Atomic and Molecular Phases of Hydrogen at Megabar Pressures

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The stable structures of the solid hydrogen have been studied by the band theoretical calculation using the plane wave basis in the local density approximation. Comparing the Gibbs free-energies for candidate structures in the atomic and molecular phases, we have discussed the stable structures. The metallization occurs around 300 GPa by the molecular dissociation. We have also studied the pressure dependences of the vibrational frequencies at the Γ -point in the molecular phase by the frozen phonon method in the harmonic approximation. Our results suggest that the molecules sit on the hcp sites and are canted from the c-axis.

[hydrogen, high pressure, molecular dissociation, vibrational mode, Raman and infrared]

1. Introduction

The insulator-metal and molecular-atomic phase transitions of highly compressed hydrogen have been of considerable interest in high pressure physics [1]. Recent shock compression experiment reported substantial increase in the conductivity of liquid hydrogen at 140 GPa [2]. At low temperatures, however, the sign of metallization of solid hydrogen has not been found up to about 220 GPa by the static compressions [3,4]. To predict the nature and the metallization pressure of compressed hydrogen it is necessary to know the structures in the molecular phase as well as the atomic phase. The recent X-ray diffraction experiment for solid molecular hydrogen observed the hcp lattice of the centers of molecules up to ~ 120 GPa at room temperature [5]. The molecular orientations at high pressures, however, are still unknown.

We have calculated the Gibbs free energies for candidate structures by the total energy calculation by the use of band theoretical treatment. We have mainly paid attention to the tetragonal diamond family [6] in the atomic phase. We have also studied the pressure dependences of vibrational frequencies assuming structures in the molecular phase and compared the results with the Raman scattering and infrared (IR) absorption experiment.

2. Metallization and Molecular Dissociation

We have performed the band theoretical calculation for candidate structures in the local density approximation (LDA), using plane wave basis and the bare Coulomb form of the atomic potential. The number of the plane-wave basis is set at $\sim 130n$ (where n is the number of atoms in the unit cell) which is equivalent to the energy cutoff of ~ 90 Ry at $r_s=1.3$, where r_s is the radius of a sphere of volume per electron in units of bohr radius a_0 . The number of k -points in the Brillouin zone is set at $\sim 4000/n$ for the molecular phase and $\sim 8000/n$ for the atomic phase. Zero point energy of the proton motion is not included in our calculation.

The cubic diamond structure has been studied and reported to be of lowest energy in the atomic phase by Natoli *et al.* [7] using the quantum Monte Carlo (QMC) calculation. We have studied the tetragonal diamond family by varying the c/a of the diamond structure. The energy of

Fig.1. The c/a dependences of energies for the tetragonal diamond structure. The arrows indicate the places of local minimum.

tetragonal diamond is shown in Fig.1 as functions of c/a . As is shown in the figure β -Sn structure ($c/a \sim 0.9$) and Cs-IV structure ($c/a \sim 3$) are of lower energies than the diamond ($c/a = \sqrt{2}$) at densities corresponding to the atomic phase. Those results come from the following. The diamond structure is a local minimum at low densities ($r_s = 1.5$).

Fig.2. Gibbs free energy differences from that of diamond structure. The solid lines are atomic phases. The dot-dashed lines are molecular phases. (I) and (II) denotes the filamentary and the planar structure.

The diamond, however, locates at the local maximum of the Madelung energy, and owing to the increased importance of the Madelung energy at higher densities a hump grows gradually at the c/a of diamond. At sufficiently high densities the diamond becomes the local maximum and at the both sides of the cubic diamond the β -Sn and the Cs-IV structures becomes local minimum.

There are other two local minima (filamentary and planar structure), whose energies are higher than those of the β -Sn and the Cs-IV structures at densities $r_s < 1.4$. Thus the filamentary, the planar, and the diamond structures of the diamond family are unstable in the atomic phase.

The pressure dependences of Gibbs free-energy differences of candidate structures are shown in Fig.2 with some structures which has been reported to be of low energy in the molecular phase. For the structures in the molecular phase we assumed ideal hcp and the intramolecular atomic distance of $1.45a_0$ around which total energy is minimum. As shown in Fig.2 we can conclude that the Pca2₁ structure, which is a molecular solid, transforms into the β -Sn, which is an atomic solid and metal, at 260 GPa. We note here that our structures of the molecular phase have not been fully optimized.

There are no stable region for the anisotropic structures like planar and filamentary structures as reported earlier [8].

If the band gap persists up to around 300 GPa in the molecular phase, though the accurate band gap can not be obtained by our LDA calculation, the possibility of metal-

lization by molecular dissociation increases.

