

Project Title:

First principles calculation of hydrogen hydrate

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I. Introduction

Ever increasing fossil energy consumption and associated global environmental concerns have provoked intensive searches for alternative energy resources. Hydrates of natural gases such as $\text{CH}_4\text{-H}_2\text{O}$ ¹⁻³ (the most abundant natural form of clathrate) prevailing in deep-sea sediments and permafrost have received active attention and been proposed as one of these energy resources⁴. An estimate of the global reserve of natural gas in the hydrate form buried in the permafrost and sediments underneath the continental shelf is significantly larger than that from traditional fossil fuels and will be a valuable future energy resource⁵. More recently, hydrogen hydrate is of great interest because it facilitates environmentally clean and highly efficient energy conversion. From astronomical point of view, water is known to be a major constituent of giant planets.⁶⁻⁹ The cores of Jupiter¹⁰ and Saturn¹¹ are believed to consist of a mixture of hot ices mostly water but also methane, ammonia, and rocks. It is also expected that Uranus and Neptune as well as some extrasolar planets contain major amounts of water in their envelopes.¹² ¹³ On the other side, hydrogen is the most abundant element in the universe, making up 75% of normal matter by mass and over 90% by number of atoms.¹⁴ Water and hydrogen under high pressure may form hydrogen hydrates. Therefore, study of water and hydrogen at high pressures has wide implications in astrophysics and knowing its physical properties is also important for understanding the structure and the formation history of these planets. The behavior of hydrates under pressure can also provide valuable

information on water–water interactions and interactions of water with a wide range of guest molecules. Furthermore, studying H_2O and H_2 mixtures may provide insight into the nature of hydrogen-rich atmosphere in the large-body interstellar ice embryos postulated to exist during planet formation.^{15, 16}

At present, three forms of hydrogen hydrates are known to exist stably in different conditions. The first one is a clathrate hydrate, sII structure,^{17, 18 19, 20 21} and the other two are filled-ice type compounds, C_1 and C_2 .²²⁻²⁵ The filled ice type compounds consist of a host ice structure which forms an H_2O sublattice and the hydrogen molecules contained in voids in the host ice structure. The hydrogen molecules in C_1 are located interstitially in ice II lattice and those in C_2 are in ice Ic lattice or can also be recognized by replacing one H_2O sublattice completely in ice VII structure ²² as displayed in Fig.1. The molecular ratios of hydrogen to water are 1:6 and 1:1 for C_1 and C_2 , respectively. Due to such high hydrogen content, especially for C_2 , these compounds are also considered to be potential candidates for hydrogen storage material, although their stable pressure regions are fairly high; i.e., C_1 and C_2 are synthesized above 0.8 and 2.4 GPa at room temperature, respectively. Thus, an attempt to stabilize C_2 under low pressure was made by lowering the temperature and its existence at 500 MPa and 77 K was reported.¹⁹ In particular, pressure-induced phase transitions were investigated using x-ray diffraction (XRD) and Raman spectroscopy.^{24, 25} In the low pressure region, C_2 hydrogen hydrate remains a cubic crystal structure and the structural transitions were

observed at approximately 35-40 and 55-60 GPa, and that the high-pressure phase can survive up to at least 80.3 GPa.²⁵ However, these two high-pressure phases are not yet determined by the experiments. On the other hand, research has focused on the behavior of hydrogen bond (H-bond) in materials under compression for many years. The pressure at which H-bond symmetrization occurs in C_2 was predicted to be considerably lower than that in ice VII through measurements of pressure dependence of both O-H frequency measured by Raman spectroscopy and the intermolecular O-O distance with X-ray diffraction up to 60 GPa of C_2 hydrogen hydrate.²³

