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Mixed Molecular and Atomic Phase of Dense Hydrogen

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We used Raman and visible transmission spectroscopy to investigate dense hydrogen (deuterium) up to 315 (275) GPa at 300 K. At around 200 GPa, we observe the phase transformation, which we attribute to phase III, previously observed only at low temperatures. This is succeeded at 220 GPa by a reversible transformation to a new phase, IV, characterized by the simultaneous appearance of the second vibrational fundamental and new low-frequency phonon excitations and a dramatic softening and broadening of the first vibrational fundamental mode. The optical transmission spectra of phase IV show an overall increase of absorption and a closing band gap which reaches 1.8 eV at 315 GPa. Analysis of the Raman spectra suggests that phase IV is a mixture of graphenelike layers, consisting of elongated H_2 dimers experiencing large pairing fluctuations, and unbound H_2 molecules.

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The behavior of hydrogen at very high pressures is still poorly understood due to the limitations imposed on conventional experimental techniques. Currently, three solid phases of hydrogen and deuterium (labeled I, II, and III) are known (see Fig. 1) [1,2]. Phase I has a hexagonal closed-packed structure with freely rotating molecules. Phase II (the broken symmetry phase), which possesses some degree of orientational order and may differ from the lattice symmetry of phase I, exists at temperatures below 135 K and up to ~160 GPa [3,4]. Phase III is separated from phase II by an almost vertical phase line from 0 to 125 K at ~155 (165 for D_2) GPa [5,6], and the transition between the two is characterized by a large discontinuity (~ 100 cm^{-1}) in the vibron frequency. Phases I, II, and III coexist at a triple point at 125 K and 155 GPa (135 K and 165 GPa for D_2), above which a phase line with positive slope separates phases I and III. The I-III transition exhibits a similar discontinuity in vibron frequency which rapidly decreases with increasing temperature, disappearing at 250 K [7]. At 77 K and pressures in excess of 275 GPa, a change of color [8,9] and band gap of the order of 2 eV has been reported with an estimation that the band gap would close at pressures of 420–450 GPa [8–10]. Because of the difficulties associated with the containment of hydrogen at high pressures and elevated temperatures (> 250 K), the highest pressure reached at 300 K prior to this study is approximately 180 GPa [11]. Therefore, experimental high-pressure 300 K studies of hydrogen are of fundamental interest, as they may reveal new facts relevant to the I-III and other possible phase transformations or even shed light on the behavior of the melting curve at high pressures [12–14] and predicted unusual liquid state [15]. Vibrational spectroscopy is crucial for making direct measurements on the state of bonding of the material at high pressures and temperatures. In addition to information on bonding, these spectroscopic techniques have been the sole means for identifying phase transitions in H_2 at above 150 GPa, because vibrational excitations are extremely sensitive to changes in crystal structure, including melting [5,6,12]. The combined experimental evidence, from the shock-wave study on hot dense liquid hydrogen [16] and from static studies [12,14] on solid and liquid hydrogen states, indicates that the application of "*high*"

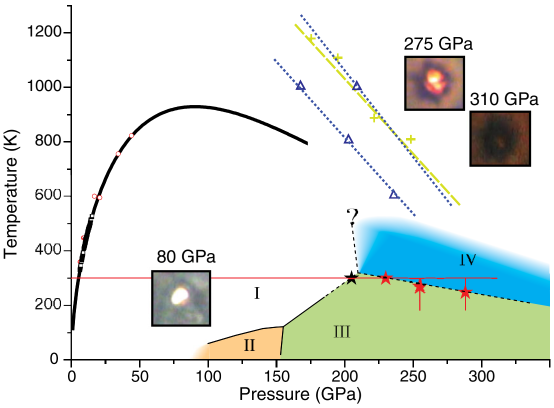

FIG. 1 (color online). Proposed phase diagram of H_2. The melting curve (thick solid line) is a Ketchin fit from Ref. [12], and the symbols along it are from Refs. [12,27]. The solid lines separating the phases I, II, and III are from Ref. [28]. The thin solid lines show the *P*-*T* paths taken in this study, and the stars along them show phase I to III and III to IV transformations. The dashed lines are proposed boundaries between I–III, III–IV, and I–IV phases. The calculated transition lines between molecular and atomic liquid are shown with dashed lines and crosses [24] and triangles [25]. The microphotographs show the appearance of deuterium in phase I and hydrogen in phase IV.

