New High-Pressure Excitations in Parahydrogen

Alexander F. Goncharov, Russell J. Hemley, Ho-kwang Mao, and Jinfu Shu
Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington,
5251 Broad Branch Road N.W., Washington, D.C. 20015

(Received 18 July 1997)

Raman and infrared spectroscopy of para-H_2 to pressures in excess of 200 GPa and to 8 K using new ultrapure synthetic diamond anvils reveals numerous new vibrational excitations in the three high-pressure phases. Highly resolved Raman-active librons indicate differences in orientational ordering between phases II and III, including evidence for changes within phase II. The librons in phase III are strongly pressure dependent and reflect a substantial increase in ordering with pressure. Multiple vibrons in all three phases (I, II, and III) are observed. The results place new bounds on predicted crystal structures and dynamics of the dense molecular solid. [S0031-9007(97)04895-3]

PACS numbers: 62.50.+p, 61.50.Ks, 78.30.−j

Experimental and theoretical investigations of dense solid hydrogen continue to reveal numerous intriguing but incompletely understood properties of its high-pressure phases [1]. Three solid molecular phases (I, II, and III) persist at megabar pressures (>100 GPa). The behavior of the system is characterized by vibrational discontinuities, remarkable increases in infrared vibrational response, and a surprisingly complex phase diagram exhibiting aspects of both classical and quantum orientational ordering [2,3]. Recent theoretical calculations predict novel behavior associated with new classes of crystal structures and orientational ordering schemes [4–11], intermolecular and intramolecular charge transfer [4–7], spontaneous polarization and development of a charge density wave [1,6], an antiferroelectric instability [7,10], as well as superconductivity [12], and superfluid order [10]. The predicted energy differences between structures are extremely small and very sensitive to the approximations made in the calculations (e.g., treatment of zero point motion, local density approximation). Detailed measurements of the vibrational excitations in the dense solid are crucial for testing these predictions and establishing the connection with existing experimental data. This includes obtaining information on the crystal symmetry from the distribution of Raman- and IR-active modes in the pure $J = 0$ solid and effects of disorder due to temperature or ortho-para state.

The vibrational excitations of solid hydrogen consist of vibrons (intramolecular vibrations), phonons (intermolecular translations), and rotons (free molecular rotations). At low densities, the Raman modes form multiplets associated with splitting of the $Q_1(J)$ ($\Delta\nu = 1$; $\Delta J = 0$) and $S_0(J)$ ($\Delta\nu = 0$; $\Delta J = 2$) bands. The splitting of the $S_0(0)$ roton into a triplet and a single phonon are characteristic of the rotationally disordered hcp structure of phase I, confirmed by x-ray diffraction to 120 GPa (room temperature only) [13]. The vibrational spectrum is particularly sensitive to predicted changes in structure and dynamics. On ordering, the rotons should be supplanted by librons (lattice phonons derived from restricted rotational motion). Such measurements thus also permit examination of the extent to which J remains a valid quantum number and ortho-para states are distinguishable at high pressure.

The identification of phase II as one of quantum mechanical ordering [3] implies that its stability should depend critically on the initial ground rotational state of the molecules [$J = 0$ or 1, para (p) or ortho (o) species]. In fact, pure o-H_2 transforms to the ordered ($Pa3$) phase at ambient pressure and 3.8 K [14]. In contrast, p-H_2 (consisting of spherically symmetric rotating molecules) transforms to an ordered (so-called broken symmetry, BSP) phase at 110 GPa and 8 K, presumably due to an increase in anisotropic intermolecular interaction [15]. The structure of this phase is not known and spectroscopic data are extremely limited. For example, Lorenzana *et al.* [15] reported a complete disappearance of low-frequency spectrum, although proposed structures (e.g., Ref. [16]) should exhibit rotons (or librons) and phonons that depend on crystal symmetry. These results contrast with studies of the transition to phase II at >80 K in mixed (50%-50%) o-p H_2 crystals [3,17,18]. The persistence of the optical phonon implies that the hcp structure of molecular centers is not strongly affected by the phase transition. Surprisingly, Raman measurements [17] of the broadened $S_0(0)$ and $S_0(1)$ rotational bands as well as IR measurements [3,18] of the $Q_1(J) + S_0(0)$ and $Q_1(J) + S_0(1)$ combination bands are remarkably unaffected by the I-II transition in the mixed crystals.

