Proton tunneling in phase IV of hydrogen and deuterium

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Using *in situ* optical spectroscopy we have investigated the temperature stability of the mixed atomic and molecular phases IV of dense deuterium and hydrogen. Through a series of low-temperature experiments at high pressures, we observe phase III-to-IV transformation, imposing constraints on the *P-T* phase diagrams. The spectral features of the phase IV-III transition and differences in appearances of the isotopes Raman spectra strongly indicate the presence of proton tunneling in phase IV. No differences between isotopes were observed in absorption spectroscopic studies, resulting in identical values for the band gap. The extrapolation of the combined band gap yields 375 GPa as the minimum transition pressure to the metallic state of hydrogen (deuterium). The minute changes in optical spectra above 275 GPa *might* suggest the presence of a new solid modification of hydrogen (deuterium), closely related structurally to phase IV.

The recent experimental discovery of phase IV of hydrogen and deuterium is exemplary of how studies of hydrogen at multimegabar pressures is constitutive to the understanding of the pressure-induced complexity in simple systems at extreme compressions.[1] Raman studies have shown that, at 300 K, hydrogen transforms to a new phase (phase IV) at pressures above 220 GPa. Quite unique and unusual features of the Raman spectra, e.g., the appearance of the second fundamental vibrational mode, were interpreted as phase IV, consisting of graphene-like six-member rings made up of elongated H_2 dimers, which experience large pairing fluctuations, and unbound H_2 molecules. This unusual structure, having *Pbcn* symmetry and 48 atoms per unit cell, was earlier proposed by density functional theory (DFT) as a possible candidate for phase III at 0 K.[2] The newly found experimental ability to compress hydrogen at room temperature above 180 GPa in the diamond anvil cell has resulted in major revision of the hydrogen phase diagram.[1] However, the new findings did not answer many questions and both experimental[3] and theoretical[4,5] studies produced somewhat contradictory results, posing many more uncertainties about the possible states of dense hydrogen. For example, in one experimental study at 300 K, H_2 phase IV was probably observed (which is not supported by the data presented on deuterium) however the authors did not suggest a mixed atomic-molecular state, instead claiming pressure-induced molecular dissociation and metallization above 260 GPa.[3] On the other hand, theoretical studies[4,5] predict the transformation of phases III and IV into molecular phase V at pressures above 250 GPa, which is at variance with many experimental observations.[1,6–8]

Our previous study focused on the behavior of hydrogen and deuterium at 300 K and[1] reported some preliminary results on H_2 phase IV at low temperatures. Compared to the three other molecular phases (I, II and III),[9] little is known about the low-temperature stability field of H_2 phase IV[1] and nothing is known about the stability field of deuterium phase IV. As hydrogen and deuterium have the highest relative isotopic mass difference among elements, the effects of zero point energy (ZPE) might play an important role. Based on the fact that phase IV exists at relatively "high" temperatures and the transition line separating it from phase III has a negative slope with respect to the pressure axis, we surmised[1] that the transition to the mixed state (phase IV) is entropy driven. This suggestion is supported by the significant differences in the Raman spectra of phase III vs phase IV, which is indicative of very dissimilar structures of these phases. Since the structure of phase III is not known and the proposed structural model for phase IV needs confirmation, it is impossible to make a quantitative comparison of entropies and ZPEs of both phases. Therefore, experiments aimed at determining the stability fields of hydrogen (deuterium) are highly desirable and of fundamental interest, because they are expected to provide a clear picture of the hydrogen (deuterium) phase diagram and therefore reveal new aspects relevant to the theoretical modeling and interpretation.

In this study, we mapped out phases III and IV of deuterium (hydrogen) up to 300 GPa and between 200 and 300 K. We investigate the low-temperature stability of deuterium (hydrogen) phase IV, revealing the differences in the stability fields of the isotopes and similarities in the electronic structures. We show that the phase III-to-IV transformation is accompanied by a large discontinuity of the fundamental vibrational mode frequency, the largest discontinuity observed between different phases of hydrogen (deuterium). We also demonstrate that the full width at half-maximum (FWHM) of the vibrational fundamental reaches ~ 450 cm^{-1} for H_2 and ~ 250 cm^{-1} for D_2 in phase IV while staying below ~ 150 cm^{-1} for both isotopes at pressures above 250 GPa in phase III. The large difference between the peak widths of the main vibrational modes of the two isotopes in phase IV indicates substantial proton tunneling in hydrogen, probably due to the higher ZPE of the lighter species.