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temperatures might facilitate the dissociation of the hydrogen molecule and therefore promote transformation to an atomic and metallic state at lower pressures. In this Letter, using high-pressure Raman and visible transmission spectroscopy, we show that at high temperatures ($T = 300$ K) and above 220 GPa hydrogen adopts an unusual structure containing 6-atom rings corresponding to a "predissociated" semimetallic state separated by a layer of free-like (unbound) molecules.

We have conducted several experiments at room and low temperatures on H_2 (and D_2) with the highest pressures reached 315 (275) GPa (see Ref. [17] for the details). With increasing pressure, the low energy (< 1000 cm^{-1}) bands of H_2 (D_2) broaden and decrease in intensity [Figs. 2(a) and 2(b)]. However, when pressures above ~190 GPa were reached, we observed the appearance of a new, relatively intense broad Raman band at 500 cm^{-1} (Fig. 2). The emergence of this band is accompanied by the drastic change of the slope of the main vibrational mode ν_1 from -5 to -12.7 cm^{-1}/GPa (Fig. 3). The full width at half maximum (FWHM) of the ν_1 mode also reflects changes at the transition; from the solidification point at 5.5 GPa, the FWHM increases linearly, reaching 100 cm^{-1} by 210 GPa. At this point, the broadening abruptly changes rate, and within an interval of 50–60 GPa (at 260–270 GPa) the FWHM reaches ~460 cm^{-1} (Fig. 3). Our observations of the low energy broad band are similar to a band at 450 cm^{-1} observed in H_2-III at 178 GPa and 18 K [6]. The change in slope of the ν_1 and the increase of FWHM are in good agreement with similar observations made in phase III at low temperatures (18 K for librons and 250 K for vibrons) [6,9]. The 190 GPa–300 K P-T point, where we observe an apparent phase transition, could fit on the phase I-III boundary of existing low temperature data if extrapolated to 300 K and above 190 GPa (Fig. 1).

As pressure is increased above 220 GPa and the ν_1 mode reaches a frequency of ~3800 cm^{-1}, the transition to a new phase (referred here as IV) starts. The transformation is evidenced by the profound changes in vibrational and low (< 1200 cm^{-1}) energy spectra. At above 220 GPa, the low-frequency broad band is superseded by three new sharp Raman modes. A new vibrational mode ($\nu_2 \sim 4150$ cm^{-1}) appears at 235 GPa (Fig. 2). At the same pressure, the ν_1 frequency reduces below the values expected for the vibron of phase III at 77 K (Fig. 3). This observation suggests that phase IV has a modified bonding character compared to phase III (see below). The ν_1 mode frequency softens very rapidly with pressure at a much higher rate than the vibron of phase III. At 315 GPa, the frequency of the ν_1 mode is 2750 cm^{-1} (35% reduction of frequency compared to ~4260 cm^{-1} at 40 GPa where the