The complete Raman spectrum of pure p-H_2 through the transition to phase III has not been reported. In particular, little is known about the low-frequency spectrum. Raman studies typically have been limited by the onset of strong fluorescence from conventional diamond anvils used in these experiments. One Raman-active librational band with a strong frequency shift with pressure has been reported [3]. A weak feature in a similar frequency range was reported in Ref. [15], together with an abrupt decrease in intensity upon warming below the transition to

0031-9007/98/80(1)/101(4)$15.00

phase I. A phonon was detected in phase III (80 K) [17], suggesting that the underlying crystal lattice is derived from hcp (rather than fcc). The IR activity of the vibron and presence of librational modes in phase III indicate that the structure is more complex.

To address these problems, we have performed detailed measurements of the vibrational excitations of pure p-H_2 using ultrapure synthetic diamond anvils, which we show removes the stress-induced optical features associated with natural diamond impurities. As a result we observe new sets of vibron, phonon, roton, and libron excitations in p-H_2 as a function of pressure through phases I, II, and III. The results place new constraints on the structures and orientational state of the molecules in these phases. For example, the vibrational properties of phase II for p-H_2 are consistent with the presence of the inversion center at the molecule as in an fcc-based structure. We document up to ten strongly pressure dependent libron (or phonon) modes, two Raman-active phonons, and a vibron sideband in phase III, requiring at least four molecules (eight for a centrosymmetrical structure) in the primitive cell. Major differences for pure p-H_2 and o-p mixed crystals in phases I and II are found, but these differences disappear in phase III.

High-purity n-H_2 was loaded at room temperature in modified Mao-Bell diamond-anvil cells with type IIa diamonds. Three experiments were performed, two with natural type IIa diamonds and one with synthetic diamonds [19]. In each, samples were pressurized at room temperature to several tens of GPa, cooled to 10–16 K, with spectra studied at constant temperature and pressure as a function of time. Here we focus on the results of the Raman measurements (see Refs. [20,21] for techniques); a detailed discussion of the IR results will be presented elsewhere [20]. The o-p concentration was monitored at 18 K from the intensities of the $S_0(0)$, $S_0(1)$ Raman, and $Q_1(J) + S_0(0)$, $Q_1(J) + S_0(1)$ IR bands as a function of time [22]. The $S_0(1)$ and $Q_1(J) + S_0(1)$ bands disappear when the pure para state is reached, and other spectral features appear in both IR and Raman spectra [20,22]. The pressure was increased at constant temperature, with temperature excursions to 100 K in phase III, followed by warming.

We first present measurements of the low-frequency spectrum through the I-II and II-III transitions in p-H_2 (Fig. 1). The components of the the M_J triplet derived from the $S_0(0)$ transition near 350 cm^{-1} broaden with pressure and are barely resolved just below the transition. At the transition, the band does not disappear but transforms into a doublet with both components having positive frequency shifts with pressure. Moreover, two sharper bands appear at lower frequencies; the higher mode (200 cm^{-1}) is essentially pressure independent, but the lower band has a positive pressure shift. We attribute these modes to librons. At 146 GPa the low-frequency libron suddenly increases in intensity, and a new lower frequency libron appears. Also, the higher libron splits into a doublet. This behavior could reflect changes in orientational ordering within the phase (e.g., in average directions of librational motion [8]), a premonitory change associated with the transition to phase III, or yet another phase transition. In addition, the intensity of the phonon mode near 900–1000 cm^{-1} becomes extremely weak above 115 GPa (in phase II).

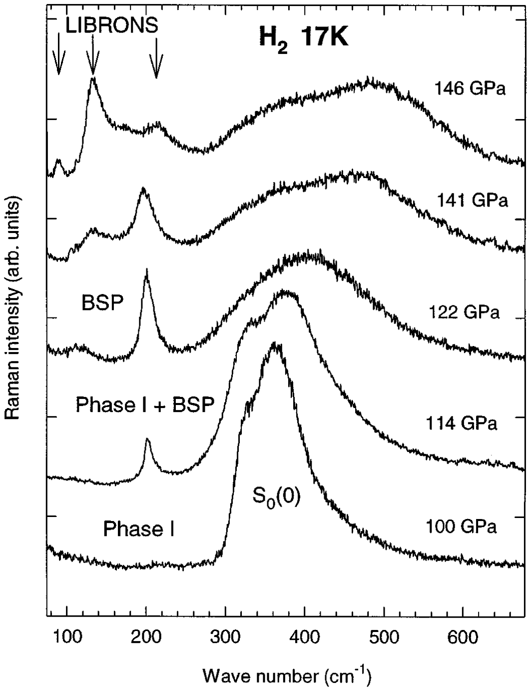

FIG. 1. Raman spectra of roton/librational excitations in p-H_2 through the transition to phase II (BSP).

