# High-Pressure Behavior of Hydrogen and Deuterium at Low Temperatures

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*In situ* high-pressure low-temperature high-quality Raman data for hydrogen and deuterium demonstrate the presence of a novel phase, phase II′, unique to deuterium and distinct from the known phase II. Phase II′ of $D_2$ is not observed in hydrogen, making it the only phase that does not exist in both isotopes and occupies a significant part of $P$-$T$ space from ∼25 to 110 GPa and below 125 K. For $H_2$, the data show that below 30 K the transition to phase II happens at as low as 73 GPa. The transformation from phase II to III commences at around ∼155 GPa and is completed by 170 GPa with the average pressure of ∼160 GPa being slightly higher than previously thought. The updated phase diagrams of $H_2$ and $D_2$ demonstrate the difference between the isotopes at low temperatures and moderate pressures, providing new information on the phase diagrams of both elements.

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Elemental hydrogen under compression has been an alluring topic in the high-pressure sciences for several decades [1]. Despite numerous theoretical and experimental studies [2–11], several outstanding problems remain, such as the structure of phase II, the influence of the isotopic mass difference, quantum motion, and para-ortho equilibrium on the transition pressure to phases II and III. The discovery of phase IV [12,13] has recently reignited interest in the field. As a result of this discovery, the phase diagrams of hydrogen and deuterium above 180 GPa and at 300 K have been extensively studied experimentally [14–21] and theoretically [22–24]. The experimental studies radically expanded both phase diagrams by pushing the achievable $P$-$T$ conditions to new limits; cf. phase diagrams in Refs. [25,26] and in Ref. [21]. Despite the remarkable progress in our understanding of the behavior of both isotopes at very high compressions, there has been no attention given to the $P$-$T$ regimes where phase II exists. But such studies of the hydrogen isotopes at medium compressions are important to understand the evolution of the system during its transformation from the weak intermolecular state with strong intramolecular forces (e.g., phases I, II, and III) to the layered phases (e.g., phases IV and V) with weaker intramolecular bonding and stronger intermolecular interactions.

Phase I of $H_2(D_2)$ is known to adopt a hexagonal close-packed structure with freely rotating molecules at an equilibrium of ortho-para concentration, known as normal $n$-$H_2(D_2)$. The application of high pressures and low temperatures forces the molecules to adopt a broken symmetry phase, phase II, whereby the quantum-mechanical rotational motion is present, though hindered by the increased density [2]. The x-ray and neutron diffraction studies suggest that phases II and III have the centers of the molecules also located on the hcp lattice sites [9,27]. Despite the relatively low pressures needed to reach phase II (for deuterium $P > 20$ GPa at 20 K), the shape and the degree of the molecular deformation and the molecular orientation is still unknown [9]. In the currently accepted picture, the transition between phase I and II is thought to involve the quantum ordering of the molecules while the transition from phase II to III could be described as the classical one [6,11]. Recently, *ab initio* calculations, which took into account the quantum nuclei fluctuations, implied further complexity. It was suggested that in phase II of deuterium the molecular orientations are well defined and therefore the structure could be described as a "classical" one with a given symmetry [11]. On the other hand, the calculations showed that due to the large quantum fluctuations in hydrogen, one cannot identify the underlying classical structure, implying that phases II of $D_2$ and $H_2$ are structurally different [11].

The most recent phase I to II transformation lines are given in Ref. [26] and were determined using optical spectroscopy. In para-$H_2$ the transformation to phase II happens above ∼110 GPa at low temperatures (e.g., ∼20 K [3,4,28]), while for mixed ortho-para-$H_2$, the phase line was only mapped out to 100 GPa and 60 K. In deuterium, the phase line separating phases I and II is well established, requiring pressures as low as 20 GPa (at $T < 25$ K) to reach phase II [8]. Nevertheless, due to its heavier weight, the Raman spectra of phase II in $D_2$ appear to demonstrate more complex behavior than in its lighter counterpart. For instance, Raman studies up to 45 GPa observe 11 weak vibrational sidebands in mixed ortho-para $D_2$ [8]. By analyzing the pressure dependence of these sidebands, Ref. [8] suggested that a phase II′ existed in a very narrow pressure range between 20 and 24 GPa below

40 K. The same authors subsequently presented another observation, that the $D_2$ $\nu_1$ mode frequency gradient change with temperature [26] at pressures around 130 GPa.

