

Megabar Pressure Triple Point in Solid Deuterium

Lijing Cui, Nancy H. Chen, S. J. Jeon,* and Isaac F. Silvera

Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

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Solid orthodeuterium and mixed ortho-para crystals have been studied by infrared and Raman spectroscopy to a pressure of 186 GPa. We observe two clear phase transition lines and a triple point where they meet; no critical point is observed as reported for hydrogen. We believe that previous reports of a critical point in hydrogen are erroneous. Symmetry arguments are used to identify and narrow down the possible structures for the various phases.

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Solid molecular hydrogen, rich in phase transitions at high pressure, has been the objective of intensive efforts to produce the metallic phase. Solid deuterium, studied here, is expected to display very similar properties at high pressure. Lorenzana, Silvera, and Goettel [1] showed that a phase line which starts at 149 GPa at low temperature has a steeply rising transition temperature with increasing pressure. This high pressure phase was named the hydrogen-*A* or H-*A* phase and is of unknown structure. It has been suggested that the H-*A* phase might be metallic molecular hydrogen; however, there is no direct evidence for this. The H-*A* phase line was later reported to terminate at a critical point [2,3], implying that the H-*A* phase had the same symmetry as the low pressure insulating phase [4] ($P6_3/mmc$ hexagonal close packed, hcp). For D_2 a single point for a phase transition has been found at 77 K at a pressure reported as 190 GPa [5] and later revised to 165 GPa [6]; from the similarity of the Raman spectrum to that of hydrogen it has been suggested that this is the corresponding deuterium-*A* (D-*A*) phase. In this Letter we determine the D-*A* phase line using infrared (IR) measurements and confirm this to be the analog of the H-*A* phase with an onset between 143 and 151 GPa at $T=8$ K. At lower pressure, parahydrogen and orthodeuterium have a transition from a symmetric hcp lattice to an orientationally ordered phase called the BSP (broken symmetry phase). In deuterium the BSP line has been determined from 28 to 40 GPa by Silvera and Wijngaarden [7]; in hydrogen only a single point has been determined at 110 GPa and liquid helium temperatures [8]. In this Letter we report the triple point for the intersection of the BSP line with the D-*A* line. Our results suggest that the reported critical point in hydrogen was incorrectly identified as such and is most likely a triple point, with the phase line continuing beyond the triple point, to separate the H-*A* phase from the insulating hcp phase, as we have observed in deuterium. Finally, our results, using both Raman and IR spectra, provide a powerful tool for determining the structures of the high pressure phases.

It is useful to briefly review the theoretical picture. Electronic band structure calculations have been used to predict band gap closure or metallization pressures. Early on Ramaker, Kumar, and Harris [9], as well as Friedli

and Ashcroft [10], predicted that hydrogen in the $Pa3$ structure would become a metal in the region of a few hundred GPa. Later, Barbee *et al.* [11] showed that a much lower energy high pressure structure is the hcp lattice with molecules oriented along the c axis (hcp- c), having a metallization pressure of 60 GPa. The predicted metallization pressures suffered from the fact that local density approximation calculations predict gaps a factor of 2-3 too small. Garcia *et al.* [12] used a modified approach to show that hcp- c would metallize at about 180 GPa. Subsequently, Kaxiras, Broughton, and Hemley [13] showed that there are lower energy structures on the hcp lattice with molecules rotated away from the c axis, so that the symmetry is lowered. Nagara and Nakamura [14] enlarged the basis of the hcp lattice to four molecules/unit cell and found, with increasing pressure, a still lower energy space group, hexagonal $Pca2_1$. Surh, Barbee, and Mailhot [15] considered the effect of vibronic zero-point motion on the $Pca2_1$ structure and found that the hcp- c structure became the ground state for the insulator-metal transition. It seems clear that an experimental determination of the possible space groups at high pressure would be an important guide to theory.

Similar uncertainty exists for the BSP transition. Hydrogen (deuterium) molecules exist in the para and ortho species which we shall characterize here by even or odd (odd or even) rotational states with free rotor quantum numbers J, M [16]. For para- H_2 (ortho- D_2) at low temperatures only the $J=0$ state is occupied and the molecules are in spherically symmetric quantum states. The low pressure solids have the hcp structure. At a sufficiently high pressure at $T=0$ K, J breaks down as a good quantum number and the lattice orientationally orders. For pure electric quadrupole-quadrupole (EQQ) interactions the lowest energy structure is predicted to be $Pa3$ [16]. Calculations for a more realistic intermolecular potential by Runge *et al.* [17] predict that ortho- D_2 orders in the $Pa3$ structure and then changes to a hexagonal ordered structure at higher pressures, while para- H_2 orders directly into a hexagonal structure. Experimentally, the structure of the BSP is undetermined.