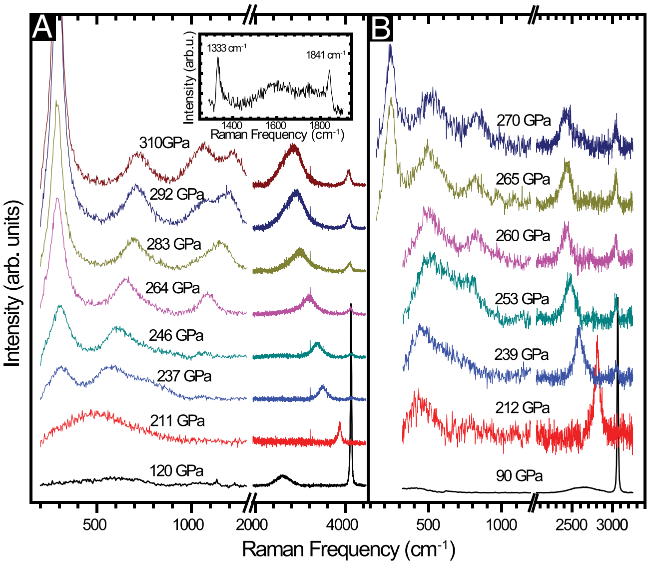

FIG. 2 (color online). Representative Raman spectra of H_2 (a) and D_2 (b) at different pressures (shifted vertically for clarity). The weak broad peaks at ~2400 cm^{-1} on spectra at 120 GPa for H_2 and 90 GPa for D_2 are due to the 2nd-order Raman from diamond. The inset in (a) shows the stressed diamond peak at 315 GPa.

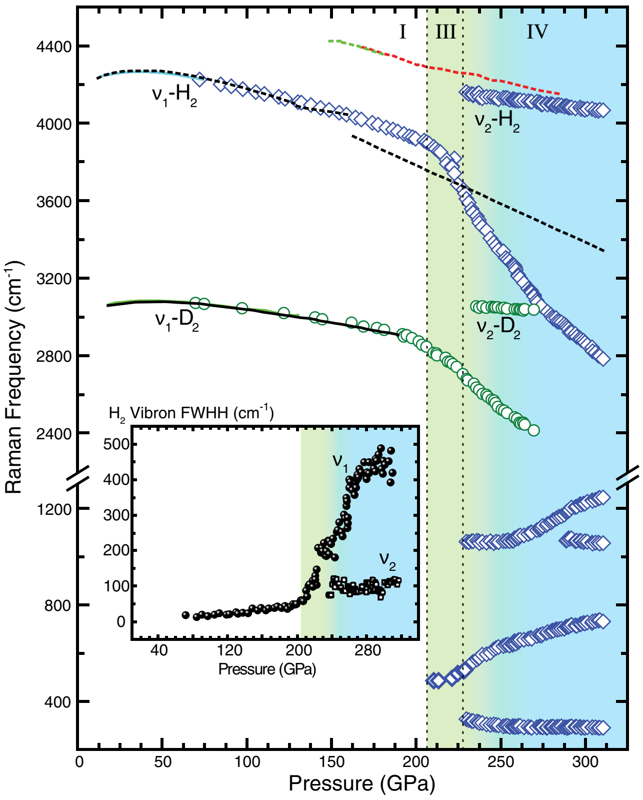

FIG. 3 (color online). H_2 and D_2 phonons frequency shifts as a function of pressure. Open squares are the ν_1, ν_2, and low energy modes of hydrogen; open circles are ν_1 and ν_2 modes of deuterium. The dashed lines are infrared and Raman measurements at low temperatures from Refs. [6,8,20]. The solid line is the ν_1 mode of deuterium at 300 K from Ref. [11]. Inset: Hydrogen ν_1 (solid circles) and ν_2 (open squares) modes FWHM as a function of pressure.

ν_1 mode goes through the maximum of its frequency), which is much lower than that in phase III at 77 K and 320 GPa ($\nu_1 \sim 3400$ cm^{-1} [8]). The FWHM of the ν_2 mode lies on the linear extrapolation of the vibron mode of phase I (Fig. 3) and is clearly driven by the normal pressure-induced broadening unlike the ν_1 mode, indicating two very different local atomic environments involved in these modes (see below). In the high-pressure regime, the frequency of the ν_1 versus pressure shows a slope change (slope changes from -12.7 to -7 cm^{-1}/GPa), and a 1050 cm^{-1} band branches off to give rise to another weakly softening band above 280 GPa (Figs. 2 and 3), which rapidly increases in intensity. The relative intensity of the lowest-frequency band at 295 cm^{-1} significantly increases, while the mode shows small softening with pressure (Fig. 2). This complex behavior suggests that the ν_1 mode couples to other modes of the same symmetry (e.g., Ref. [18]) with the gain of intensity for the 295 and 1050 cm^{-1} modes. The strong coupling between the modes also forces a small upturn of the ν_1 vibron frequency with pressure above 275 GPa (Fig. 3).

