

## Phase Transition in Solid Molecular Hydrogen at Ultrahigh Pressures

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Solid normal hydrogen was compressed in a diamond-anvil cell to pressures above 200 GPa. Spontaneous Raman spectra demonstrate that the solid undergoes a structural phase transformation beginning at 145 GPa at 77 K, as evidenced by an abrupt discontinuity in the intramolecular vibron frequency as a function of pressure. The magnitude of the vibron-frequency shift and the pressure-temperature conditions of the phase transformation are consistent with its identification as the theoretically predicted pressure-induced orientational ordering of the molecular solid.

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The phases of solid hydrogen at high density are currently the subject of great theoretical and experimental interest.<sup>1-13</sup> Recent advances in experimental high-pressure techniques have provided a number of fundamental constraints on the phase diagram of hydrogen at pressures below 100 GPa,<sup>2-4</sup> including recent direct crystal-structure determination by single-crystal x-ray diffraction.<sup>5</sup> At higher pressures, solid molecular hydrogen is predicted to undergo a series of phase transformations, including orientational ordering, molecular band overlap, and eventually dissociation of the molecular bond to form an atomically bonded metallic solid.<sup>7-13</sup> Static compression of hydrogen to pressures where such structural transitions are predicted to occur, together with successful measurement of physical properties under these extreme conditions, has proved to be a difficult challenge. Previously, we compressed hydrogen in a diamond-anvil cell to maximum pressures of 147 GPa at room temperature.<sup>6</sup> Raman measurements carried out to these pressures indicated that the molecular solid is stable to these pressures.<sup>6</sup> There was no evidence of structural phase transformations in the molecular solid, although the Raman-active intramolecular stretching mode was observed to soften appreciably above 100 GPa. In the present study, Raman-scattering measurements of solid normal hydrogen were performed at low temperatures to pressures in the 200-GPa range. The Raman spectra demonstrate that a discontinuous change in the molecular vibron frequency and bandwidth occurs at 145( $\pm 5$ ) GPa at 77 K indicative of a structural phase transformation in the molecular solid. The spectroscopic observations are consistent with an orientational ordering transition of the molecular solid driven principally by electric quadrupolar interactions at high densities.

The experiments were performed with use of a diamond-anvil cell with bevelled diamonds, as in previous studies.<sup>6</sup> Ultrahigh-purity (normal) hydrogen gas was loaded in the high-pressure cell at 300 K with techniques described elsewhere.<sup>14</sup> At pressures above 10 GPa, the cell was cooled to 77 K. The high-pressure Raman measurements were performed primarily at 77 K, with

several temperature excursions to 130 K. The Raman measurements were performed with an optical system described previously.<sup>6</sup> The pressure was determined from the ruby fluorescence method. In the present experiments a small number of micron-sized ruby grains were contained within the cell. For each pressure measurement we used the wavelength shift of  $R_1$  fluorescence bands indicative of ruby confined under near quasihydrostatic pressures (i.e., free of bridging between the diamond anvils). We therefore used the quasihydrostatic ruby pressure scale which has been demonstrated to be appropriate for weak solids at ultrahigh pressures.<sup>15</sup> This pressure scale has recently been confirmed above 100 GPa.<sup>16</sup> The zero-pressure  $R_1$  peak of  $\lambda_0 = 693.41$  nm at 77 K was used.

The results of high-pressure Raman measurements in the region of the molecular vibron at 77 K are shown in Fig. 1. A single, well-resolved band which decreases in frequency with pressure above 30 GPa was observed initially, as in previous studies.<sup>4,6</sup> At 145 GPa, however, a second, broader peak appeared 103( $\pm 5$ )  $\text{cm}^{-1}$  below that of the first. The two peaks coexisted over a small pressure interval with the intensity of the new peak growing at the expense of the first with increasing pressure. At 160 GPa, the first peak completely disappeared. This behavior was found to be reproducible to within  $\approx 5$  GPa from run to run. Moreover, in experiments in which a larger pressure gradient in the hydrogen was produced, this behavior was observed to occur in different regions of the sample at different stages whenever the pressure reached 145–150 GPa. No discontinuous change in optical properties (e.g., visible absorption due to band overlap<sup>9,11</sup>) across the transition was observed. In addition, the transition did not appear to have a large temperature dependence at these pressures on the basis of measurements carried out on increasing the temperatures to  $\approx 130$  K.

