

Orientational Phase Transitions in Hydrogen at Megabar Pressures

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(Received 3 August 1989)

We have studied solid molecular hydrogen in various ortho-para concentrations at megabar pressures and down to liquid-helium temperatures. From changes of Raman spectra of rotational and vibrational modes we have identified three new phases. We show evidence for the orientationally ordered phase of parahydrogen at a pressure of 110 GPa (1.1 Mbar) and 8 K and for molecular orientational ordering within the newly discovered hydrogen-*A* phase.

PACS numbers: 62.50.+p, 64.70.Kb, 67.80.Cx

Solid hydrogen and deuterium have fascinating phase diagrams which depend on ortho-para concentration, as well as pressure and temperature. At low temperature and pressure, orientational ordering occurs in pure *o*-H₂ or *p*-D₂ (species with rotational quantum number $J=1$) and in ortho-para mixtures rich in the $J=1$ species. At intermediate pressures, solids of pure *p*-H₂ or *o*-D₂ (molecules in the spherically symmetric $J=0$ state for low pressure) are predicted to order orientationally due to a fundamental lowering of the symmetry of the wave function. This ordering is called the broken-symmetry phase (BSP) transition. At very high pressures, the solids are predicted to metallize due to band overlap. Recently, Hemley and Mao¹ reported spectroscopic observation of a transition in hydrogen near 150 GPa. Lorenzana, Silvera, and Goettel² showed that the high-pressure phase diagram is richer than had been anticipated by demonstrating that this transition is to a new phase, called hydrogen-*A* (H-*A*), which only exists at megabar pressures. Here we present new results for orientational ordering of hydrogen at pressures greater than 100 GPa (1 Mbar). Our results include (1) observation of the BSP transition in *p*-H₂ at 110 GPa, (2) determination of a phase line for orientational ordering of *p*-H₂ in the H-*A* phase, and (3) demonstration that ortho-para mixtures order within the H-*A* phase.

In order to understand the transitions we have observed, we first review the orientational properties of hydrogen. At low pressures in the solid state, hydrogen molecules are in almost free-rotor states, with spherical harmonics, Y_{JM} , as the single-molecule wave functions. Here J is the rotational quantum number and M is its projection. At low temperatures, only the $J=0$ or $J=1$ levels are thermally populated due to the large separation of the rotational energy levels.³ At low pressure, hydrogen solidifies in the hexagonal-close-packed (hcp) structure. *o*-H₂ molecules are in the *p*-orbital-like Y_{1M} states and the molecular axes can be ordered in space. At zero pressure *o*-H₂ orientationally orders into the Pa3 lattice at 2.8 K.³ In this structure the molecular axes are oriented along the body diagonals of a face-centered-cubic (fcc) lattice. This ordering minimizes the anisotropic intermolecular interactions which are dominated by the electric quadrupole-quadrupole interaction.

The physics of the ordering in *p*-H₂ is fundamentally different from that in *o*-H₂.⁴⁻⁷ At low pressure the single-molecule wave function is the spherically symmetric state, Y_{00} . Therefore, *p*-H₂ cannot orientationally order and remains hcp down to $T=0$ K. However, with increasing pressure anisotropic interactions increase relative to the spacing of the rotational levels and J begins to break down as a good quantum number. It is easily seen, using first-order perturbation theory,³ that the admixture of higher- J states into the $J=0$ ground state is proportional to the ratio of the anisotropic energy to the splitting of the free-rotor energy levels. At a critical density the anisotropic potential becomes so large that the ground-state wave function of *p*-H₂ distorts anisotropically and the molecules orientationally order at $T=0$ K. This transition from the symmetric phase to the BSP was predicted to take place at pressures substantially below 100 GPa in hydrogen.⁴⁻⁷ Ceperley and Alder⁸ have recently predicted this phase transition to occur at a pressure near 100 GPa in hydrogen, using a quantum Monte Carlo calculation. Because of the smaller rotational splitting, the BSP occurs in D₂ at a lower pressure than in H₂. This phase transition has been observed in *o*-D₂ at 28 GPa by Silvera and Wijngaarden.⁹

The experimental setup and procedures utilized the same diamond-anvil cell, cryostat, and pressure-measuring methods described in our recent report² of the identification of the H-*A* phase at about 150 GPa. We studied the rotational and vibrational¹⁰ spectra of H₂ (internal rotational and vibrational modes of solid H₂ are called rotors and vibrons, respectively) using Raman scattering for pressures up to 167 GPa and temperatures from 4.3 to 150 K.