The structures of high-pressure phases of hydrogen are unknown, which makes the definitive interpretation of the observed phenomena difficult. We use the structure(s) recently proposed by the *ab initio* theoretical calculations for phase III of hydrogen [19] to analyze our findings. With the inclusion of the zero-point energy, the calculations suggest 3 structures ($C2/c$, $Cmca$-12, and $Pbcn$) as the most plausible candidates for phase III. In $C2/c$ and $Cmca$-12 structures, all H_2 molecules have approximately the same bond length (within 1%) but would have the second Raman vibrational mode due to the Brillouin zone *doubling* with respect to phase I. This is in some agreement with the experimentally observed infrared [10,20] and ν_2 Raman [6] modes. The extremely weak Raman ν_2 vibron was observed in phase III and was assigned to a folded mode from the Brillouin zone boundary; the frequency of this mode is quite close to that of the strong IR mode (Fig. 3), as they both correspond to the vibrational states near the top of the vibrational band [21]. Both IR and Raman (at ~175 GPa) are relatively close in frequency (~ 4400 cm^{-1}) to the unbound state [21]. On the other hand, the proposed for H_2-III $Pbcn$ structure could explain all features of the Raman spectra of phase IV reported here. This structure is highly unusual; it consists of unbound molecules sandwiched between the honeycomb graphenelike layers made of 6-atom rings, which have different size lengths (from 0.85 to 1.04 Å; see Fig. S2 in [17] and Ref. [19]), yielding both molecular and atomic hydrogen at the same time. The density-functional theory calculations give the positions of Raman active modes [19] for the $Pbcn$ structure; we observe 6 out of 16 predicted fully symmetric modes (A_g) which are expected to be the most intense. The spectral positions of all observed modes agree well with the theoretical calculations (see Fig. S3 in [17]). Using empirical formula relating the frequencies (ν) and the bond lengths (r), $\nu r^3 = \text{const}$ [22], we *qualitatively* assign the observed vibron frequencies in the $Pbcn$ structure. The 0.72 Å length, which is very close to the bond length of an unbound molecule, could be easily assigned to the ν_2 mode ($\nu_2 \sim 4150$ cm^{-1}), and the ν_1 2800 cm^{-1} mode could be assigned to the 0.82 Å bond length. At this point we note that 1.04 and 1.03 Å bond lengths *could* correspond to a calculated (see Fig. S3) and observed doublet at 1050 and 1200 cm^{-1}. We have not observed the band at ~1800 cm^{-1}, corresponding to the 0.95 Å length, but this band most probably is hidden behind the stressed diamond signal, covering the area from 1333 to 1850 cm^{-1} at 315 GPa (inset in Fig. 2). Two other modes observed here below 700 cm^{-1} (Fig. 3) correspond to the out-of-plane translational and librational modes.

