

Low-Frequency Vibrational Dynamics and Structure of Hydrogen at Megabar Pressures

R. J. Hemley, H. K. Mao, and J. F. Shu

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, N.W., Washington, D.C. 20015

(Received 1 May 1990)

Low-frequency rotational and lattice-phonon spectra of solid H₂ have been measured to 162 GPa at 77 to 295 K. Rotational bands broaden continuously up to and through the 150-GPa phase transition, with no sign of orientational transitions. The optical phonon, identified at low pressures as the transverse-optical mode of the hexagonal-close-packed structure, persists into the high-pressure phase, which indicates the underlying lattice remains hexagonal to these pressures. The measurements are consistent with the 150-GPa transition being largely electronic in origin and associated with metallization.

PACS numbers: 67.80.Cx, 62.50.+p

Knowledge of the structural and dynamical properties of solid molecular hydrogen at very high densities is crucial for detailing its eventual transition to high-pressure metallic forms.¹ As a result of developments in diamond-anvil cell techniques, static pressures above 200 GPa have been reached on hydrogen samples.²⁻⁴ By use of Raman spectroscopy, we have discovered major low-temperature phase transitions in hydrogen² and deuterium³ beginning at 150 GPa. The transition is characterized by a large discontinuity of approximately 100 cm⁻¹ in the frequency of the intramolecular stretching mode (vibron). We have also observed large changes in optical properties at visible wavelengths in the solid at pressures above 200 GPa; this result suggests that metallization may occur in the molecular solid at lower pressures by closure of an indirect gap, perhaps at the 150-GPa transition.⁴ In addition to the possibility of band overlap,⁵⁻⁷ order-disorder transitions are expected in this pressure range, and this rotational ordering may be coupled to structural transitions.^{2,8} Ordering may occur as a first-order crystallographic phase change such as the hcp to *Pa*3 transition observed in high-(*J*=1)-content solids at low temperatures and pressures (<1 GPa).⁸ Alternatively, the ordering may proceed continuously or discontinuously without lattice reconstruction.⁶ In the very-high-pressure metallic-molecular phase, it is not known if the molecules are freely rotating or aligned, and the rotational state of the molecules is expected to have a significant effect on the pressure of the insulator-metal transition.⁷ In addition, theoretical calculations indicate that there is an important crystal-structure dependence of electronic properties: Significantly different metallization pressures are predicted for cubic and hexagonal structures with different ordering schemes.⁵⁻⁷

High-pressure diffraction studies have shown that hydrogen and deuterium remain in the hexagonal-close-packed structure to at least 30 GPa.⁹ The extension of such measurements to the ultrahigh pressure range above ~100 GPa is not yet feasible. As an alternative to diffraction studies, structural constraints may be obtained by measurements on the low-frequency rotational and lattice-phonon states by Raman measurements below 1000 cm⁻¹. Broadening of rotational bands has

been used as an indication of the onset of phase transitions.¹⁰ The measurement of the Raman-active lattice modes (optical phonons) provide a more definitive probe because, in general, these excitations are structure specific. Measurements of the *E*_{2g} optical phonon of hcp hydrogen at high pressure have been reported, but only up to 23 GPa.¹¹ Measurements at higher pressures are difficult because of the very low scattering cross section for this excitation. In the present study, we have extended measurements of both the low-frequency rotational (librational) bands and the *E*_{2g} optical phonon of solid normal H₂ to 162 GPa at 77 to 295 K. The results provide the first constraints on the crystal symmetry of hydrogen above 30 GPa, including its behavior in the high-pressure phase above 150 GPa.

The present experiments were performed using high-pressure Raman-scattering techniques similar to those described previously.²⁻⁴ We used modified megabar diamond-anvil cells¹² with single-bevel anvils with central flats of 50–100 μm, and composite gaskets consisting of T-301 stainless steel and rhenium. A 30–50-μm hole was drilled to contain the sample. These samples were considerably larger than those studied previously²⁻⁴ so that the weaker lower-frequency Raman bands could be measured. Pressures were determined with the ruby-fluorescence technique.¹³ Raman spectra of hydrogen at 77 K in the low-frequency region as a function of pressure to 158 GPa are shown in Fig. 1.

