Evidence for a Structural Phase Transition in Solid Hydrogen at Megabar Pressures

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We have studied solid molecular hydrogen at pressures up to 167 GPa (1.67 Mbar) and temperatures from 4.3 to 150 K. We have investigated the phase transition recently observed by Hemley and Mao near 150 GPa and identified as orientational ordering by studying the Raman vibrational and rotational excitations. The phase line determined for this transition differs significantly from that expected for the extension of the low-pressure orientational ordering. We conclude that this transition is to a new high-pressure molecular phase which only exists at megabar pressures.

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Solid molecular hydrogen has a fascinating phase diagram which has only been studied experimentally in detail at low pressures. Theoretical considerations predict both structural and orientational-ordering phase transitions as well as a very-high-pressure insulator-to-metal transition.[1] Recently, Hemley and Mao[2] reported the spectroscopic observation near 150 GPa of a transition to a new phase which they tentatively identified as an extension of the well-known low-pressure orientationally ordered phase.[3] We have studied this transition using Raman scattering in a diamond-anvil cell (DAC) up to pressures $P=167$ GPa from temperatures $T=4.3$ to 150 K. Our results indicate that this transition is not the continuation of the low-pressure orientationally ordered-phase line. Rather, we conclude that the transition is to a new molecular phase that only exists at megabar pressures.

Molecular crystals, including H_2, can undergo orientational ordering which is a special type of structural phase transition in which the molecular axes order with respect to the crystallographic directions. By convention, in molecular crystals, a structural transition is referred to as one in which the space group of the molecular centers changes. A given transition can be orientational, structural, or both. In H_2, the crystal structure as a function of temperature and pressure depends upon the ortho-para (*o-p*) concentration.[3] At low pressure, single molecules are in almost free-rotor states. Parahydrogen molecules are in the spherically symmetric state with rotational quantum number $J=0$ and cannot orientationally order, whereas o-H_2 molecules are in the $J=1$ states and the molecules can order along crystallographic directions. Orthohydrogen has an hcp (hexagonal-close-packed) to fcc (face-centered-cubic) transition at zero pressure and 2.8 K in which the space group of the molecular centers changes and the molecules orientationally order along the body diagonals (Pa3 structure).[3] This order minimizes the lattice energy arising from the dominant electric quadrupole-quadrupole (EQQ) interaction which varies as R^{-5}, where R is the intermolecular separation. The critical temperature for ordering is expected to have a $\rho^{5/3}$ density dependence, which has been observed in H_2 by Silvera and Jochemsen[4] up to $P=0.5$ GPa for varying ortho-para concentrations. Hemley and Mao tentatively identified the transition observed near 150 GPa in H_2 with 0.5 ortho concentration as an extension of the experimental low-pressure order-disorder phase line.[4]

Subsequently, Barbee *et al.*[5] calculated the relative stability of several phases of H_2 as a function of pressure. They predicted that hcp-H_2 orientationally orders at low pressure without a change in symmetry; this possibility was pointed our earlier by Lagendijk and Silvera.[6] Such ordering would be difficult to detect by Raman or infrared spectroscopy. Therefore, Barbee *et al.* speculated that, since Hemley and Mao had spectroscopic evidence for a change of symmetry, the observed transition may be associated with a structural or insulator-metal transition, rather than being an extension of the low-pressure orientational ordering. This conclusion, however, may not be well founded because the hcp-Pa3 ordering transition, which is strongly dependent on ortho-para concentration, is expected to occur in the *P-T* region studied. The analysis of Barbee *et al.* suppresses the ortho-para distinction because the interactions are not averaged over single-molecule rotational or vibrational states. Therefore, the hcp-Pa3 ordering transitions of o-H_2 or ortho-para mixtures are absent from their theoretical treatment.

