Change in intramolecular vibration of hydrogen molecules and intermolecular interaction in hydrogen hydrate under high pressure

Shin-ichi Machida[1]; Hisako Hirai[2]; Takehiko Yagi[3]

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

Hydrogen hydrate is expected to become a clean energy. And hydrogen hydrate is thought to be one of the major components of outer planets and their moons. Hydrogen hydrates were synthesized under high pressure at room temperature as filled-ice type compounds, C1 and C2. C1 is synthesized above 0.8 GPa, and hydrogen molecules are contained in the H2O sublattice of ice II. C1 transforms to C2 at 2.4 GPa, Hydrogen molecules in C2 are contained in the H2O sublattice of ice Ic, and C2 is recognized as an ice VII structure in which one H2O sublattice is replaced by H2. This C2 of hydrogen hydrate can remain under pressure as high as 60 GPa. The reason for the stability has not yet been explained. In this study, high-pressure experiments of hydrogen hydrate were performed in a pressure range of 0.1 to 50 GPa at room temperature, and intramolecular vibration modes of hydrogen molecules in 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 method. The samples were synthesized by filling the gasket hole with water and H2. The optical microscopy, X-ray diffractometry (XRD) and Raman spectroscopy were performed for characterization.

Under the optical microscope, no change was observed after the transformation into C2 at 2.4 GPa. In the XRD pattern, the typical diffraction peaks of the C2 were observed from 2.4 GPa to 35.0 GPa. In the Raman spectra, the slope of the Raman shift versus pressure clearly changed at around 16 GPa and 40 GPa for vibron of hydrogen molecules. And at around 44 GPa, roton of hydrogen molecules almost disappeared.

The XRD patterns showed that C2 was kept up to 35 GPa, therefore, the change of the slope of Raman shift versus pressure was occurred without structural change. This change of intramolecular vibration was induced by the interaction between neighboring hydrogen molecules and between hydrogen molecules and water molecules. This interaction are considered to contribute to the remarkable stability.

From the O-O distance of the neighboring water molecules in the C2, the symmetrization of hydrogen bond could occur at around 40 GPa. Therefore, the changes of intramolecular vibration modes were induced by the symmetrization.

For the examination of intermolecular interaction in hydrogen hydrate and symmetrization of hydrogen bond, the neutron diffraction study of the hydrogen hydrate is expected.