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MOLECULAR DYNAMICS STUDIES ON GUEST MOLECULES IN N_2-, O_2-CLATHRATE HYDRATE (ABSTRACT)

Shinichiro HORIKAWA[1], Hidenosuke ITOH[2], Katsuyuki KAWAMURA[3] and Takeo HONDOH[1]

[1]*Institute of Low Temperature Science, Hokkaido University, Kita-19, Nishi-8, Kita-ku, Sapporo 060*
[2]*Department of Applied Physics, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060*
[3]*Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Meguro-ku, Tokyo 152*

Air-hydrates found in deep parts of polar ice cores enclose ancient air as guest molecules. The behavior of gas molecules in clathrate structure cages is important to reveal past changes in the composition of the atmosphere. Recently, IKEDA *et al.* (Proceedings of Natural Gas Hydrate Symposium '96, 117, 1996) carried out polarized Raman spectroscopy measurements on single air-hydrate crystals and found that the intensity of stretching vibrational spectra of N_2 and O_2 molecules varied depending on crystal orientations with respect to the polarized plane of the incident laser beam. This result is attributed to the anisotropic arrangement of guest molecules in the crystal structure.

We carried out molecular dynamics simulation on N_2- and O_2-hydrate in order to understand the behavior of N_2 and O_2 guest molecules, using the KKY (KUMAGAI, KAWAMURA and YOKOKAWA, Mol. Sim., **12**, 177, 1994.) potential model. Taking advantage of this atom-atom potential model, we calculated intramolecular vibrational spectra in addition to the motion and orientation of whole molecules. We found that guest molecules in a large cage are distributed apart from the center and move around in the cage while those in a small cage were located at the center, and have a preferred orientation which lies on a crystallographic {111} plane. These two results can be explained in terms of the size difference of the two cages and the compressive distortion of small cages along the ⟨111⟩ direction. The vibrational spectra of the N_2- and O_2-stretching modes showed double maxima for those in large cages and a single maximum for those in small cages.

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