Dense molecular hydrogen: Order, disorder, and localization

Russell J. Hemley *, Ho-kwang Mao

Geophysical Laboratory and Center for High-Pressure Research, Carnegie Institution of Washington, 5251 Broad Branch Rd. N.W., Washington, DC 20005-1305, USA

Abstract

Recently discovered high-pressure transitions in hydrogen isotopes (H$_2$, D$_2$ and HD) exhibit phenomena associated with order, disorder, and localization in their vibrational, rotational, and electronic excitations. Rotational disorder persists in hcp phase I to very high pressures, despite the dramatic increase in intermolecular coupling. Symmetry breaking of hcp occurs on passage into phase II with decreasing temperature, where the axis of rotational quantization adopts specific orientations. Above 150 GPa, a radical symmetry breaking occurs, which is characterized by a large increase in infrared vibron intensity, quasiclassical orientational ordering, and loss of even and odd rotational parity. Synchrotron infrared measurements reveal no evidence for intraband electronic excitations down to 0.15 eV in phase III. Metallization in the molecular solid appears to be controlled by the orientational state, and possibly by order–disorder associated with large-amplitude vibrational motion. The $P$–$T$ phase diagram to 200 GPa is surprisingly rich, exhibiting both triple and tricritical points.

1. Introduction

At low pressures and temperatures, hydrogen forms a quantum molecular solid. As such, it is characterized by large zero-point motion, rotational disorder, and the distinguishability of molecules into even and odd parity species (para and ortho states) [1]. With increasing pressure, the interactions between the molecules increase, giving rise to phase transitions that depend on ortho–para state and isotope, as well as pressure and temperature. At higher pressures, we now know that the interactions increase to such an extent that the solid can no longer be considered a system of weakly interacting molecules but instead evolves toward a network solid [2]. Eventually, at sufficiently high pressure, theory predicts that the hydrogen molecules must break down and form a high-density atomic metal, a dense plasma [3]. As a quantum metal, it is predicted that the strong dynamical character associated with the low mass may give rise to very-high-temperature superconductivity and/or cause the materials to remain in a liquid state even to the lowest possible temperatures, forming a quantum fluid ground state.

With the development of the diamond-anvil cell during the past fifteen years, the unusual behavior of hydrogen over a wide range of pressures has been explored in detail under static conditions [2]. Static pressures on hydrogen approaching 300 GPa have been reached, a greater than 12-fold compression relative to the density of the solid at ambient pressure. Moreover, the accuracy, precision, and sensitivity of the measurements have improved markedly. Three molecular phases have been studies in detail
(Fig. 1): phase I is the high-temperature, low-pressure phase; phase II is a low-temperature, high-pressure phase; and phase III is a high-pressure molecular phase existing above 150 GPa. A broad range of physical and chemical properties of hydrogen in these phases have been determined over a wide range of pressures. These may be viewed as a variety of symmetry breaking transitions induced by pressure (and temperature). We briefly review several of these phenomena, focusing on the properties associated with order–disorder of the rotational, vibrational, and electronic degrees of freedom.

2. Rotational disorder in phase I

Vibrational spectroscopy has been used extensively to study the rotational disorder and orientational state in hydrogen as a function of pressure, temperature, and ortho–para state. Rotational Raman spectra to megabar pressures showed that rotational disorder persists throughout the region identified as phase I, that is, to pressures above 150 GPa (higher at higher temperatures) [5]. The presence of rotational disorder is indicated by the persistence of rotational excitations (i.e., $J$ is a good quantum number) over this $P$–$T$ range. This was subsequently confirmed by infrared measurements of the vibron–roton combination bands [6]. The rotational disorder is remarkable, considering the large increase in intermolecular coupling ($\kappa'$) over this pressure range ($6\kappa'$ increasing from 3 to 510 cm$^{-1}$ from zero-pressure to 180 GPa [6]). Notably, the lattice symmetry (of molecular centers) for phase I has been determined by X-ray diffraction first to the 40 GPa range [2,7,8] and more recently to record pressures of 120 GPa (295 K) [9]. One of the key advances in this effort was the growth of 15–30 $\mu$m single crystals of hydrogen and deuterium within a surrounding medium of solid helium to help preserve the integrity of the crystals to very high pressures. The measurements demonstrate that the structure remains hcp throughout the range studied, confirming the Raman and infrared data [5,6].

