Editors' Suggestion

Phase transitions in H_2-HD-D_2 mixtures up to 350 GPa

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Utilizing the high-pressure low-temperature Raman and optical transmission/absorption spectroscopies, we have mapped out the phase diagram of H_2-HD-D_2 alloy with the initial H:D concentration 50:50 up to 350 GPa between 10 and 300 K. We followed the phase lines between all known solid phases [I, II, III, IV, and IV′ (IV + V)] of pure H_2 and D_2 constraining their locations in the wide P-T space. We trace the phase boundary separating phases III and IV(IV′)/V demonstrating that this phase line has a steep negative slope (−0.95 K/GPa), which becomes shallower at above 250 GPa (−0.55 K/GPa). The phase line follows the trend observed in the pure species. Additionally, we find that the band gap of the mixture between 300 and 360 GPa is close to those of the pure species suggesting that alloying one isotope by another would not significantly shift the metallization pressure. These observations imply that hydrogen deuteride (HD) has very similar properties to those exhibited by the pure species.

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I. INTRODUCTION

Hydrogen (deuterium) molecule is deceptively simple but when many of them arrange themselves into the crystalline state, they unexpectedly create the solid with one of most intricate and complex phase diagram among the elements [1–7]. As the result both hydrogen and deuterium phase diagrams attract considerable attention and were extensively studied in a wide pressure and temperature range. Currently there are 5 known solid phases of hydrogen, while phase V of deuterium is believed to happen at higher pressures than those required for H_2-V and was not yet experimentally observed [4]. Hydrogen deuteride (HD), on the other hand, was studied significantly less than pure H_2 and D_2 most probably due to its prohibitively high price.

Nevertheless, the absence of the *ortho-para* distinction and therefore lack of the quantum effects pertinent to those effects observed in pure species, and "in between" two isotopes mass, make HD an interesting object to study and compare with two other species. To the best of our knowledge there are very few papers which deal with HD and/or hydrogen-deuterium mixtures at high pressures [9–12] and only 2 studies presented the phase diagrams in a wide pressure-temperature range [13,14]. The phase diagram of pure HD was studied up to the claimed 340 GPa at low temperatures by the infrared (IR) spectroscopy [14], while the low-temperature phase II and its transformation to the phases I and III were explored as function of concentration of the constituent hydrogen and deuterium using the Raman spectroscopy [13]. The room-temperature high-pressure study of hydrogen-deuterim mixtures of different concentrations suggested that they form alloys, where the mass disorder leads to the Anderson localization of the vibrational modes [12]. Later, it was found that in HD the phase transitions at room temperature (as detected by the changes of vibrational frequencies) in hydrogen-rich mixtures (75:25) are very close to those observed in pure hydrogen [4]. The critical pressures for the transitions III-IV, IV-IV′, and IV′-V were found to be 220, 275, and 325 GPa, respectively [13].

In general, the behavior of the hydrogen isotopic mixtures at high pressure is quite similar to that of the pure isotopes, as was reported in Refs. [4,9,10,12], see Fig. 1, and compare to the phase diagrams of H_2/D_2 in Ref. [4]. However, the low-temperature infra-red (IR) spectroscopic study [14] presented a phase diagram markedly different from those of pure hydrogen and deuterium without providing any explanation. The study [14] did not convincingly demonstrate any measurements from which pressure was estimated and did not provide any raw data (one spectrum within a very limited energy range was given in Supplemental Material) to support the findings. The claims of several novel phases and phenomena were based on fitted spectra only, without any remarks on the quality of the fits. According to Ref. [14], at low temperatures HD-III transforms HD-IV*, which coincides with the dissociation of HD molecules into pure H_2/D_2. At even higher pressures, HD-IV* was claimed to transform to another phase (HD-PRE) [14], Fig. 1 [14]. On the other side, the Raman study [13] was mostly focused on how the H:D concentration influences the phase transitions between phases I, II, and III in isotopic mixtures. It demonstrated that H_2-HD-D_2 mixtures exhibit identical phase sequence to the pure species but the

