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Ab initio lattice dynamics evidence for the broken-symmetry phase of solid hydrogen

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Abstract

The lattice dynamics of solid hydrogen in the broken-symmetry phase (phase II) are extensively studied using density functional linear-response theory. The full phonon dispersion curves in the whole Brillouin zone for the previously proposed candidate structures are examined for the first time. It is found that the energetically preferred $Pca2_1$ structure shows exclusively dynamical stability in the pressure range of phase II (110–150 GPa), as indicated by the absence of phonon softening. A pressure-induced soft transverse acoustic (TA) phonon mode is identified and the TA mode completely softens at the zone boundary of the Y point at ~ 151 GPa, which coincides well with the experimentally observed transition pressure (150 GPa) from phase II to phase III. Moreover, the analysis of the eigenvector of the TA soft mode suggested that this phonon softening will result in enlarged intramolecular bond lengths. This fact might serve to explain the experimental observation of a sudden decrease in Raman and IR active vibron frequencies during the phase II to phase III transition. The physical reason for the reduction of Raman vibron frequency with pressure has been discussed. The newly proposed $P\bar{3}$ structure with $Pa\bar{3}$ -type local order has been explored for the first time. However, the calculated results of total energy, band structure, and phonon do not support the choice of $P\bar{3}$ structure.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Despite a great deal of effort starting with the first theoretical predictions in 1935 [1], experimental and theoretical investigations of solid hydrogen continue to reveal numerous intriguing but incompletely understood properties of its high-pressure phases [2]. The phase diagram has been investigated by several research groups at room temperature and below, based on the optical measurement performed in diamond anvil cell devices [3]. At zero temperature

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and lower pressures (below 110 GPa), quantum rotational effects overcome librational barriers, so that the molecules rotate freely (phase I). At higher pressures (110–150 GPa), anisotropic intermolecular interactions freeze the molecular rotations into an ordered broken-symmetry phase (phase II). Above 150 GPa, a new orientationally ordered phase (phase III) is observed.

Although a large body of theoretical investigations has been performed on the broken-symmetry phase of solid hydrogen, the determination of the structure is still under debate [4]. The first-principles calculations based on density functional theory (DFT) suggested that $Cmc2_1$ [5, 7], $Pca2_1$ [6–10], or $P2_1/c$ [11] structures are preferred in phase II. A path integral Monte Carlo simulation [12] proposed a $Pa3$ -type local orientational order without displacement of the molecular centres from the hexagonal closed packed (*hcp*) lattice. These structures can be derived from the *hcp* lattices by changing the ordering of the molecular axes, and they contain two or four hydrogen molecules in the unit cell. Very recently, Goncharenko *et al* performed x-ray and neutron diffraction measurements up to 60 GPa in solid deuterium [13]. The neutron intensities in a unit cell of $P\bar{3}$ symmetry with $Pa3$ -type local orientational order were calculated and compared with experimental measurements. Their results suggested that phase II of solid deuterium might be an incommensurate structure with $Pa3$ -type local orientational order.

By considering that the structure of phase II could depend on the isotope [13, 14], the incommensurate structure with $Pa3$ local order of solid hydrogen in phase II is, thus, not conclusive. The available experimental measurements for solid hydrogen in phase II are less reported due to the well-known difficulties described in [3]. The only well documented experiments are Raman and infrared (IR) measurements. Optical measurements in phase II of solid hydrogen indicated the presence of two IR active vibrons, in contrast to phase I, where only one is observed [3]. Raman vibron spectra in phase II show a single peak lower than that of the IR modes, and the frequency abnormally decreases upon compression. There exist many theoretical works [6–8, 15–19] on the lattice vibrations to analyse the vibrational spectra and determine the structures and molecular orientations for phase II. However, the full picture of lattice dynamics in the whole Brillouin zone (BZ) is less reported. Lattice dynamics plays an important role in determining crystalline structures, and stability requires that the energies of phonons must be positive for all wavevectors in the BZ. Moreover, dynamic instabilities are often responsible for phase transitions under pressure [20–22, 33]. In this work, the lattice dynamics of solid hydrogen for the previously proposed candidate structures have been extensively investigated using *ab initio* calculations based on density functional linear-response theory. The full phonon dispersion curves are calculated, for the first time, to provide more lattice dynamics evidence for phase II of solid hydrogen. To probe the validity of the $Pa3$ local order, we adopt the periodic $P\bar{3}$ structure, instead of an incommensurate structure, as our target structure to explore the nature of phase II.