High purity normal D_2 was loaded and pressurized in diamond anvil cells (DACs) by techniques described elsewhere [18]. Two separate samples were studied: a thicker

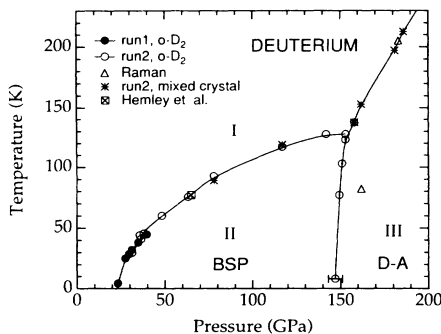


FIG. 1. Various phases of high pressure solid deuterium identified by IR absorption in this Letter; points determined by Raman studies are indicated by triangles. Mixed crystals at a given pressure were produced by letting the sample convert from o -D₂ to equilibrium D₂.

sample (run 1) to search for weak absorptions, but limited to lower pressures, and a thinner sample (run 2) that has reached very high pressures. The thick sample was 15 μ m thick at 40 GPa; the thin sample was 7 μ m at 36 GPa and reduced to approximately 5 μ m at 162 GPa. Pressure was determined at lower pressure by the ruby fluorescence spectrum from a few micron-sized grains of ruby. In the thin sample, for pressures above 78 GPa, our ruby signal was undetectable and we used the frequency of the Raman active vibron as a pressure gauge, measured earlier by Hemley and Mao [6]. Ortho-para conversion rates at high pressure have been observed to be accelerated [8]; by holding the samples at liquid helium temperatures for a few days they converted to ortho-deuterium. This is extremely important: Our IR and Raman measurements correspond to modes at crystal momentum $k=0$ of a pure lattice and reflect the symmetry allowed transitions, whereas studies of equilibrium crystals of hydrogen and deuterium at liquid nitrogen temperature are mixed ortho-para crystals so that there is no translational invariance and transitions for all k are allowed; in the latter case there are no simple symmetry arguments for allowed or disallowed modes. After a sample's ortho content stabilized at a temperature T_s , conversion was slow enough that rapid excursions in temperature allowed measurement essentially at the ortho content corresponding to T_s .

We have primarily studied the infrared absorption, although we have also made some Raman scattering measurements in our samples. The latter was by fairly standard techniques; the IR studies used a computer controlled tunable (2.2–3.3 μ m) Burleigh color center laser. Normalization of absorption spectra measured below a transition temperature T_c , by spectra measured above T_c , effectively removed background absorption such as that arising from the diamond anvils. Our usual method of study was to fix the pressure and then vary the temperature to traverse phase lines.

It is clearer to discuss our results in terms of the three regions in the P - T phase diagram shown in Fig. 1. We

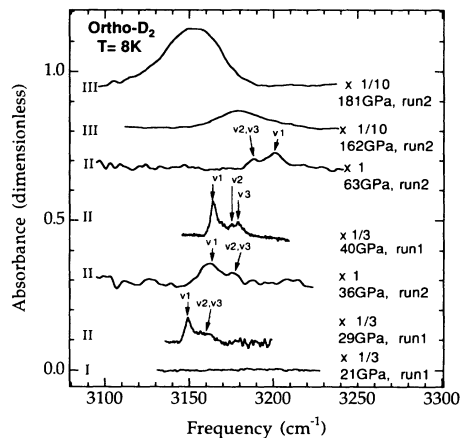


FIG. 2. IR absorption spectra of ortho-deuterium at various pressures and 8 K, offset along the vertical axis for clarity. We plot the absorption coefficient times the sample thickness, scaled as indicated. Phase regions are indicated on the left; the arrows indicate resolved peak centers. The narrower lines in run 1 are probably due to a smaller pressure distribution in the sample. Note that the integrated absorption in region III is orders of magnitude larger than in II.

anticipate some of our results in identifying these regions: I is the insulating molecular phase with the hcp structure: For ortho-D₂, molecules are in the spherically symmetric states, whereas for mixed ortho-para crystals the molecules are disordered. II is the BSP phase for ortho-D₂, and III is the D-A phase. Absorption spectra are shown in Fig. 2 and the pressure dependence of the peak frequencies in Fig. 3. There is no infrared activity for a pure hcp lattice [19], in agreement with our observations in region I, as our samples are high purity ortho-D₂.

