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New Phases and Dissociation-Recombination of Hydrogen Deuteride to 3.4 Megabar

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We present infrared absorption studies of solid hydrogen deuteride to pressures as high as 340 GPa (100 GPa=1 megabar) in a diamond anvil cell and temperatures in the range 5 to 295 K. Above 198 GPa the HD sample transforms to a mixture of HD , H_2 and D_2 , interpreted as a process of dissociation and recombination. Three new phase-lines are observed, two of which differ remarkably from those of the high-pressure homonuclear species, but none are metallic. The time-dependent spectral changes are analyzed to determine the molecular concentrations as a function of time; the nucleon exchange achieves steady state concentrations in ~ 20 hours at ~ 200 GPa.

In 1935 Wigner and Huntington predicted that hydrogen would transform to an atomic metallic solid at high density [1]. There is a decades long effort to metallize the hydrogens (H_2 , D_2 , and HD) in the solid state at high pressure and low temperature or moderate pressures and high temperatures. We have studied HD to very high pressures. With increasing pressure we first observe the line separating phases I-III; then when entering a new phase at 198 GPa, HD transforms to HD , H_2 , and D_2 . We propose that the nucleon exchange is due to a process of dissociation followed by recombination that we call **DISREC** (see discussion ahead). At still higher pressures and low temperatures, yet another phase is entered. In contrast to pure isotopic systems, the new phase lines are almost vertical and appear to intersect the $T=0$ Kelvin axis. The observation of new phases are unexpected with a significant departure from the behavior of the pure isotopic solids; DISREC confirms phenomena that have only been observed in theoretical simulations. None of the newly observed phases are metallic.

The hydrogens form remarkable solids whose properties are dominated by quantum effects: the ortho-para isomers due to the Pauli principle and large zero-point energies/motions in the crystal lattice. At low pressure, ortho and para, fundamentally distinguished by their nuclear spin states, have distinct structures and properties. The ortho-para concentrations are metastable with slow conversion to equilibrium [2]. At megabar pressures there are predictions that hydrogen may be a liquid at $T=0$ K or low temperature due to the zero-point energy [3, 4]. HD is a special case because the nucleons are distinguishable, and thus the ortho-para distinction is not a feature and molecular states rapidly thermalize. A distinction of HD is that the free molecules have a small permanent electric-dipole moment (5.85×10^{-4} D) [5]. Our ultimate goal is to extend the phase diagram to higher static pressures and low or modest T for any of the isotopes to achieve the metallic phase. A first-order phase transition to liquid metallic hydrogen (**MH**) at static pressures and high temperatures has recently been observed [6], and liquid metals of hydrogen and deuterium have been observed in high-temperature shock experiments [7, 8]. There have been a number of very high static pressure studies of the solid homonuclear species at lower temperatures, but none have achieved metallization [9-14].

To understand *HD* in the context of the hydrogens we first discuss the known phases of the isotopes. Ideally the structures of phases are determined by x-ray or neutron diffraction techniques, but these are very challenging measurements for the high-pressure hydrogens as the samples are very small and the molecules are very weak scatterers. In practice the phase lines of the hydrogens have been determined by optical methods, studying Raman or IR active modes. At a phase transition, modes disappear, appear, or undergo discrete shifts, as the symmetry of the lattice changes; these changes pinpoint the phase lines. Samples with mixed ortho-para concentrations are disordered and lack translational symmetry but still demonstrate similar phase transitions as determined by optical measurements. The loss of translational symmetry is more distinct for isotopic mixtures due to the different masses (a much larger distinction than nuclear spin states), yet in this paper we present clear evidence of phase transitions in these disordered systems. We believe that the observed transitions are structural, for example, transitions to structures having graphene like planes with translational disorder within the planes. There are a small number of ways that clusters of isotopes can be formed and these can lead to distinct spectra.