Although we have no direct information on the crystal structure of the high-pressure phase in the present experiment, the Raman data provide important constraints on the nature of the transformation. The orientationally

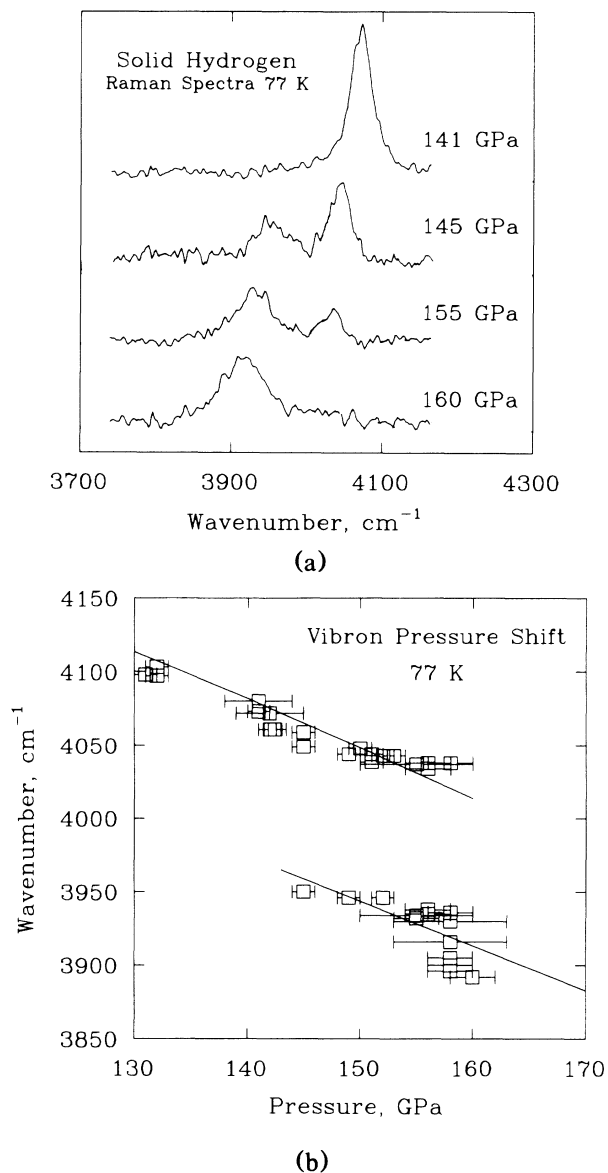


FIG. 1. (a) Raman spectra of solid hydrogen in the region of the  $k=0$  intramolecular stretching modes (vibrons) through the phase transformation at 77 K. A sloping baseline due to diamond-anvil fluorescence has been subtracted. (b) Pressure dependence of the two vibrons in the region of the phase transformation. The lines are weighted least-squares fits to the data.

disordered hexagonal-close-packed structure (space group  $P6_3/mmc$ ) has been shown to persist to 26.5 GPa according to our recent single-crystal x-ray diffraction studies.<sup>5</sup> The continuity of the Raman spectrum with a decrease in temperature to 77 K and an increase in pressure indicates that this structure is preserved to 145 GPa. For the transition, we consider the effect of orientational ordering at very high densities on the Raman spectrum using the low-temperature ordered structure