3. Vibrational localization transitions

With recently improved sensitivity of the Raman technique, we have studied the vibron bands corresponding to the double vibron excitation in a single hydrogen molecule and simultaneous excitation of vibrons on two different molecules. This was done to explore a novel transition in which the double excitation transforms from being localized on a single molecule to being delocalized throughout the crystal to give a bound–unbound transition [10]. We performed detailed Raman scattering measurements on solid deuterium, where the intensity of the bands corresponding to the double excitations were a factor of $10^{-4}$ to $10^{-5}$ times weaker than those of the single excitation vibron bands described above [11]. The increase in intermolecular coupling with pressure causes a shift in the frequency of the sharp localized vibron excitation to reach that of the broad continuum of delocalized states. At this point, the sharp vibron band vanishes. The results of theoretical calculations, which are free of adjustable parameters, agree nearly exactly with the experimentally observed transition.

Localization effects are also observed in the spectrum of the principal vibron, or intramolecular stretching mode, in both hydrogen and deuterium (Fig. 2). Raman spectra of the vibrons in the ortho–para hydrogen samples exhibit localization phenomena and parallel the physics of a random binary alloy [12]. The disorder is associated with vibrational excitations on the $J = 0$ and $J = 1$ molecules. The exper-
pressure are accurately determined, in contrast to the results of coherent potential approximation calculations. All of these calculations are parameter-free, in the sense that the intermolecular vibrational coupling $\varepsilon'$ is determined by independent experiments (e.g., infrared and isotopic Raman studies).

4. Symmetry breaking in phase II

At higher pressure, the increasing crystal field breaks the rotational symmetry of the $J = 0$ solids by mixing higher rotational levels into the ground state [13]. At low temperatures (below 10 K), this quantum ordering transition was reported in o-D$_2$ at 28 GPa [14] and in $p$-H$_2$ at 110 GPa [15]. The high-pressure, low-temperature phase (now called phase II), in ortho–para mixtures has been studied in detail recently by infrared spectroscopy [4,16,17]. The transition in such hydrogen samples occurs at 110 GPa (at 85 K) and is characterized by a new, sharp vibron that appears 45 cm$^{-1}$ below the broader principal vibron which is continuous with that observed in phase I. Notably, the infrared spectra of normal samples of deuterium at the same temperatures and pressures are more complex, with up to four vibrons observed [4]. The additional vibrons indicate that the

Fig. 2. Top: Raman spectrum of solid hydrogen in the region of the intramolecular vibrons as a function of pressure at 77 K [12]. Bottom: (a) The difference in frequency between the $J = 0$ and $J = 1$ peaks as a function of pressure as determined experimentally and determined from supercell calculations with a tight-binding model Hamiltonian. (b) The ratio of integrated intensities as a function of pressure. The results of coherent potential approximation (CPA) calculations are also shown. The parameter $\varepsilon'$ is the intermolecular vibrational coupling.

Fig. 3. Raman vibron spectrum, including the sideband multiplets observed for deuterium in phase II at 36 GPa and 6 K, together with the vibron dispersion calculated for the hcp structure [18]. The sideband features can be understood as arising from zone-boundary modes folded into zone center in a $3 \times 5$ superstructure derived from hcp. The energy scale is normalized to the difference between the band center (near the frequency of the infrared mode) and the bottom of the band (Raman frequency).
ordered phase II has lower symmetry than hcp but alone do not reveal the space group.

The lower pressure portion of the phase diagram of deuterium (both ortho–para mixtures and ortho–rich samples) has been studied in more detail by Raman spectroscopy [18]. We found significant changes in low-frequency rotational excitations as well as a huge increase of intensity of high-frequency vibron sidebands at the transition to phase II. The transition is characterized by the appearance of a new roton and vibron band, changes of their intensities, and narrowing and splitting of the bands, which indicate an increase of molecular ordering. Detailed study of the multiple vibrons and roton reveals that the deuterium has a structure in which the molecules orient themselves in different directions in successive planes of the original hexagonal close packed solid to form an orientational superstructure (Fig. 3). An additional surprise is the existence of an intermediate phase between the high-temperature hexagonal-close packed structure and this orientational superstructure. The intermediate phase may be an orientational glass, similar to that observed at very low temperatures at ambient pressure [19].