Before presenting experimental results, we briefly describe our experimental apparatus and methods. The DAC design and cryogenic loading techniques used for this experiment have been described elsewhere.[7] Two runs were made using single beveled diamonds (bevel angle 7°) with 300-μm culet diameters and 50-μm flats. The performance of such a design at high pressures has been described by Moss and Goettel.[8] Above 100 GPa the rhenium gasket had a sample chamber approximately 17 μm in diameter and an estimated thickness of 6 μm. A number of 1–2-μm-size ruby grains (0.5% $\mathrm{Cr}_3{}^+$) interspersed within the sample were used for pressure determinations,[9] which were corrected for thermal shifts.[7] Ruby constituted less than 5% of the final sample volume. At the highest pressures, the pressure varia-

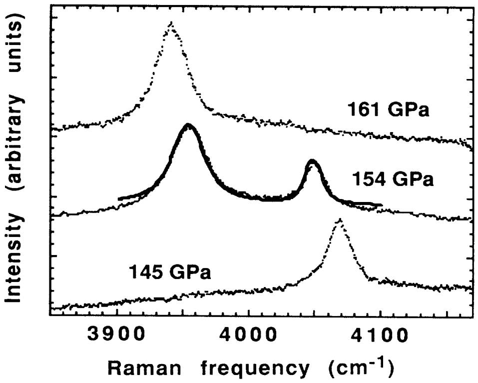

FIG. 1. Raman scattering intensity vs frequency shift for the vibron in the low-pressure, the mixed, and the high-pressure phase of hydrogen at 77 K. The solid line represents a fit using the gradient model described in the text.

tion within the sample, as determined from the ruby spectra, was 6 GPa, which is reasonable agreement with that obtained from the vibron data as discussed later.

We investigated the pressure and temperature dependence of the Raman-active vibron mode[10] (internal vibration of H_2), as well as rotational Raman spectra, to probe the transition observed near 150 GPa. Because the most important evidence emerged from the vibron spectra, we emphasize these data in this work. In Fig. 1 we show $T=77$-K vibron spectra below the critical pressure, P_c, for the transition, near P_c where two vibron peaks were observed to coexist, and above P_c. In Fig. 2(a), we show our 77-K vibron-frequency data as a function of pressure as well as the data of Hemley and Mao. A mixed-phase regime, represented by the double peaks in Fig. 1 and the overlap region in Fig. 2(a), could exist for several reasons, including (1) the presence of a pressure gradient, and (2) hysteresis in the transition which allows the coexistence of two phases over a finite pressure or temperature range.[11] To determine the phase line for this transition, it is necessary to understand the existence of the mixed-phase regime and the possible effects of hysteresis on our measurements.

Our data indicate that the observed properties of the two-phase region can be explained by the presence of a pressure gradient without the transition demonstrating significant hysteresis. The transition temperature for the appearance or disappearance of a phase was reproducible to within 1 K when raising or lowering the temperature at a constant pressure. Given this lack of hysteresis, we modeled the transition as occurring sharply at a well defined pressure with the vibron frequency varying linearly with pressure as shown by the dashed line in Fig. 2(a). Using a linear pressure variation across the sample as observed from our ruby pressure determinations, we calculated the effect of pressure inhomogeneity on the measured spectral frequencies and line shapes.[12]

