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Retraction

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Toshiaki Iitaka and Toshikazu Ebisuzaki 2004

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It has come to the attention of IOP Publishing that this article should not have been submitted for publication because it duplicates the authors' earlier paper (Toshiaki Iitaka and Toshikazu Ebisuzaki 1993 Methane hydrate under high pressure *Phys. Rev. B* **68** (2003) 172105).

It was included in the proceedings of the joint 19th AIRAPT and 41st EHPRG International Conference on High Pressure Science and Technology (Bordeaux, 7–11 July 2003) through an oversight. Therefore, this article has been retracted by IOP Publishing.

Filled ice structure of gas hydrates—a density functional study

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Abstract

The structural, electronic, and spectroscopic properties of a high-pressure phase of methane hydrate (MH-III) are studied by first-principles electronic structure calculations. A detailed analysis of the atomic positions suggests that *ionization* of hydrogen-bonded water molecules occurs around 40 GPa and *centring* or symmetrization of hydrogen bonds occurs around 70 GPa. These pressures are much lower compared with ionization around 55 GPa and centring around 100 GPa in pure ice. The transition may be observed with low-temperature IR/Raman spectroscopy of OH stretching modes or neutron diffraction.

(Some figures in this article are in colour only in the electronic version)

Methane hydrate (MH), known as *clathrate ice*, is a special class of ice that contains methane molecules in cages or networks of hydrogen-bonded water molecules. The low-pressure phase of methane hydrate (MH-I) has the sI structure of cages [1]. MH-I, abundant in the deep ocean, has been attracting the attention of industry as a key new energy resource material, whose amount is estimated to be twice as much as the total fossil fuel reserve [1].

MH is also known as an important material for understanding the mystery of the atmosphere of Titan, the largest satellite of Saturn. Conventional theory [2] could not explain the abundant methane gas in Titan's atmosphere because the MH-I inside Titan was assumed to decompose into water and methane around 1 or 2 GPa, and escape to the atmosphere to be photodecomposed in the early stage of Titan's history. To understand this mystery is one of the goals of Cassini-Huygens spacecraft, which started its journey in 1997 and will arrive at the Saturn system in 2004 [3].

On Earth, in 2001, Loveday *et al* [4, 5] discovered new phases of MH by x-ray and neutron diffraction experiments at high pressure: MH-I transforms to MH-II (sH cage structure) at 1 GPa, and then to MH-III phase (orthorhombic filled ice structure) at 2 GPa, which survives

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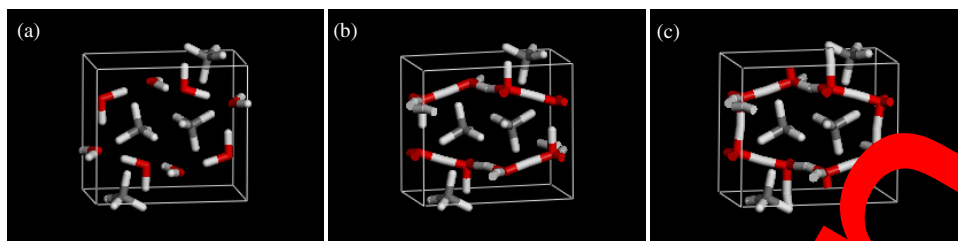


Figure 1. Crystal structure of MH-III: (a) 40 GPa; (b) 60 GPa; (c) 80 GPa.

at least up to 10 GPa. Other researchers reported similar high-pressure phases [6]. Recently, Hirai *et al* [8] reported that MH-III survives up to 42 GPa at room temperature. Shimizu *et al* [9] have measured the site and pressure dependence of CH- and OH-vibration frequencies in these phases up to 5.2 GPa. Discovery of these high-pressure phases allows for a new explanation of the abundant methane gas in Titan's atmosphere: methane is not reserved in thick layers of MH-III under Titan's surface and gradually escaped to the atmosphere from the reservoir [4].

In this paper, we focus on the features of MH-III as a promising material for investigating *centring* or symmetrization of hydrogen bonds between water molecules. The advantage of using MH-III for studying the centring is that it is expected to occur at much lower pressure than that of pure ice (ice VII–ice X transition) [10–12], which may make the difficult high-pressure experiments easier. In the following, we calculate the crystal structure and vibrational spectra of MH-III by using the density functional theory, so that we can predict and analyse experimental results.

