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Ab initio calculation of the zero-point energy in dense hydrogen

Tomoki Takezawa[1]**, Hitose Nagara**[1,2] **and Kazutaka Nagao**[3]

[1] Division of Materials Physics, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
[2] CREST, Japan Science and Technology Corporation (JST), Japan
[3] Laboratory of Atomic and Solid State Physics, Cornel University, Ithaca, NY 14853-2501, USA

E-mail: takezawa@hbar.mp.es.osaka-u.ac.jp

Abstract
We have studied the vibrational modes and their frequencies in both atomic and molecular phases of dense hydrogen to find the stable structures and evaluated the zero-point energies (ZPEs) and the effect on molecular dissociation. The most probable structure in the atomic phase is Cs IV whose vibrational modes have real frequencies over the whole Brillouin zone. And the structure in the molecular phase is very close to *Cmca*, whose vibrational modes with imaginary frequencies work as guides to the stable structure. Our estimates of the ZPE are very close to those of Kagan *et al* (Kagan Yu, Pushkarev V V and Kholas A 1977 *Sov. Phys.–JETP* **46** 511). Adding the ZPE to the static energy, we estimated its effect on the pressure of the molecular dissociation. The reduction of the dissociation pressure due to the inclusion of the ZPE becomes over 100 GPa.

1. Introduction

No experimental evidence, so far has been observed at room or lower temperatures, while at elevated temperatures significant increase of the electrical conductivity, up to 342 GPa [2] has been observed in a shock compression experiment [3].

In the meantime, large numbers of theoretical studies have been carried out by the use of the *ab initio* band theoretical methods. The pressure of the metallic transition, however, is still unclear although new attempts are being made to cope with difficulties contained in the theories [4, 5].

The pressure-induced molecular dissociation in hydrogen is another interesting problem. Most of the dissociation pressures have been predicted without the zero-point energies (ZPEs) of the proton motions [6]. The hydrogen in the atomic phase is thought to be a metal, and the pressure of the molecular dissociation gives the upper bound of the metallization pressure even if the molecular phase remains an insulator.
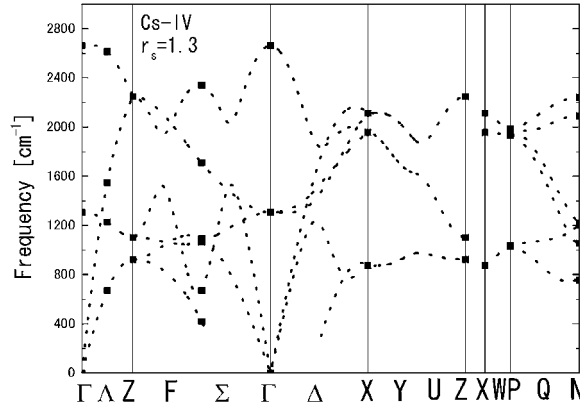
Figure 1. Phonon dispersion of compressed hydrogen for the Cs IV structure at $r_s = 1.3$ ($P \sim$ 320 GPa). The solid squares show the frequencies at the q_L-points which are defined in [8] and the dotted curves are the 'interpolated' curves. The curves for the lowest branch are not shown in the vicinity of the Γ point because of some ambiguities.

In this paper, taking some structures in both atomic and molecular phases, we calculate the vibrational frequencies for all modes over the Brillouin zone based on the first-principles band theoretical method and evaluate the ZPEs of proton motions. We compare the ZPEs with those of previous calculations. We also study the effect of the ZPE on the pressure of the molecular dissociation.

2. Calculation and results

Among the several methods used to calculate the phonon dispersion in the framework of first-principles band theoretical treatments [7, 8], we adopt straightforward method using the super-cell, which was used by Parlinski *et al* [8]. We calculate the effective force constants by band calculations based on the LDA, where we use the plane-wave basis and the conjugate-gradient method to obtain the electronic states [9]. Then we calculate dynamical matrices from these effective force constants. We use the pure Coulomb form of the atomic potential, and use about 4000 plane waves and $3 \times 3 \times 3$ mesh for the k-point sampling over the Brillouin zone. This number of the k-point sampling is equivalent to 8–16 times the number if the calculations were done with the primitive cell. With the above number of the plane waves, the energy cut-off is $\sim$75 Ryd at $r_s = 1.35$ and $\sim$95 Ryd at $r_s = 1.2$. (The density parameter r_s is defined by the relation $V = (4\pi/3)r_s^3 a_0^3$ where V is the volume per electron with a_0, the Bohr radius.)

As the structures in the atomic phase, we take the tetragonal diamond family with special attention paid to the Cs IV, the β-Sn, and the cubic diamond structure, of which the latter two were first studied by Natoli *et al* [10, 11] in their quantum Monte Carlo studies. The above three structures interchange by expansion or compression of the cubic diamond structure along the c-axis, and have been indicated as the structures of lowest energy ever studied in the atomic phase [12, 13]. For those structures we calculate the force constants using a super-cell containing 32 atoms, i.e. the super-cell that consists of 16 primitive cells each of which contains two atoms. We use the symmetry properties of the structures to reduce the number of the independent force constants. Using the force constants, we calculate the dynamical matrix at each q-point, whose dimension is 6×6 for the diamond family.