Extending our measurements to phase III (>150 GPa), we again find numerous new excitations. Between 146 and 168 GPa, the low-frequency Raman spectra and IR combination bands transform gradually as a result of two-phase coexistence, and finally above 174 GPa we observe a completely different manifold of low-frequency excitations (Fig. 2). Increasing pressure further leads to a substantial sharpening and shift of these bands to higher frequencies. Moreover, the Raman-active phonon mode, which is unobservable in the BSP phase, becomes strong and splits into a doublet in phase III.

Figure 3 shows the pressure dependence of low-frequency excitations measured either directly by Raman or deduced from combination IR bands [18]. The phonon of p-H_2 in phase I (near 800 cm^{-1}) follows the pressure dependence of the mode in o-p mixed crystals at 80 K [17]. We observe up to ten librons (or lower frequency phonons) in phase III. The spectral positions of the newly observed Raman modes are in good agreement with those deduced from the IR for samples starting out as o-p mixed crystals [3], but the new bands are much better resolved, particularly at the highest pressures (e.g., 205 GPa). The results for both phases can be interpreted as arising from a gradual increase in the potential barriers

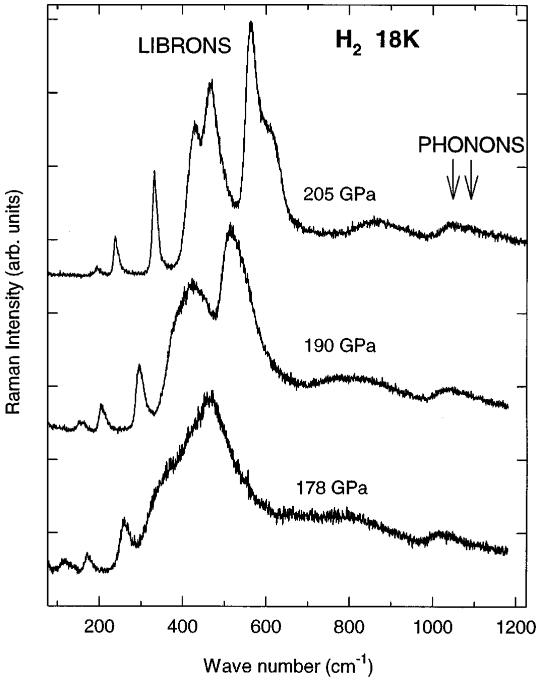

FIG. 2. Low-frequency Raman spectra of p-H_2 in phase III.

between different molecular orientations with pressure. Once the barriers become comparable to the libron energy, the levels split and give rise to new transitions.

The measurements also reveal new features in the vibron spectrum of p-H_2 (Fig. 4). With the disappearance of the $S_0(1)$ transition in forming the pure para state of phase I, a new high-frequency Raman band appears together with narrow IR bands [20]. We assign this band to the $S_1(0)$ vibration-rotation transition [25], previously observed only in the zero-pressure solid having high $J = 0$ species concentrations [23]. At the I-II phase transition, the $S_1(0)$ transition disappears in Raman (and IR spectra) and a new Raman vibron appears near 4520 cm^{-1} with a linewidth similar to the previously observed vibron (labeled ν_1). We assign it to a second symmetry allowed vibron fundamental ν_2. For phase III we also observe a second narrow band (near 4400 cm^{-1}), which we tentatively assign as a second Raman vibron in this phase. All newly observed fundamentals follow the pressure dependence of the principal vibrons and lie within the vibron exciton bandwidth determined at these pressures [18].

These observations provide important constraints on the crystal structures of the phases of p-H_2. The presence of the $Q_1(0)$ and $S_1(0)$ vibrons is consistent with continuity of the rotationally disordered hcp structure to 110 GPa (18 K). Our results indicate that the crystal structure of the BSP phase has Raman allowed low-frequency excitations. However, the significant decrease in intensity of the phonon at the I-II transition strongly suggests that it is symmetry forbidden. This result (as well as the disappearance of the $S_1(0)$ IR excitation [20,23]) indicates a possible change in crystal structure of molecular centers from hcp to fcc. The additional vibron ν_2 and lower frequency librons require an increase in the number of molecules in the primitive cell by at least a factor of 2 relative to phase I. All of the above are consistent with the