We modelled the crystal structure of MH-III at 50 GPa by using the $Pm\bar{c}n$ symmetry, the lattice parameters and the positions of atoms determined by the diffraction experiment [5]. We chose the orientation of methane and water molecules so that the molecules become close packed. The model consists of four methane and eight water molecules in the unit cell, of which one methane and two water molecules are asymmetrically different. This structure was found to be stable after full geometrical optimization, in which the enthalpy $H = E + PV$ was minimized by varying the lattice vectors and the positions of atoms without any constraints such as crystal symmetry. The structures at high pressures (figure 1) were calculated in a similar manner.

The details of the electronic structure calculation [21] are as follows: the valence wavefunctions are expanded in a plane-wave basis set truncated at a kinetic energy of 1520 eV. The electron–ion interactions are described by the Vanderbilt-type ultrasoft pseudopotentials [22]. The effects of exchange–correlation interaction are treated within the generalized gradient approximation of Perdew *et al* (GGA-PBE) [23]. The Brillouin zones are sampled with $4 \times 2 \times 2$ Monkhorst–Pack k -points [24] by using time-reversal symmetry only. In the geometrical optimization, the total stress tensor is reduced to the order of 0.01 GPa by using the finite basis set corrections [5].

Figure 2 shows the pressure dependence of the calculated lattice parameters at zero temperature. It agrees with the experimental data at room temperature by Hirai *et al* [8]. The cell is the softest along the c -axis. This feature is also evident from figure 1. The compression of the cell along the c -axis is mainly caused by the flattening of the two graphite-like wrinkled sheets along the c -axis. As a result, the hydrogen-bond network at very high pressures becomes an sp_2 -like structure in contrast to the sp_3 structure of ice Ih.

In pure ice, centring of the hydrogen bond $O-H \cdots O$ occurs as the oxygen–oxygen distance $d(OO)$ decreases with pressure increase [10, 11]. At large $d(OO)$ the proton occupies

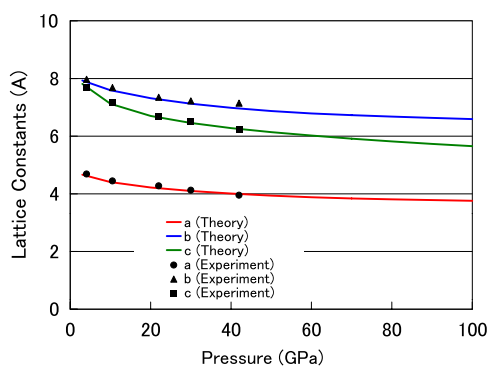


Figure 2. Lattice parameters: the solid curves indicate the present density functional theory calculation. The symbols indicate the experimental results of Hirai *et al* [8].

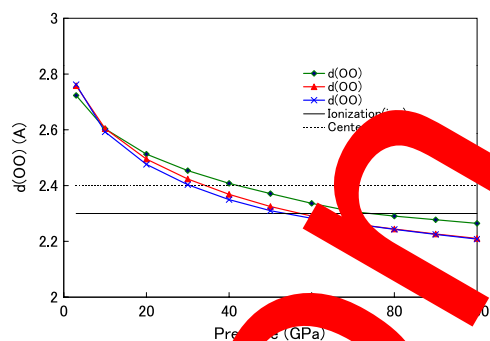


Figure 3. Three symmetrically different distances between oxygen atoms, $d(OO)$, as a function of pressure: the dashed and solid horizontal lines indicate the $d(OO)$ at which ionization and centring occur in pure ice, respectively [12].

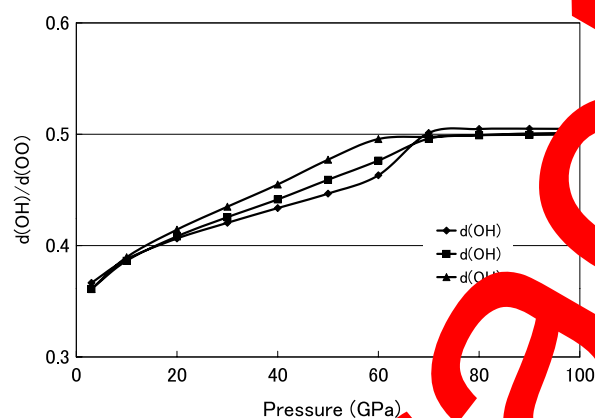


Figure 4. Hydrogen position: the ratio $d(OH)/d(OO)$ calculated by density functional theory is shown as a function of pressure.

