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. Hydrogen hydrate has been proposed as one of these resources of energy because it facilitates environmentally clean and highly efficient energy conversion. On the other side, water is known to be a major constituent of giant planets.[1] The cores of Jupiter and Saturn are believed to consist of a mixture of hot ices mostly water but also methane and 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.[2] The knowledge of water and hydrogen at high pressures has wide applications in astrophysics. Water and hydrogen have been found also in the outer solar system. In addition to energy applications, studying H2 and H2O mixtures may provide insight into the nature of hydrogen-rich atmosphere in the large-body interstellar ice embryos postulated to exist during planet formation.[3] Some of them may consist of water, hydrogen and other elements. Water and hydrogen under high pressure may form hydrogen hydrate. Therefore knowing its physical properties is important for understanding the structure and formation history of these planets

At the present, three hydrogen hydrates are known to exist stably under high pressure. One is a clathrate hydrate, sII structure,[4] [5,6] [7]and the other two are filled-ice type compounds, C1 and C2.[8-10] The filled ice type compounds consist of a host ice structure which forms an H2O sublattice and the hydrogen molecules contained in voids in the host ice structure. The hydrogen molecules in C1 are located interstitially in ice II lattice and those in C2 are in ice Ic lattice or can also be recognized by replaced one H2O sublattice completely in ice VII structure, as displayed in Fig.

1.[8] The molecular ratio of ratios of hydrogen to water are 1:6 and 1:1 for C1 and C2, respectively. Due to such high hydrogen content, especially for C2, these compounds are also considered to be potential candidates for hydrogen storage material, although the stable pressure regions are fairly high; i.e., C1 and C2 are synthesized above 0.8 and 2.4 GPa at room temperature, respectively. Thus, an attempt to stabilized C2 under low pressure was made by lowering the temperature and its existence at 500 MPa and 77 K was reported.[5] In particular, pressure-induced phase transitions were investigated through x-ray diffraction and Raman spectroscopy.[10] Structural transitions were observed at approximately 35-40 and 55-60 GPa, and that the high-pressure phase survived up to at least 80.3 GPa. However, the structures after transitions are not yet determined. On the other hand, under extremely high pressure, symmetrization of the hydrogen bonds was examined up to 60 GPa by measuring the OH-stretching mode. The pressure at which symmetrization occurs in C2 was predicted to be considerably lower than that in ice VII.[9] 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 of the surrounding water molecules and also may relate to their stabilities. Further studies are required in vibration modes and structures. As well, knowledge regarding the change of vibron is very useful for technology involving hydrogen, like Raman spectroscopy.
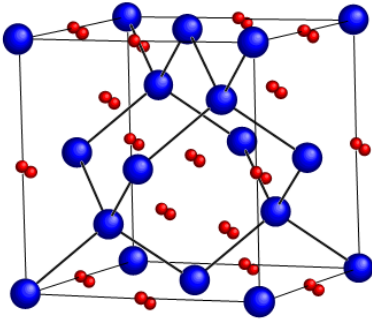
Fig.1 C2 structure with blue balls indicating water molecule without hydrogen atoms and red balls representing hydrogen molecule.

II. Computation methods

The molecular dynamics (MD) simulations were obtained by means of density functional theory (DFT) calculations using a pseudopotential plane wave approach implanted in Quantum-Espresso[11] with ultrasoft pseudopotential using the functional of BLYP[12]. These simulations are carried out with 8 water molecules and 8 hydrogen molecules at constant temperature of 300 K and different pressures. We used a plane wave basis cutoff energy of 40Ry and a 9×8×8 Monkhorst-Pack (MP) grid (*k*-mesh) for the electronic BZ integration. A more strict condition with cutoff energy up to 100 Ry in the phonon calculation using the linear-response method.[13]   In this work, we also used a dynamical approach to obtain the vibrational frequencies of H2 by analyzing the MD trajectories obtained from first-principles simulations. This approach allows us to separate the frequencies of the stretching modes in which we are interested from the translational and rotational molecular motions. Besides, we can trace the evolution of the stretching frequencies with variation of the local environment during the dynamics. 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