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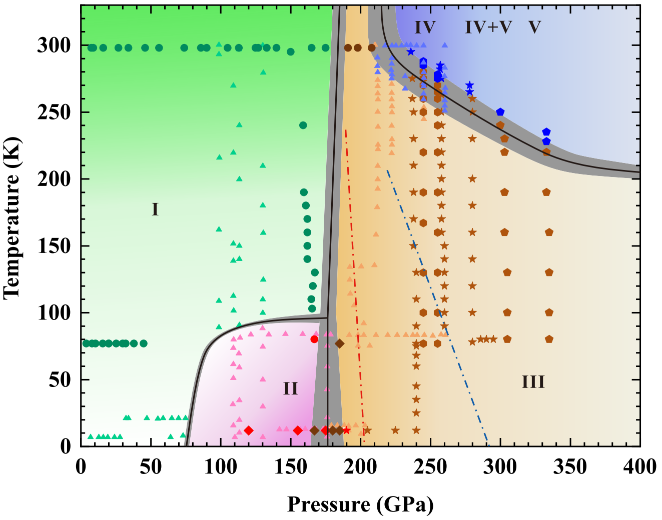

FIG. 1. The phase diagram of H_2-HD-D_2. The color scheme used in the figure corresponds to Refs. [4,8,13]. The small triangle symbols represent the data from Ref. [13]; The two dot-dashed lines indicate the claimed phase transitions from Ref. [14].

phase lines of the mixtures were noticeably shifted to higher pressures and equivalently to lower temperatures compared to those in pure isotopes. Quantitatively, the phase transition pressures of phase II to III increased by 10–30 GPa for all concentrations. The transformation to the low-temperature phase II required temperatures slightly lower than those needed to reach D_2-II for the deuterium rich mixture while the 50:50 and 75:25 (H:D) mixtures yielded temperatures comparable to those at which transition to H_2-II happens, see Fig. 1 in Ref. [13]. Clearly, there is a need for the convincing phase diagram of HD to test its consistency with those of the pure isotopes.

In this work, we have investigated H_2-HD-D_2 mixtures of three different concentrations (H:D 50:50, 60:40, and 70:30) with the focus on the alloy with equal amounts of hydrogen and deuterium (50:50). The phase diagram of this mixture is mapped out up to 350 GPa between 10 K and 300 K by utilizing the Raman spectroscopy. The Raman spectra indicate that H_2-HD-D_2 alloy displays identical to the pure-species phase sequence. We obtain high-quality Raman spectra in a wide energy range covering the rotational/librational and vibrational pasts of the spectra observing the characteristic features of each phase but find no evidence of the previously claimed new phases [14]. We trace the phase line between phases III and IV demonstrating that it has a negative with respect to pressure slope, which becomes close to being horizontal at above 300 GPa. Using the transmission/absorbance measurements we estimate that the band gap of the mixtures is very close to that of the pure species suggesting that alloying one isotope by another would not significantly shift the metallization pressure.

II. METHODS

For this study we conducted a total of twelve independent experiments. We have covered the *P-T* between 300 and 10 K and from 0.2 to 350 GPa. We have generated high pressures in the long piston-cylinder cells of our own design with diamonds having culet sizes from 15 to 50 microns. The rhenium foils of 250 microns thick were used as gasket material. The hydrogen/deuterium gas mixture was clamped at 1850–2000 bar and usually pressurized to around 1 GPa while in the gas loader. The cell was mounted into the custom built continuous–flow cryostat which allows to conduct *in situ* optical measurements in a wide temperature range. The Raman spectra were excited using 532 and 660 nm laser excitation wavelengths and collected with a spectrograph equipped with charge coupling device (CCD) array detector and pressure was calculated from the position of the diamond edge [15]. We prepared the gas mixtures by combining hydrogen and deuterium from gas cylinders at room temperature using the partial pressures to achieve the desired concentration. The isotope exchange reaction $H_2 + D_2 \rightleftharpoons 2HD$ happens within minutes in the fluid state and can be monitored using the Raman spectroscopy. After loading the concentration C was confirmed spectroscopically by using the areas of the fundamental vibrational ν_1 modes A_{H_2}, A_{HD}, and A_{D_2} using the following formula: $C = \frac{A_{HD}}{(A_{H_2}+A_{HD}+A_{D_2})}$. For further experimental and technical details the reader is referred to Refs. [8,12,13] and Supplemental Materials therein.