one of two potential minima along the $O-H \cdots O$ bond. As $d(OO)$ becomes smaller the barrier between the two minima becomes lower. When $d(OO)$ becomes smaller than some critical distance, the proton occupies the single minimum at the midpoint between the two oxygen atoms (centring). In the following we neglect the effect of finite temperature and the quantum nature of the hydrogen atom unless otherwise stated. Figure 3 shows $d(OO)$ as a function of pressure. There are three curves corresponding to the three symmetrically different $O-H \cdots O$ bonds. Around 70 GPa $d(OO)$ values become sufficiently small for hydrogen-bond centring in pure ice [12]. Indeed, figure 1 shows that the centring occurs around this pressure. Figure 4 shows the ratio $d(OH)/d(OO)$ as a function of pressure. The ratio starts from 0.35 (water molecule) at 3 GPa and reaches 0.5 (centring) around 70 GPa.

Next we look into quantum effects. Benoit *et al* [12] recently proposed a *three-stage scenario* to explain the hydrogen-bond centring [13] of pure ice with increase of pressure at room temperature: ice stays in the *molecular state* under low pressures where H_2O remain water molecules; hydrogen atoms start to jump between two potential minima in the *ionized state* under medium pressures; finally, hydrogen atoms sit at the midpoints between two oxygen atoms in the *centring state* under high pressures. The $d(OO)$ at which ionization and centring occur in pure ice are indicated by dashed and solid horizontal lines in figure 3.

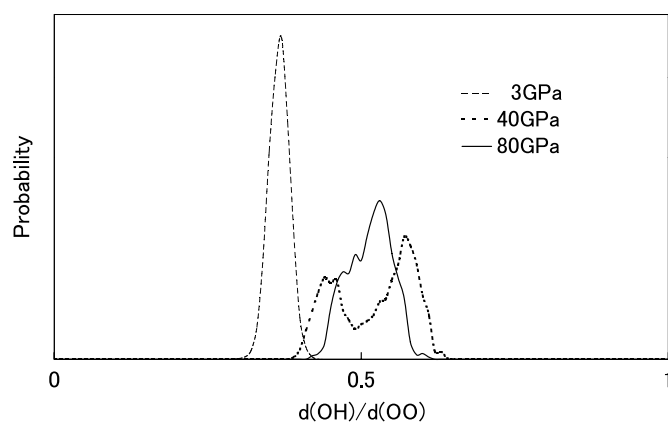


Figure 5. Distribution of hydrogen atoms in a hydrogen bond of MH-III at 30 K.

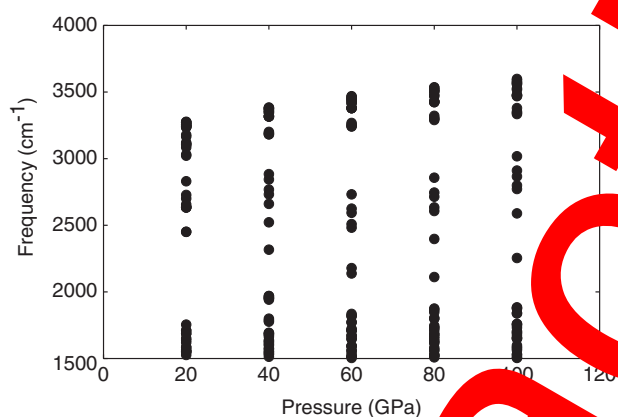


Figure 6. Normal mode frequencies calculated with the density functional linear response theory as a function of pressure.

From this figure we can read that the ionization and centring in MH-III are expected around 40 and 70 GPa, respectively. The probability distributions of $d(\text{OH})/d(\text{OO})$ for a hydrogen bond of MH-III at room temperature and with pressure 3, 40, and 80 GPa are calculated with Car–Parrinello molecular dynamics [26] (figure 5), which clearly shows that the *three-stage scenario* is also valid in MH-III but with much lower pressure than pure ice.

Figure 6 shows the pressure dependence of normal mode frequencies of MH-III calculated with the density functional linear response theory [27]. The modes between 3000 and 3500 cm^{-1} are the CH vibrations, whose frequencies monotonically increase with pressure. The modes between 2000–3000 cm^{-1} are OH-stretching modes. Their frequencies decrease monotonically up to 70 GPa, where centring occurs, and then start to increase. This tendency is qualitatively in accordance with that of pure ice [14].