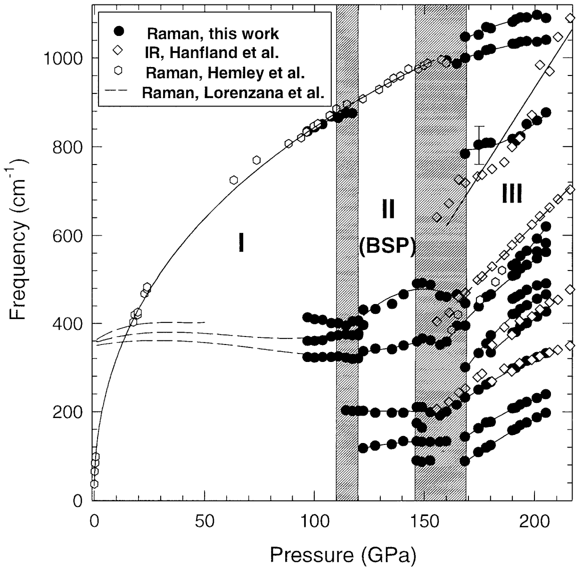

FIG. 3. Pressure dependence of the low-frequency excitations in p-H_2 through the transitions to phases II and III. The solid lines are guides to the eye; the Fermi resonances between the rotons and phonon at lower pressure (e.g., [17]) are not shown. The dashed lines are from Ref. [15]. The shaded area gives the regions of the two-phases coexistence, typically observed in such experiments [2].

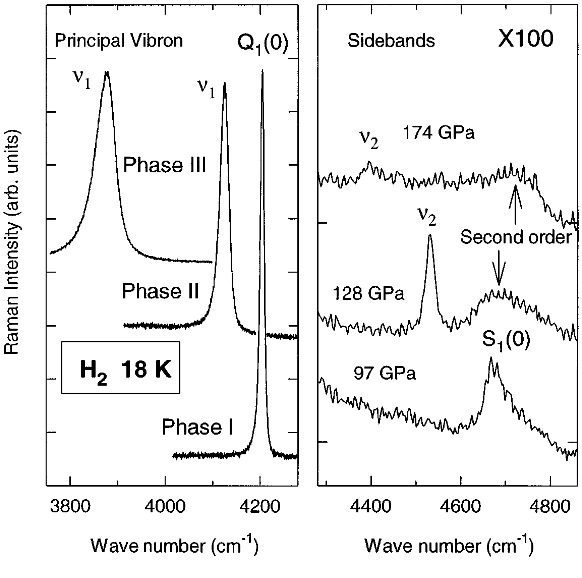

FIG. 4. Raman spectra of the vibrons of p-H_2 in phases I, II, and III. Measurements within the panel have the same spectral resolution: 3 cm^{-1} (left) and 20 cm^{-1} (right). The vibron fundamentals in phases II and III are labeled ν_i. The broad, asymmetric high-frequency features are assigned to second-order (multiphonon) scattering. The new vibrons are distinguished from the second-order bands by their narrower linewidths.

$Pa3$ [26] or $Cmca$ structures. Although the presence of the IR vibron [20] would seem to rule out these structures, this (very weak) band could be formally symmetry forbidden and its IR activity induced (e.g., by strain). Indeed, very similar IR activity of the N_2 vibron is observed in α-N_2 [27], which is known to have the $Pa3$ structure. We find the intensity and number of IR vibrons is dependent on the o-p ratio. The results also suggest possible differences in structure of phase II for o-p mixed crystals [21] versus pure p-H_2.

The extensive data obtained here for phase III also allow us to draw important conclusions about its structure. The number of low-frequency Raman-active modes and possible second Raman vibron indicate that the primitive cell should contain at least four molecules. This is consistent with the $Pca2_1$ structure, extensively discussed in the literature [6,9–11]. Alternatively, the fact that the IR and Raman vibrons and phonons have different frequencies implies that the crystal structure for phase III may possess a center of symmetry; the presence of Raman-active phonon(s) means that any center of inversion is between molecules. In this case, the number of molecules in a primitive cell should be doubled. No additional phase line [15] within the stability field of phase III was found. Instead, we find a strong frequency increase and a remarkable linewidth narrowing of librational bands. Together with the increase in vibron IR oscillator strength [4], these findings indicate a gradual increase in ordering with pressure, perhaps coupled with a continuous structural change [6,7,10] within phase III.

In conclusion, new spectroscopic techniques together with synthetic diamond anvils have revealed a great deal of new information about the high-pressure phases of hydrogen. The number of new excitations places crucial bounds on recently proposed structures and dynamical behavior in the dense solid. Differences in spectral features, phase lines, and possibly structures between pure p-H_2 and o-p mixed crystals are observed in phases I and II. However, these differences disappear in phase III, where single-molecule o-p distinguishability is lost. The new experimental data provide a crucial testing ground for theory, including quantum effects associated with rotational barriers and librational dynamics.