III. RESULTS AND DISCUSSION

A. Isothermal compression

The representative isothermal Raman spectra of the mixture as function of pressure at 3 different temperatures are shown in Fig. 2. The presented spectra at all temperatures are broadly similar to those of the pure species, yielding the identical phase-transition sequence as the pure elements. The low-frequency part of the spectrum is dominated by the rotational/librational modes, which are very well defined and separated at low pressure (see spectrum at 8 GPa in Fig. 2(a) and Ref. [16]) but quickly merge and broaden under pressure forming a wide continuous band [17]. At room temperature phase I extends for almost 180 GPa from the solidification at 5.5 GPa to transition to phase III at around 175 GPa. This transition is very subtle, for instance, there is no noticeable change of the frequency with pressure *c.f.* Fig. 3(a) here and Fig. 3 in Ref. [3], and can be only detected by the relatively abrupt change of the vibrational modes' width, see Fig. 3(b). We note that the hydrogen vibrational mode(s) appear(s) to be the weakest. The phenomenon can be explained by the fact that hydrogen molecule being the lightest scatters the most, broadening the peak(s) [12], and partially by the decreased sensitivity of the CCD at higher wave numbers (> 3500 cm^{-1}) if the red laser (660 nm) is used. In order to increase the intensity of the hydrogen-related modes in some experiments we have used additional concentrations H:D such as 60:40 and 70:30 which allowed us to observe the $H_2 - \nu_1$ at higher pressures.

At low temperatures the phase transitions are much better defined due to the abrupt changes in frequencies, width, and overall appearance of the spectrum in different phases. At 12 and 300 K the mixture enters phase III at around 165–170 GPa as witnessed by the sudden softening of the vibrational frequencies, Fig. 3(a), and by the discontinuous increase of the width of the corresponding peaks, Fig. 3(b). However, unlike at 300 K the low-frequency region (<1000 cm^{-1}) undergoes profound changes and is readily observable in the spectra,