High-purity normal D_2 (H_2) was loaded at 0.2 GPa into a long piston-cylinder diamond anvil cell and compressed at room temperature. At the desired pressure, the cell was mounted in a custom-built continuous-flow cryostat and Raman measurements were performed on cooling/warming scans between 200 and 300 K. We have used both 514-nm Ar$^+$ ion and 647-nm Kr$^+$ ion laser excitation wavelengths for optical measurements. Pressure was determined from the shift of the T$_{2g}$ Raman band of the stressed diamond using
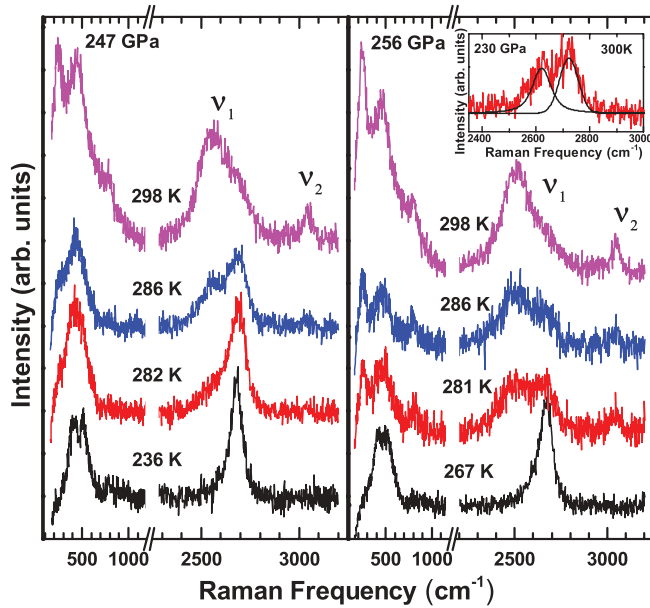
FIG. 1. (Color online) Representative Raman spectra of deuterium upon cooling (left) and warming (right) showing phase IV-III transformations at 247 and 256 GPa. Inset: Coexistence of the ν_1 modes at 300 K and 230 GPa in phases III (higher frequency mode) and IV (lower frequency mode)

the relation proposed in Ref. 10. For a full description of the experimental procedures see Refs. 1 and 11–14.

Selected Raman spectra of deuterium at 247 and 256 GPa and at various temperatures are shown in Fig. 1. At room temperature (phase IV) both ν_1 and ν_2 vibrational modes are clearly visible, having very different widths. Upon cooling at

247 GPa the ν_1 mode of D_2 shows splitting, with a higher frequency band emerging from phase III and the lower band from the remaining phase IV (Fig. 1). Upon cooling the intensities of all Raman modes associated with phase IV decrease, while new peaks appear and grow (Fig. 1). By 285 K, the transition to phase III is complete, the ν_2 mode disappears, and the ν_1 hardens significantly. To our knowledge, there are no published Raman spectra of low-frequency modes in phase III of deuterium to compare our data with. However, the overall spectrum appearances[1,15] and $\sqrt{2}$ scaling of the corresponding modes frequencies between hydrogen and deuterium[1,16] unequivocally demonstrate that the phase at low temperatures is phase III. The temperature scans at higher pressures (e.g., the 256 GPa run in Fig. 1) show identical changes in the Raman spectra, although at different transition temperatures. We find that the III $\leftrightarrow$ IV transformation in both isotopes is very well defined, happens within a 10 K range, and is reversible without any hysteresis in either pressure or temperature, which is expected from light materials with high ZPEs. The spectral positions of the fundamental vibrational modes of both isotopes shift considerably during the phase transition and the value of the shift increases with increasing pressure and decreasing temperature [Fig. 2(a)]. For example, when phase IV is reached for deuterium at 300 K and 230 GPa the discontinuity between the vibron modes in two phases is around 60 cm^{-1} (see inset in Fig. 1) but as the pressure is increased above 230 GPa and the temperature lowered, the vibron mode frequencies undergo more pronounced hardening upon entering phase III from phase IV, reaching discontinuity values of above 200 cm^{-1} [Fig. 2(a); see also below and Fig. 3].