2. Computational details

Ab initio calculations were carried out using the plane-wave pseudopotential method within the framework of density functional theory (DFT) [23]. The phonon frequencies were calculated based on the density functional linear-response method [20, 24, 25]. In this approach, the dynamical matrix is expressed in terms of the inverse dielectric matrix describing the response of the valence electron density to a periodic lattice perturbation. One of the greatest advantages is that it allows one to calculate phonon frequencies at arbitrary wavevectors q avoiding the use of supercells and with a workload that is essentially independent of the phonon wavelength. Particular attention was paid to generate a reliable hard hydrogen pseudopotential for calculations at high pressures. The generalized gradient approximation (GGA) of the

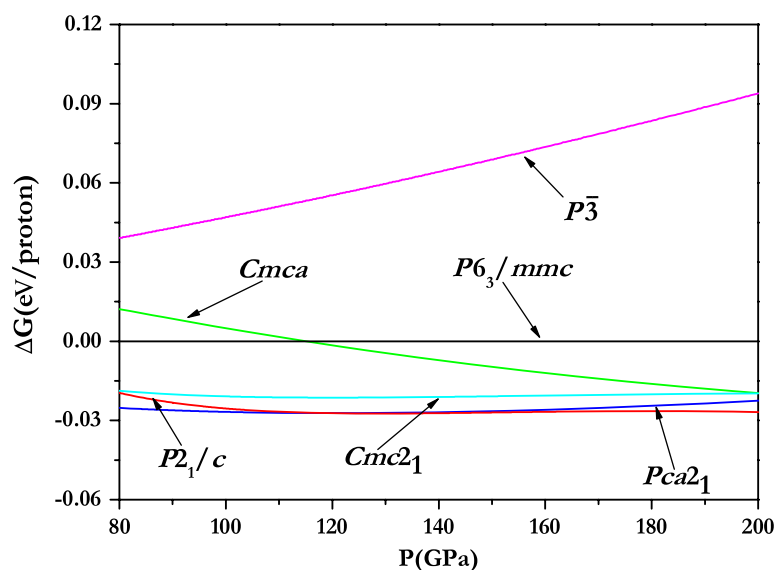


Figure 1. Gibbs free-energy curves (relative to the *m-hcp* structure) as a function of pressures for candidates of the solid molecular hydrogen considered.

exchange–correlation functional [26] was used. The Troullier–Martins [27] norm-conserving scheme was employed to generate the pseudopotentials for H with a matching radius of 0.6 au. The kinetic-energy cutoff in all calculations was chosen as 80 Ryd. To test convergence with respect to these choices, we repeated several other calculations using pseudopotentials with different matching radius and kinetic-energy cutoff. The results show that the current choice of the pseudopotential and the kinetic-energy cutoff are well converged for the total energy and forces needed here. The convergence test gave uniform Monkhorst–Pack (MP) grids of $16 \times 16 \times 10$ for molecular-hexagonal closed packed (*m-hcp*), *Cmc2₁*, and *Cmca*, $10 \times 16 \times 10$ for *Pca2₁*, $10 \times 10 \times 16$ for *P2₁/c*, and $12 \times 12 \times 12$ for $P\bar{3}$, respectively, in the electronic BZ integration. In lattice dynamics calculations, the above MP *k* mesh is found to yield phonon frequencies that converged to within 0.05 THz. A *q* mesh in the first BZ of $5 \times 5 \times 3$ for *Cmc2₁*, $3 \times 5 \times 3$ for *Pca2₁*, and $3 \times 3 \times 5$ for *P2₁/c* was used in the interpolation of the force constants for the phonon dispersion curve calculations.