The phase diagrams of the solid hydrogens at high pressure are similar; we discuss these with the help of Fig. 1, where we show known phase diagrams, as well as our new data that we shall discuss later. Since the phase diagrams of hydrogen and deuterium are similar, for comparison to HD we shall focus on one of these, D_2 . For pure solid ortho- D_2 , a transition from the low pressure (LP) hexagonal phase to an orientationally-ordered structure called the BSP (broken symmetry phase) takes place at 28 GPa [15]; a second transition occurs at ~ 150 GPa [16] to the D-A phase, which is also orientationally-ordered. For mixed ortho-para concentrations, which lack translational symmetry, the LP, BSP, and D-A are called phases I, II, and III. Recently, at higher pressures (~ 230 GPa) and around room temperature, an insulating phase named IV has been observed for H_2 and D_2 [11, 12, 17], having a P,T phase line with a rather weak pressure dependence [17, 18].

A number of years ago Brown and Daniels [19] showed that when a mixture of H_2 and D_2 is pressurized (pressures between 1.4 and 60.5 GPa) at room temperature, a process takes place to form HD, leaving an H_2 , D_2 , HD mixture (this process has recently been confirmed with higher pressure studies by Howie et al up to almost 300 GPa [20]). Subsequently, Moshary,

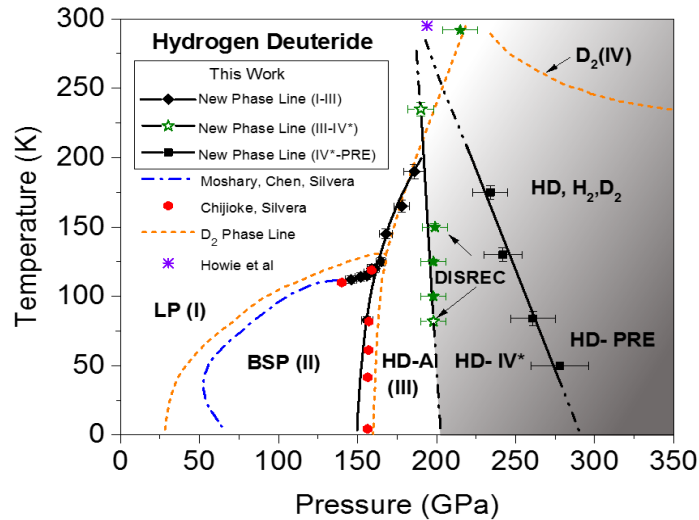


Fig. 1. The phase diagram of HD , extending the earlier measurements beyond the triple-point to establish the I-III line. For comparison we show the phase diagram of D_2 . Solid lines (above ~ 200 GPa) indicate new phase-lines of mixtures of isotopes. For the III to HD-IV* line we only traversed the phase line at $P \sim 198$ GPa and $T = 82$ and 240 K, indicated by open stars, while DISREC was observed all along the phase line (filled stars). The shaded area shows where hydrogen, deuterium, and hydrogen deuteride spectra were observed. We also show a DISREC point at room temperature and a point from Howie et al where they observed a phase transition.

Chen, and Silvera [21] studied a sample of HD to 110 GPa at 77 K, showing that $2HD \rightarrow H_2 + D_2$ does not take place, while Chijioke and Silvera [22] saw no evidence of isotope changes to 159 GPa at 160 K. In this letter we report on a study of HD to a pressure of ~ 340 GPa. No changes of HD were observed after 14 hours at 184 GPa and 82 K. Above 198 GPa and temperatures ranging from 5 to 295 K, we observe the formation of H_2 and D_2 , while HD remains a component. We extend the phase diagram for HD, studied earlier [22, 23], to our highest pressures. The lattice is not metallic at the pressures studied and we conclude that the process $2HD \leftrightarrow H_2 + D_2$ can take place at ultra-high pressure.