The most interesting observation is the discontinuity of the FWHM of the ν_1 mode at the III $\leftrightarrow$ IV transition, which reflects fundamental changes during the phase transformation
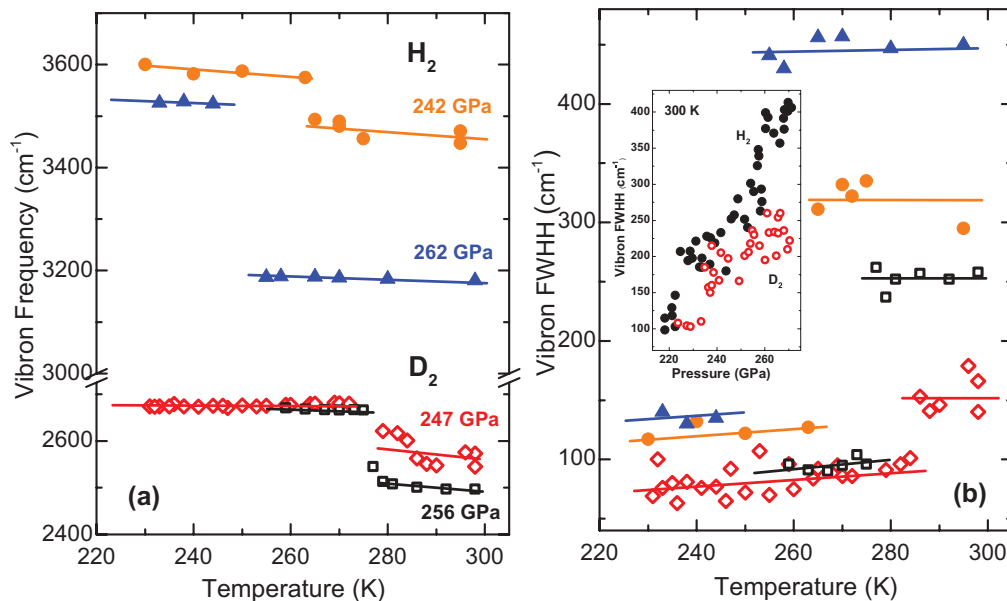