( $Pa3$ ) as a model.<sup>1</sup> If we assume only nearest-neighbor electric quadrupole-quadrupole (EQQ) interactions on a static lattice, the stabilization energy is  $E = (38/3)\Gamma$ , where  $\Gamma$  is the EQQ coupling constant given as  $\Gamma = 6Q^2e^2/25R^5$ ;  $eQ$  is the quadrupole moment and  $R$  is the nearest interatomic distance.<sup>1</sup> It is convenient to write  $\Gamma_{\text{eff}}(\rho) = \xi(\rho)\Gamma(\rho)$ , where  $\xi$  is a scale factor of order unity that includes the effects of vibrational motion<sup>17</sup> and of higher-order contributions to the intermolecular potential which may become significant at high densities.<sup>1</sup> We assume the experimental value of  $\Gamma_{\text{eff}}(\rho_0) = 0.56 \text{ cm}^{-1}$  (Ref. 1) and a constant ratio of the quadrupole moments in the ground ( $v=0$ ) and excited ( $v=1$ ) states,<sup>18</sup> and use the recently measured equation of state<sup>5</sup> to determine the density at the phase transition. With these assumptions we calculate that  $\Delta\nu$  is negative and undergoes a significant increase in magnitude from  $-1.6 \text{ cm}^{-1}$  at 0.1 MPa to  $-60 \text{ cm}^{-1}$  at 145 GPa; the experimental values are approximately  $-0.5 \text{ cm}^{-1}$  (Ref. 19) and  $-100 \text{ cm}^{-1}$  at these pressures, respectively, which is comparable to the predicted shift. The  $\Delta\nu$  measured at 145 GPa would require  $\xi \approx 1.7$ , an increase in  $\xi$  with density which is likely to reflect increasing non-EQQ anisotropic interactions<sup>1</sup> and diminishing vibrational renormalization effects at high pressures; a higher  $\Gamma_{\text{eff}}$  (and hence larger  $|\Delta\nu|$ ) may also be expected for an ortho-para mixture,<sup>20</sup> as is the case for our samples.

In addition to the frequency shift at the transition, the pressure-temperature conditions of the transition are consistent with the predictions based on lower-pressure data for a transition driven by EQQ interactions. Silvera and Jochemsen<sup>21</sup> studied the ortho-para and pressure dependence of the transition temperature  $T_c$  to pressures of 0.6 GPa and found that  $T_c \sim [\xi(\rho)/\xi(\rho_0)](\rho/\rho_0)^{5/3} \times T_c(\rho_0)$ . The transformation observed in the present study at 145 GPa and 77 K is shown together with the lower-pressure results in Fig. 2. The reference transition temperature  $T_c(\rho_0)$  decreases with decreasing ortho concentration  $c_1$ . Hence the high-pressure point in the figure is considered a lower bound on  $T_c(\rho)/T_c(\rho_0)$  because of the expected drop in  $c_1$  with temperature [i.e., at equilibrium  $c_1 \approx 0.75$  at 300 K;  $c_1 \approx 0.50$  at 77 K (Ref. 1)]. The kinetics of ortho-para conversion at these very high pressures, however, has not yet been studied. For orthohydrogen ( $c_1=1$ ) Silvera and Jochemsen<sup>21</sup> found that the density dependence of  $T_c$  scaled nearly as  $(\rho/\rho_0)^{5/3}$  at low pressures; this curve is also shown in the figure. We find that the present result is consistent with the trends observed in the earlier data.

There have been numerous theoretical predictions of the orientational ordering of the hydrogen isotopes under pressure. Several early calculations predicted that the transformation observed at 0.1 MPa from the orientationally disordered hexagonal-close-packed structure ( $P6_3/mmc$ ) to the ordered cubic-close-packed structure

