

Isotopic effects and intramolecular interactions in hydrogen hydrate under high pressure

Shin-ichi Machida[1]; Hisako Hirai[2]; Taro Kawamura[3]; Yoshitaka Yamamoto[3]; Takehiko Yagi[4]

[1] Life and Environmental Sci., Tsukuba Univ; [2] Geoscience, Tsukuba Univ.; [3] MHRL, AIST; [4] Inst. Solid State Phys, Univ. Tokyo

Filled ice structures of hydrogen hydrates, filled ice II and filled ice Ic, are formed under high pressure at room temperature. The filled ice II structure is synthesized at around 0.8 GPa, and the filled ice II structure transforms to the filled ice Ic structure at 2.3 GPa. The filled ice structure for hydrogen hydrate is maintained to at least 80.3 GPa. At about 35 to 40 GPa, symmetrization of hydrogen bond in the host water molecules was suggested to occur. This filled ice structure for hydrogen hydrate shows the outstanding stability under high pressure. Therefore, it is expected that intermolecular interactions which induce the stability for the filled ice structure might occur. However, the intermolecular interactions in the filled ice structure have not yet been clarified. In this study, high pressure experiments of deuterated hydrogen hydrate were performed, and the phase changes and the vibrational changes of the filled ice structures were examined. And, the results obtained from deuterated hydrogen hydrate were compared with those from H₂-H₂O hydrogen hydrate. Then, the isotopic effects and intermolecular interactions in the filled ice structure for hydrogen hydrate were examined.

A lever-and-spring type diamond anvil cell was used in the high-pressure experiments. The pressure was measured by ruby and Sm:YAG fluorescence methods. In the experiments of H₂-H₂O and H₂-D₂O systems, the samples were prepared by the reaction between water and supercritical hydrogen fluid. In the case of D₂-H₂O system, liquid deuterium cooled by liquid helium was loaded. In situ optical microscopy, X-ray diffractometry and Raman spectroscopy were performed to characterize the samples.

Raman spectra of H₂-D₂O system revealed that D₂ and HD molecules existed in the filled ice Ic structure. These results indicated that the replacement between the hydrogen atoms of framework water molecules and those of guest hydrogen molecules might occur. In the XRD measurements, the compressibility of the filled ice Ic structure for H₂-D₂O system was different with that of H₂-H₂O system. These isotopic effects observed in the Raman and XRD measurements could be induced by the differences of the intermolecular interactions between H₂-H₂O system and H₂-D₂O system.