FIG. 2. (Color online) (a) Frequency discontinuities of the ν_1 modes of H_2 (filled triangles, 262 GPa; filled circles, 242 GPa) and D_2 (open squares, 256 GPa; open diamonds, 247 GPa) across the III-to-IV transformations. (b) FWHM of the ν_1 vibrons of H_2 (filled triangles, 262 GPa; filled circles, 242 GPa) and D_2 (open squares, 256 GPa; open diamonds, 247 GPa) plotted versus temperature. Note the quite similar values of FWHM for both isotopes in phase III. Lines in (a) and (b) are guides for the eye only. Inset: FWHM of the H_2 (filled circles) and D_2 (open circles) ν_1 vibron versus pressure at 300 K.
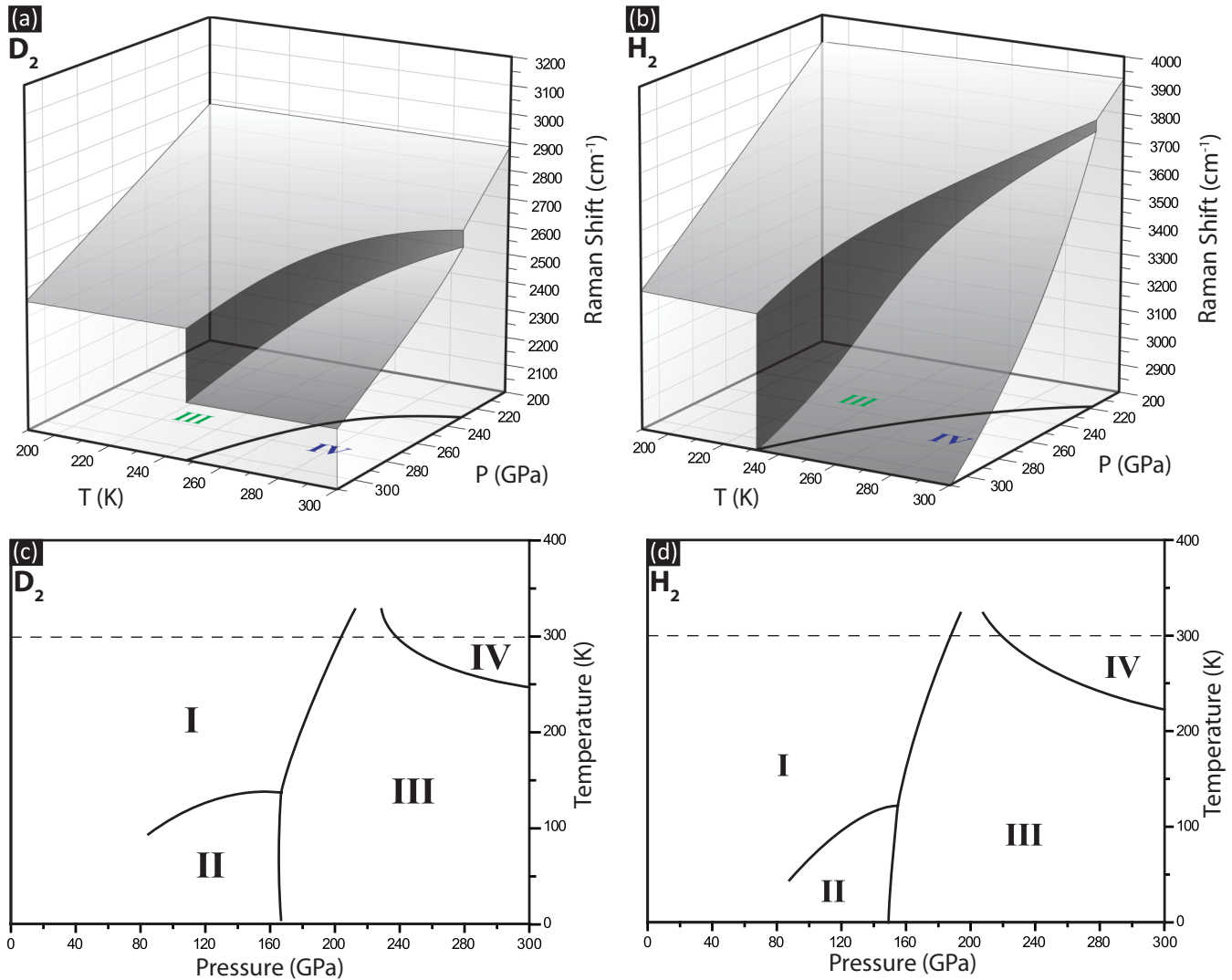
FIG. 3. (Color online) Generalized P-T-ν_1 diagrams for (a) D_2 and (b) H_2 showing the difference in the vibron frequency landscapes. P-T phase diagrams for (c) D_2 and (d) H_2. The lines separating the phases I, II and III at temperatures below 200 K are from Ref. 9.

and demonstrates the quite unusual character of phase IV. Figure 2(b) shows the FWHM of the ν_1 vibron of D_2 (H_2) versus temperature at different pressures. In phase III, the FWHM of ν_1 is marginally larger for hydrogen—between 290 and 250 GPa the width of ν_1 varies from 150 to 100 cm^{-1}—while for D_2 it is from 100 to 75 cm^{-1} [Fig. 2(b)]. However, in the same pressure range (290 to 250 GPa), the picture changes quite drastically upon warming by 10 K and entrance into phase IV: at 290 GPa ν_1 for H_2 broadens to ~450 cm^{-1} (350 cm^{-1} at 250 GPa), while ν_1 for D_2 reaches ~250 cm^{-1} at 290 GPa (150 cm^{-1} at 250 GPa). The most plausible explanation for the increased FWHM of ν_1 in phase IV is the intermolecular proton exchange and reduced lifetime of molecules. The expanded intramolecular bond length and association of these elongated molecules in six-member rings[1,2] would facilitate such intermolecular proton tunneling in one phase (IV) compared to another (III) under nearly identical P-T conditions; particularly, this effect will be enhanced in lighter hydrogen as reflected by its much larger FWHM. It is important to note that some other factors