The samples of HD gas (our virgin sample of HD had $\sim 4\%$ H_2 impurity) were cryogenically loaded in diamond anvil cell (DAC). The DAC was mounted in a cryostat similar to an apparatus described elsewhere [24]. Conic shaped type II diamonds with 50-micron diameter culets were coated with alumina that acts as a hydrogen diffusion barrier; a rhenium gasket was used. IR spectra were obtained in the temperature range 5-295 K with a Nicolet FTIR interferometer that uses an internal thermal light source. The experiment lasted 6 weeks and terminated with failure of the diamond anvils. At the highest pressures the diameter of the sample was about 14 microns (see photo in Supplementary Information, SI); interferograms were averaged for about 35 minutes to obtain adequate signal-to-noise (see SI). Although the sample contained a ruby particle for pressure determination, our studies extended far beyond the calibrated ruby scale [25]. As is common for ultra high-pressure experiments on the hydrogens, we used frequencies of the IR vibron modes for pressure determination [26, 27], calibrated against the diamond phonon scale [28] (see SI).

Spectra of the sample were obtained as a function of pressure and temperature. In Fig. 2 we show fits to the IR absorption spectra (also see SI). Remarkably, the IR spectral lines that we

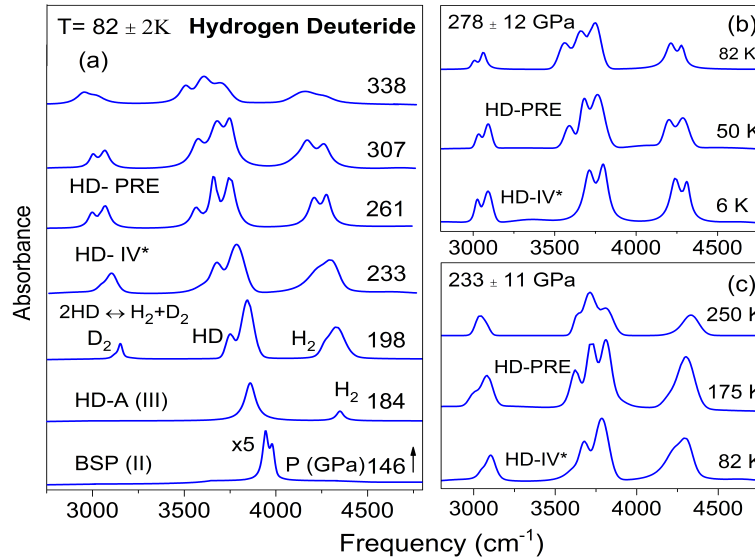


Fig. 2. Left: infrared spectra as a function of pressure at a temperature of 82 K. At 146 GPa the impurity hydrogen vibron line is too weak to be observed in phase II. With increasing pressure one sees the onset of deuterium lines and growth of hydrogen lines, evidence of DISREC, as well as splitting of the spectral lines. For the spectrum at 198 GPa the sample was in the process of transformation and not at final equilibrium concentrations. Right: IR spectra as a function of temperature for the indicated pressures. (b) As temperature is lowered, a transition from PRE to IV* is observed; (c) shows the reversal, IV* to PRE.

observe from the three species remain rather sharp and resemble spectra in the pure isotopic samples, in spite of the conceptual picture that any molecule is in a cluster of neighbors of mixed isotopic composition. This is probably because the intermolecular interactions average out for mixed samples and impurity modes (due to isotopes doped into an otherwise isotopically pure sample) are experimentally known to follow the IR mode pressure dependence, as discussed in ref. [21]. Figure 2a shows IR spectra at a fixed temperature (82 K). At 198 GPa we see the appearance of a D_2 vibron line (after ~ 11 hours), splitting of the HD vibron line, and growth of the H_2 vibron line intensity; all spectral lines clearly show a splitting at 261 GPa. Figures 2b,c show spectra for the crossing of phase lines at fixed pressures and varying temperatures. The splittings, shifts, and changes for all of our measurements are summarized in Fig. 3, which shows the peak frequencies of the IR lines as a function of pressure at 82 K. It is not surprising that the splittings for H_2 and D_2 are different from splittings for the pure species [14, 17]; the isotopic concentrations are very different. Furthermore, the phase lines in the case of the HD isotopic