We have observed the long-sought BSP transition in *p*-H₂ at 110 GPa and 8 K. As was shown by Silvera and Wijngaarden in the observation of the BSP in *o*-D₂,⁹ the collapse of the $J=0 \rightarrow 2$ rotor bands is the principal indicator of this phase transition; we observed similar behavior in *p*-H₂ (Fig. 1). At low pressure the $J=0 \rightarrow 2$ rotational Raman spectrum consists of three well-resolved transitions to rotor bands. These lines are narrow as there are no excitations in the lattice with sufficient energy to relax them and conserve energy and crystal momentum. However, Lagendijk and Silvera⁶

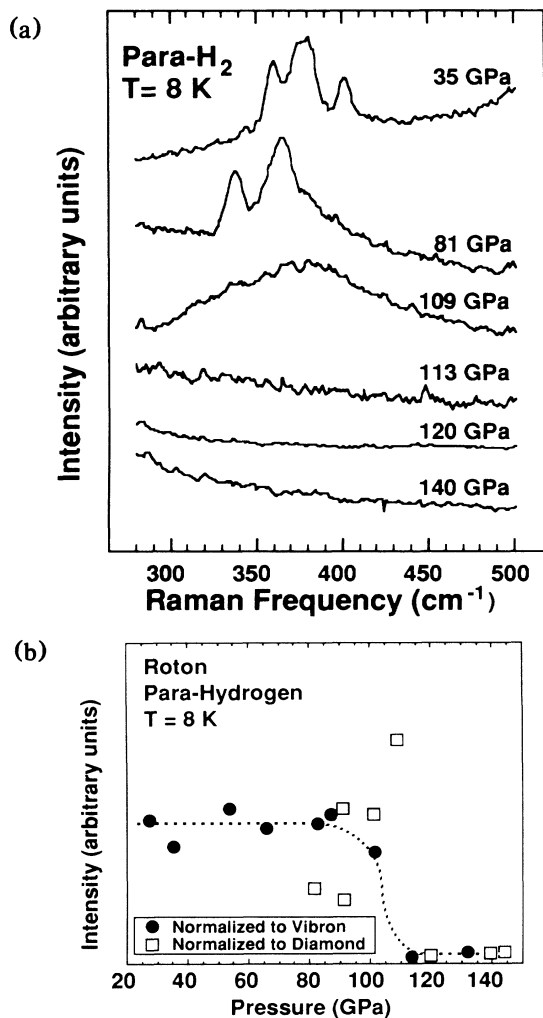


FIG. 1. Pressure dependence of the roton bands in p -H₂. We identify the disappearance of the roton band between 109 and 113 GPa as the BSP transition. (a) Spectra at different pressures. (b) The integrated intensity as a function of pressure. The dashed line is a guide to the eye. The roton intensity was normalized to either the vibron intensity or the intensity of a pressure-independent feature in the diamond-fluorescence spectrum as discussed in the text: (a) has the latter normalization.

and Igarashi¹¹ have calculated that the roton bands broaden to lower energy as the BSP transition is approached. These lower-energy states can then relax the Raman-active zone-center rotors resulting in severe lifetime line broadening. The broadening of the spectra as a function of pressure at $T=8$ K is evident in Fig. 1(a) and is similar to that observed for o -D₂ prior to the BSP transition. For D₂, a single broadened roton peak below the critical pressure became a broad weak librational doublet as the system underwent the transition. For H₂, in contrast, we observe a single broadened peak before the transition that disappears between 109 and 113 GPa [Fig. 1(b)].¹² In two separate experiments, we detected only a flat background above the critical pressure,