such as larger anharmonicity or enhanced electron-photon coupling could also be responsible for the observed mode broadening. The ultimate explanation of the described effects should come from theoretical studies. In fact, a very recent *ab initio* variable-cell molecular dynamics simulations[17] study observed "intralayer proton transfer" increasing with pressure and temperature in phase IV, in broad agreement with the present work.

The effect of the increased FWHM of the vibrational mode is already present in phase III,[1,7,18] but phase III has only one type of molecule with characteristic lifetime and bond length, with the FWHM being from 75 to 150 cm^{-1} for both isotopes in a wide P-T range [Fig. 2(b)]. In phase IV, the $Pbcn$ structure was shown to be dynamically unstable,[4] but several $Pbcn$-like structural models with P_c-48 (which still has imaginary phonons),[4] P_c-96,[4] and C_c[5] (both dynamically stable) symmetries having six-member rings were proposed. X-ray diffraction studies are needed to unambiguously determine the structure of phase IV but such experiments are exceedingly difficult at the moment. Our observations of the

FWHM behavior across the III-IV transformation illustrate the importance of temperature effects and that phase IV is a thermally driven partially disordered phase, thus adding additional weight to the proposed mixed atomic and molecular state of dense hydrogen (deuterium).[1,2]

By combining the P-T scans of the ν_1 mode frequencies we constructed three-dimensional P-T-ν diagrams of both species [Figs. 3(a) and 3(b)]. The overall appearance of the phase diagrams is markedly similar but there are several subtle differences. The III-to-IV transition pressures are shifted to slightly higher values for D$_2$. As a result, the III-IV phase line of D$_2$ lies above the one for H$_2$ [Figs. 3(c) and 3(d)]. Our measurements for H$_2$ yield a III-IV line gradient of −1.6 K/;GPa, while the slope is twice as shallow for D$_2$ as shown in Fig. 3. Another difference between the isotopes during the III-IV transformation is the very different values of the vibron frequency discontinuities. With increasing pressure the discontinuity upon the III ↔ IV transition increases (see Figs. 2 and 3), reaching much larger values for hydrogen, e.g., ∼500 cm^{-1} for H$_2$ at 315 GPa and 250 cm^{-1} for D$_2$ at 300 GPa.

These are the largest discontinuities observed between the different phases; for comparison the largest value of the frequency softening of the ν_1 mode upon entering phase III from phase II is only around 100 cm^{-1} for *both* H$_2$ and D$_2$.[19,20]

