RAPID COMMUNICATION

High-pressure Raman study of solid hydrogen up to 300 GPa*

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The high-pressure behavior of solid hydrogen has been investigated by *in situ* Raman spectroscopy upon compression to 300 GPa at ambient temperature. The hydrogen vibron frequency begins to decrease after it initially increases with pressure up to 38 GPa. This softening behavior suggests the weakening of the intramolecular bond and the increased intermolecular interactions. Above 237 GPa, the vibron frequency softens very rapidly with pressure at a much higher rate than that of phase III, corresponding to transformation from phase III into phase IV. The phase transition sequence has been confirmed from phase I to phase III and then to phase IV at 208 and 237 GPa, respectively. Previous theoretical calculations lead to the proposal of an energetically favorable monoclinic $C2/c$ structure for phase III and orthorhombic *Pbcn* structure for phase IV. Up to 304 GPa, solid hydrogen is not yet an alkali metal since the sample is still transparent.

Keywords: ultrahigh pressure, diamond anvil cell, phase transition, Raman spectra

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1. Introduction

As an electrical insulator at ambient conditions, solid hydrogen was predicted to become an alkali metal under extreme compression.[1] Since Ashcroft pointed out that the metal hydrogen would be a room temperature superconductor in 1968,[2] the quest for metallic hydrogen at high pressure represents a longstanding problem in condensed matter physics. Ceperley *et al.* reported that the metallic pressure of hydrogen was about 3.0 ± 0.4 Mbar by the quantum Monte Carlo calculation.[3] The two earliest static pressure experiments were done by Narayana *et al.* and Loubeyre *et al.*, and both of them reported that solid hydrogen did not become an alkali metal up to 342 GPa.[4,5] Besides, Loubeyre *et al.* further proposed that metal hydrogen should be observed at about 450 GPa when the direct gap closes.[5] Recently, Eremets *et al.* found that hydrogen became opaque and electrically conductive above 220 GPa by electrical measurement.[6] Subsequently, Howie *et al.* have proposed a new phase IV and measured its band gap which reaches 1.8 eV at 315 GPa by the optical transmission spectra.[7] The recent experimental result showed that the solid hydrogen remained transparent until 360 GPa.[8] Therefore, the quest for the metallization of solid hydrogen is still underway.

As an important thermodynamic variable, high pressure provides an effective means to probe the structures in a wide parameter space by modifying molecular distances of the crystals.[9–11] In recent decades, it has become possible to perform static experiments under pressure calibrated above 300 GPa with the diamond anvil cell as a vehicle. While multimegabar pressures had been achieved consistently with other samples, the study of hydrogen at ultrahigh pressures presented many experimental challenges.[12] Two difficulties have to be overcome: one is that hydrogen is difficult to load into the sample chamber physically and chemically, and another is that many of hydrogen's high-pressure properties are hard to measure. In addition, hydrogen embrittlement causes failure in pressure confinement. Therefore, it is a challenging and tough thing to study solid hydrogen under megabar pressure.

The crystal structure is considered a key to understanding its intriguing physical properties especially for pressure-induced metallization. Up to now, three high-pressure phases of solid hydrogen exist to 200 GPa at or below room temperature. Phase I has a hexagonal close-packed structure with freely rotating molecules.[13,14] Phase II differs from the lattice symmetry of phase I, possesses some degree of orientation order, and exists at temperatures below 135 K and up to 160 GPa.[15,16] Phase III was identified by Raman and infrared absorption measurements, which currently are the most sensitive means for identifying phase transitions of these materials at multimegabar pressures.[13] Phase III is separated from phase II by an almost vertical phase line from 0 to 125 K at 155 GPa.[17] There are still many disputes between experimental results and theoretical calculations about the crystal struc-

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tures of solid hydrogen. However, hydrogen has the smallest electron-scattering cross-section among all elements, resulting in extremely weak x-ray diffraction intensity for structural determination. Furthermore, the small sample volume at ultrahigh pressures provides an additional challenge for measurements of other various properties. Raman spectrum has become a vital tool to study the vibration properties and phase transitions of materials particularly for low atomic number element.[18–24]

In this work, we have performed *in situ* ultrahigh pressure Raman spectroscopy investigation to explore the phonon behaviors and phase transitions of solid hydrogen at room temperature. Our results revealed that the phase transition sequence is from phase I to phase III and then to phase IV at 208 GPa and 237 GPa, respectively. Up to 304 GPa, solid hydrogen is still not metal since the sample is still transparent.