5. Phase III: symmetry breaking at 150 GPa

The most striking example of symmetry breaking is the large enhancement of IR vibron absorption in the high-pressure phases above 150 GPa (Fig. 4). The IR vibron suffers a low-temperature discontinuity [16], similar to that observed in the Raman spectrum [21]. The onset of intense IR vibron absorption at 150 GPa seems to parallel the spectral properties of organic charge-transfer salts, including pressure-induced neutral-to-ionic transitions. Recently, the role of intramolecular versus intermolecular charge transfer has been examined [20]. To understand this behavior, we consider the charge redistribution associated with a vibron excitation as a superposition of two effects. The first is a fixed ionic charge, which is the main source of infrared activity of the optical phonons in ionic solids. The application to solid hydrogen has been discussed recently [22,23]. The second is a dynamic charge redistribution, which simply means that upon atomic displacement, the ionicity changes. This effect is usually quantified by the notion of dynamic charge, defined as

\[ Q^* = Q_i + Q_d = dD/du, \]

where \( D \) is the induced dipole moment, \( Q_i \) is ionic charge, and \( u \) is ionic displacement. For a vibron, \( Q_d = R(dQ_i(R)/dR) \), where \( R \) is the H–H bond length. The charge is related to the oscillator strength, \( f \), determined in Ref. [20] as \( Q^* \sim e(Mf)^{1/2} \), where \( e \) is the electron charge, and \( M \) is the reduced mass of the vibrational mode. At the highest pressures of our measurements in phase III (216 GPa), \( Q^* \) reaches a value of 0.04 \( e \) [24]. This represents a significant increase over that found at low pressures. Interestingly, the magnitude of the charge is in the range of that found in some elemental crystals. The results are consistent with the strong interaction between molecules at these pressures. However, the magnitude of the increase rules out the recently proposed hypothesis of a fully ionic state in phase III consisting of \( H^+H^- \) ions [23], where \( Q^* \sim 1 \).
6. Hydrogen deuteride

Under equilibrium conditions, a 50:50 mixture of hydrogen and deuterium will combine to form a solution of 50% HD, and 25% each of H₂ and D₂. Measurements on the mixture afford the opportunity to study an isotopic alloy in which spectroscopic features throughout the exciton band can be observed as a result of the breakdown in selection rules arising from the lack of translational invariance. We wished to examine whether the vibrons in the alloy would undergo a discontinuity or whether the effect of disorder would smear out the transition. It was also of interest to determine whether the intensity change would occur in all three vibron components [4]. Indeed, a discontinuity is observed in all three vibrons together with an intensity increase. Although the change occurs at approximately the same pressure, the change is first noticeable in the H₂ molecule, followed by HD and then D₂. This follows the order of the transition pressures for the pure samples (i.e., \( P_n(H_2) < P_n(D_2) \)). We also note that the structure of the bands differ from one another and from that observed for the pure samples as a result of the disorder. For example, the H₂ peak can be resolved into a doublet, and there is a broad component on the high frequency side of the sharper D₂ vibron. The absorption associated with the weak permanent dipole moment [25] is negligible in comparison to the strong intensity observed in phase III (for all three species).

7. Critical versus tricritical points

The vibron discontinuity associated with the transition to phase III disappears above a critical or tricritical point [26,27]. The existence of such an invariant point on I–III phase boundary places a strong constraint on possible types of transformations by ruling out transitions involving reconstruction of the crystal lattice. A critical point implies that phase III can be derived from phase I through both continuous and discontinuous routes. There is an isotope effect on the phase III transition pressure (\( \sim 10 \) GPa lower in hydrogen relative to deuterium), which provides additional constraints on the nature of the transition and possible evidence for new phenomena. As described above, three univariant phase boundaries (I–II, II–III, and I–III) meet at an invariant triple point above which the I–III transition is discontinuous but the discontinuity diminishes with increasing temperature. Cui et al. [28] reported a similar phase diagram for deuterium but failed to detect a discontinuity in either Raman or IR vibron at I–III transition. Consequently, they proposed that previous reports of evidence for a critical point in hydrogen are actually that of a triple point. Moreover, the II–III boundary of deuterium reported by Cui et al. [28] was \( \sim 10 \) GPa lower than that previously reported for deuterium but identical to that of hydrogen, implying zero isotope effect.

Recent studies of both hydrogen and deuterium have clarified this issue. In fact, a surprisingly rich phase diagram at higher pressures is revealed [29]. Both isotopes undergo a major change at the transition to phase III [16]. The measurements show that the lower pressure phase line in hydrogen intersects the 150 GPa phase line in a triple point at 114 K and \( \sim 160 \) GPa [4]. More detailed measurements have been performed for deuterium (Fig. 5) [29]. A well-defined Raman vibron discontinuity is observed across the I–III phase line above the I–II–III triple point at 167 GPa and 130 K. Evidence for additional invariant points is found, including one at 182(\( \pm 3 \)) GPa and 235(\( \pm 15 \)) K where the discontinuity disap-
pears. As pointed out above, there is also evidence at lower pressures for an intermediate glassy phase between the I–II transition in ortho–para mixtures (where ortho–para states are distinguishable) [18].