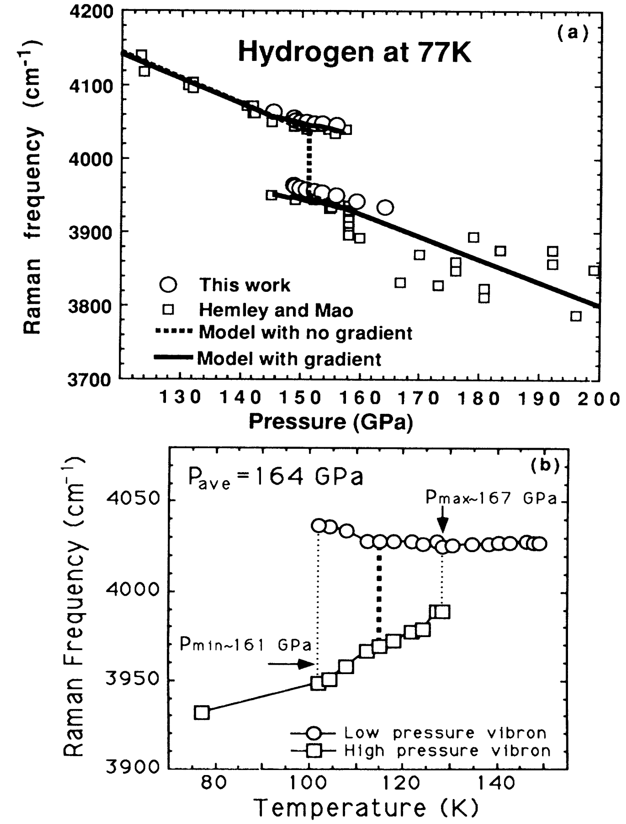

FIG. 2. (a) Comparison of the vibron-frequency data in the vicinity of the phase transition to the model of the sample having a sharp pressure transition with a pressure variation of 12.6 GPa across the sample. (b) Temperature dependence of the vibron frequencies in the vicinity of the phase transition. The two vibrons coexist over a range of temperature because of the pressure gradient across

This pressure-variation model does a good job of reproducing the experimental results as shown in Fig. 2(b) for a representative pressure of 164 GPa. First, it explains the coexistence of two peaks at a given pressure. At an average pressure near the transition, part of the sample will be above and part will be below the transition pressure which will yield a double-peak spectrum (Fig. 1) because of the finite sampling area of the laser. The model also predicts weakly asymmetric line shapes as a result of the combined effect of the linear pressure gradient and the circular sampling area.[13] Such asymmetry is indeed observed but is not readily apparent on the scale of Fig. 1. The model also correctly predicts the unusual reduction of the slope $d\nu/dP$ (where ν is the frequency) in the two-phase region [Fig. 2(a)]. Based on our temperature and pressure data, we are confident, therefore, that pressure gradients are mainly responsible for the two-phase region in our spectra and that hysteresis is not significant for this transition. Using this pressure-gradient model, our data and the data of Hemley and Mao yield 153 and 151 GPa, respectively, for the pressure of the transition at 77 K.[14]

We have determined points on the *P*-*T* phase line for the transition by studying the temperature dependence of the vibron spectra at several pressures as shown in Fig. 2(b). The overlap of the vibrons in temperature is not due to hysteresis, but rather is analogous to the overlap of the vibrons in pressure [Fig. 2(a)].[15] Portions of the sample at different pressures have different critical temperatures for the transition. The *P*-*T* phase line determined for this transition is shown in Fig. 3.[16]

We have also examined other *P*-*T* regions of the phase diagram. At 9 K where the ortho content is close to zero, we monitored the vibron spectrum from 27 to 144 GPa. There was no evidence of the high-pressure phase as indicated by the open-square symbols in Fig. 3. At 144 GPa, we rapidly warmed a p-H_2 sample from 9 to 77 K and then held the sample at this temperature for over 24 h to let it approach ortho-para equilibrium. There was no evidence of the high-pressure phase along this *P*-*T* path. At 77 K, the high-pressure phase appeared after increasing the pressure. The solid squares at 9 K are for a sample with an initial ortho concentration of 0.5 which was allowed to convert to p-H_2 It remained in the high-pressure phase for all ortho concentrations.

We explored the effect of the ortho concentration on the phase line. We could not measure the ortho concentration, but by observing time-dependent changes in spectra features, we could determine when the sample approached equilibrium. We have no evidence suggesting that ortho concentration significantly affects the transition.[17]

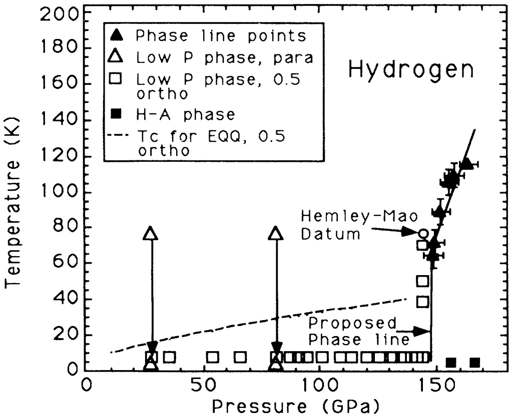

FIG. 3. The proposed *P*-*T* phase diagram for hydrogen. The solid triangles represent the measured phase boundary for H-*A*. The open squares indicate *P*-*T* points in which the sample was established to be completely in the low-pressure phase, whereas it was completely in the H-*A* phase for the filled squares. The open triangles denote the *P*-*T* points for which there was no spectral evidence of the H-*A* phase in cooling down from 77 to 4.2 K.