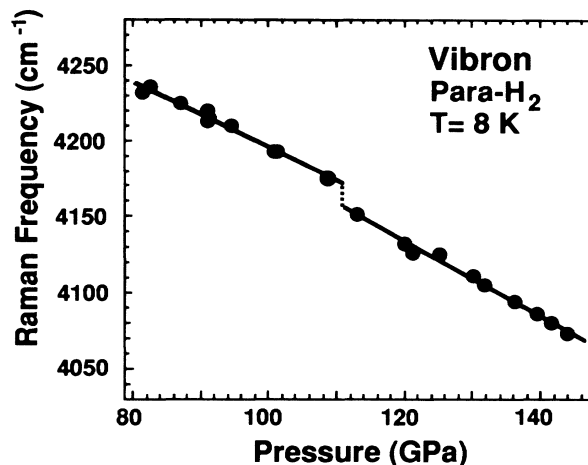


FIG. 2. Vibron frequency vs pressure showing the discontinuities which occur at the BSP transition in p -H₂ at 110 GPa. The statistical significance of the discontinuity is discussed in the text.

perhaps due to a combination of lifetime line broadening, pressure inhomogeneity broadening, and fluorescence background from the diamond.¹³ We can place an upper-bound limit of about 3% on the amplitude of the roton with respect to the vibron. We believe that lifetime broadening is the major factor leading to this lack of signal, though we cannot rule out that the BSP in H₂ may have a different crystal structure from D₂ so that the librational excitations are Raman inactive.

Our identification of the BSP transition based on the roton-spectrum changes is strongly correlated with a discontinuous change in the vibron frequency as a function of pressure, as shown in Fig. 2. Because the vibron remains sharp near the phase transition, it is a sensitive indicator of the BSP transition as demonstrated in D₂ where a frequency shift of 3 cm⁻¹ was observed. This is in reasonable agreement with a mean-field calculation by Igarashi.¹¹ Since the frequency of the $\nu=1, J=2$ vibron differs from the $\nu=1, J=0$, the frequency of the molecular vibron shifts when the $J=2$ is mixed into the ground state at the BSP transition. The shift is expected to be about 3 times larger in H₂ than in D₂.^{11,14} In traversing the BSP phase line in H₂ we measure a sharp 15-cm⁻¹ shift of the vibron frequency which we observed in two separate runs. In contrast, the vibron shift is about 100 cm⁻¹ at the H-A transition.^{1,2} Consequently, detection of the BSP transition is more subtle. We estimated the standard deviation of our frequency measurements to be less than 3 cm⁻¹ at a given pressure.¹⁵ The two-line fit shown in Fig. 2 has an extremely significant goodness-of-fit value of 0.71.¹⁶ We reject single-curve linear and quadratic fits because of their significantly worse goodness-of-fit values, 0.00099 and 0.0010, respectively. Because of the smaller vibron discontinuity, natural linewidths, and a 6-GPa pressure variation across the sample, the coexistence of two peaks, as observed in the H-A transition, is difficult to resolve

for the BSP transition.¹⁷ The *P-T* point for the BSP transition which we have determined from our vibron and roton data is plotted in Fig. 3, our high-pressure phase diagram of hydrogen.

At pressures above 150 GPa, H₂ is in the H-A phase. The H-A phase line was found to be insensitive to ortho content.² We decided to study *p*-H₂ in the H-A phase. By keeping the sample at a temperature of 4.3 K for a sufficiently¹⁸ long time, the sample approached equilibrium, i.e., about 100% *p*-H₂. At low temperature, we observed a broad Raman band in the 300–400-cm⁻¹ region, the energy range corresponding to rotational (or librational) transitions [Fig. 4(a)]. It is not surprising that the Raman band appears in roughly the same region as the low-pressure roton. In D₂, for example, the BSP transition is believed to involve a crystallographic change of the molecular axes, and yet the rotational and librational excitations remain in roughly the same energy range. In H₂, as the sample was warmed, the band intensity decreased markedly at a critical temperature [Fig. 4(b)]. Upon subsequent cooling below this temperature, the intensity increased again.¹⁹ The vibron, on the other hand, showed no measurable change in either frequency or intensity as a function of temperature. Since only the rotational bands were significantly affected, it is consistent to associate the intensity change of the rotational spectra as a function of temperature with an orientational-ordering transition. The temperature observed for this change increased with pressure as expected because anisotropic interactions that drive the ordering of molecules increase with increasing pressure. We interpret the measurements as representing an orientational-order-partial-disorder transition in *p*-H₂ within the H-A phase (Fig. 3). We believe that partial order remains in the high-temperature phase, as the rotational

intensity does not completely disappear. Further work will be necessary to fully characterize and understand this transition, which may require other subtle explanations. We cannot rule out some other subtle displacive transition that affects the rotational but not the vibrational states.