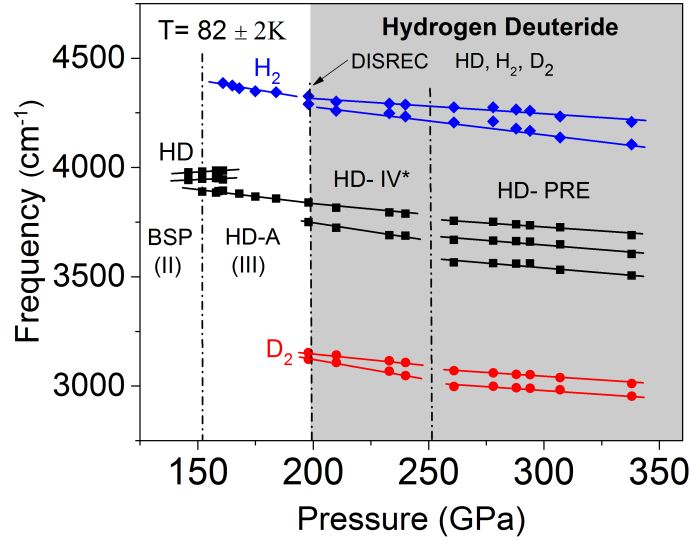


Fig. 3. Peak frequencies of the IR modes as a function of pressure, indicating phase transitions where splittings or new modes appear. The shaded area is where a mixed isotope sample, due to DISREC was observed.

mixtures are almost vertical, indicating possible different structures.

Figure 1 shows the P,T data points for the phases of HD. First of all, our data confirm the triple point found in ref. [22] and we determine the phase-line between phase I and III. We observe two additional phase-lines, very different from the phase-line for pure deuterium or hydrogen. We call the lower-pressure phase HD-IV*; the higher-pressure phase may precede the transition to metallic hydrogen deuteride and we have named it *HD-PRE*. Both phases have negative slopes with regard to pressure and extrapolate to 200 and 290 GPa at the T=0 K axis. These phase lines, that are almost vertical, are quite different from the behavior in the pure isotopic samples in which phase IV only appears at relatively high temperature with a weak dependence on pressure (see Fig. 1 for phase IV of D_2).

Simulations have shown that there are several structures, close in energy, that are composed of hexagonal graphene-like planes for the pure isotope solids [29-34]. We do not have an explanation for the difference between the phase lines for pure or mixed isotope samples exhibited in our data, as the solid structures are unknown. We comment that in the pure

homonuclear species the transition is believed to be entropy driven [32] which may be mitigated by a mixed molecular sample. Raman spectroscopy supports a structure with alternating hexagonal layers in the pure isotopic solids. Two distinct Raman vibrons were observed, corresponding to the two proposed hexagonal planes. We note that only the structures of the lowest-pressure phases are known [2] and the structures of phases II-IV are at best calculated and compared to spectroscopic observations.

Phase IV of H₂ and D₂ has been interpreted by Howie et al [12] as being composed of distinct hexagonal layers, called a mixed molecular-atomic phase with molecular and atomic layers, however our measurements, as well as a simulation [32], do not support this assertion. The existence of the two distinct vibron modes arising from two distinct sets of planes is incompatible with the existence of atomic layers; planes of atoms do not have vibron modes. If the model proposed by Howie et al [12] were correct, that alternate layers are atomic, then when phase IV is entered, half of the molecules would dissociate and this should have a large impact on the intensity of the vibron modes.