In this Letter, we present the results of *in situ* high-pressure low-temperature Raman spectroscopic studies that are used to systematically map out phase II of mixed ortho-para $H_2$ and $D_2$. The changes in the raw Raman spectra of deuterium with pressure and/or temperature indicate the presence of a previously unknown solid phase existing between 20 and 110 GPa and below 130 K. The novel phase, called phase II′ here, occupies the larger part of the $P$-$T$ area that used to be known as phase II. If pressure is further increased at above 110 GPa, phase II′ transforms into phase II. We demonstrate that mixed ortho-para $H_2$ enters phase II from phase I at pressures as low as 73 GPa (at $T = 20$ K). The pressure needed to reach phase III from phase II is around 160 GPa, slightly higher than previously thought and almost equal to the corresponding pressure required to reach phase III of deuterium.

A detailed description of the sample preparation, ortho-para states, experimental details, and pressure measurements are given in the Supplemental Material [29]. The evolution of the Raman spectrum of $H_2$ at 20 K with pressure is given in Fig. 1(a). At pressures above 73 GPa, low frequency peaks at $\sim$90 and 235 cm$^{-1}$ appear, signaling the phase I to II transformation. In the experiments on para-$H_2$, similar excitations were observed above 114 GPa [28]. Such a difference in the transition pressures is due to the difference between pure para-$H_2$ used in Ref. [28] and the mixed ortho-para state in our study for which the transition pressure is lower. In Fig. 1(b), the evolution of the Raman spectrum at a constant pressure of 92 GPa with temperature is shown. If the temperature is reduced below 50 K, then low frequency excitations similar to those shown in Fig. 1(a) appear and phase II is reached (the additional $P$-$T$ paths are shown in Ref. [29]). We also note that a single weak vibrational mode $\nu_2$, which was observed in phase II in para-$H_2$ at 128 GPa, 18 K [28] was not observed in our experiments.

Figures 1(c) and 1(d) show the Raman spectra of $D_2$ that follow similar $P$-$T$ paths to $H_2$. These similar spectroscopic features are exhibited by both $D_2$ and $H_2$ but, there are some important differences between the isotopes. The transformation in $D_2$ at above 20 GPa and at 20 K is not only indicated by the emergence of the low-frequency bands similar to the ones observed in $H_2$, but also by changes in the vibrational activity. Several weak $D_2$ vibrational sidebands appear at a slightly higher frequency than $\nu_1$ at around 3250 cm$^{-1}$ (see also additional figures in Ref. [29]). The small changes of these bands with temperature were interpreted in Ref. [8] as the transformation from phase II′ to II. We find that due to the complexity and low intensity of these sidebands, no definitive statements can be made, but if there is a phase transformation as suggested, then the *phase* II′ described in Ref. [8] is occupying an extremely small $P$-$T$ area, with a width of 2 to 4 GPa, and would be different to phase II′ described here. If a different $P$-$T$ path is taken (e.g., a quasi-isobaric cooling), the same changes occur, namely, the appearance of the secondary vibrational and low energy modes, signaling the entrance into phase II′ [Fig. 1(d)].

