

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. More recently, hydrogen hydrate is of great interest because it facilitates environmentally clean (water is the only by-product) and highly efficient energy conversion. From astronomical point of view, water is known to be a major constituent of giant planets.<sup>1-4</sup> The cores of Jupiter<sup>5</sup> and Saturn<sup>6</sup> 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.<sup>7, 8</sup> 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.<sup>9</sup> Water and hydrogen under high pressure may form hydrogen hydrate. Therefore, study of water and hydrogen at high pressure has wide implications in astrophysics and knowing its physical properties is also important for understanding the structure and the formation history of these planets. At present, three forms of hydrogen hydrates are known to exist stably in different conditions. The first one is a clathrate hydrate, sII structure,<sup>10, 11, 12, 13, 14</sup> and the other two are filled-ice type compounds, C<sub>1</sub> and C<sub>2</sub>. The filled ice type compounds consist of a host ice structure which forms an H<sub>2</sub>O sublattice and the hydrogen molecules contained in voids in the host ice structure. The hydrogen molecules in C<sub>1</sub> are located interstitially in ice II lattice and those in C<sub>2</sub> are in ice Ic lattice or can also be recognized by replacing one

H<sub>2</sub>O sublattice completely in ice VII structure<sup>15</sup> as displayed in Fig.1.

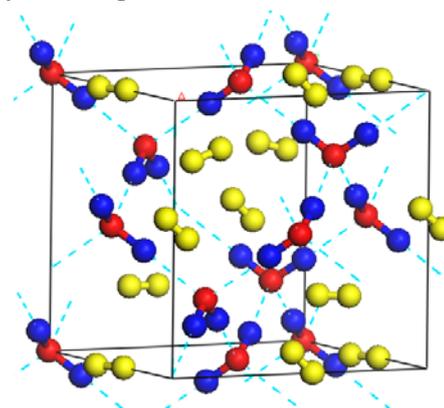


Fig. 1 (Color online) A structural model of C<sub>2</sub> phase illustrated from the structural analysis (Ref. 10). The red balls represent oxygen atoms in water molecules, the blue balls indicate hydrogen atoms in water molecules, the yellow balls indicate the hydrogen atoms of the hydrogen molecules while the dashed lines indicate hydrogen bonds.

In particular, pressure-induced phase transitions were investigated using x-ray diffraction (XRD) and Raman spectroscopy.<sup>16, 17</sup> In the low pressure region, C<sub>2</sub> hydrogen hydrate remains a cubic crystal structure and the structural transitions were observed at approximately 35-40 and 55-60 GPa and the high-pressure phase can survive up to at least 80.3 GPa.<sup>17</sup> However, these two high-pressure phases are not yet determined by the experiments. In ice, there are enormous investigations on proton ordering transitions in which ice I<sub>h</sub>/XI<sup>18-23</sup>, V/XIII, VI/XV, VII/VIII<sup>24-28</sup>, XII/XIV. Similarly, we would also like to study the proton ordering in the H<sub>2</sub>-H<sub>2</sub>O. 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<sub>2</sub> hydrogen hydrate under high pressure. Therefore, further theoretical studies were motivated in structural and vibrational properties under compression.

## 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 Package<sup>29-31</sup> with ultrasoft pseudopotential using the functional of BLYP<sup>32</sup>. These simulations are investigated with 8 water molecules and 8 hydrogen molecules at constant temperature of 300 K with pressure range from 3 GPa to 100 GPa. The simulations ran around at least 15 ps for all the pressure points with time step of 0.5 fs. We used a plane wave basis cutoff energy of 35 Ry and a 2×2×2 Monkhorst-Pack (MP) grid (*k*-mesh) for the electronic Brillouin zone integration. A more strict condition with cutoff energy up to 100 Ry and 9×9×6 MP grid was employed in the phonon calculation using the linear-response method.<sup>33</sup> In this work, we also used a dynamical approach to obtain the vibrational frequencies by analyzing the MD trajectories obtained from first-principle simulations, in which we can trace the evolution of the stretching frequencies with variation of the local environment during the dynamics. We have broadened the theoretical spectra with a Lorentzian of full width at half maximum FWHM = 30 cm<sup>-1</sup>. Another advantage of the method is that anharmonic effects, which can have an important contribution at high temperatures, are automatically included in the computed frequencies.