From Fig. 1, there is good agreement between calculated EOS at 300 K and experimental data below 30 GPa. We attribute the deviation at higher pressure to the fact that experimentalists still use cubic structure to calculate the

volume while actually the phase transition happening. Moreover, the large discrepancy between EOS at 0 K and experimental data highlight the importance of temperature effect in this system.
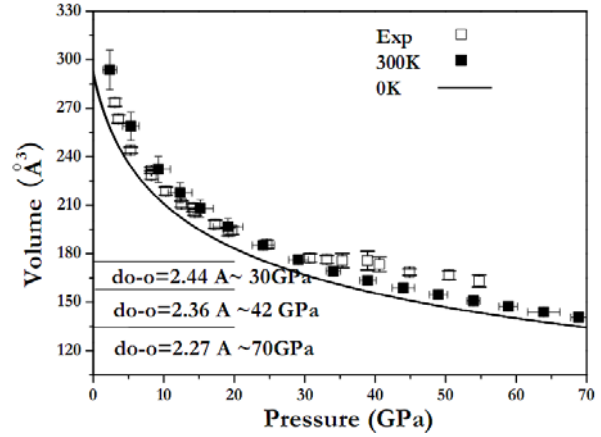

Fig.2 Comparison of calculated EOS at 0 K and 300 K (solid line and solid squares, respectively)with experimental data (open squares with error bar)

As mentioned above, experimentalist observed phase transitions through XRD and Raman spectroscopy. However, no structure information was provided after the transitions. We proposed that the structure changed from cubic symmetry into tetragonal around 60 GPa, as displayed in Fig. 3.
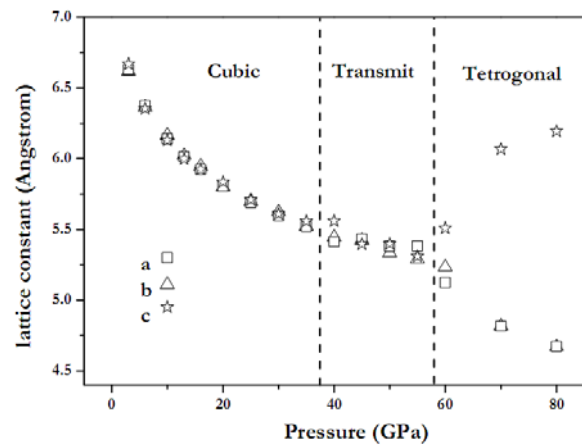

Fig. 3 Lattice constant evolution under pressure.

In order to extract the vibrational frequencies from the MD trajectories, we have used the velocity autocorrelation method[14], in which the vibrational power spectrum is derived from the Fourier transform of the velocity autocorrelation function. Therefore, we first define the stretching coordinate of each molecule as the distance between the two hydrogen atoms. We then compute the velocity autocorrelation using only this coordinate.

We compared phonon density of states calculated from MD trajectory and frequency from linear response theory. Stretching frequency of H2 shows blue-shift trend as usual H2 behavior under pressure. The OH stretching splitted into two groups according to the linear response theory results while the frequency value decrease and then increase with pressure.
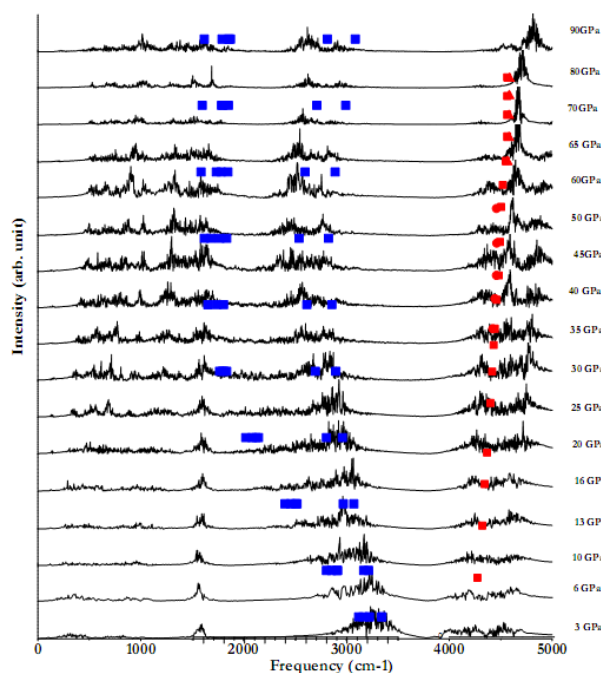

Fig. 4 Simulated phonon density of states (solid line) from MD trajectory and the frequency (solid symbols) calculated with linear response theory.