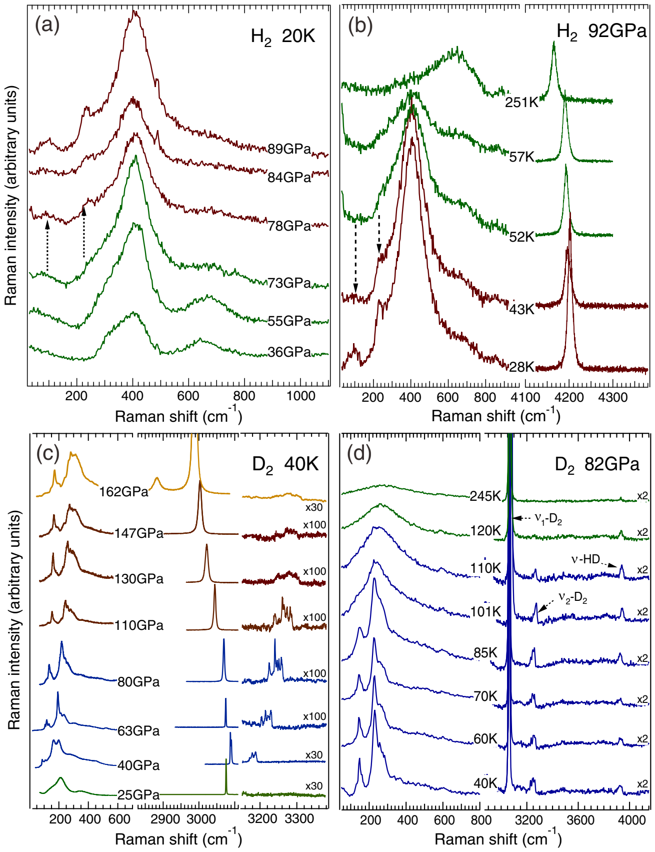

FIG. 1. Representative Raman spectra at different $P$-$T$ conditions. (a) Representative spectra of $H_2$ as a function of pressure at 20 K. (b) Representative spectra of $H_2$ as a function of temperature at 92 GPa. (c) Representative spectra of $D_2$ as a function of pressure at 40 K. (c) Representative spectra of $D_2$ as a function of temperature at 82 GPa. The different colors of the curves represent different phases: green, I; blue, II′; maroon, II.

Besides the spectral changes seen in the raw spectra, the phase transition between phases II′ and II can be also observed in the frequency dependence of the different excitation lines. For example, the main vibrational excitation, being more energetic and less sensitive to the ortho-para concentrations than rotational or librational modes, is a good indicator of phase transitions. In the $P$-$T$ runs at nominally constant pressure (see the Supplemental Material [29]) we collected data on the vibrational excitations in 2–3 K steps (see Fig. 2). These high quality, small temperature interval data allow us to detect the phase transition if the frequency of $\nu_1$ is taken as an order parameter. Figure 2(b) shows the temperature dependence of the $H_2$ $\nu_1$ frequency collected at different pressures. As temperature is increased or decreased (we observed very small $< 10$ K hysteresis) the $H_2$ $\nu_1$