3. Results

We first investigate the energetics of the candidate structures [3, 4, 13] with space group *P6₃/mmc* (*m-hcp*), *Pca2₁*, *P2₁/c*, *Cmc2₁*, *Cmca*, and $P\bar{3}$ for the broken-symmetry phase of solid hydrogen through total energy calculations based on the DFT. For each selected structure we fully optimized the bond lengths, molecular orientations and cell parameters at each density². The free-energy difference among the candidate structures is presented in figure 1. We find that the energy of the $P\bar{3}$ structure is the highest among the selected structures,

² For the $P\bar{3}$ structure, we found that full optimization will lead to the axes of all molecules being aligned parallel to the *c*-axis (similar to the *m-hcp* structure), which has seriously deviated from the *Pa3*-type local order. In order to keep the *Pa3* local order, we have to reduce the convergence threshold on forces to 1.0×10^{-2} au (in other structures, the value is 1.0×10^{-3} au) Although this is not appropriate according to the principle of physics, it can however help us to gain a basic understanding of properties for $P\bar{3}$ structure.

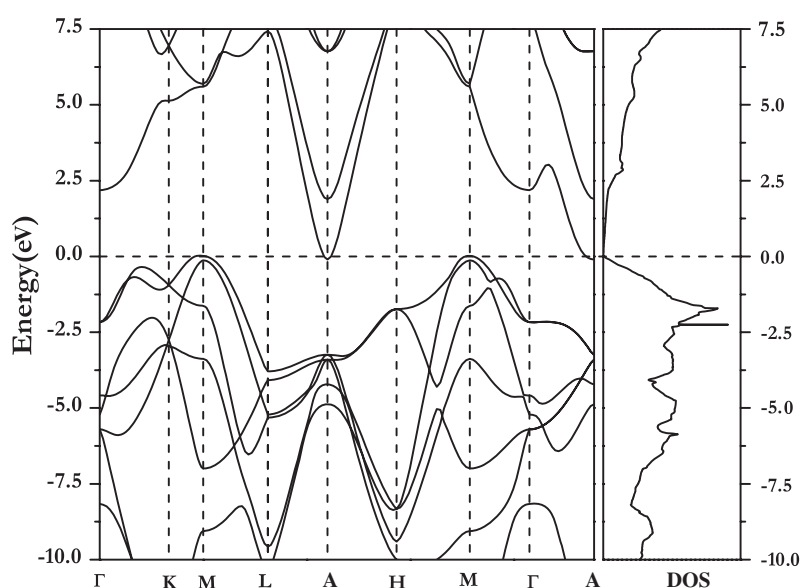


Figure 2. Left panel: the calculated electronic band structure at 110 GPa for solid hydrogen with the $P\bar{3}$ structure. Right panel: the calculated electronic DOS at 110 GPa with the $P\bar{3}$ structure.

indicating an energetically unfavourable condition. The calculated electronic band structures and electronic density of states (DOS) for the $P\bar{3}$ structure at 110 GPa is presented in figure 2, in which the $P\bar{3}$ structure shows an indirect band gap feature. It is important to note that the Fermi level crosses the energy band at the M and A points of the BZ with very low electronic DOS at the Fermi level, signifying a weak metal nature of the $P\bar{3}$ structure. This is also in apparent contradiction with the fact that solid hydrogen is an insulator in phase II. There are no stable regions for the $Cmc2_1$ and $Cmca$ structures which are energetically unfavoured. It should be pointed out that the $Pca2_1$ and $P2_1/c$ structures have almost the same energy among the selected structures in the energetically lowest region, in agreement with the previous *ab initio* calculations [6, 11, 28].