ZPE and thermal effects must play a crucial role in the formation of phase IV under the P-T conditions described here. The competition between ZPE and entropy would shape the appearance of the phase diagrams [Figs. 3(c) and 3(d)] and create differences in the slopes. Recent DFT studies proposed more energetically stable then $Pbcn$ candidate structures for the phase IV with Pc[4] or Cc[5] symmetries. These calculations suggest that hydrogen would transform to phase IV above 220 GPa and ∼300 K and that this phase would be separated from the phase III by phase line having negative (with respect to pressure axis) slope, in good agreement with our current and previous results.[1] The calculated Raman spectral positions and intensities of the Pc structure[4] are in much better agreement with our experimental observations than $Pbcn$, although they are still not a perfect fit (Fig. 4). The DFT calculations also proposed a $C2/c$ structure as a possible candidate for phase III
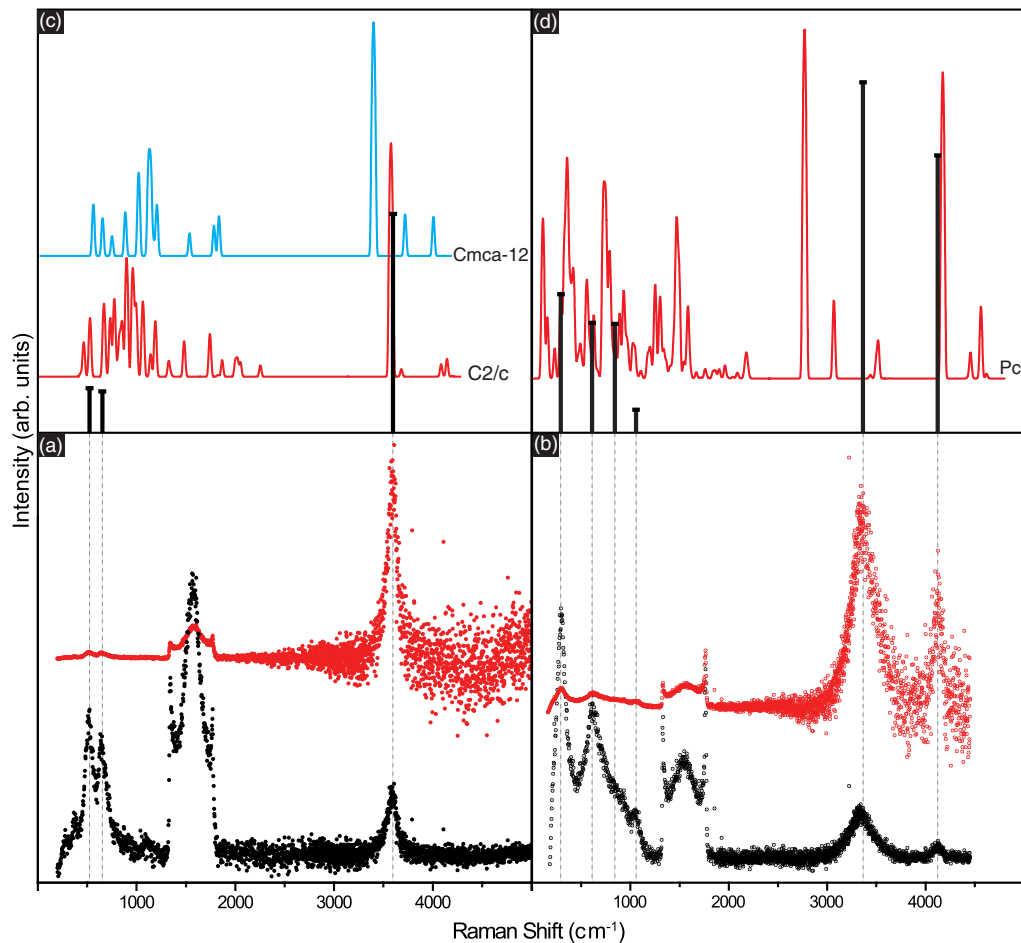

FIG. 4. (Color online) Comparison of experimentally observed and theoretically calculated[2] Raman intensities and spectral positions of the hydrogen bands at 250 GPa. (a, b) Experimental raw spectra observed in phases III (a) and IV (b) are shown below (in black); spectra corrected for decreasing sensitivity of the detector are shown above (in red). The broad peaks between 1333 and ∼1800 cm^{-1} are due to the first-order Raman from diamond. (c, d) Experimental renormalized spectra plotted as Gaussian distributions for phases III (c) and IV (d) [vertical (black) lines]; theoretically calculated spectra for (c) $C2/c$ (red) and $Cmca$-12 (blue) and (d) P_c (red). Note that the intensities for renormalized and theoretically calculated spectra are given on a logarithmic scale to show much weaker low-frequency modes and additional vibrational bands besides ν_1 and ν_2.
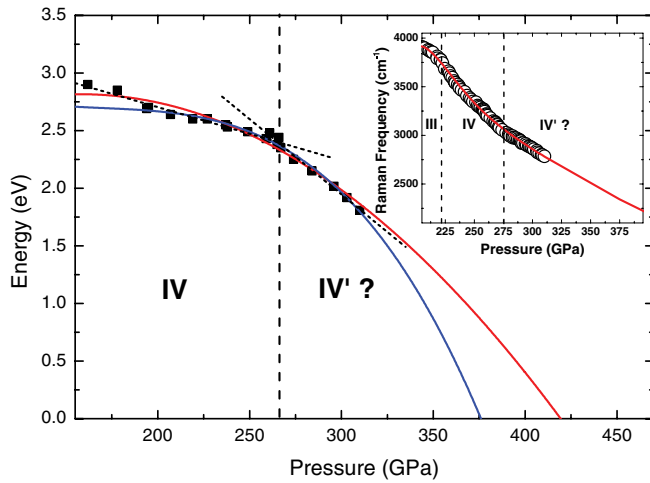
FIG. 5. (Color online) Hydrogen and deuterium combined band-gap points (filled squares) as a function of the pressure at 300 K. Dotted (black) straight lines are linear fits to the measured data points in phases IV and IV′. Quadratic [upper (red) curve] and cubic [lower (blue) curve] polynomial fits extrapolated to higher pressures are shown as solid lines. Inset: Frequency of the ν_1 mode of hydrogen as a function of pressure. Open circles are measured ν_1 vibron frequencies versus pressure. The solid (red) line shows the nearly linear (from 275 to 400 GPa) extrapolation of the ν_1 frequency up to above 375 GPa—the minimal pressure needed to close the optical band gap. Dashed vertical lines indicate the proposed phase transition between phase IV and phase IV′.