In figure 7(a), vibrational spectra of MH-III at 3 GPa are calculated as a Fourier transform of the velocity–velocity correlation function obtained from Car–Parrinello molecular dynamics [26] and compared with the normal mode frequencies calculated with the density functional linear response theory [27]. The peak around 3100 cm^{-1} characteristic of OH-stretching vibration of hydrogen-bonded water molecules is prominent at 30 K but disappears at 300 K. This is in agreement with the experimental observation that the Raman peak around 3100 cm^{-1} appeared in MH-III at room temperature [9], and can be interpreted as the result of the strongly anharmonic potential. Figure 7(b) shows vibrational spectra of MH-III at 80 GPa. The OH-stretching modes of centred hydrogen bonds are located between 2000 and

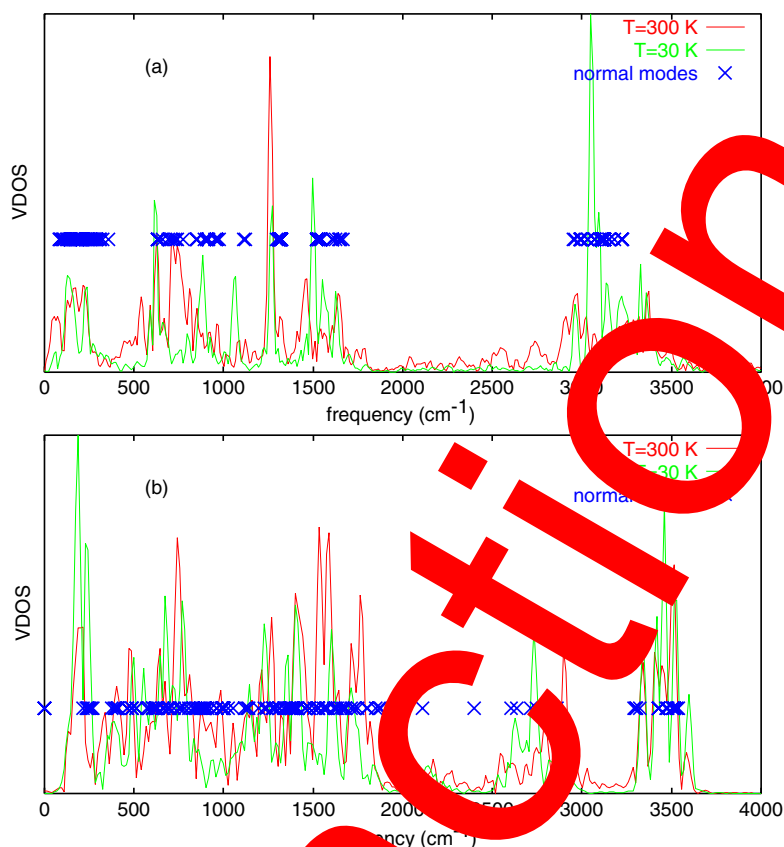


Figure 7. Vibrational spectra of MH-III at (a) 30 K and (b) 80 GPa calculated by Car–Parrinello molecular dynamics are compared with the normal mode frequencies calculated with the density functional linear response theory. The solid curve indicates the result of CPMD at 300 K, the dashed curve at 30 K, and crosses are normal mode frequencies calculated with the density functional linear response theory [27].



Figure 8. Phonon dispersion of MH-III at 80 GPa calculated with the density functional linear response theory [27].

300 cm^{-1} . At low temperature the peaks agree well with the normal modes, while the peaks are blue-shifted at high temperature probably due to weak anharmonicity. The disappearance of the peak of the OH-stretching mode in molecular and ionized states at room temperature and the survival of the peak due to the OH-stretching mode in the centred hydrogen bond in MH-III are analogous to those in ice VII and ice X [16].

Figure 8 shows the phonon dispersion of MH-III at 80 GPa calculated with the density functional linear response theory [27]. All frequencies at all wavenumbers have positive frequencies, indicating the mechanical stability of this structure at zero temperature. However, further experimental and theoretical studies are necessary to prove the thermal stability at room temperature.

In summary, we have studied the structural and spectral properties of the high-pressure phase of methane hydrate (MH-III) with density functional theory, and showed that ionization and centring of hydrogen bonds in MH-III may be observed around 40 and 70 GPa, respectively, which are much lower pressures than those of pure water ice. Therefore, MH-III may provide precious information about ionization and centring of hydrogen bonds between water molecules as the second example after pure ice. From the viewpoint of planetary science, studying physical and chemical properties of clathrate hydrates such as MH will become more and more important to interpret and to understand the information on the outer solar system sent from space missions such as the Cassini–Huygens spacecraft arriving at the Saturn system in 2004.

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