Phase changes of hydrogen and deuterated hydrates induced by guest orientational ordering

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Introduction and Method

A filled ice structure of hydrogen hydrate, C2, consists of ice Ic host framework and hydrogen molecules filled in the voids of the framework [1]. The symmetry of the structure has been thought to be cubic because of ice Ic host. A theoretical study, however, has predicted that the symmetry changes to tetragonal at low temperatures and higher pressures [2]. Our experimental study confirmed the lowering symmetry by X-ray diffraction (XRD) study, and also showed existence of a high pressure phase (HP-phase) above 40 GPa [3]. The reason for forming tetragonal structure has been inferred to be orientational ordering of guest hydrogen molecules [3], and so it is required to confirm this experimentally, as well as, to clarify the reason for HP-phase. In this study, hydrogen hydrate (H_2-H_2O) and deuterated hydrate (D_2-D_2O) were examined on vibration modes of the guest molecules and structural changes of the host framework using XRD and Raman spectroscopy in the range of 10-300K and 7-65GPa.

Results and Discussion

Raman spectroscopy for H_2-H_2O hydrate revealed that clear change in vibron, $Q_1(1)$ was not observed, but that distinct splits in roton, $S_{0(}0)$ was observed. The splitting of roton means that rotational symmetry of hydrogen molecules lowers from spherical to lowered symmetry, e.g. ellipsoidal one. This indicates that the free rotation is suppressed, in other words, orientational ordering (probably partially) takes place. Such orientational ordering of the guest molecules may lead to deform the cubic host structure to a tetragonal one.

For D_2-D_2O hydrate, additional splitting of diffraction line from the tetragonal structure and additional splitting of vivron besides roton were observed. The results indicate that the structure of HP-phase is lower than tetragonal one with further ordered state of guest molecules. The three phases of hydrogen hydrates observed in this study can be characterized by disordered, partially ordered, and fully ordered state of guest hydrogen molecules in a manner analogous to solid hydrogen.

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[2] Zhang *et al*. (2012) *J. Chem. Phys*. **137**, 084505.
[3] Hirai *et al*. (2012) *J. Chem. Phys*. **137**, 074505.