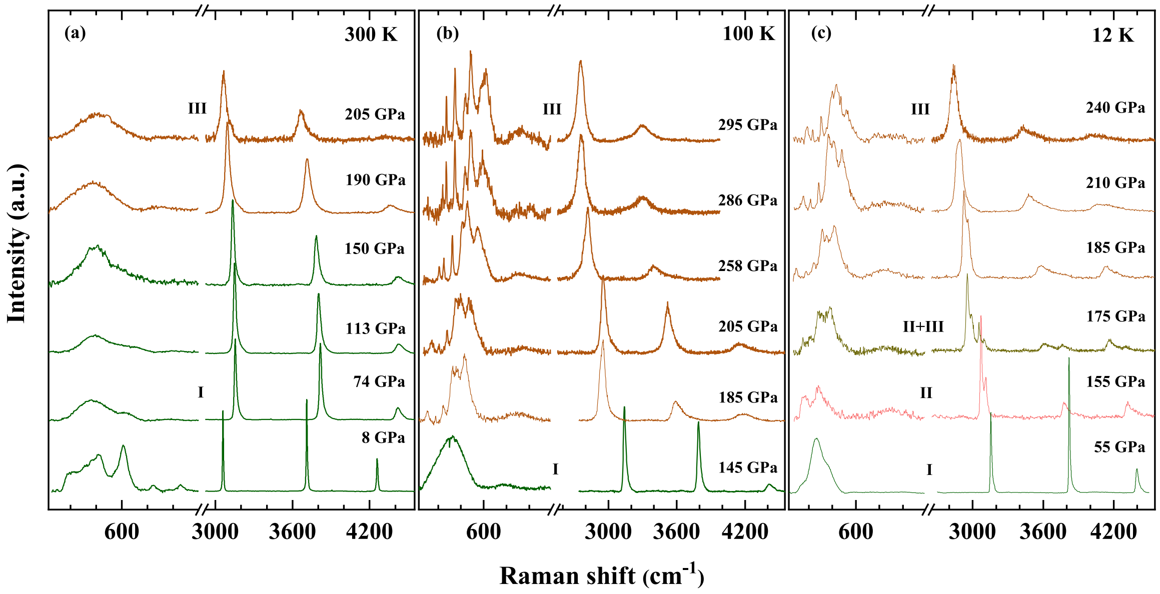

FIG. 2. The Raman spectra of H:D 50:50 mixtures as function of pressure at 300, 100, and 12 K. (a) Raman spectra at 300 K from 8 GPa to 205 GPa; (b) Representative Raman spectra at 100 K showing the transitions from I to III; (c) Raman spectra of the phase transition I-II-III at 12 K. The different spectra colors represent different phases. Phase I: green, phase II: red, phase III: dark orange.

Fig. 2(b) and Fig. 2(c). The broad vibrational density of stateslike feature is replaced with well-defined and narrow phonons (librons) which become sharper as pressure is increased. The emergence of the well-defined narrow phonons indicated the molecular ordering with pressure and gradual lowering of symmetry although the underlying lattice remains *hcp*-like [18].

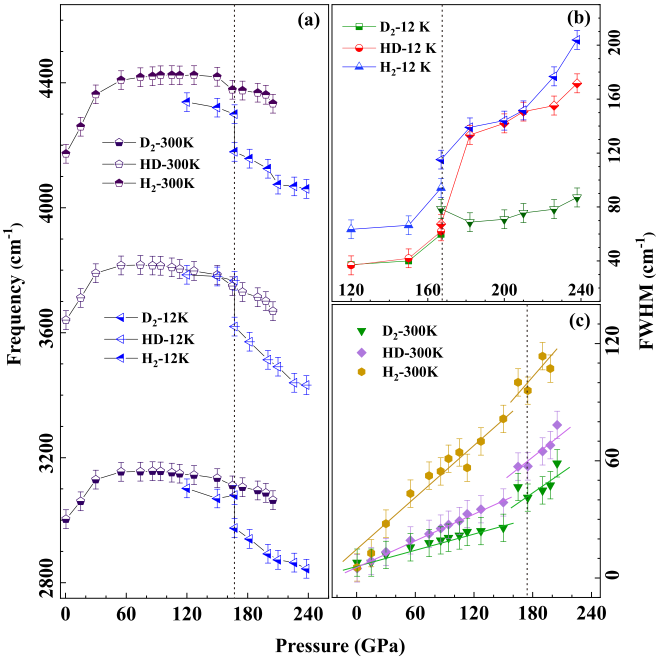

FIG. 3. The frequency and full widths at half maximum (FWHM) of the vibrational modes as function of pressure up to 240 GPa at 12 and 300 K. (a) The vibrational frequency as function of pressures at 12 K, 300 K; the FWHM as function of pressure at 12 K in (b) and 300 K in (c).

B. Isobaric heating and phase III to IV(V) transformation

Phase transition between phases III and IV at high pressures (above ∼250 GPa) is arguably the most interesting transformation observed in dense hydrogens due to the very shallow slope of the phase line separating phases III and IV(V) [4,19]. The phase transition is purely temperature driven and was not observed in the H:D mixtures at such high pressures before. The changes in the Raman spectra through the III to IV(V) phase transition are striking, abrupt, and very easily detectable. One of the most interesting features of phase IV(V) is the presence of two vibrational modes due to the two different atomic environments, which are usually described as graphene like (G) and free molecules (B) layers [20]. Figure 4 presents 3 selected temperature scans collected at nominal pressures of 236, 278, and 335 GPa, while Fig. 5 shows the librational and vibrational frequencies as a function of pressure in phases III and IV(V). There are several interesting features/tendencies in the evolution of the spectra with temperature. Deep in the stability field of phase III, all librational modes exhibit distinct, very well-defined peaks with the spectra resembling those of the pure species. Nevertheless, it is interesting to note that unlike the vibrational part of the spectra, the low-frequency part cannot be represented as the linear combination (summation) of three isotopes, e.g., the spectra of mixtures at low frequencies. Phase III of the mixtures has *less* number of peaks (around 8, see Fig. 4) than the individual species at these conditions (9 for H_2 [21] and 13 for D_2 [5]).