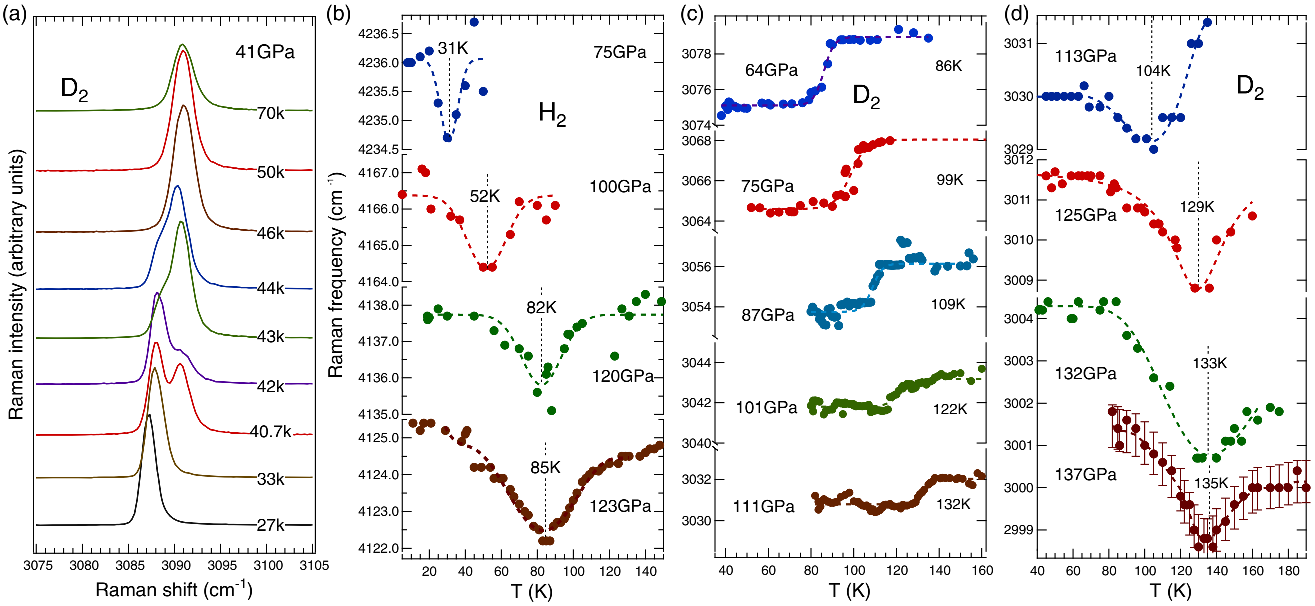

FIG. 2. (a) The representative Raman spectra of the vibrational excitation of $D_2$ as a function of temperature. The vibrational excitation split and shift happen during the phase I to II′ transition. The Raman frequency of $H_2$ (b) and $D_2$ (c), (d) as a function of temperature at various pressures. The solid circles are the experimental data, the dashed lines are only a visual aid. The error bars are only shown on one curve for clarity.

frequency softens abruptly by $\sim 3\ \mathrm{cm}^{-1}$ and then regains its pretransition values creating a "dip" in the frequency versus temperature plot [Fig. 2(b)]. The temperature at which the minimum of the dip is located coincides with the phase transition temperature obtained from the spectroscopic changes described above. The width of the dip increases with pressure from around 10 K at 75 GPa to around 40 K at above 100 GPa. The same analysis of the deuterium vibrational frequency indicates the presence of two different frequency patterns, depending if deuterium is cooled or warmed above or below 110 GPa [Fig. 2(c)]. At below 110 GPa, in the vicinity of the phase I to II′ transition, the $D_2$ $\nu_1$ frequency discontinuously shifts to lower frequency by $\sim 5\ \mathrm{cm}^{-1}$ with decreasing temperature, producing a steplike function [Fig. 2(c)]. The frequency midpoint of the steplike function corresponds to the spectral changes described at the I–II′ phase transition above. As pressure is increased, the discontinuous step becomes smaller, with the steplike shift almost disappearing at around 110–111 GPa. Above this pressure, the temperature dependence of the vibrational frequency changes and starts to resemble the one described above for hydrogen. For both isotopes, the $\nu_1$ frequency of $H_2$ and $D_2$ becomes strongly temperature dependent in phase II. Although the binary mixtures of varying concentration could have different phase diagrams, the changes described here, e.g., the change of the frequency vs temperature dependence or dip vs steplike are distinctly pressure dependent (see also Ref. [29]). This rules out that the observed effects are due to the ortho-para concentration.

Since the structures of neither phase II or II′ are known it is difficult to explain the different behavior of the $D_2$ $\nu_1$ frequency vs temperature relation below and above 110 GPa. Such change is most probably caused by the slightly different atomic environment phase II and II′ might have. For example, two quite similar and energetically competitive structures such as $C2/c$ [11,33] and $P6_3/m$ [10] were seen in calculations at the pressure range where phase II exists. One could speculate that the phase transition described here could be the transformation between two similar structures having different stacking order or different degree of orientational order or disorder, which would lead to the minute changes in the temperature behavior of the optical spectra. We note that the Raman spectra in phases II of $H_2$ and $D_2$ are distinctly different; e.g., phase II of $D_2$ has a much more complex low-frequency part of the spectrum and has a dozen vibrational sidebands, suggesting that the structures of phase II of $H_2$ and $D_2$ are rather different. Our experimental results seem to confirm that this difference might be due to the classical nature ($D_2$) vs strong quantum fluctuations structures ($H_2$) [11] but this picture awaits x-ray spectroscopy confirmation or disproval.