2. Experimental details

Ultrahigh-purity hydrogen gas was loaded into tungsten or rhenium gaskets of diamond anvil cells by a gas-loading system. The sealed pressure was about several GPa after hydrogen loading, and one of the loading Raman spectra and the sample chamber are shown in Fig. 1. Various reasons have been proposed to explain the pressure limit of hydrogen under static compression: the chemical reaction of dense hydrogen with components of the diamond cell environment, including gasket, pressure calibrant or diamond anvil; the line broadening due to the non-hydrostaticity of hydrogen and the onset of strong fluorescence from the diamond anvils that causes a dramatic decrease of the signal-to-noise ratio, etc. To achieve higher pressure and obtain Raman spectra with good-quality, eight experimental runs were investigated in total. Samples were compressed and measured at room temperature. Pressure was determined from the sharp edge of the first-order diamond Raman band produced at the diamond–sample surface of the stressed anvil.[25–27] The maximum acquisition time was about 30 s. Below 200 GPa, one pair of diamonds with 100 μm culets were used to reach a pressure of 180 GPa. Above 200 GPa, because of the limitations of sample volume, no ruby or other pressure sensors were loaded into the sample chamber. The diamonds with 20 μm or 50 μm culets were used for obtaining the vibron information up to 300 GPa. The sample sizes typically ranged between 6 μm and 10 μm when the pressure was above 300 GPa.

The Raman spectra were collected as a function of pressure. Backscattering geometry was used, with both 532-nm and 646-nm laser lines as the Raman excitation wavelength. Prior to each measurement, the spectrometer was calibrated using an Si line. No dissolution of hydrogen into the gasket and no evidence of hydride formation were found during the experiment which achieved 304 GPa.

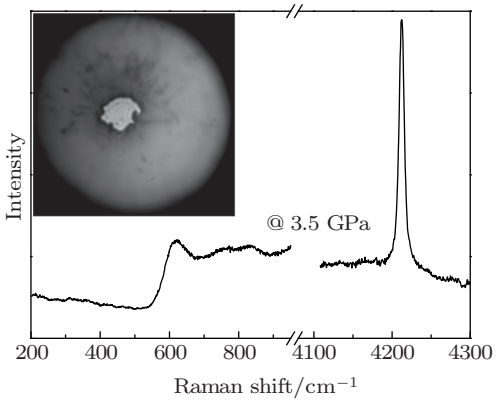


Fig. 1. The Raman spectra and sample chamber of the sample just after loading at 3.5 GPa. The used diamond culet is 100 μm and the sample chamber is about 20 μm.

3. Result and discussion

At lower pressures and room temperature, hydrogen crystallized into phase I with space group $P6_3/mmc$ is a diatomic molecular solid with strong covalent molecular bonds, weak intermolecular interactions, and a filled valence band with a large band gap, which makes the material a good insulator.[13] The most prominent feature associated with the transition at these pressures is the change of the strong Raman vibron. As shown in Fig. 2(a), Raman scattering experiments were carried out at pressures up to 180 GPa. The vibron frequency initially increases with pressure increasing, which is normal behavior resulting from the increased repulsion between neighbor molecules. However, this trend stops at about 38 GPa, above which the frequency decreases with pressure increasing. This behavior gives rise to considerable excitement in the field, since a decrease in frequency suggests the weakening of the intramolecular bond and the increased intermolecular interactions, perhaps in anticipation of an eventual transition to a monatomic solid. Subsequently, similar behavior was also observed in solid D_2.[28] Figure 2(b) shows the pressure dependence of the line width of the vibron band. The line width increases rapidly with pressure. The full width at half maximum (FWHM) of the band is about 2 cm^{-1} at first and then reaches 27 cm^{-1} at 181 GPa, which was also observed in other previous results.[29,30] The increase in a line width is caused by the increase of an intermolecular interaction.