In order to check the dynamical stabilities for the above candidate structures, we calculated their phonon dispersion curves in the whole BZ. For the $P\bar{3}$ structure, three acoustic and nine optical phonons at the zone centre show large imaginary values, indicating that the $P\bar{3}$ structure is dynamically unstable. Similar behaviours also appear in the *m-hcp* structure, of which three acoustic modes at the centre of BZ are imaginary. We present the calculated phonon dispersion curves at 130 GPa with the $Cmc2_1$ (a) and $P2_1/c$ (b) structure in figure 3. In general, the dispersion curves are obviously divided into two parts, of which the high-frequency parts are the vibrons, while the low-frequency parts are mid-lying phonons (translational modes of the molecular centres) and other low-lying phonons and librations (the motions of the molecular orientation). In the $Cmc2_1$ structure, imaginary phonon frequencies are clearly found at the zone boundary points (Y and S) suggesting a dynamical instability. The energetically favoured $P2_1/c$ structure is also predicted to be dynamically unstable by evidencing a softening mode at the zone boundary B point. The $Cmca$ structure is a metallic molecular phase based on our calculation, and is also unstable from the phonon calculations (not shown) in the pressure range of phase II. It is very important to note that in the current phonon calculations, the $Pca2_1$ structure is the only structure with dynamical stability for phase II of solid hydrogen.

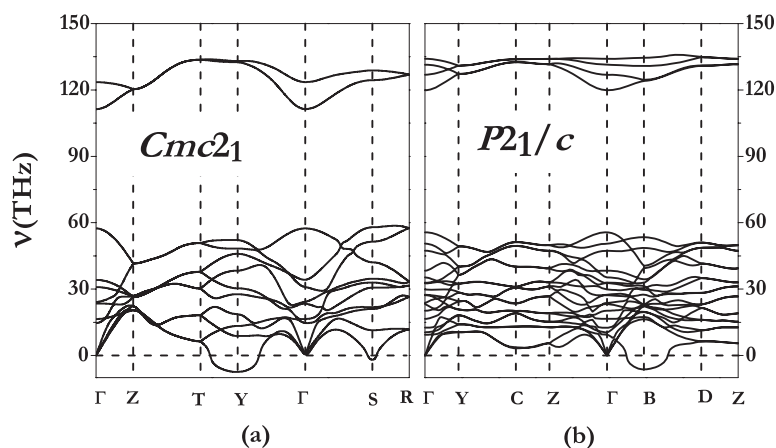


Figure 3. The calculated phonon dispersion curves for solid hydrogen at 130 GPa with the $Cmc2_1$ (a) and $P2_1/c$ (b) structure, respectively.

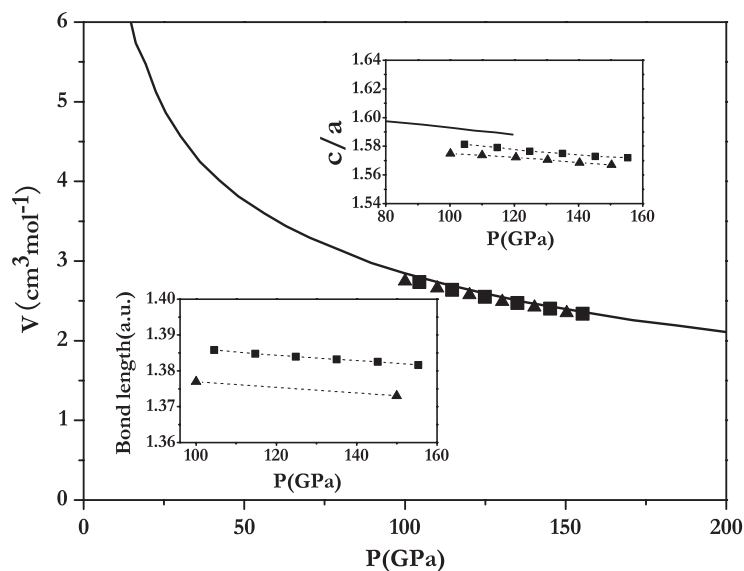


Figure 4. Main figure: the calculated equation of states (EOS) for phase II of solid hydrogen with the $Pca2_1$ structure. Solid squares are the optimized results of volume versus pressure. Solid triangles are the results of AIMD calculations [6]. The experimental data of the EOS [31] are also plotted as a solid line. Top and bottom insets: the variation of c/a ratios and the bond lengths with pressure, respectively. Solid squares, solid triangles, and the solid line denote the results from this work, AIMD calculations, and experiments, respectively.