8. Broad band absorption

Shortly after the discovery of phase III [21], theoretical calculations suggested that the new phase could be metallic [30]. Indeed, a large number of subsequent calculations predicted significant changes in electronic properties at these pressures, and one of the major theoretical problems was how to preserve the band gap at these pressures [31–33]. The measured features observed at the 150 GPa transition indicated that the transition involved orientational and structural changes. In addition, the sample remained transparent in the high-pressure phase to at least 250 GPa [34]. To test the theoretical prediction of metallization, optical experiments were designed and conducted. Eggert et al. [35] measured the index of refraction to 70 GPa and on the basis of an extrapolation of a single-oscillator model for the index predicted band-overlap metallization at 148 GPa from an apparent dielectric catastrophe 1. Direct measurements of the index of refraction at these pressures revealed no dielectric catastrophe [37]. Moreover, it was shown that closure of the indirect gap predicted by theory should not give rise to such a change in the visible, and that any such changes are associated with the pressure variation in the direct gap, which should not be visible until pressures of 300 GPa or above are reached, consistent with previous direct observations [34]. Reflectivity and absorption measurements carried out to 0.5 eV showed a systematic and reproducible increase at the low energy limit of the spectrum [38,39]. Several hypotheses were proposed to explain the observations. These included Drude absorption (due to indirect gap closure), vibron excitation, electronic interband transition [39]. In addition, it was pointed out that sample texture due to the anisotropy of the material, thin film effects, and diffraction could be important.

Recently, we have extended the infrared measurements to significantly lower energies [40]. A representative spectrum of deuterium in phase III at 170 GPa and 83 K is shown in Fig. 6. The strong vibron of phase III is readily observed. Measurements down to 0.15 eV extend the energy range compared to previous measurements by over a factor of two [17,39]. Measurements at longer wavelengths are complicated by diffraction effects. A small increase at the lowest energies is suggestive but most likely is associated with decreasing signal to noise and/or diffraction effects. Fig. 6 also shows Drude model curves for phase III deuterium taken from the recent paper of Cui et al. [17], which were consistent with measurements reported in that study (to 0.35 eV).

We find that none of these models are consistent with the present direct measurements. The strong transmission observed to 0.15 eV puts a strong bound on possible carrier density in phase III; specifically, if the phase is metallic at this pressure, the plasma frequency \( \omega_p \) is less than 0.3 eV. Theory predicts

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1. The pressure extrapolation was revised in an addendum [36] where theoretical calculations together with refractive index data were used to argue that phase III is metallic.
closure of the band gap at these pressures, but this is strongly dependent on the orientational state of the molecules. Moreover, it has also suggested that there is localization of electrons due to persistent rotational disorder [3]. In view of the evidence for orientational ordering in phase III [2,29], the controlling factor may in fact be large amplitude vibrational motion. It has been suggested that localization may arise from differences in ortho–para state [17]. However, there is no evidence for the distinguishability of single molecule ortho–para states at these pressures. Moreover, there is strong evidence that the even and odd $J$ states are mixed in phase III, a phase with characteristics of a classical orientationally ordered material [29,41].

9. Conclusions

There is evidence for new phenomena associated with order, disorder, and localization in the rotational, vibrational, and electronic states in hydrogen over a range of densities. Rotational motion persists in hcp phase I, despite a dramatic increase in intermolecular coupling with pressure [2]. This rise in intermolecular coupling provides the basis for understanding localization transitions associated with the vibron excitations, including the pressure-tuned bivibron bound–unbound transition [11] and the unusual variation in $J = 0$ and $J = 1$ vibron peaks with pressure [12]. There are fundamental differences in the symmetry breaking associated with the transitions to phase II and to phase III. The transition to phase II has a quantum mechanical origin, with the axis of rotational quantization adopting specific orientations and even and odd $J$ states mixing in separate manifolds [18]. In all three isotopic species above 150 GPa, a radical symmetry breaking occurs that is characterized by a large increase in infrared vibron intensity and orientational ordering similar to that documented in classical systems (although zero-point motion is still likely to be significant). The stronger interactions in phase III associated with charge transfer [20] cause a mixing of even and odd $J$ states [41,42] and hence a breakdown of the ortho–para distinctions that exist at lower pressures. The phase diagram for both $H_2$ and $D_2$ to 200 GPa and temperature is surprisingly rich, exhibiting both triple and tricritical points. Detailed synchrotron infrared absorption measurements carried out for $D_2$ in phase III to 170 GPa reveal no evidence for intraband electronic excitations down to 0.15 eV [40], which rules out recent Drude models fit to higher energy data. Theoretical calculations indicate that metallization at these pressures may be suppressed by the effect of disorder or by the formation of excitonic states [3], a proposal that requires further experimental study.

Acknowledgements

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