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低温高圧下における水素ハイドレート低対称化のラマン分光による原因推定
A possible reason for forming tetragonal phase of hydrogen hydrates under low-T and high-P by Raman spectroscopy

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Hydrogen hydrates are composed of hydrogen-bonded host water molecules forming cages or ice frameworks that include guest hydrogen molecules. One type of hydrogen hydrate, filled-ice Ic structure (HH-C2), is thought to have cubic structure. High pressure experiments of HH-C2 at room temperature revealed that HH-C2 survived from 2.3 GPa up to at least 80.3 GPa with structural changes at around 40 and 60 GPa. The structural change at around 40 GPa was explained to be relating to symmetrization of the hydrogen bond in the host water molecules. Another experiment reported that the structure of HH-C2 persisted to 11 K at about 4 GPa.

An ab initio calculation predicted that the cubic structure of HH-C2 transforms to a tetragonal structure under high-pressure and low-temperature. Such phenomenon has not yet been experimentally examined. Recently, in situ X-ray diffractometry (XRD) confirmed that the cubic structure of HH-C2 transforms to a tetragonal structure at low-temperatures and high-pressures. So, in this study, in order to estimate the reasons for the transformation to the tetragonal structure, Raman measurements were performed for the vibrational and rotational modes of the guest hydrogen molecules under low-temperature and high-pressure.

Clamp-type diamond anvil cells (DAC) made of copper-beryllium was used. The DAC was cooled by liquid nitrogen in an open-flow DAC holder. The pressure and temperature ranges were 5.0 to 33.0 GPa and 90 to 300 K, respectively. For pressure measurements, a ruby ?uorescence method was used. For temperature measurements, alumel-chromel thermocouples were used. Initial samples were prepared by gas-loading method at ISSP, Tokyo University. The samples were characterized by optical microscopy and Raman spectroscopy manufactured by Photon Design.

The transformation of HH-C2 to a tetragonal structure was inferred to be produced by changes in the rotational or vibrational modes of the guest hydrogen molecules (referred as roton and vibron, respectively). At room temperature the vibron obtained from 5 to 33 GPa was consistent with the previous study. At lower temperatures, the slope of wavenumber of the vibron versus temperature was slightly changed at around 210 to 230 K in the case of 16 GPa. On the other hand, distinct split of roton S0(0) was observed at 173 K, 8 GPa. At 300 K the split of the roton S0(0) was expected to occur at around 20 GPa from the XRD study, but it was unclear possibly because of thermal disturbance. The pressure and temperature conditions at which the roton split occurred in the present Raman study were good agreement with those of phase boundary between the cubic and the tetragonal phase determined by the XRD study.

Hydrogen molecules in the cubic HH-C2 structure are thought to be rotationally disordered at lower pressure and higher temperature. The single roton peaks indicate disordered rotating state of hydrogen molecules. The splitting roton observed suggested that the rotational mode changed from the disordered (spherical) mode to ordered (ellipsoidal) one, which induced the deformation of the lattice, namely transformation to a tetragonal structure.

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