This structure was first described by Kitaigorodskii and Mirskaya [29] for the ground state of a classical quadrupolar system, and later proposed for solid hydrogen [30] in phase II. The following calculations are, thus, mainly focused on this energetically preferred and dynamically stable structure.

The volume, cell shape, and atomic positions for the $Pca2_1$ structure were fully optimized at selected pressures. The calculated equation of states (EOS) is shown in figure 4 as indicated by the symbols of solid squares. For comparison, the previous *ab initio* molecular

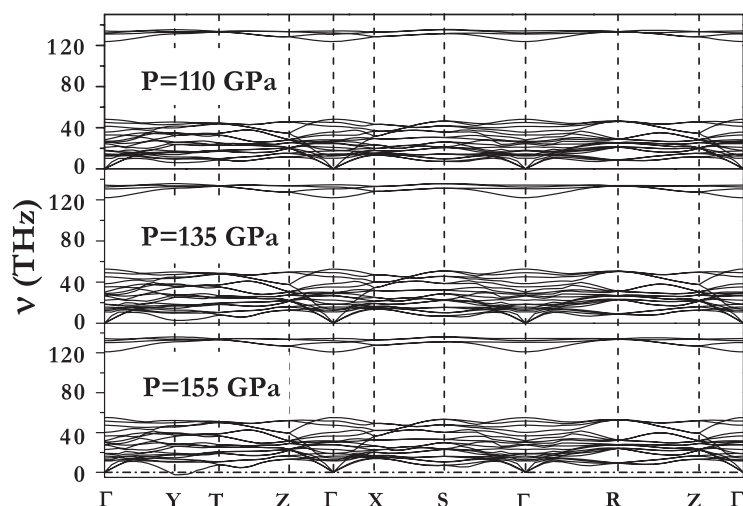


Figure 5. The calculated phonon frequencies of solid hydrogen with the $Pca2_1$ structure at pressures of 110, 135, and 155 GPa, respectively.

dynamics (AIMD) calculations [6] and the experimental measurements [31] are also presented in figure 4 as solid triangles and a solid line, respectively. One observes that the agreement of our calculations with the previous calculations and the experimental data is excellent. The optimized c/a ratios and the bond lengths with pressure are also presented in the insets of figure 4. It is found that the c/a ratio (solid squares) show almost linear decreases of the hexagonal cell with pressure, coinciding with the trend of experimental observations. The optimized bond lengths as plotted by solid squares in the bottom inset of figure 4 are slightly larger than those in AIMD calculations. However, the bond lengths in both theoretical works show a clearly decreasing trend with pressure. It is noteworthy that the centres of hydrogen molecules occupy the sites of a slightly distorted hcp lattice. Note also that the excellent agreement between the calculated EOS and experimental data strongly supports the choice of our pseudopotentials and the validity of the current theoretical mode at high pressures.

The calculated phonon dispersion curves of solid hydrogen with the $Pca2_1$ structure at different pressures are shown in figure 5. At 110 and 135 GPa, no imaginary phonon frequency is observed in the whole BZ, indicating that solid hydrogen with the $Pca2_1$ structure is dynamically stable. With increasing pressures, most of modes slightly shift to higher frequency, while the transverse acoustic (TA) mode decreases, indicating a negative Grüneisen parameter $\gamma_j(q) = -\partial \ln \omega_j(q) / \partial \ln V$ for mode j at the zone boundary point (Y), where q is the wavevector, ω is frequency, and V is volume. At a pressure of 155 GPa, the phonon frequency of the TA mode at the Y (0, 0.5, 0) point becomes imaginary, signalling a structural instability in the $Pca2_1$ structure of solid hydrogen. We have presented the variation of the TA mode at the Y point with pressure in the main figure of figure 6. The estimated pressure for phonon softening to zero frequency from figure 6 is ~ 151 GPa. The squared phonon frequencies ν^2 for the TA mode at the Y point with pressure P are also plotted, as shown in inset (a) of figure 6. A near perfect linear relation between ν^2 and P was obtained. Such behaviour is consistent with the Landau theory of pressure-induced soft mode phase transitions [32]. It is significant to note that the calculated transition pressure, 151 GPa, is in excellent agreement with the experimental transition pressure from phase II to phase III of 150 GPa. Kohanoff *et al* [33] reported an instability of TA phonon mode at the X (1, 0, 0) point of the BZ, only