We also have evidence that orientational ordering within the H-A phase can occur for ortho-para mixtures. Samples of *p*-H₂ were held at temperatures (56 and 77 K) above the critical temperature for the *p*-A transition for long periods of time. After conversion to the equilibrium ortho-para concentration, the intensity of the rotational (or librational) band increased. In conjunction

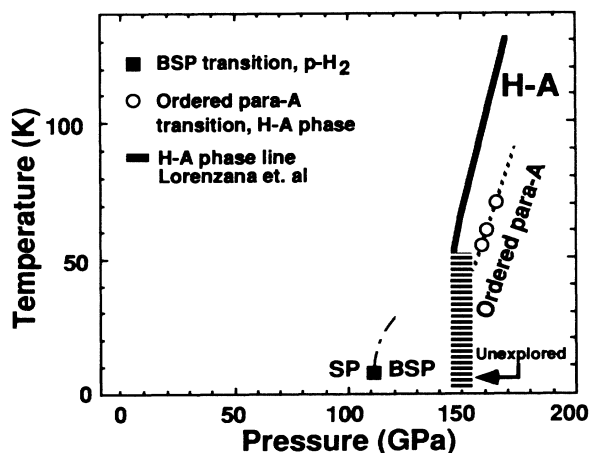


FIG. 3. Our proposed high-pressure phase diagram for hydrogen, which includes data for *p*-H₂ and ~50% ortho mixtures. The dashed line from the SP- (symmetric-phase-) BSP phase-line point is an indication of where we expect the phase line to lie. The dashed line from the ordered *p*-A phase line is a linear extrapolation.

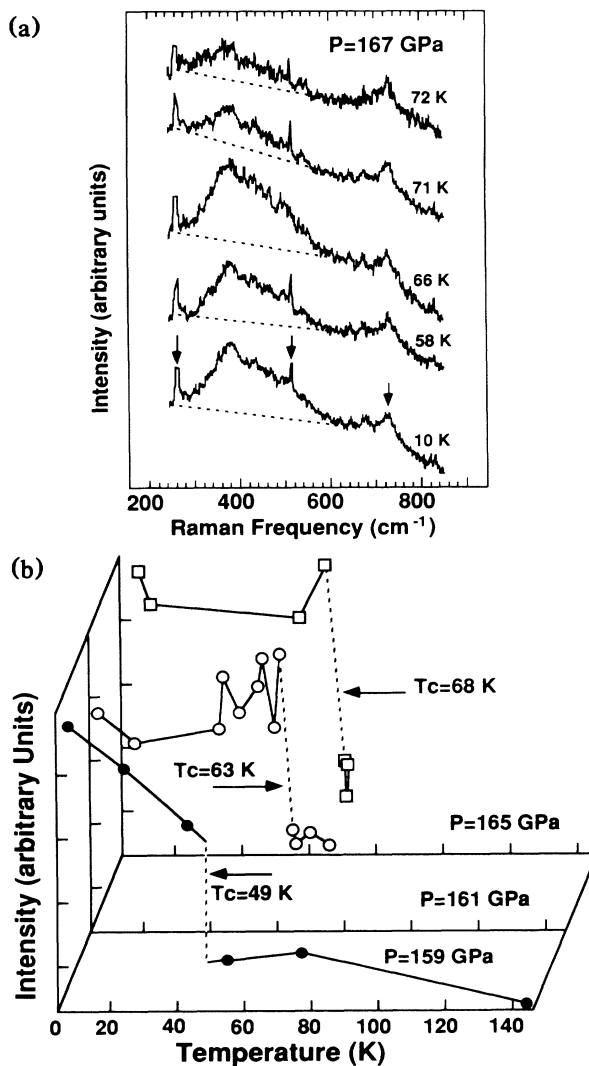


FIG. 4. Temperature dependence of the rotational (or librational) bands in *p*-H₂ in the H-A phase at 167 GPa. The bands undergo a change in intensity at a given temperature range, which we interpret as the ordered *p*-A transition. (a) Selected spectra of the Raman signal. The arrows point to background spectral features; the sharp lines arise from the laser, and the broad line is from the diamonds. (b) The temperature dependence of the integrated intensity at different pressures.