We first discuss the lower-pressure behavior. The two lowest-frequency bands correlate with the *S*₀(0) ($\Delta J = 2, J = 0$) and *S*₁(0) ($\Delta J = 2, J = 1$) rotational transitions in the normal solid (rotons in *p*-H₂). At low densities the first is composed of three individual peaks that arise from $\Delta M = \pm 1, \pm 2, 0$ transitions split by the crystal field in the hcp solid.¹⁴ These bands are inhomogeneously broadened in the normal solid at 77 K but become resolved at lower temperatures (decreasing ortho content). With increasing pressure the positions of the rotational transitions change little but begin to broaden. Above ~50 GPa, the *S*₀(0) band evolves into a doublet at 350 and 410 cm⁻¹ that persists up to the highest pressures. The pressure dependences of the low-frequency Raman bands are shown in Fig. 2, along with previous

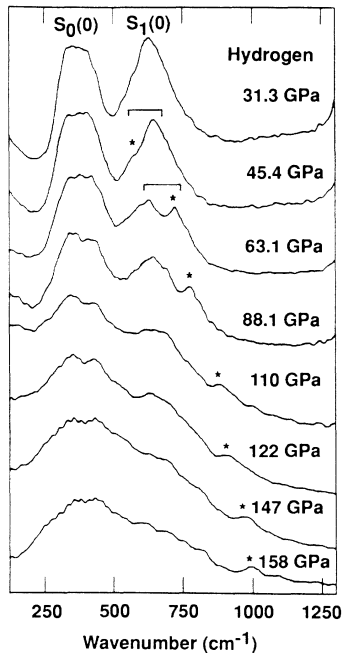


FIG. 1. Representative Raman spectra of hydrogen as a function of pressure at 77 K. The $S_0(0)$ and $S_1(0)$ rotational bands are indicated. The asterisks identify the optical phonon correlated with the transverse optical E_{2g} mode. There is some evidence for additional peaks, including a possible splitting of the $S_1(0)$ band at higher pressures, but these have significantly lower intensities (comparable to the noise level). The brackets in the 45.4- and 63.1-GPa spectra indicate the region of mixing of the E_{2g} -phonon and rotational states.

results from much lower pressures. The weak pressure shift of the $S_0(0)$ agrees with previous results for p - H_2 ; however, the splitting of the component bands differ, a detailed analysis of which will be presented elsewhere.

A striking change in the region of the $S_1(0)$ band is observed beginning at ~ 40 GPa. At higher pressure a weaker but clearly resolved peak with a very large pressure shift becomes apparent. To exclude the possibility that this change is associated with a transformation (e.g., order-disorder) we examined the temperature dependence of the spectrum between 77 and 295 K. We found that the intensity variations were independent of temperature. On the basis of the continuous change in the spectrum at this pressure, we interpret this behavior as arising from a hybridization of the strongly pressure-dependent E_{2g} phonon and the $S_1(0)$ rotational band ($J=3$ level) at 40–60 GPa. This effect is directly analogous to mixing of the E_{2g} phonon with one of the $J=2$ rotors in p - H_2 at 13 GPa, as reported by Wijngaarden and co-workers.¹¹ The mixing may be represented by $\omega^\pm = \frac{1}{2}(\omega_R + \omega_P) \pm \frac{1}{2}[(\omega_R - \omega_P)^2 + 4W_1^2]^{1/2}$, where ω_R and ω_P are the unperturbed rotational and phonon frequencies, and W_1 is a density-dependent interaction energy. In the region of the avoided crossing (40–60 GPa), we find $W_1 = 36(\pm 8)$ cm^{-1} , which is sig-