In region II, we observe three peaks in the thick sample (run 1); the two weaker peaks are barely resolved. In the thin sample we only observe two peaks, the weaker peak presumably being two unresolved peaks with low signal to noise. Silvera and Wijngaarden [7] first identified the BSP transition using rotational Raman scattering. We have observed the phase line by changes in the IR spectra

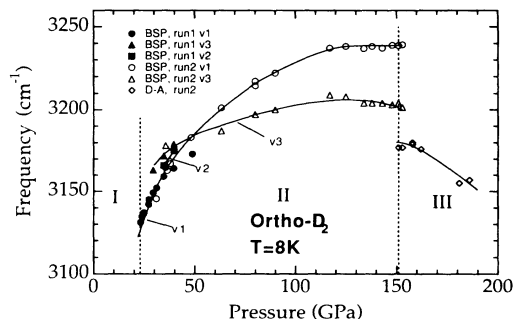


FIG. 3. IR vibron peak frequencies as a function of pressure in the various phases of ortho-D₂. We believe that the peak represented by the open triangles actually represents the ν_2 and ν_3 lines, but as can be seen in Fig. 2, these lines are unresolved in the thin sample. The solid lines are guides to the eye.

in regions I and II. However, we find a critical pressure $P_c = 23.3$ GPa (in the $T=0$ K limit), compared to the 28 GPa which they reported. This may be an indication that our sample had slightly more para content than theirs did, as recent studies by Moshary, Chen, and Silvera [20] on the BSP transition in HD show that P_c is sensitive to extremely small levels of the complementary species.

We have also studied the phase line for 77 K equilibrium mixed ortho-para crystals at a few pressures. Pure para-D₂ orders at 3.8 K at zero pressure due to EQQ interactions and the critical temperature increases with pressure [16]; eventually this phase line is expected to merge with that for the BSP transition [21]. At the lowest pressure that we examined, 78 GPa, the measured transition point coincides with that for pure ortho-D₂. Hemley, Eggert, and Mao [22] recently reported evidence for a transition at 65 GPa in a 77 K equilibrium crystal of D₂. We plot this point in Fig. 1 and identify this transition as orientational order in a mixed crystal, similar to that observed in HD [20]. We conclude that the phase lines for pure and mixed crystals have merged above this pressure.

Region III is characterized by an IR active vibron that grows rapidly in intensity with increasing pressure, as observed in hydrogen by Hanfland *et al.* [23] in mixed crystals. The abrupt change in the spectra in traversing into this region provides an easy method to determine this phase line. The D-A phase has an onset between 143 and 151 GPa at $T=8$ K, which is essentially the 0 K limit. At 77 K we find P_c between 148 and 151 GPa. This differs from the value of 165 GPa reported by Hemley and Mao [5] using Raman scattering. We also detected the phase line by Raman scattering at higher pressure and 77 K, which must agree with Hemley and Mao, as we use their spectra for pressure determination for both IR and Raman experiments. These results are shown in Fig. 1. This pressure difference between IR and Raman determinations for the D-A transition may be attributable to pressure gradients in the sample, which we believe were between 5 and 10 GPa (determined by the Raman signal from different parts of the sample) in combination with a difference in relative sensitivity of the IR and Raman measurement techniques. The transition pressure determined by Raman measurements is by convention [1] taken at the point in which the intensities of the Raman lines for the low and high pressure phases are equal, which corresponds to half of the sample in the D-A phase. In our measurements there was intense background fluorescence from the diamonds which limited the signal-to-noise ratio to about 5 when the sample was in a single phase. By contrast, the IR absorption in the D-A phase is strong and it is possible to observe the onset of the transition when only a small fraction of the sample is in the D-A phase. There is no means of determining when the sample is 50-50 in both phases as the absorption continues to grow and increases rapidly with pressure in the D-

A phase, so the onset is taken as the transition point. We do not believe that there is a small new slice in the phase diagram, but rather that this observation is an artifact of the measurement technique.

We have also determined the experimental integrated intensity as a function of temperature at selected pressures. This should be proportional to the square of the order parameter and useful in characterizing the order of the transition. We are unable to determine whether these are first or second order phase transition lines from these data, due to the pressure gradient in the sample. As a result of this gradient, in the transition region part of the sample is in one phase and part in another, with the percentage varying as the temperature is changed. As a consequence the possibly abrupt change in the integrated absorption, characteristic of a first order transition, becomes smoothed, typical of a second order transition. We have also studied the temperature dependence of the Raman vibron frequency in traversing from III to I at 180 GPa. We observe a continuous change from the low temperature value to the high temperature value, rather than a discontinuous change seen in going from III to II at 77 K, here or elsewhere [3].