The dispersion curves are shown in figure 1 for the Cs IV structure at $r_s = 1.3$ ($P \sim 320$ GPa[4]). All frequencies at the $\boldsymbol{q}_L$-points are real. The 'interpolated' curves are shown in the figure by the dotted curves. The frequencies become slightly imaginary in the vicinity of the Γ point. We think that this arises from the small super-cell size used in our calculation. As the density is increased, the frequencies increase due to the stronger interaction among the atoms.

In the dispersion curves for the β-Sn structure, there are two unstable modes with high imaginary frequencies near zone boundaries out of a total of six modes. The high imaginary frequencies will mean instability of this structure. For the cubic diamond structure, we point out that this structure is located at the local maximum above $P \sim 200$ GPa ($r_s < 1.40$), when we plot the static energy as a function of c/a [12].

In the molecular phase, $Pca2_1$, $Cmc2_1$, and $Cmca$ are the structures which have been predicted to be probable above 250 GPa [6, 13], although some modifications of those structures have been proposed [14]. These three structures are transformed continuously into one another by changing the molecular orientations and the molecular centres. We study $Cmca$ in the molecular phase because $Cmca$ or a slight modification has been predicted to be energetically favourable over $\sim$250 GPa [6, 13].

We calculate the force constants using a super-cell containing 32 atoms, i.e. the super-cell that consists of eight primitive cells each of which contains four atoms. The dispersion curves of $Cmca$ structure have some unstable modes, with small imaginary frequencies. One of the unstable modes corresponds to the displacement of the molecular centres toward the $Cmc2_1$ structure. We expect the structure with slight modification obtained from the $Cmca$ structure to become stable. So we assume in the present study that molecular dissociation occurs between Cs IV and $Cmca$ structure, because we think the static energy and the ZPE of the real structure in the molecular phase are not so different from those of the $Cmca$ structure.

We evaluate the ZPE, sampling 1000 $\boldsymbol{q}$-points over the Brillouin zone, using the force constants. We simply discard the frequencies of those modes with imaginary frequency. We confirm that the contribution of the discarded modes to the ZPE is small. The results are shown in figure 2, with some of the Kagan *et al* results (see footnote 4). We note here that the values of the ZPE of the present calculation are very close to those of Kagan *et al* but are about a half of those obtained by the quantum Monte Carlo calculation (QMC) of Natoli *et al* [10, 11]. The large discrepancies between the QMC and those of the phonon calculations will need to be studied more.

Adding the ZPE to the static energy, we discuss the molecular dissociation between Cs IV and $Cmca$. The pressure of the molecular dissociation can be obtained from the condition of the crossing of the Gibbs free energy which is identical with the enthalpy at $T = 0$. The crossing occurs at around 300 GPa if we include the ZPE in the Gibbs free energies. This pressure is much lower than the pressure around 450 GPa obtained without the ZPE.

The large reduction of the dissociation pressure will also be explained by the first order charge of the transition pressure which is obtained from enthalpy crossing with and without the ZPE:

$$\Delta p = -\frac{E_m^{(zp)}(V_m) - E_a^{(zp)}(V_a)}{V_m - V_a}. \tag{1}$$

The above formula shows that the ZPE reduces the transition pressure if $V_m > V_a$ and $E_m^{(zp)} > E_a^{(zp)}$. These are the cases for the transition between Cs IV and $Cmca$ as shown by the inset of figure 2. If we use the above formula, we obtain the shift of the dissociation pressure: -90 GPa.

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[4] These theoretical values of the pressures are calculated without the ZPE.
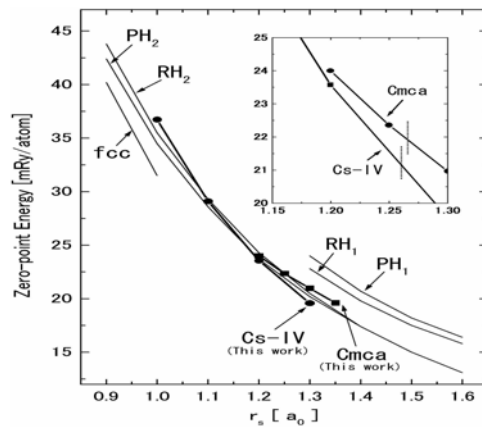
Figure 2. Comparison of the ZPEs. The filled circles and squares show our data points and the curves connecting those points are guides to the eye. ZPEs of other structures are from Kagan *et al* [1]. Inset: details of Cs IV and *Cmca*, in which the vertical dotted lines show the densities at the transition pressure obtained by the enthalpy crossing without the ZPE.

3. Summary and conclusions

We have studied the phonon dispersion and the ZPE with its effect on the pressure of the molecular dissociation. Our results on the phonon dispersion of Cs IV suggest that Cs IV is stable and expected to be one of the most probable structures in the atomic phase while the β-Sn structure is unstable. In the molecular phase, we have studied the *Cmca* structure. The dispersion curves show the probability of slight modification of the *Cmca* structure.

We have estimated the effect of the ZPE on the molecular dissociation which we assumed to occur between Cs IV and the *Cmca*. The ZPE decreases the dissociation pressure by 90–150 GPa. We note that, with further optimization of the structure in the molecular phase, the static energy of the molecular phase will be lowered and the molecular phase may remain up to higher pressures than the present prediction. We also point out that the dissociation pressure is a little higher for deuterium, by more than $\sim$30 GPa.

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