GPa.<sup>7</sup> Thus a clearly isotopic effect exists in the high-pressure limitation as a crystal structure between the H<sub>2</sub>-D<sub>2</sub>O and H<sub>2</sub>-H<sub>2</sub>O systems. These results indicate that the intermolecular interactions in FIICs are significantly different between the H<sub>2</sub>-D<sub>2</sub>O and H<sub>2</sub>-H<sub>2</sub>O systems and that this difference of the intermolecular interactions induces the isotopic effect in the stability of the crystal structure for hydrogen hydrate. We were not able to clarify the intermolecular interactions in the present study. Therefore, in order to examine and quantify these interactions, other hydrogen hydrate experiments in other compositions and other systems must be performed in the future.

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