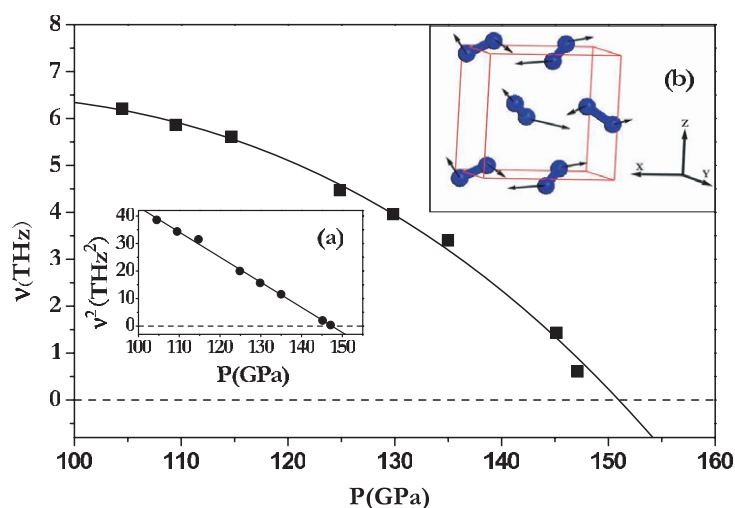


Figure 6. Main figure: the calculated transverse acoustic (TA) frequencies at the Y point with pressure. The solid line through the calculated data points represents fitted curves using a B spline. Insets: (a) The calculated square phonon frequency ν^2 as a function of pressure; the solid line through the data points is a linear fit. (b) The eigenvector for the TA phonon mode at the Y point.

through computing the zone centre and the zone boundary phonon frequencies [33]. However, their suggested transition pressure is ~ 180 GPa, which is 30 GPa higher than the experimental measurement. This large difference between their theory and experiment does not provide sufficient evidence for the transition from phase II to phase III. Many lattice dynamics studies under pressure [22, 34] suggested that if the predicted transition pressure from the phonon softening is much higher than the experimental measurements, then this phonon softening might not be independently responsible for the phase transition. Therefore, from their phonon calculation, one could not give a very clear answer to whether the transition from phase II to phase III is attributed to the phonon softening at the X point. The schematic representation of eigenvectors for the TA phonon mode at the Y point is shown in inset (b) of figure 6. On the one hand, the motion of hydrogen atoms would lead to the rotation of hydrogen molecules, changing molecular orientations, which might lead to the new orientationally ordered phase. On the other hand, the atomic movements in the eigenvector tend to stretch the bond lengths of the hydrogen molecules. Thus, the TA phonon mode at the Y point softening to zero frequency will result in enlarged intramolecular bond lengths. As a consequence, the intramolecular interaction between two hydrogen atoms will be weakened. This fact might serve to explain the experimental observation of a sudden decrease in Raman and IR active vibron frequencies during the phase transition from phase II to phase III [3]. Therefore, here the predicted TA phonon softening behaviour at the Y point provides a significant implication for the transition from phase II to phase III, and particularly for further investigating the structure of phase III.