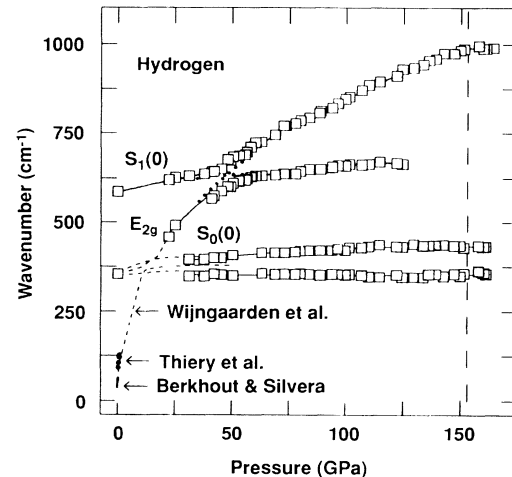


FIG. 2. Pressure dependence of the low-frequency Raman bands of hydrogen at 77 K. The low-pressure results were obtained at 4 K (p - H_2). The dotted line between 40 and 60 GPa shows the frequencies of the unperturbed phonon and rotational band frequencies. The pressure dependence of the rotational band [correlated with $S_1(0)$] is not shown above 125 GPa because it broadens significantly. The pressure of the high-pressure transition at 77 K is indicated by the vertical dashed line.

nificantly higher than that obtained for the mixing of the phonon with the $J=2$ rotor [$W_1 = 12(\pm 2)$ cm^{-1} (Ref. 11)] as a result of the larger crystal field at the higher densities. From such an analysis we find a continuous shift of the E_{2g} band with pressure up to the 150-GPa transition. The shift is consistent with previous measurements carried out at low pressures by Thierry *et al.*,¹⁵ Berkhout and Silvera,¹⁶ and Wijngaarden and co-workers,¹¹ who documented the extremely large initial pressure dependence of the E_{2g} band.

The continuous shift and broadening of the rotational bands and the persistence of the optical phonon above 100 GPa provide evidence that the normal solids do not undergo any major structural transitions from hcp below the vibron discontinuity of 150 GPa. The vibron itself was also measured as a function of pressure and temperature in these samples and found to shift continuously with pressure over this range, consistent with previous observations.^{2,3} These measurements indicate that any discontinuities in the vibron frequency with pressure must be less than 2 cm^{-1} . Hence, our results indicate that the underlying structure of the molecular solid remains hexagonal. This result is particularly significant because most electronic structure calculations to date for the high-density molecular solid have used an assumed cubic structure (e.g., Ref. 5). In contrast, calculations by Barbee *et al.*⁶ and Raynor¹⁷ indicate that structures based on a hexagonal-close-packed configuration are significantly more stable than cubic forms (e.g., $Pa3$ structure). Specifically, an hcp structure with the molecules aligned parallel to the c axis is found to be most

stable; Barbee *et al.*⁶ further proposed that the molecules order continuously in this configuration with increasing pressure. In this ordering scheme, there is no change in space group ($P6_3/mmc$), and only one E_{2g} lattice mode will appear. This is consistent with the present measurements, although we cannot yet rule out other ordering schemes or small distortions (e.g., superlattices) of the hcp structure.¹⁸ It may be of interest to note that the recently described ordered molecular form^{6,17} was actually predicted by Abrikosov¹⁹ in 1954 to be the structure of the molecular solid in this density range (i.e., prior to molecular dissociation).

Recently, Lorenzana, Silvera, and Goettel^{20,21} carried out a Raman study of hydrogen using a megabar diamond-anvil cell.¹² They have confirmed our observation of the 150-GPa vibron discontinuity in hydrogen and have reported measurements of the temperature dependence of the transition down to 5 K.²⁰ Evidence was also reported for a broken-symmetry transition in p -H₂ at 5 K on the basis of broadening and loss of the rotational bands at 110 GPa.²¹ In contrast, we find that the rotational bands (e.g., lower-frequency doublet) in the normal solid at 77 K persist through this pressure interval. If their assignment proves correct, the results suggest rather different behaviors between the pure para and the normal solids at these temperatures prior to the 150-GPa transition. This result is somewhat surprising in view of the fact that the 150-GPa transition appears to have a weak dependence on temperature (ortho-para state²²) in this range. Unfortunately, the lattice vibrations were not measured in their study,²¹ so the spectra contain no information on the crystal structure of the proposed ordered molecular phases of hydrogen above and below the 150-GPa transition.