In the liquid state and more importantly in phase I at lower pressures both the rotational and vibrational modes can be described as the linear combination of two isotopes indicating that all atomic species participate in these modes. There, each of the isotopes contributes all available rotational modes and one vibrational mode each to the corresponding rotational and vibrational density of states, for example see Fig. 4(b). But in phase III the picture changes and the low-frequency

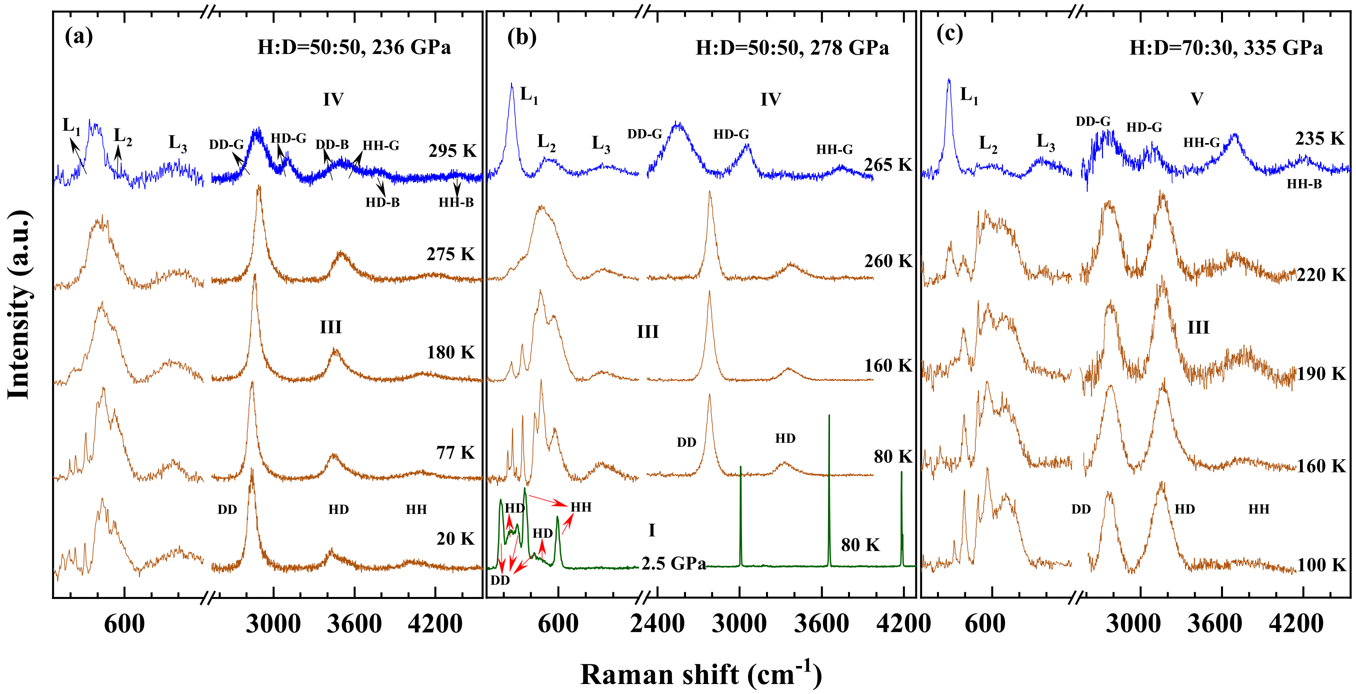

FIG. 4. Representative Raman spectra of H_2-HD-D_2 mixtures as function of temperature at different pressures. The isotopic ratio of H:D is 50:50 in (a),(b) and 70:30 in (c). Orange color represents phase III, and blue color represents phase IV. The low-frequency excitations in phase IV are marked L_1, L_2, L_3 [4].