3. Lattice Vibration in the Molecular Phase

In addition we have studied the vibrational modes at the Γ -point by the frozen phonon method in the harmonic approximation. We calculated the Hellmann-Feynman forces by the LDA band theoretical calculation using plane wave basis and evaluated the dynamical matrices from the force. The number of the plane-wave basis is set at $\sim 130n$ which corresponds to the energy cutoff of ~ 75 Ry at $r_s = 1.4$. The number of k -points in the Brillouin zone is set at $\sim 2000/n$.

We have studied the Cmc2₁ structure in detail. This structure is known to have low energy among structures with two molecules in the unit cell by both the band theoretical calculation [9] and the QMC [10]. The vibrational modes of Cmc2₁ at the Γ -point in the Brillouin zone belong to the four irreducible representations, A_1 , A_2 , B_1 , and B_2 , among which we focused on the A_1 and B_2 because they contain the vibronic modes as well as the translational modes of the center of the molecules. Those modes are both Raman and IR active from the group theoretical point of view. In our calculation we assumed the centers of molecules to form the ideal hcp lattice and optimized the angle between the molecular axis and the c -axis, θ , and the intramolecular atomic distance.

In the frozen-phonon calculation we set the displacements according to the symmetry coordinates which have the vibronic, phonon-like, and librational character. To calculate the force constants we generated the displacement of $0.002a_0$ for the vibronic coordinates and $0.01a_0$ for both the phonon-like and librational coordinates. We have found that mixing among the vibronic, phonon-like, and librational modes are very small. Hence we use the terms, vibron, phonon, and libron, to designate the modes below. The pressure dependences of A_1 -vibron, B_2 -vibron, and B_2 -phonon frequencies of the Cmc2₁ are shown in Fig.3. The A_1 -vibron and B_2 -vibron respectively corresponds to the in-phase and the out-of-phase stretching modes and B_2 -phonon corresponds to the translational motion of the molecular centers along the c -axis. Comparing our results with experiments we assigned A_1 -vibron to the Raman-vibron and B_2 -vibron to the IR-vibron. Although the calculated vibron frequencies are smaller than the experiment by $\sim 200\text{cm}^{-1}$, which difference is about 5% of the experimental value, the frequency difference between two vibrons and the pressure dependence of the frequencies are in good agreement with the experiment. The pressure dependence of the B_2 -phonon is close to the experimentally observed phonon branch in the frequency region from 1200 cm^{-1} to 1900 cm^{-1} [11,3].

We have examined the vibrational frequencies for the P6₃/mmc structure (m-hcp) setting $\theta = 0$, and using the same symmetry coordinates as those of the Cmc2₁. The result is also shown in Fig.3. A_{1g} -vibron, B_{1u} -vibron, and B_{2g} -phonon in the m-hcp correspond to A_1 -vibron, B_2 -vibron, and B_2 -phonon in the Cmc2₁. The out-of-phase vibron has higher frequency than the in-phase vibron as in the Cmc2₁. The pressure dependences of vibron frequencies, however, are considerably deviated from the experiment. On the other hand pressure dependence of the phonon is similar to that of the Cmc2₁. Thus the B_2 -phonon seems to be insensitive to the molecular orientations. These results

Fig.3. The pressure dependences of frequencies for Cmc2₁, P6₃/mmc(m-hcp), and Pca2₁. The (v) and (p) denotes the vibronic and phonon-like modes.

suggest that in the molecular phase molecular centers form hcp lattice and they are canted from c-axis.

We have studied further the Pca2₁ vibrons. This structure is energetically more favorable than the Cmc2₁. As can be seen in Fig.3 vibrons do not soften as much as the experiments. However it should be noted that we have not optimized the structure in the Pca2₁.

4. Conclusions and Remarks

We have studied the stable structures and the molecular dissociation by comparing the Gibbs free-energies calculated by the band theoretical treatment. Owing to the appearance of the β -Sn or the Cs-IV structure in the atomic phase, the highly anisotropic structure of planar or filamentary struc-

ture do not appear. We have found that the metallization occurs at around 300 GPa by the molecular dissociation. The structures in the molecular phase may need further optimization. The transition pressures, however, will not change appreciably owing to the crossing of the free energy curves with large angles.

We have also studied the vibrational frequencies in the molecular phase at the Γ -point. The frozen-phonon calculation at the Γ -point is thought to predict the transverse optical mode frequencies [12]. We compared our results with the experimental results though we are lacking the information about the polarizations in the IR experiments. The present results suggest that the molecular centers sit at the hcp sites and the molecules are canted from the c-axis is plausible as the structure in the molecular phase. Our results exclude the m-hcp structure.

We have based our study on the adiabatic and the harmonic approximation. Large effects of non-addiabaticity and anharmonicity, however, have been expected in the compressed hydrogen, and further studies may be needed for such effects.

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