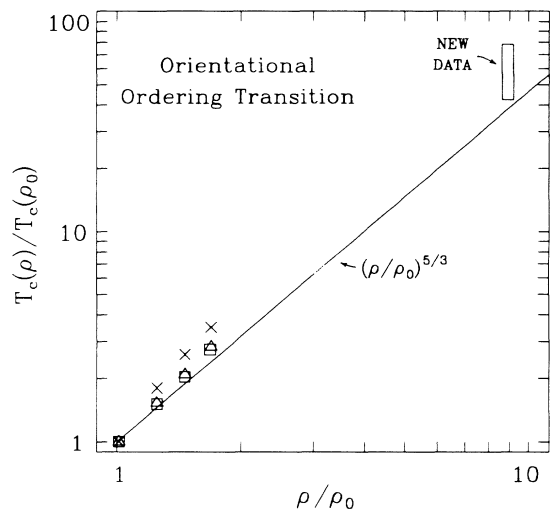


FIG. 2. Temperature and density phase diagram for the orientational ordering transition in solid hydrogen. The present high-density result is given by the rectangular symbol, the height of which illustrates the dependence of  $T_c(\rho)/T_c(\rho_0)$  on the ortho-para concentration in the sample at 145 GPa. The lower and upper bounds of  $T_c(\rho)/T_c(\rho_0)$  at 77 K correspond to  $c_1=0.75$  and  $c_1=0.60$ , respectively, where  $c_1$  is the fraction of orthohydrogen, with  $\rho_0=0.0881$  g/cm<sup>3</sup> (Ref. 1) and  $\rho=0.769$  g/cm<sup>3</sup> at 145 GPa (Ref. 5). The low-density data are from Ref. 21; the crosses, triangles, and squares correspond to  $c_1=0.60, 0.75$ , and  $1.00$ , respectively.

(Pa3) in ortho-rich crystals will occur in parahydrogen in the 10-GPa pressure range (at low temperature).<sup>7,8</sup> The transformation has not yet been observed in hydrogen according to measurements carried out to  $\approx 50$  GPa,<sup>18</sup> although the transformation has been reported in orthodeuterium at 28 GPa by Silvera and Wijngaarden.<sup>22</sup> Recent quantum Monte Carlo calculations predict the transition to occur in hydrogen in the 100-GPa range (at  $T=0$  K).<sup>12</sup> The present results for normal hydrogen are consistent with the recent calculations, although the transformation in the pure para system is expected to occur at still higher pressures. It is noteworthy that the pressure-temperature conditions of the transformation documented here are very close to that predicted by Silvera<sup>13</sup> for orthohydrogen using trends in low-pressure-low-temperature experimental data.<sup>21</sup>

On further increase in pressure above the transition, the new vibron remained an identifiable peak and continued to soften with pressure, as shown in Fig. 3. At pressures above 170 GPa, the determination of the pressure became increasingly difficult due to the weakened ruby-fluorescence signal from the sparse ruby in the sample. The uncertainty in the pressure is reflected in the scatter in the data in this pressure range. Under maximum load, we note that fluorescence peaks indicating pressures as high as 248 GPa were observed in the center of the diamond flat; in this region of the sample, molecular hydro-

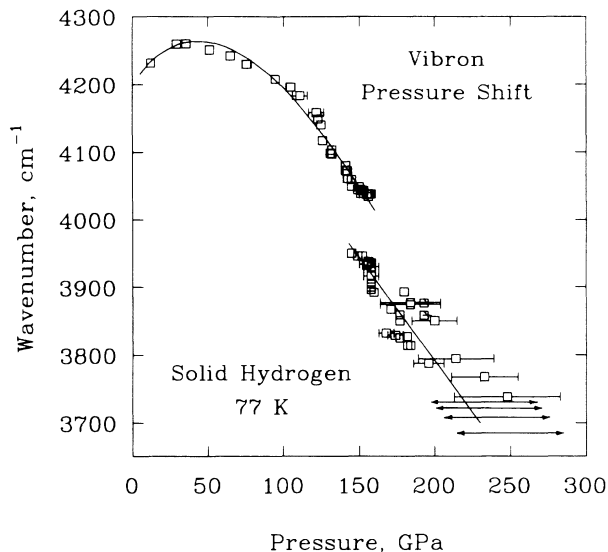


FIG. 3. Pressure dependence of the vibron of solid hydrogen in the low- and high-pressure phases at 77 K.

gen was observed in the Raman measurements with vibron frequencies as low as  $3738$  cm<sup>-1</sup>. Still lower vibron frequencies to  $3685$  cm<sup>-1</sup> were observed in regions of the sample that did not contain ruby. Although pressures therefore could not be determined, a simple linear extrapolation of the lower-pressure data suggests peak hydrogen pressures in the 250-GPa range. Further discussion of the optical properties of the molecular solid in this pressure range will be presented elsewhere. The maximum pressures reported here may serve as a new lower bound on the molecular-to-atomic transition pressure in this material.

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