part, having less peaks than the individual isotope, cannot be represented as the sum of two spectra anymore. This interesting effect was attributed to the Anderson localization driven by the mass disorder and was observed in phase IV at room temperature [12]. Here, we observe an identical effect but for phase III at very low temperature. That suggests that the Anderson localization, which was thought to be partially influenced by the geometry of the six-atom-ring G layer in phase IV [12], is present in the “standard” hcp-like structure of phase III [22]. The evolution of these low-frequency modes with increasing temperature is gradual, the well-defined narrow peaks slowly merging into the broad but relatively intense excitations, which eventually transform into the phase IV characteristic-looking 4 phonons (labeled $L_{1,2,3,4}$ [3,12]). At the same time the vibrational modes drastically soften through the III-IV phase transition and a new vibrational excitation appears signifying the emergence of the freelike molecules layer (B) [3]. The temperature of the III-IV transformation slowly goes down with pressure simultaneously changing the slope. The phase line has some rather unique characteristics such as being essentially vertical at between 200 and 230 GPa, having negative with respect to pressure slope and as pressure increases the slope flattens out with the phase line becoming almost horizontal at pressures above 300 GPa, Fig. 1.

C. Band gap as function of pressure

Ref. [14] claimed two novel phases of hydrogen deuteride, which do not exist in pure isotopes. At the highest pressures the paper suggested that “*the higher pressure phase may precede the transition to metallic hydrogen deuteride and we have named it HD-PRE*” although no explanation was given why this phase, if real, should precede the metallization. In order to gain more information about the electronic properties of mixtures at these compressions, and because the band gap of HD was never measured before, we have optically measured the band gap of the 50:50 mixtures at 100 K between 135 and 350 GPa, (135 GPa was used as the reference point). Figure 6 presents the band gaps of the H:D mixture and pure hydrogen [3,6] and deuterium [23] in the same pressures range. We observe the gradual closure of the alloy’s band gap linearly with pressure, which is in excellent agreement with the previously published works on pure isotopes. The alloy’s band gap lies almost exactly in between the band gaps of hydrogen and deuterium, Fig. 6. Note that at the same pressures the deuterium’s band gap is around 0.5–0.6 eV larger than that of hydrogen [23]. Interestingly, the 50:50 alloy’s band gap values do not lie exactly in the middle between those of the pure isotopes but seems to be shifted upwards towards the deuterium’s ones. If this is really the case (it also might be the artifact of the systematic error) then it would appear that alloying one element with another does not decrease the band gap, as it was speculated by suggesting the existence of HD-PRE phase [14]. On the contrary, the alloying is marginally increasing the band gap resulting in the slightly larger values, which are closer to those of pure deuterium. Thus, the effect of alloying, if any, would move the metallization pressure of the mixture above the one required to metallize pure hydrogen.

IV. CONCLUSIONS

By combining our data from our previous studies [12,13] and the Raman and transmission/absorbance measurements from this work, we are able to constrain the phase diagram