For our high-pressure observations we believe that the mechanism to form hydrogen and deuterium molecules is a process involving fluctuating dissociation-recombination of molecules. There is a probability for recombination with atoms from dissociated neighbor molecules, that we call DISREC. This is the importance of studying HD, as the recombined atoms can form molecules of hydrogen and deuterium that can be spectroscopically detected. This is theoretically supported by the simulations [33, 35] (see films in their SI) which showed that of the alternate hexagonal layers, layer I contained orientationally disordered molecules and layer II orientationally ordered molecules (Refs. [32, 35] name these B and G-layers, respectively). Layer I was stable against nucleon transfer with increasing pressure, while the molecules in layer II (which have expanded bonds) could dissociate and recombine. We believe that this process occurs in HD. For random processes, DISREC would lead to a 25-25-50% concentration of H₂, D₂, and HD, respectively.

HD can be used as a diagnostic tool to understand very high-pressure structures. Since we observe that HD molecules are stable until phase *HD-IV** is entered, then one should see a growth of the H₂ and D₂ concentration due to the DISREC process. In transitioning from phase III to *HD-IV** we observe the growth of H₂ and D₂ IR modes. When the molecular concentrations

arrive at equilibrium, the composition of our sample is $\sim 56\%$ HD , $\sim 26\%$ H_2 and $\sim 18\%$ D_2 (our HD sample starts with 4% H_2 impurity) determined from the integrated intensities of the IR modes. This implies that for pressures above ~ 198 GPa, the entire sample undergoes DISREC as the composition is $\sim 0.5HD + 0.25(H_2 + D_2)$, when our final concentrations are corrected for the initial H_2 impurity.

Howie et al [20] studied H_2 , D_2 , HD mixtures at room temperature and observed splitting of the Raman vibron lines above about 195 GPa, suggesting a transformation to phase IV (called IV') correlated to the vibron frequencies arising from different layer types. However, they did not study the temperature dependence of the phase line. A linear extrapolation of the HD -IV* $-HD$ -PRE phase lines (our data) to room temperature (Fig. 1) shows that with increasing pressure at room temperature they may have been in the HD -PRE phase, rather than the phase they identified as similar to IV and named HD -IV'. In our mixed sample the HD IR vibron line shown in Fig. 3 splits into three lines with the entry into the HD -PRE phase, while H_2 and D_2 IR vibron lines do not split, which is unexpected. Howie et al, studying mixed samples [20], suggest that the transformation at 198 GPa is one involving double hexagonal layers. Apparently they used the pressure dependence of the Raman vibrons from Phase IV of the pure species for layers I (B) and II (G) to identify their structure. In the SI we re-plot some of their data for a 50-50 H_2 - D_2 mixture that after transformation should be quite similar to our composition. For the pure species their B modes are approximately constant with increasing pressure while the G modes have a steep negative slope. This is the case for the modes that they associate with deuterium and hydrogen deuteride, but this is not the behavior for the hydrogen G mode, implying a problem with the mode identification. This is a complex system that should be reanalyzed to investigate possible structures and associated Raman and IR active modes.

We have used the integrated intensities of the IR lines to determine the concentrations of the various species as a function of time at a pressure of 198 ± 8 GPa and temperature of 82 ± 2 K. Observation of the sample for 14 hours at $P=184$ GPa, $T=82$ K showed no DISREC, i.e. the HD concentration was stable. The change of concentration vs. time for HD -IV* is plotted in Fig. 4. To describe the spectral kinetics data (see Fig. 4), we used Avrami's equation [36-39]

$(x(t) - x_e)/(x_0 - x_e) = \exp(-bt^n)$, where x is the concentration of a species at time t , x_0 and x_e are