with our results for para H-A, we interpret this increase in intensity as indicating that orientational order exists in the mixed ortho-para H-A phase. Traversing the H-A phase line in temperature, the rotational band intensity disappeared and reappeared reversibly, which we interpret as possible evidence for orientational disorder in this phase, based on analogy to the low-pressure behavior of H₂.²⁰ This is not necessarily contradictory to the interpretation of the BSP transition, where the intensity disappeared as pressure was increased in the zero-temperature limit; reasons were offered for the disappearance of the intensity. Here, the intensity exists in the zero-temperature limit, so that the sharp decrease of rotational intensity with increasing temperature can be interpreted as a reduction in orientational order. However, definitive conclusions here await a detailed determination of the nature of the H-A phase and the high-temperature phase.

In summary, we have found that hydrogen has an unexpectedly rich and complex phase diagram at high pressures. We have presented evidence for the BSP transition in *p*-H₂. Within the new H-A phase, we have presented evidence that *p*-H₂ orientationally orders and that ortho-para mixtures orientationally order and then disorder above the H-A line. In order to verify the phase diagram presented here, it is important to determine accurately more points on the phase lines as a function of temperature and pressure. Studying these transitions under decreasing pressure would be valuable except that it is difficult to decompress in controlled steps without loss of the sample.²¹ It would be interesting to determine if both *p*-H₂ and ortho-para mixtures have tricritical points at megabar pressures, as seems to be indicated by the provisional phase diagram presented here. In addition, points on the extension of the well-known phase line for orientational order-disorder of mixed ortho-para crystals have yet to be measured.

We thank Jon Eggert for useful discussions. We thank the Department of the Air Force (Air Force Avionics Laboratory), Contract No. F04611-89-K-0003, and the Harvard Materials Research Laboratory, National Science Foundation Grant No. DMR-14003, for support.

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¹²In our almost forward-scattering geometry, we found that a diamond fluorescence peak ($\sim 730 \text{ cm}^{-1}$) and the roton band both had their maximum intensity when the system was well aligned. The rotational band intensity, therefore, was normalized to either or both of two markers, the diamond fluorescence peak or the vibron band intensity. We plot the vibron-normalized data preferentially, although both methods yielded similar results. Where the alignments for the roton and vibron measurements were known to have been significantly different, the diamond-fluorescence normalization was chosen. A realignment of the optical path was necessary when the pressure was changed, and we believe that this leads to the scatter observed in our data. The lack of signal in our data above 110 GPa cannot be ascribed to poor alignment.

¹³The diamond-fluorescence background rises significantly with increasing pressure and interferes with both Raman and ruby-fluorescence measurements. The Raman signal is about 300–400 counts/sec whereas the background signal is about 2000–5000 counts/sec.

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¹⁵To ascertain this, we recalibrated our diode array, realigned, and remeasured the vibron frequency numerous times. We never obtained extrema that differed by more than 5 cm^{-1} . Hence our standard deviation is very conservative.

¹⁶The goodness-of-fit value is the probability of obtaining a χ^2 value that exceeds the observed χ^2 . See W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes: The Art of Scientific Computing* (Cambridge Univ. Press, New York, 1986).

¹⁷To show this, we modeled the BSP transition as taking place at a sharply defined pressure. The effects of the factors discussed in the text were combined using the model developed by Lorenzana, Silvera, and Goettel (Ref. 2).

¹⁸We have observed that about 3 days are required for conversion to equilibrium at 30 GPa. At 80 GPa, about 1 day is required. By monitoring the time dependence of the spectral features measured in this work, we believe equilibrium is reached in less than a day at 150 GPa.

¹⁹There was apparent thermal hysteresis in these measurements. This can be explained by the inopportune placement of our thermometer. Subsequent studies at temperatures of $\sim 77 \text{ K}$ with thermometers placed on both the cell body and the diamonds showed a time lag of approximately 10 min between the two in response to a change in temperature. In order to minimize this, we effected temperature control prior to data taking. In our previous work (Ref. 2), we established that the hysteresis in the H-A phase line is 1 K or less. In this work, however, we did not always wait to reach thermal equilibrium to the accuracy of our previous work because we worried about ortho-para conversion effects.

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