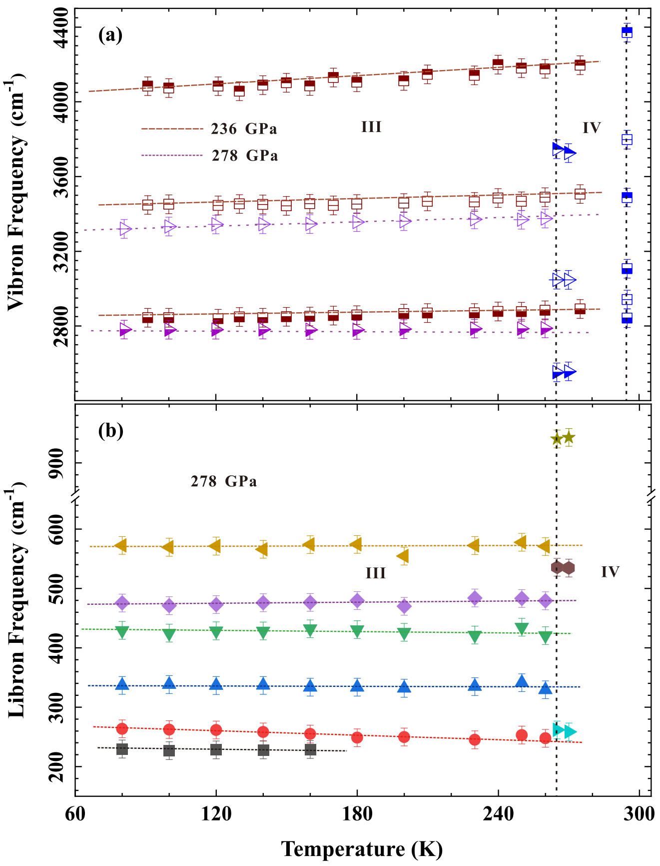

FIG. 5. The frequency of vibrational and librational modes as function of temperature at different pressures. The isotopic ratio is H:D=50:50 in the isobaric heating process from phase III to phase IV. (a) The vibrational frequency versus temperature; (b) the librational frequency versus temperature. The vertical dashed lines indicate the phase transitions to phase IV at ∼295 K at 236 GPa and ∼245 K at 278 GPa.

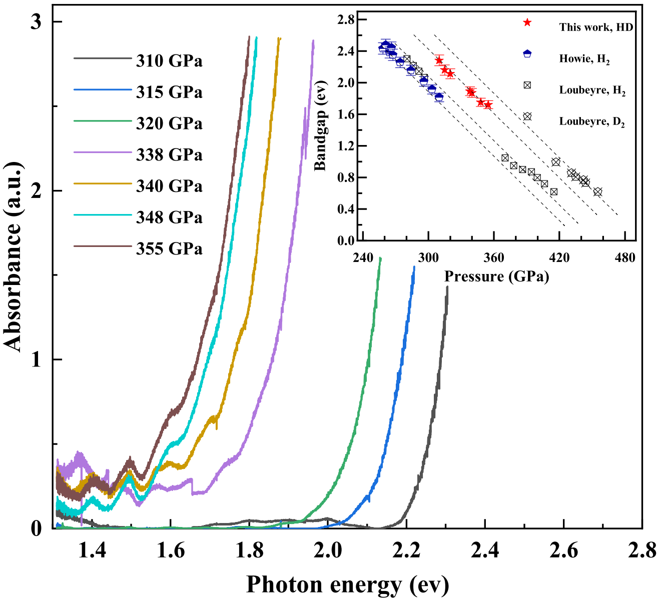

FIG. 6. The absorbance spectra of D_2-HD-H_2 as function of pressure compared to the band gaps of pure isotopes. The insert: the band gap of HD at 300–360 GPa and 80 K (phase III). The band gap of pure isotopes (H_2, D_2) are taken from Refs. [6,19,23].

of H_2-HD-D_2 between 0 and 350 GPa from 10 to 300 K. Our measurements are in excellent agreement with previously published works both on mixtures and on pure isotopes. We do not confirm the existence of the previously reported phases claimed on the basis of the infrared spectroscopy [14]. We demonstrate that the phase diagram of the mixture of hydrogen deuteride (HD), hydrogen (H_2), and deuterium (D_2) is almost identical to that of the pure individual species. We observe the mass-driven Anderson localization at low temperatures in phase III, the effect which is also fundamental in shaping the appearance of the Raman spectra of the H:D mixtures in phases IV. The Anderson localization, driven by the mass difference, is the phenomenon that could be only observed in alloys but apparently does not play any role in determining their phase diagram. The measurements of the mixture's band gap show that it is slowly closing under pressure, in line with all other gradual changes demonstrated by solid dense hydrogen and deuterium under compression.

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