## III. Results and Discussions

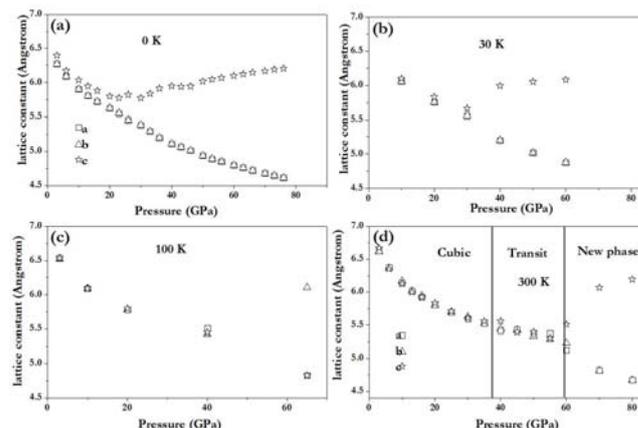


Fig. 2 Lattice constant evolution at 0K , 30K, 100K, and 300 K as a function of pressure in which *a*, *b*, *c* was indicated as empty squares, triangles, and stars, respectively.

The evolution of lattice constant (*a*, *b*, and *c*) under pressure in MD simulation was investigated in Fig. 2(b)-(d). There is obvious trend that the temperature stabilizes the ‘cubic’ structure from Fig. 2 (b) to Fig. 2 (d). It is easy to see that the structure is ‘cubic’ ( $a = b = c$ ) below 35 GPa and transit into ( $a = b < c$ ) symmetry which confirms the experimental structural change findings as illustrated in Fig. 5(d). The transition starts around 40 GPa evidencing by non-identical lattice constants and completely finish around 60 GPa. We double-checked with a larger cell MD run with 16 H<sub>2</sub>O molecules and 16 H<sub>2</sub> and similar results are achieved.

And then, we took one more step towards mapping the phase diagram of H<sub>2</sub>-H<sub>2</sub>O as illustrated in Fig. 3. Considering the hydrogen bond network orderd (disordered) or the H<sub>2</sub> rotation (non-rotation) in the influence of temperature, there are going to be four combinations. For the H<sub>2</sub> rotation phase and non-rotation phase, it is easy to observe from the trajectory movie. For the phase boundary line between hydrogen bond ordered-disordered phases, we could roughly estimate from formula  $\Delta G = TS = k_b \ln(3/2)T$ . Hence, the transition temperature from hydrogen bond ordered phase to the disordered phase lies around 29 K which is similar to the ice I<sub>b</sub>-XI transition (around 72 K).<sup>34</sup>

Since the configuration entropy does not depend on the pressure, so this phase boundary line is parallel to the pressure axis. From the experimental point view, neutron diffraction might be the effective tool to determine the hydrogen bond ordered phase of  $\text{H}_2\text{-H}_2\text{O}$  which showed great success in the host lattice ice system, i.e. ice VIII<sup>25, 28, 35</sup>, ice XI<sup>19, 21, 34, 36</sup>, ice XIII and ice XIV<sup>37</sup>, ice XV<sup>38</sup>. We proposed to use Raman spectra to measure the  $\text{H}_2$  roton frequency to determine the  $\text{H}_2$  rotation-nonrotation phase boundary which was commonly used in this hydrogen hydrate system.<sup>14, 15, 17, 39-41</sup>