Our extended measurements of the low-frequency vibrational spectrum above 150 GPa (Figs. 1 and 2) are useful for the understanding of the nature of this transition. Details of the Raman spectrum in the region of the phonon and vibron at 147–162 GPa are presented in Fig. 3. Despite the pronounced discontinuity in the vibron, the optical phonon remains essentially unchanged. The result indicates that the transition can proceed with at most minor changes in crystal structure. The pressure dependence of the phonon appears to change abruptly at the transition, possibly softening in the high-pressure phase (Figs. 2 and 3). These observations are consistent with a transition whose character is principally electronic. We have shown on the basis of optical measurements that band overlap may occur in the vicinity of the transition if the gap is indirect.^{3,4} Recent direct measurements of near-infrared reflectivity²³ and evidence for a critical point in the low-temperature phase boundary²⁴ are consistent with this proposal and support assignment of the transition to one associated with band-gap closure.

The evidence for rotational (or librational) excitations that persist above 100 GPa is germane to the problem of predicting accurately the pressure at which band overlap

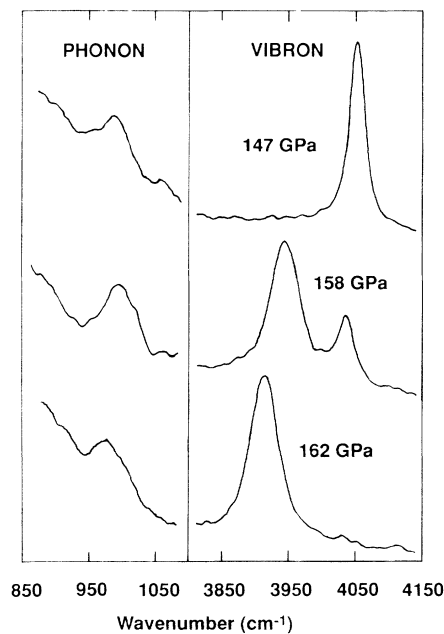


FIG. 3. Optical phonon and vibron spectra through the phase transition at 77 K.

occurs. Anisotropic hexagonal structures, particularly those in which the molecules are aligned parallel to the c axis,¹⁹ provide a condition favorable for band overlap. For example, static lattice calculations for this structure based on the local-density approximation predict the transition at 40 GPa,⁶ whereas in the $Pa3$ structure the transition is delayed to much higher pressures (> 170 GPa).^{5,7} The proper treatment of large-amplitude (e.g., rotational) motion within the hexagonal forms is likely to be crucial for accurate theoretical description of both the insulator-metal transition and properties of the molecular metallic phase.²⁵ These results suggest that rotational ordering may be coupled with metallization. Although our measurements indicate that the rotational envelope initially remains unchanged on passing into the high-pressure phase above 150 GPa (Fig. 1), the relative intensities of the rotational bands vary with increasing temperature. These changes appear to be distinct from the vibron transition, however. Additional temperature-dependent, low-frequency Raman bands (200–600 cm^{-1}) are observed at these pressures, but these features have been identified as new stress-induced transitions in the diamond anvils and should not be mistaken for hydrogen excitations.²⁶ We do observe systematic changes in the intensity of background signal from hydrogen samples above 160 GPa; similar results have been reported previously and attributed to orientational ordering.²¹ The broadness of this signal suggests that it could also arise from scattering by free carriers of hydrogen in the metallic state,^{23,24} although further work is required to confirm this result.

We thank M. Hanfland for help with the experiments,

and R. J. Wijngaarden for useful discussions. This work was supported by the NSF (Grants No. EAR-8720320 and No. DMR-8912226), NASA (Grant No. NAGW-1722), and the Carnegie Institution of Washington.

¹E. Wigner and H. B. Huntington, *J. Chem. Phys.* **3**, 764 (1935).

²R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.* **61**, 857 (1988).