Besides the investigation of the hydrogen vibron below 200 GPa, we also did other experimental runs in order to obtain ultrahigh pressure above 300 GPa searching for the metallization of hydrogen. Recent improvements on the throughput and spatial resolution of our Raman set-up allowed us to collect signals from samples with 5 μm in diameter. We used 532-nm laser excitation wavelengths to measure the Raman spectra. We found that minimizing the exposure time significantly decreases the risk of diamond failure. The whole ex-

perimental measurement is investigated using a symmetric diamond anvil cell with 20-μm culet diamonds, and the sample diameter is about 10 μm after loading hydrogen into the cell with pressure 30 GPa. Figure 3 shows the transmission of the incident white light through the sample at 92 GPa, 225 GPa, and 304 GPa, respectively. The transmitted light appears yellow owing to the absorption by the diamonds. The transmission at 92 GPa appears unchanged from that at 225 GPa, as does the transmission when the torque was increased. There was no measurable change in the shape or size of the sample area between 225 GPa and 304 GPa. Up to 304 GPa at 300 K, solid hydrogen is not yet an alkali metal since the sample is still transparent. When compressed to 304 GPa, the diamond was crushed after measuring the Raman spectra. The front diamond through which the laser light was introduced to the sample chamber failed first, as is shown in Fig. 3(f). Figure 4 shows selected diamond Raman spectra and hydrogen vibron spectra upon compression up to 300 GPa. In this experimental run, the acquisition time is 10 s while the acquisition time is 20 s above 237 GPa. The frequency of the hydrogen vibron spectra shows persistently blue-shift up to 263 GPa. Synchronously, the intensity of the hydrogen vibron peak decreases rapidly above 237 GPa, and begins to drop continuously under ultrahigh pressures.[7,31,32]

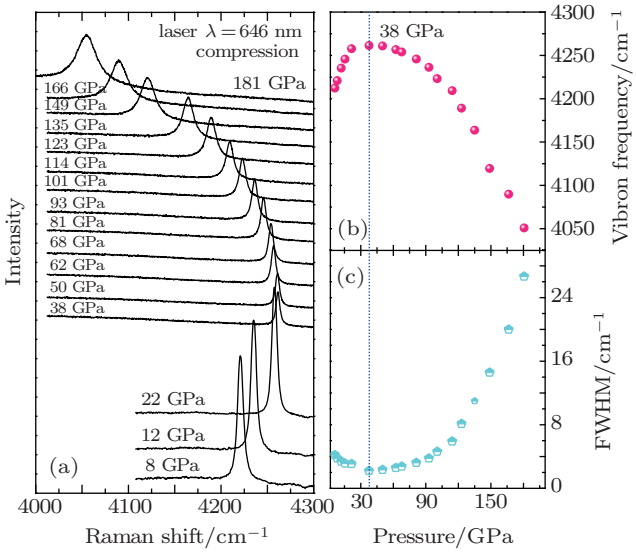


Fig. 2. (color online) (a) Hydrogen vibron spectra under different pressures. (b) Pressure dependence of vibron frequency at 300 K. (c) Pressure dependence of the line width of the hydrogen vibron.