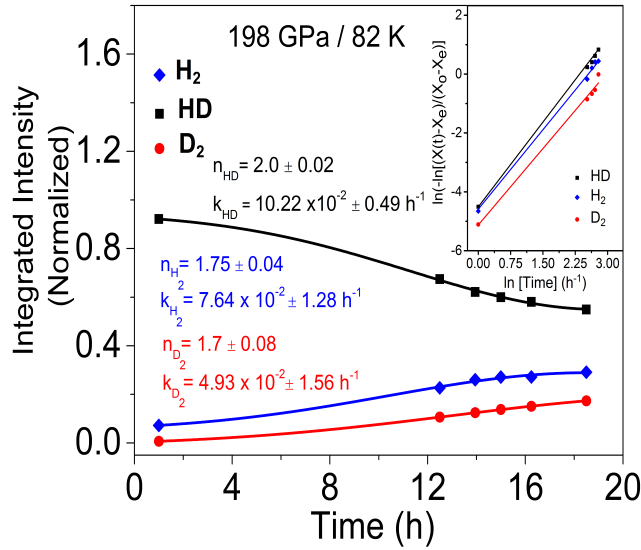


Fig. 4. The normalized IR integrated intensity changes of hydrogen isotopes plotted as a function of time, showing the kinetics associated with the DISREC at 198 GPa and 82K. These time-dependent intensity changes are fitted to Avrami's equation (see the inset) to yield the rate constants and Avrami exponent marked on the plots.

initial and equilibrium values, and b and n are the parameters relating to the rate of reaction and the processes that characterize the reaction (the Avrami exponent). The reaction rate k is equal to $b^{1/n}$. We obtained the best fit with the Avrami parameters (see inset in Fig. 4) of $n_{HD} = 2 \pm 0.02$, $n_{H_2} = 1.75 \pm 0.04$, and $n_{D_2} = 1.7 \pm 0.08$, which indicates that the reaction is in the nucleation dominated regime [40]. We believe that the nucleation process is one in which nuclei grow in the HD lattice which transforms to hexagonal graphene-like planes such as the I, II (or B, G), studied in simulations, followed by DISREC. Our measurements are consistent with the transformation being homogeneous throughout the sample; our measurements cannot determine if the H_2 impurities influence the nucleation.

In summary, we have studied hydrogen deuteride up to ~ 340 GPa and compared its behavior with that of pure molecular hydrogen and deuterium. HD transforms to an isotopic mixture for pressures above ~ 200 GPa. Three phase lines were determined: HD-IV*, HD-PRE, and the I-III line. The new high-pressure phases reported here are evidently different from those of the homonuclear species, in particular the pressure slopes of the phase lines; simulations may offer insight. In the goal of metallization of the hydrogens at lower temperatures, HD remains an important candidate, with the caveat that it would be challenging to transform from pure HD to atomic metallic H and D. When the phase HD-IV* is entered, DISREC commences. Our view,

based on results of simulations, is that in this region the structure is layered; a negligible density of atomic species exists and all atoms are bound as molecules, probably with bond lengths that depend on the planes they occupy. Atoms can exist due to bond-breaking fluctuations, but they rapidly recombine, so that the expectation value of free atoms in the lattice is very small. It is interesting to note that nucleon exchange probably takes place in the pure homonuclear samples at all pressures, but this is difficult to detect as there is no change in concentrations. The HD sample offered a unique opportunity to observe this exchange. At low pressure the process $H_2 + D_2 \leftrightarrow HD$ is probably due to tunneling rather than DISREC. A reason why the reverse process does not take place for lower pressures may be energetics. In this case the probability to tunnel back is blocked by energy conservation, that is, back tunneling requires additional thermally populated excitations to conserve energy between the initial and final states. Low density HD is also of special astronomical interest with the recent detection of HD in interstellar clouds [41, 42]. Deuterium is believed to have been created primordially in the Big Bang nucleosynthesis. Determination of the deuterium abundance, relative to hydrogen in the atmospheres of planetary systems and nebulae provides important cosmological constraints on planetary and stellar formation [43]. In this regard, the dissociation and recombination process is quite important and abundances must also consider the HD concentrations.

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