Vibrational spectroscopy is one of the main materials characterization tools, since it can yield information about the form in which hydrogen is present in the material. However, the interpretation of vibrational spectra involves the assignment of the observed frequencies to microscopic atomic configurations, which is usually facilitated if there are theoretical predictions available for comparison. The vibron (intramolecular vibration mode) of hydrogen molecules is expected to reflect the interaction between hydrogen molecules and the surrounding water molecules and also may relate to the hydrate stabilities. Knowledge regarding the change of vibron frequency is also very useful for technology involving hydrogen, like Raman spectroscopy. Up to now, to our best knowledge, there is little theoretical report carried out on C_2 hydrogen hydrate under high pressure. Therefore, further theoretical studies were motivated in vibrational properties and pressure-induced phase transitions under compression.

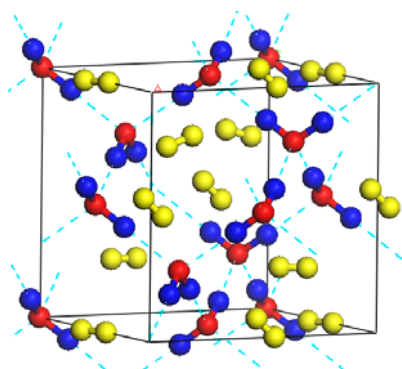


Fig. 1 A structural model of C_2 phase illustrated from the structural analysis (Ref. 10). The red balls represent oxygen atoms in water molecules, the blue balls indicate hydrogen atoms in water molecules, the yellow balls indicate the hydrogen atoms of the hydrogen molecules while the dashed lines indicate hydrogen bonds.

II. Computation methods

The molecular dynamics (MD) simulations at finite temperature and geometry optimization at 0 K were carried out by means of density functional theory (DFT) calculations using a pseudopotential plane wave approach implemented in Quantum-Espresso Package²⁶⁻²⁸ with ultrasoft pseudopotential using the functional of BLYP²⁹.

III. Results Summary

In this work, we have studied the vibrational properties and “predicted” structure after phase transition under pressure using first principles MD study. Experimentally reported ‘*cubic*’ structure was found not stable in the zero temperature simulation and it is the thermal effects playing an essential role in its stabilization below 30 GPa at room temperature. We proposed that the ‘*cubic*’ filled ice C_2 phase transformed into a tetragonal phase from 40 GPa and completed around 60 GPa in the MD simulation at 300 K, as shown in Fig. 2, which offers theoretical evidence for further experiments.

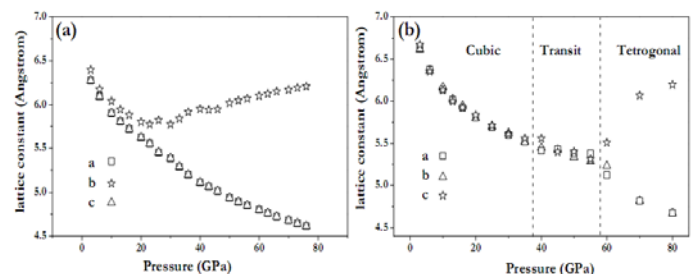


Fig. 2 Lattice constant evolution at 0K (left panel) and 300 K (right panel) as a function of pressure in which a , b , c was indicated as empty squares, triangles, and stars, respectively.

PDOS was extracted from Fourier analysis of the MD trajectories, which are in good agreement with experimental data. H-bond symmetrization was inferred to happen below 60 GPa from analysis of soft mode O-H vibrational frequency and radial distribution of $g(\text{OH})$ under compression. One interesting phenomenon is the pressure dependence of the intermolecular O-O distance is significantly larger in ice VII than in C_2 hydrogen hydrate. It appears that the relationship is in close agreement with those of ice VII at twice the pressure. Moreover, it indicates that the C_2 hydrogen hydrate serves as a model system for ice at pressures reduced by a factor two.

IV Future work

We are keen to extend our account in the next fiscal year and we almost finished most of the work in this project. Further detailed analysis of the vibrational properties need to be done.

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