We thank V. Struzhkin, R. Lu, and T. Schindelbeck for experimental help. This work was supported by NSF (DMR-9624050, CHiPR), NASA (NAGW-1722), and DOE (DE-AC02-76-CH00016; DE-FG02-96ER14651).

[1] N.W. Ashcroft, Phys. World **8**, 43 (1995).

[2] R.J. Hemley and H.K. Mao, J. Non-Cryst. Solids **205–207**, 282 (1996).

[3] I.I. Mazin, R.J. Hemley, A.F. Goncharov, M. Hanfland, and H.K. Mao, Phys. Rev. Lett. **78**, 1066 (1997).

[4] R.J. Hemley, Z.G. Soos, M. Hanfland, and H.K. Mao, Nature (London) **369**, 384 (1994); R.J. Hemley, I.I. Mazin, A.F. Goncharov, and H.K. Mao, Europhys. Lett. **37**, 403 (1997).

[5] J.S. Tse and D.D. Klug, Nature (London) **378**, 595 (1995).

[6] B. Edwards, N.W. Ashcroft, and T. Lenosky, Europhys. Lett. **34**, 519 (1996); B. Edwards and N.W. Ashcroft, Nature (London) **388**, 652 (1997).

[7] I. Souza and R.M. Martin, Bull. Am. Phys. Soc. **42**, 672 (1997); R.M. Martin (private communication).

[8] I.I. Mazin and R.E. Cohen, Phys. Rev. B **52**, R8797 (1995).

[9] J. Kohanoff, S. Scandolo, G.L. Chiarotti, and E. Tosatti, Phys. Rev. Lett. **78**, 2783 (1997).

[10] M.P. Surh *et al.*, Phys. Rev. B **55**, 11 330 (1997).

[11] K. Nagao, H. Nagara, and S. Matsubara, Phys. Rev. B **56**, 2295 (1997).

[12] C.F. Richardson and N.W. Ashcroft, Phys. Rev. Lett. **78**, 118 (1997).

[13] P. Loubeyre *et al.*, Nature (London) **383**, 702 (1996).

[14] I.F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).

[15] H.E. Lorenzana, I.F. Silvera, and K.A. Goettel, Phys. Rev. Lett. **64**, 1939 (1990).

[16] L. Cui, N. H. Chen, and I.F. Silvera, Phys. Rev. B **51**, 14 987 (1995).

[17] R.J. Hemley, H.K. Mao, and J.F. Shu, Phys. Rev. Lett. **65**, 2670 (1990).

[18] M. Hanfland, R.J. Hemley, and H.K. Mao, *High-Pressure Science and Technology—1993*, edited by S.C. Schmidt *et al.* (AIP, New York, 1994), p. 877.

[19] The diamonds were chemically pure crystals obtained from General Electric Superabrasives, Worthington, OH. Optical properties of similar diamonds under pressure have also been studied by J. Liu and Y. Vohra [Appl. Phys. Lett. **68**, 2049 (1996)].

[20] A.F. Goncharov, R.J. Hemley, H.K. Mao, and R. Lu (to be published).

[21] A.F. Goncharov, J.H. Eggert, I.I. Mazin, R.J. Hemley, and H.K. Mao, Phys. Rev. B **54**, R15 590 (1996).

[22] This is easily deduced from the intensities of the 4870 cm^{-1} $Q_1(J) + S_0(0)$ and 5100 cm^{-1} $Q_1(J) + S_0(1)$ bands, which are proportional to $aC_pC_o + bC_p^2$ and $a'C_o^2 + b'C_oC_p$ [23], where C_p and C_o are fractional concentrations of para- and orthomolecules, and $a/b = 3$, $a'/b' = 0.4$ are constants. The conversion rate increases drastically with pressure to about 100 GPa [24] (see also, [21]). When the pure para state of phase I is reached, the crystal field splitting of the $S_0(0)$ is observed, as found previously [15]. Also, the Raman vibron increases in frequency by some 10 cm^{-1}.

[23] H.P. Gush, W.F.J. Hare, E.J. Allin, and H.L. Welsh, Can J. Phys. **38**, 176 (1960).

[24] J.H. Eggert, E. Karmon, A.F. Goncharov, R.J. Hemley, and H.K. Mao, Bull. Am. Phys. Soc. **41**, 615 (1996); (to be published).

[25] The frequency (4670 cm^{-1}) is too high to assign it to a vibron, which also would not be allowed in hcp-structured pure p-H_2.

[26] K.J. Runge, M. P. Surh, C. Mailhiot, and E.L. Pollock, Phys. Rev. Lett. **69**, 3527 (1992).

[27] H.J. Jodl, W. Loewen, and D. Griffith, Solid State Commun. **61**, 8 (1987).