A reasonable structure for the broken-symmetry phase of solid hydrogen would be compatible with the optical measurements on vibrons, where a strong Raman peak and two IR modes are observed [3]. For the $Pca2_1$ structure, there are four vibrons (labelled as A_1 , A_2 , B_1 , and B_2); all of them are Raman active (A_1 is the in-phase oscillation mode, while A_2 , B_1 , and B_2 are out-of-phase modes), and three of them (A_1 , B_1 , and B_2) are IR active. In figure 7, the calculated frequencies of vibrons (solid symbols) with pressure are compared with experimental results [3] (dashed and solid lines) and two previous theoretical calculations

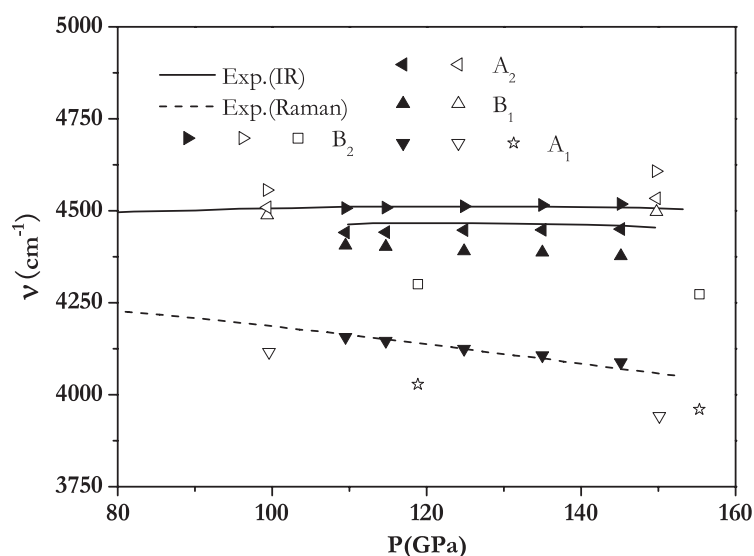


Figure 7. The calculated vibron frequencies of solid hydrogen with the $Pca2_1$ structure as a function of pressure. The lower dashed line and the two upper solid lines are experimental Raman and IR data [3], respectively. Solid triangles are the results of this calculation. Open triangles are data from AIMD calculations with quantum effects included [6]. Up and right triangles are calculated IR active vibrons (modes B_1 and B_2 respectively). Down triangles are calculated Raman active vibron (mode A_1). Left triangles are the Raman-only vibron (mode A_2). Open squares and stars are previously calculated IR and Raman modes (modes B_2 and A_1) from [7].

(open symbols) [6, 7]. The agreement between the calculated Raman mode A_1 (solid down triangles) and the experimental Raman measurements is excellent. It is clear that the softening trend of Raman active vibron as a function of pressure is well produced by this theory. This trend is also verified by [7] and by [6] with quantum effects included, as indicated by the open stars and the open down triangles, respectively, in figure 7. The small intensities for the other three Raman modes (A_2 , B_1 , and B_2) which are not observed in experiments might be due to contributions from out of phase vibrations cancelling out [6]. If we attribute the two experimental IR vibrons to the B_1 (solid up triangles) and B_2 (solid right triangles) modes, the agreement between theory and experiment for the upper IR mode (B_2) is excellent, while it is less satisfactory for the lower IR mode (B_1). Failure to observe the IR active mode of A_1 might be attributed to its weak peak intensity in experiments. It should also be pointed out that our results for the IR spectrum agree better with those calculated by the AIMD method (open triangles) [6] as shown in figure 7; however, they show a large difference with that of [7] (open squares). The big discrepancy might result from the different calculation methods (our calculations of lattice dynamics are based on the linear-response theory, while they use the frozen-phonon method) or exchange–correlation functionals (ours is the GGA, while theirs is the local density approximation).