For comparison to the phase line we determined, we also show the extrapolation to high pressure of the EQQ order-disorder phase line based on a $(\rho/\rho_0)^{5/3}$ density dependence (dashed line in Fig. 3).[18] Unlike the behavior of our experimentally determined phase line, we expect the order-disorder phase line to extrapolate continuously in temperature and pressure to the low-pressure phase studied by Silvera and Jochemsen.[4] To check this interpretation, we performed two measurements which traversed the theoretical EQQ line. The sample, with ortho concentration of 0.5, was cooled from 77 to 4.3 K at 27 and 81 GPa (open triangles in Fig. 3). We did not observe a vibron line shift of order 100 cm^{-1} which characterizes the transition observed near 150 GPa. We observed only much smaller shifts of about 6 cm^{-1}, which require further study.

We now address the question of the nature of the high-pressure phase. We conclude that the phase line we have measured is not an extension of the low-pressure orientational-order phase line. Therefore, the phase occurring above $P = 153$ GPa (at 77 K) is a heretofore unexpected phase which we call the hydrogen-*A* (H-*A*) phase.

Our observation of a discontinuous shift of the vibron frequency as a function of pressure or temperature (Fig. 2) is indicative of a first-order phase transition. This is consistent with the H-*A* transition being a structural phase transition.[19] Barbee *et al.*[5] proposed that the H-*A* transition may be structural rather than orientational, that it could represent an insulator-to-metal transition, and that the transition might involve the change from a molecular to a monatomic state. We have compelling evidence that the state is molecular: (1) the existence of the vibron spectrum, and (2) the existence of a weak Raman signal in our spectra in the 300–400-cm^{-1} shift region (the region of molecular rotational and librational transitions) at the highest pressures in the H-*A* phase.

Several theoretical papers[5,20] have proposed a scenario in which, with increasing pressure, hydrogen has a transition from an insulating molecular to a conducting molecular phase, followed by a transition to a conducting atomic phase. At this time we have no evidence bearing on whether the H-*A* phase could be related to these proposed insulator-to-metal transitions. Recently, Mao and Hemley[21] have claimed metallization of H_2 in this pressure range. This is controversial as compelling evidence was not provided.[22,23]

Pressure gradients in high-pressure samples can have profound effects on the interpretation of phase transitions. By use of our model, we have been able to show that H_2 has a structural transition to a new phase which only exists at megabar pressures.

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[11] See, for example, J. C. Toledano and P. Toledano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987), p. 166.

[12] We assumed Lorentzian line shapes for hydrostatic vibrons. Our laser spot size was ~15 μm; we integrated the contributions from each part of the sample weighted by its area.

[13] We obtained best fits to our data using a linewidth of 8 cm^{-1} for hydrostatic vibrons and a pressure variation of 8 GPa across the sample. These assumptions fit our experimental linewidth of 18 cm^{-1}. The data of Hemley and Mao yield a linewidth about 1.5 times larger than ours, which is consistent with their larger pressure gradient.

[14] A pressure variation of 12 GPa was used for the data of Hemley and Mao.

[15] As mentioned earlier, we can reproduce the appearance or disappearance of a phase to within 1 K upon raising or lowering the temperature, suggesting that there is little hysteresis.

[16] Hemley and Mao studied H_2 over essentially the same pressure and temperature range but did not report a significant temperature dependence of the transition. This may be because they did not fully consider the effects of pressure gradients on their experimental data.

[17] At low temperature the ortho concentration is ~0 and increases to 0.74 at 155 K. The equilibrium concentration at high pressure has not been measured. At zero pressure it requires a few weeks for a sample to approach the equilibrium *o-p* concentration. At 30 GPa we have observed that about 3 days are required, and at 80 GPa about 1 day. At pressures in excess of 150 GPa equilibrium may be approached in several hours.

[18] We do not expect the EQQ interaction to dominate the anisotropic interactions at high density; see, for example, F. H. Ree and C. F. Bender, J. Chem. Phys. **71**, 5362 (1979).

[19] There is no reason why H-*A* could not also be orientationally ordered and might exhibit an order-disorder transition at higher pressures and temperatures.

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