The increased vibron mode softening, its broadening, and the presence of the intense ν_2 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), similar to that which has been previously observed in ice VII through the hydrogen bond symmetrization [18]. In the vicinity of the symmetrization transition, the lattice becomes highly anharmonic, causing a pronounced softening and broadening of the O-H stretch mode [18] very similar to the observations in this study. We speculate that the pressure-dependent changes of the soft mode, mode coupling, and optical absorption are related to the predicted continuous structural transformation of the $Pbcn$ structure into the higher symmetry $Ibam$ [19] configuration with formation of the perfect graphenelike hydrogen layers with *equal* distances between atoms in a 6-member ring. Because of the larger zero-point energy, the higher mobility of the proton compared to the deuteron is expected, leading to the enhanced proton tunneling in the regime approaching symmetrization as was observed in water [23]. In this case, the hydrogen vibron would show larger softening of the ν_1 mode relative to deuterium as demonstrated in the divergence from the $\sqrt{2}$ ratio between H_2 and D_2 ν_1 modes (see Fig. S2 in Ref. [17]) as the lighter hydrogen tunnels more easily. This also could explain the presence of the regime of an increased optical absorption above ~280 GPa (see Fig. 4). Above 268 GPa, a strong band-gap feature appears in the spectra and shifts in red with pressure. The overall absorption increases with pressure in this regime; the sample becomes dark in appearance (Fig. 1 and Ref. [17]). Although the band-gap shift with pressure is comparable to that for phase III (Fig. 4), the overall significant increase in absorption suggests that above 278 GPa hydrogen may become semimetallic. This is in excellent agreement with the theoretical prediction that $Pbcn$ structure will metallize at above 300 GPa [19].

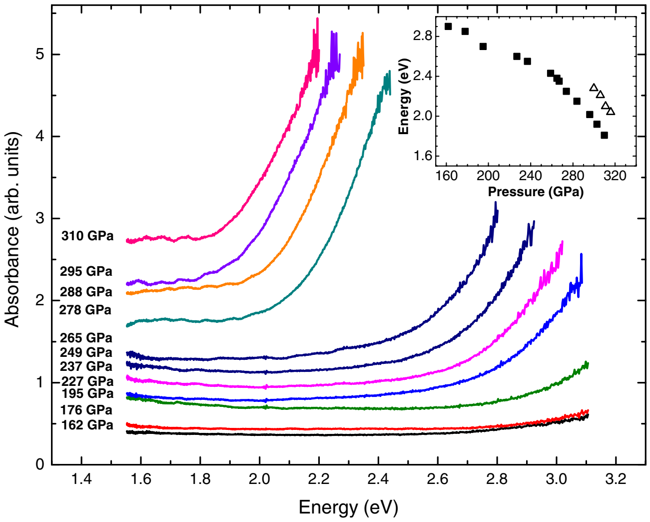

FIG. 4 (color online). Optical absorption spectra of H_2 in a visible spectral range at 300 K and different pressures. The reference transmission spectrum was measured at 75 GPa. Inset: Estimated band gap as a function of pressure at 300 K (solid squares) and at 77 K from Ref. [8] (open triangles).

We have observed reversible phase IV to III transformations between 230 and 285 GPa upon cooling or warming (see Fig. S5 in [17]). These results allow us to constrain the phase diagram of hydrogen at very high pressures. Our observations suggest that phase IV supersedes phase III at high temperatures and will most likely become metallic. The transition line between phases III and IV has a negative slope, and it is relatively shallow in *P*-*T* coordinates. This substantiates that the transition is entropy driven, which is supported by the described above difference in structure and related to it proton tunneling in phase IV. Theory [19], together with this experimental study, confirms that a unique mixed molecular and atomic state provides a route to solid metallic hydrogen at high temperatures. In order to better understand the connection between the described here phase IV, the melting curve, and predicted atomic liquid states [24,25], further investigations are clearly needed. We tentatively place the second triple point at 210 GPa and 320 K, but the slope of the I–IV boundary needs to be established. This boundary is of particular interest, because it has important consequences for the behavior of the melting curve. Independently of the I–IV slope boundary, it is very likely that the melting curve will change its slope at some *P*-*T* condition, because the phases I and IV are very dissimilar. Depending on the sign of this slope, one could expect that the predicted ground liquid state [15] could be realized at higher pressures or may be not realized at all as in case with Li [26]. Since phase IV could have strong quantum tunneling of protons within two-dimensional layers, it could possess some features of quantum proton fluid. It is interesting to note that the intersection of the molecular to atomic liquid states boundary predicted theoretically [24,25] and the extrapolation of the melting curve is in close proximity to the stability field of phase IV discovered in this work (Fig. 1). This is a clear indication of the connection between changes in both liquid and solid states in this interesting and unusual material.

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