The vibron frequencies in principle should increase with increasing pressure, resulting from the increased atomic repulsion inside the hydrogen molecules due to the decreased bond lengths. However, both the current theory and the Raman measurements of vibrons show that the Raman frequencies decrease under pressure. It was proposed that no softening occurs but a quantum effect leads to the softening in the previous AIMD calculations [6]. However, both [7] and we got the softening trend for the $Pca2_1$ structure in the harmonic approximation without

quantum effect corrections. Thus, we conclude that the softening of the Raman active vibron with pressure is not mainly induced by the quantum effects, nor by the anharmonic effects. Therefore, it is an intrinsic nature of solid hydrogen under pressure. The softening might be due to the movement of the intramolecular electron density to the intermolecular regions because of pressurization [35]. This behaviour will weaken the interatomic coupling inside a hydrogen molecule and, therefore, result in the softening of the vibron frequencies. The Raman mode A_1 is the only in-phase mode, and this mode corresponds to motion where all four molecules behave in the same manner. Yet it still remains to be fully understood why only this in-phase mode softens with pressure.

In this work, we first investigated the energetics, band structure, and phonons for the $P\bar{3}$ structure with the $Pa3$ local order. It turns out that this structure possesses a very high enthalpy, a semi-metallic nature, and phonon instability even at the zone centre. One might argue that these unfavourable conditions might result from the fact that the studied structure is periodic, and not incommensurate. It is known that, for metals, Fermi surface nesting might induce an incommensurate structure [36], while for insulators phonon softening away from the zone centre (not at the zone centre) might also result in an incommensurate phase [37]. Therefore, from the phonon softening point of view in the insulating solid hydrogen, the induced incommensurate structure from a periodic structure might have an enlarged unit cell. As a consequence, it will produce more energy bands and phonon branches. However, the choice of the incommensurate structure cannot be easily understood to lower the energy, open a band gap, and even stabilize the crystal. Thus, one has to take care when accepting the incommensurate structure with $Pa3$ local order as the candidate structure of phase II from the analysis of the currently calculated results. Unfortunately, there is no very reasonable theory to deal with the incommensurate structure from the *ab initio* point of view, except for a very large classical molecular dynamic calculation with thousands of atoms in the simulation cell. However, this kind of study is out of the scope of the current study.

It should be pointed out that the calculations might give different results if we take the ortho–para distinction [38] of solid hydrogen into account. However, our method employed here could not deal with such states or systems. We should also emphasize that a full understanding of the lattice dynamics of solid hydrogen may require consideration of anharmonic effects on the vibrations. The increasing anharmonicity with pressure might shift slightly the frequencies of vibron modes [3, 39]. However, recent Raman measurements of molecular hydrogen under simultaneous conditions of high temperature and high static pressure have implied that the anharmonicity decreases with pressure [40]. Therefore our linear-response calculations in the frame of the harmonic approximation might be a reasonable assumption at high pressures. In principle, the frozen phonon approach can be used to include anharmonic effects, but such calculations are beyond the scope of this study.

4. Conclusion

In conclusion, according to the calculations of the phonon dispersion curves in the whole BZ for previously proposed candidate structures, the $Pca2_1$ structure is found to show exclusively dynamical stability in the pressure range of phase II (110–150 GPa), as indicated by the absence of phonon softening. A pressure-induced soft TA phonon mode completely softens at the zone boundary Y point at about 151 GPa, which agrees well with the experimental transition pressure from phase II to phase III. Moreover, the analysis of the eigenvector of the TA soft mode suggested that this phonon softening will result in enlarged intramolecular bond lengths, which might serve to explain the experimental observation of a sudden decrease in Raman and IR active vibron frequencies during the phase transition from phase II to phase III. The calculated

EOS, c/a ratio, Raman and infrared spectral shifts with pressure are in excellent agreement with available experimental data. The theoretical results presented here support that the $Pca2_1$ structure is a good candidate for the broken-symmetry phase of solid hydrogen. From the results of calculated total energy, band structure, and phonon frequency, we do not observe any positive evidence for the choice of $P\bar{3}$ structure in phase II of solid hydrogen. However, further theoretical works including a full consideration of the incommensurate structure are needed to clarify the validity of the proposed $Pa\bar{3}$ -type local order.

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