Figure 1 shows that we have observed a triple point in D₂ at $P=153 \pm 5$ GPa and $T=128 \pm 2$ K. Above this point the D-A line persists; a critical point is not detected even though the Raman vibron frequency discontinuity disappears. Earlier, Hemley and Mao [2] and Lorenzana, Silvera, and Goettel [3] interpreted the disappearance of the discontinuity in frequency, used to identify the H-A line, as evidence for a critical point in hydrogen. We believe that the phase diagram observed for D₂ will be found in hydrogen, with a triple point where the BSP line meets the H-A line, rather than a critical point. This scenario is more likely, as the notion of a critical point has created some severe difficulties. Silvera [4] pointed out that a critical point implied that the symmetry of the H-A phase must be that of the region corresponding to I in Fig. 1, hcp. On the other hand, Martin, Natoli, and Zallen [24] pointed out that the IR absorption identified by Hanfland *et al.* [23] in H₂ as a vibron is not allowed in a structure with hcp symmetry. We mention here that this argument is not applicable as Hanfland *et al.* studied a mixed crystal which does not have translational invariance. Nevertheless, we believe that this vibron absorption peak will be confirmed for pure parahydrogen, as we have observed for orthodeuterium.

Lorenzana, Silvera, and Goettel [8] traversed the H-A line at about 165 GPa by increasing temperature and found evidence that this phase transition also involves orientational order-disorder, from abrupt broadening of rotational lines in Raman spectra. Hemley, Mao, and Shu [25] traversed the H-A line in pressure at fixed temperature, 77 K, and claimed that there was no evidence of orientational order-disorder. Silvera [26] pointed out that these measurements were at different regions in the

phase diagram so that they were not necessarily contradictory. If the "critical" point is actually a triple point, then we interpret these results as follows: Lorenzana, Silvera, and Goettel traversed from region III to I and observed orientational disorder, while Hemley and Mao traversed from II' (orientationally ordered mixed crystal) to III', both orientationally ordered, and thus observed no abrupt change in the rotational spectra. We conclude that if the phase diagrams of hydrogen and deuterium are similar, then the H-A and D-A phases are orientationally ordered.

Finally, we can make a number of comments about the possible crystal structures. We have performed a group theoretical analysis of IR and Raman activity of vibrons and phonons for various structures which have been considered for the high pressure phases of hydrogen. Here we show our results for the number of distinct allowed vibron transitions in curly brackets {number of IR modes; number of Raman modes}. Detailed results including the phonon selection rules with comparison to experiment [22] will be presented in a future publication. Our observation of no IR absorption and one Raman vibron mode is consistent with region I being hcp {0;1} for pure crystals. Consider the D-A phase, where a single Raman and a single IR active vibron mode have been observed. The early guess of $Pa3$ {0;2} is eliminated, as it has no IR vibron activity. The lowest energy $Pca2_1$ {3;4} structure is also eliminated. The $P2/m$ {1;1} of Kaxiras, Broughton, and Hemley [13] remains a candidate and might be further studied for the phonon modes. Now, consider the experimental observations in the BSP structure: Three IR vibrons and one Raman vibron have been observed. Again, the $Pa3$ structure predicted by Runge *et al.* [17] is eliminated, as well as $P2/m$, $Pmc2_1$ {2;2}, and $P2_1/c$ {2;2}. The $Pca2_1$ has three IR vibrons in agreement with observations, but four Raman vibron modes are expected. Perhaps these are almost degenerate and unresolved in our experiment. Calculation of mode frequencies and intensities would be useful.

In summary, using IR and Raman spectroscopy at high pressure and low temperature we have been able to fill important gaps in our knowledge of high pressure deuterium. We have observed the D-A and BSP lines as well as a triple point in the phase diagram and suggest that a critical point does not exist in hydrogen. A number of possible structures of high pressure hydrogens have been eliminated from consideration. We provide an explanation of two sets of earlier data to show that the H-A and D-A phases are most likely orientationally ordered. These results still are unable to answer the question of the possible metallic nature of the H-A and D-A phases.

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*Permanent address: Department of Chemistry, Korea University, Seoul 136, Korea.

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