³R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.* **63**, 1393 (1989).

⁴H. K. Mao and R. J. Hemley, *Science* **244**, 1462 (1989).

⁵D. E. Ramaker, L. Kumar, and F. E. Harris, *Phys. Rev. Lett.* **34**, 812 (1975); C. Friedli and N. W. Ashcroft, *Phys. Rev. B* **16**, 662 (1977); B. I. Min, H. J. F. Jansen, and A. J. Freeman, *Phys. Rev. B* **33**, 6383 (1986).

⁶T. W. Barbee, A. Garcia, M. L. Cohen, and J. L. Martins, *Phys. Rev. Lett.* **62**, 1150 (1989).

⁷N. W. Ashcroft, *Phys. Rev. B* **41**, 10963 (1990).

⁸I. F. Silvera, in *Simple Molecular Systems at Very High Densities*, edited by A. Polian, P. Loubeyre, and N. Boccaro (Plenum, New York, 1988), pp. 33-46.

⁹H. K. Mao *et al.*, *Science* **239**, 1131 (1988); V. P. Glazkov *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **47**, 661 (1988) [*JETP Lett.* **47**, 763 (1988)]; R. J. Hemley *et al.*, *Phys. Rev. B* **42**, 6458 (1990).

¹⁰I. F. Silvera and R. J. Wijngaarden, *Phys. Rev. Lett.* **47**, 39 (1981).

¹¹R. J. Wijngaarden, V. V. Goldman, and I. F. Silvera, *Phys. Rev. B* **27**, 5084 (1983); A. Lagendijk, R. J. Wijngaarden, and I. F. Silvera, *Phys. Rev. B* **31**, 1352 (1985).

¹²H. K. Mao, in *Simple Molecular Systems at Very High Densities* (Ref. 8), pp. 221-236.

¹³H. K. Mao, J. Xu, and P. M. Bell, *J. Geophys. Res.* **91**, 4673 (1986); R. J. Hemley *et al.*, *Phys. Rev. B* **39**, 11820

(1989).

¹⁴J. Van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983).

¹⁵M.-M. Thiéry, D. Fabre, M. M. Jean-Louis, H. Vu, and B. Vodar, *C. R. Acad. Sci. Paris* **278B**, 731 (1974).

¹⁶P. J. Berkhout and I. F. Silvera, *J. Low Temp. Phys.* **36**, 231 (1979).

¹⁷S. Raynor, *J. Chem. Phys.* **87**, 2795 (1987).

¹⁸Evidence for other more complex structures is suggested by the possibility of weaker peaks in the measured spectra at high densities (Fig. 1); however, this remains inconclusive with the present signal-to-noise ratio. The possibility of anisotropic structures with molecules in two-dimensional rotational states (planar rotors) is pointed out in Ref. 7.

¹⁹A. A. Abrikosov, *Astron. Zh.* **31**, 112 (1954).

²⁰H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, *Phys. Rev. Lett.* **63**, 2080 (1989).

²¹H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, *Phys. Rev. Lett.* **64**, 1939 (1990).

²²At low densities the concentration of $J=0$ (para) molecules is 50% at 77 K, and increases to $\sim 99\%$ at 5 K. These values are calculated from the low-density properties of the solid, where J is a good quantum number. Above 100 GPa, the single-molecule ortho-para distinction is expected to break down as a result of strong mixing of the zero-order rotational states. The nature and degree of the coupling with nuclear spin states under these conditions needs to be examined theoretically.

²³H. K. Mao, R. J. Hemley, and M. Hanfland, *Phys. Rev. Lett.* **65**, 484 (1990).

²⁴R. J. Hemley and H. K. Mao, *Science* **249**, 391 (1990).

²⁵D. M. Ceperley and B. J. Alder [*Phys. Rev. B* **36**, 2092 (1987)] report such calculations based on quantum Monte Carlo techniques but hexagonal molecular phases were not considered.

²⁶R. J. Hemley and H. K. Mao, *Ann. Report Director Geophys. Lab.* **1989**, 105; (to be published).