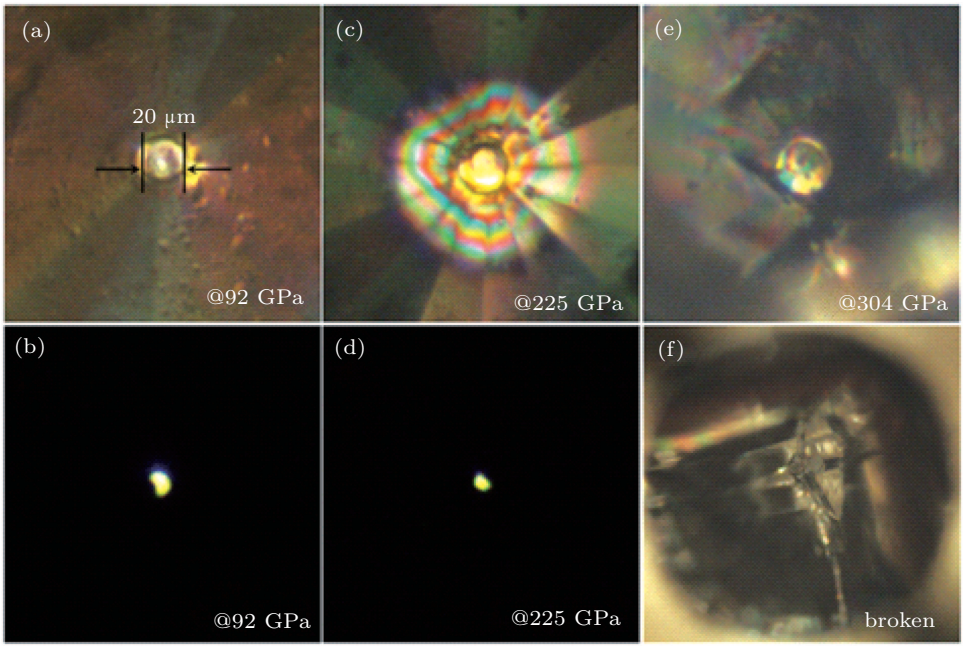


Fig. 3. (color online) Optical microscopy images of solid hydrogen sample at (a) 92 GPa with transmitted and reflected white light and (b) 92 GPa with transmitted white light, at (c) 225 GPa with transmitted and reflected white light and (d) 225 GPa with transmitted white light, at (e) 304 GPa with transmitted and reflected white light. The diamond crushed at 304 GPa after measuring the Raman spectra, shown in panel (f).

As shown in Fig. 5, the frequency of the hydrogen vibron peak is plotted as a function of pressure. An obvious softening behavior is observed in the vibron mode with increasing pressure. In 1995, Goncharov *et al.*[33] observed the phases I–III change of deuterium, along with a subtle discontinuity of the intramolecular vibron as a function of pressure. However, the observed discontinuity in the vibron frequency across the I–III transition line became vanishingly small above 254 K. Therefore, although the phases I–III transition has been studied extensively at lower temperatures, the phases I–III boundary is extrapolated to 300 K by Howie *et al.*[14] According to Zha *et al.*,[32] the transition point from phase I to phase III is close to 200–205 GPa, and the pressure range of the phase III at 300 K is narrow. In Fig. 5, the labelled pressure range of phase III is

about 208–225 GPa related to the previous literature.[14,32] It is emphasized that these pressures are all relative to the diamond Raman scale used in these studies. At the I–III transition, the reorientation of the molecule or the elongation of intermolecular distance might discontinuously take place. Above 237 GPa, the vibron mode frequency softens very rapidly with pressure at a much higher rate than the vibron of phase III, indicating phase III transforming into phase IV. The transition from phase III to phase IV was first reported by Howie *et al.*,[14] which is characterized by the simultaneous appearance of the second vibrational fundamental and new low-frequency phonon excitations. The subsequent literature also observed that the appearance of phase IV is accompanied with a new vibrational mode at higher frequency,[31,32] which suggests that phase IV has a modified bonding character compared to phase III. However, in this study, the previous reported new vibrational mode is submerged due to the background of the diamond. As identified in previous x-ray and neutron diffraction, phase I has a hexagonal close-packed structure; vibrational spectroscopy established that the structure of phase I is molecular, consists of quantum rotors, and has a wide pressure–temperature (P–T) range of stability.[13,14] There are still many disputes about phase III.[34,35] Recently, the *ab initio* random structural searches lead to the proposal of an energetically favorable monoclinic $C2/c$ structure for phase III at zero temperature. In $C2/c$ structures, all hydrogen molecules have approximately the same bond length as shown in Fig. 5(b). The increased vibron mode softening, its broadening, and the presence of the vibrational mode in phase IV can be understood by the difference in local molecular association. Phase IV provides a unique continuous route for molecular dissociation (retaining unbound molecules). Howie *et al.* proposed that phase IV possesses *Pbcn* structure,[14] which could explain all features of the Raman spectra of phase IV. This structure is highly unusual, it consists of unbound molecules sandwiched between the honeycomb graphene-like layers composed of 6-atom rings, which have different size lengths (from 0.85 to 1.04 Å), yielding both molecular and atomic hydrogen at the same time. The *Pbcn* structure of phase IV with $2 \times 2 \times 1$ supercell is shown in Fig. 5(c).