Additional signs of the phase II′-II transformation also come from both the vibrational and low frequency modes dependencies with pressure. The low-frequency excitations show the appearance of a new mode at around 95 GPa (somewhat lower than 110 GPa, where most changes occur) while the second order vibrational modes' frequencies change the slope as pressure is increased (Fig. S8, Fig. S9 in the Supplemental Material [29]). In Fig. 3 we plot the $P$-$T$ paths taken in this study and combine them with the previous known phase boundaries [26] (see also the figure with overlapping phases in Ref. [29]). Based on the

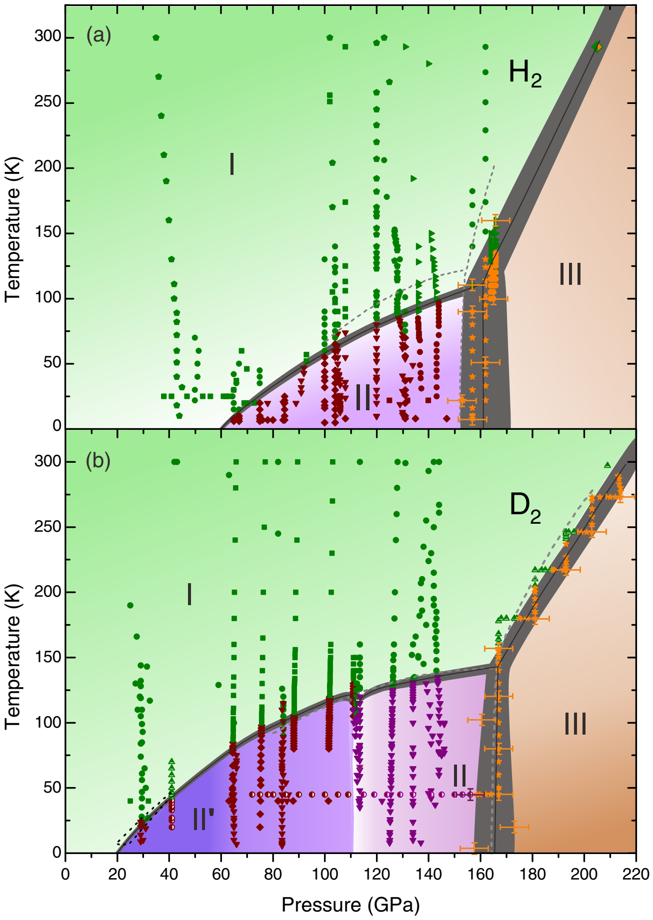

FIG. 3. Proposed phase diagrams of hydrogen (a) and deuterium (b) in a low-temperature, medium-pressure range. Different colors represent different phases in accordance with Fig. 1. The gray dashed lines are the phase boundaries from Ref. [26]. The darker shaded area around the phase transition lines indicates the area where the two phases coexist. The dashed-dotted line in (b) between 20 and 40 GPa along the I-II phase line indicates the area previously proposed as phase II′ [8].

analysis of $T_P$ and $P_T$ scans, we propose the existence of a new phase of deuterium, II′, which broadly resembles phase II. It occupies a significant part of the phase space that previously was thought to be occupied by phase II between 25 and 110 GPa. Above 110 GPa, phase II′ of $D_2$ transforms into phase II. For hydrogen, we observe the appearance of the $\nu_1$ mode characteristic of phase III at around 155 GPa while the transformation is completed by 170 GPa with the average pressures at ~160 GPa being slightly higher than previously reported [26], although still below the $D_2$ transition pressure. The I to II phase line seems to lie at lower temperatures, with the difference becoming larger with increasing compression. For the phase diagram of deuterium, the agreement between the location of the phase lines is excellent. This agreement between the data we present and previously published data on deuterium rules out a systematic error and/or different pressure scales used, e.g., ruby vs diamond edge.

Until now, the low-temperature phase diagrams of hydrogen and deuterium were identical in terms of exhibited phases. Phase II′ would be the first instance of a phase that does not occur in both isotopes. The appearance of phase II′ in $D_2$ is clearly driven by the quantum effects and we attribute its existence to a lower zero-point energy (compared with hydrogen) and more complex rotational movement due to the stronger intermolecular interactions. Therefore, the presence of another phase in deuterium could almost be expected due to the interplay between the classical and the comparatively weaker quantum behavior of the heavier isotope. This raises an interesting question about the behavior of mixtures of $H_2$, $D_2$, and HD at these conditions. The absence of para-ortho distinction in HD, and the random distribution of the isotopes [23] in the sample, could create "phase II" with properties that would be very different to those described in this study.

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