(a comparison between observed and calculated Raman spectra in phase III is shown in Fig. 4) and, more importantly, the re-entrance back into a molecular phase V (*Cmca*-12 above 280[4] or *Cmca*-4 above 250 GPa[5]) which appears to have metallic properties in both studies. These predictions of a new metallic phase seem to be in agreement with the recent claims of metallization of $H_2(D_2)$ at above 260 GPa.[3] However, our optical spectroscopy results above 260 GPa are in strong disagreement with Ref. 3, where the *total* disappearance of the Raman signal, increased reflectivity, and a closed band gap were reported. We observed an *increase* in Raman signal intensities with pressure (in our studies higher pressures than in Ref. 3 were reached for both isotopes, as evidenced by the lower vibron frequencies) and an optical band gap of ∼2 eV persisting above 300 GPa. This metallization claim contradicts several experiments conducted at identical compressions[6,7] including a quite recent infrared study of phase III of H_2 at low

temperatures and up to 360 GPa.[8] The theoretically proposed molecular metallic phases (*Cmca*-12 and *Cmca*-4) are Raman active (see Fig. 4), which would also be at variance with the claimed disappearance of Raman modes in Ref. 3. Therefore we attribute the experimental findings in Ref. 3 to the changes in the sample chamber geometry and partial sample loss rather than to the claimed "metallic liquid atomic state."

However, the slight changes in optical properties at 275 GPa, such as the appearance of the fourth low-energy mode (see Fig. 2 in Ref. 1), the change in slopes of the ν_1 frequency, and the value of the D_2/H_2 band gaps with pressure (Fig. 5), *might* indicate the presence of a new solid structure (phase IV′) of dense H_2 (D_2). The very similar Raman spectra suggest that if phase IV′ exists, it is structurally very closely related to phase IV. Phase IV′ appears to be semiconducting in our measurements but one can estimate the pressures needed to close the band gap and reach the metallic state. We have combined D_2 and H_2 band-gap points and used different polynomials to fit and extrapolate our data (Fig. 5). The pressures at which the band gap is fully closed vary widely depending on the power of the polynomial but the lowest value is approximately 375 GPa (Fig. 5). It is instructive to estimate the frequency of the Raman ν_1 mode at this pressure. Indeed, the frequency and increasing intensity of the ν_1 mode are very sensitive to compression (inset in Fig. 5). Therefore the frequency should be considered as an absolute pressure gauge in the experiments with H_2 (D_2) and could be used for direct result comparison in both experimental and theoretical studies. The extrapolation of hydrogen frequency versus pressure is almost linear (Fig. 5) and yields 2350 ± 50 cm^{-1} at 375 GPa. We note that this value is about 55% of the vibron frequency under ambient conditions and is much lower than any frequencies ever reported in experiments.

In summary, we have mapped out the transformation between phase III and phase IV of H_2 (D_2), demonstrating increased proton tunneling in phase IV. We estimate that the H_2 (D_2) will metallize above 375 GPa, a pressure which is in good agreement with several previous experimental measurements.[6,7]

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