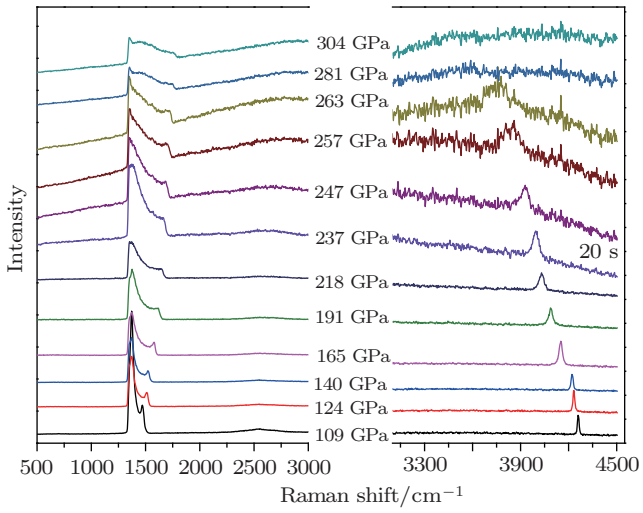


Fig. 4. (color online) Selected diamond the first-order Raman spectra (left) and hydrogen vibron spectra (right) upon compression up to 304 GPa. The acquisition time of the hydrogen vibron spectra is increased to 20 s above 237 GPa.

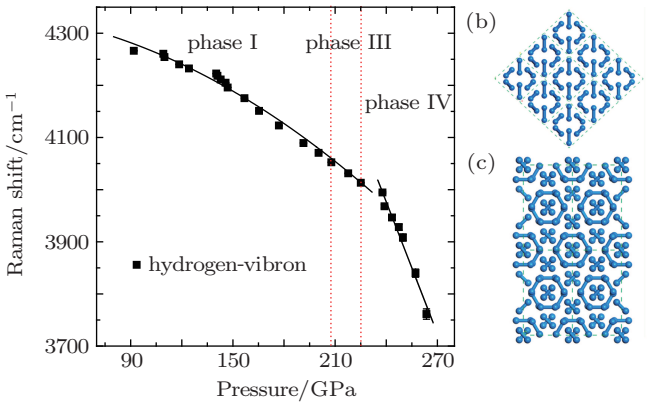


Fig. 5. (color online) (a) Pressure dependence of vibron frequency at 300 K, and the error bar is shorter than the size of the symbol. The labeled pressure range of phase III with dotted curves is about 208–225 GPa refereed to the previous literatures.[14,32](b) The candidate structure $C2/c$ of phase III with $3 \times 3 \times 3$ supercell and (c) the candidate structure *Pbcn* of phase IV with $2 \times 2 \times 1$ supercell. These two structures are viewed along x–y plane.

4. Conclusions

In summary, the high pressure behavior of solid hydrogen has been studied by *in situ* Raman spectra measurements under ultrahigh pressures at 300 K. It is found that the vibron frequencies decrease with the increase of pressure above 38 GPa. This softening behavior suggests the weakening of the intramolecular bond and the increased intermolecular interactions. Under ultrahigh pressures, the frequency of hydrogen vibron changes at pressures of 208 and 237 GPa, respectively, which corresponds to the phase transition sequence from phase I to phase III and then to phase IV. The previous *ab initio* random structural searches lead to the proposal of an energetically favorable monoclinic $C2/c$ structure for phase III and orthorhombic *Pbcn* structure for phase IV. Up to 300 GPa, solid hydrogen is not yet an alkali metal since the sample is still transparent. Continued experiments and theoretical calculations are needed to provide more information of this fundamental system under extreme conditions.

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