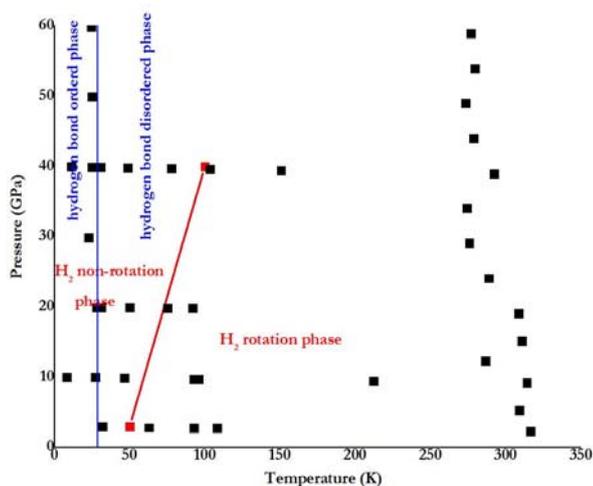


Fig. 3 Phase diagram of  $\text{H}_2\text{-H}_2\text{O}$ 's four possible states and all the (P,T) conditions in our MD simulation shown in solid squares.

### B. H-bond symmetrization

The symmetrization of H-bond in ice is intimately related to the quantum motion of protons and has been one of the major subjects in chemistry and physics of ice for over a half century.<sup>42-45</sup>

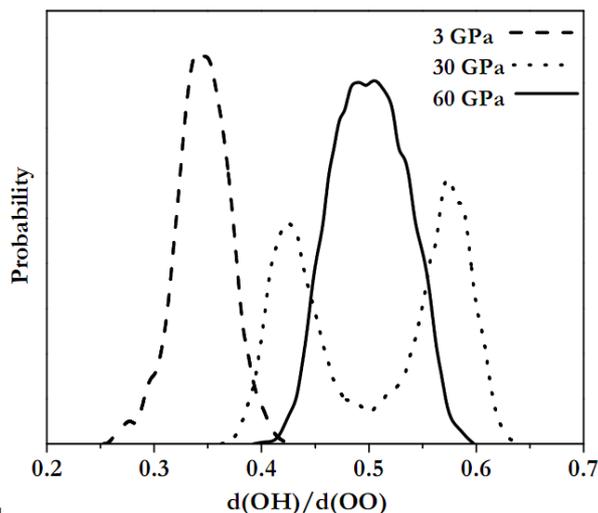


Fig. 4

bond of  $\text{C}_2$  hydrogen hydrate at 300 K and 3, 30, 60 GPa, respectively.

We further investigate the thermal hopping behavior of the hydrogen atoms, we plotted the probability distribution of hydrogen atom along a hydrogen bond at room temperature. Benoit *et al*<sup>46</sup> proposed a three stage scenario theory for illustrating the H-bond symmetrization of pure ice with increasing pressure in which under low pressure the ice is a molecular state with normal H-bond, then under medium pressure hydrogen atoms start to jump between two potential minimum (deep tunneling region or ionization), finally under high pressure hydrogen atoms move to the midpoint between two neighboring oxygen atoms (symmetrization). From Fig. 10, the probability distribution of  $d(\text{OH})/d(\text{OO})$  clearly shows that the three-stage scenario is also valid for hydrogen hydrate as it was shown for methane hydrate<sup>47</sup>.

## IV. Summary

In this work, structural changes, phase diagram, and vibrational properties were investigated using first principles MD. 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. A new phase is also observed in the room temperature simulation which

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confirms the experimental finding. Furthermore, phase diagram of four phases (hydrogen bond ordered-disorder, H<sub>2</sub> rotation-nonrotation) was estimated at a first approximation which could provide hints for further experiments

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**Fiscal Year 2011 List of Publications Resulting from the Use of RICC**

**[Oral presentation at an international symposium]**

*(Oral Presentation)* Jingyun Zhang and Jer-lai Kuo, Toshiaki IITAKA, "First principles molecular dynamics study on filled ice hydrogen hydrate under pressure" Sep.5-10, 2010, 12th International Conference on the Physics and Chemistry of Ice, Sapporo, Japan.

**[Others]**

*(Poster Presentation)* Jingyun Zhang, Jer-Lai Kuo, Toshiaki Iitaka "First principles molecular dynamics study on filled ice hydrogen hydrate under pressure", Nov. 7-12, 2010, 5th Asian Conference on High Pressure Research, Japan.