In Fig. 5, we displayed the H2 vibron frequency in C2 structure. It is easy to see that the linear respond theory frequency is higher due to the simulations done at 0 K.
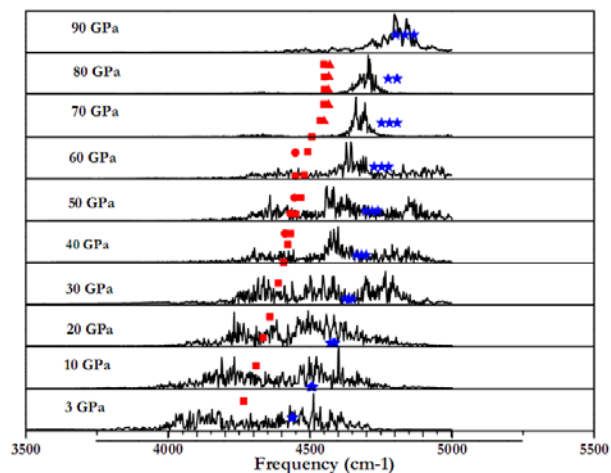

Fig 5. Comparison of calculated H2 vibron frequency (solid line) and frequency from linear respond theory (blue stars) with experimental value (red symbols).
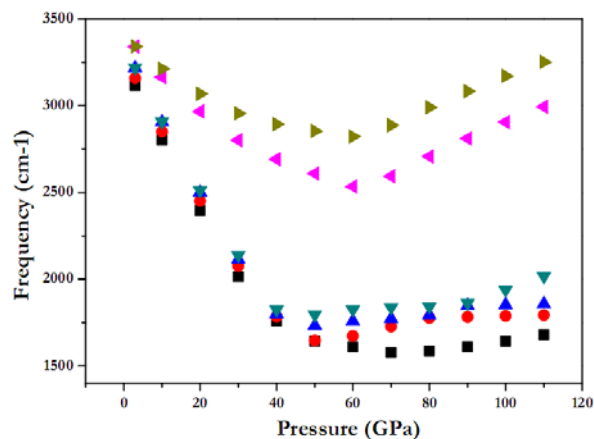

Fig. 6 Calculated OH frequency as a function of pressure from linear response theory.

The symmetrization of hydrogen bond in ice is intimately related to the quantum motion of protons known as tunneling and has been one of the major subjects in chemistry and physics for over a half century.[15] The energy potential for the proton motion along the hydrogen bonded O-O axis can be described as a double-minimum potential with an energy barrier on the midpoint. As oxygen atoms are pushed closer by applying pressure, the potential barrier will gradually be depressed and eventually the potential may converge into a single minimum at a sufficiently high pressure. Hydrogen-bonded protons initially located at asymmetric positions of the O-O separation will relocate to the symmetric midpoints. The predicted transition to the symmetric phase is related to displacements of the protons into the mid-point between two oxygen atoms. Therefore, it has some features of displacive-type phase transitions-namely, soft-mode behavior of the proton related vibrations. We deduced that the H-bond symmetrization took place around 60 GPa from the cross point of the OH stretching frequency in Fig. 6, which is larger compared with the experimental value of 40 GPa. This is understandable that we did not include the quantum effect of hydrogen tunneling.

IV. Conclusion

We carried out an extensive study on H2-H2O under high pressure by density functional theory. A good agreement in EOS below 30 GPa is achieved. We proposed the structure transited from a cubic phase into a tetragonal phase around

40 GPa and completed around 60 GPa. We deduced the H-bond symmetrization happened around 60 GPa from the OH stretching frequency.

V. Prospects

We would like to explore the H2-H2O low pressure phase sII structure and study about CH4-H2O system, which is of great importance of energy resource and scientific society.

VI 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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