DENSE HYDROGEN IN THE OUTER SOLAR SYSTEM: IMPLICATIONS FROM RECENT HIGH-PRESSURE EXPERIMENTS

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ABSTRACT

Recent high-pressure experiments on hydrogen and related low-Z materials from ~1 GPa to 300 GPa have uncovered a range of phenomena relevant to understanding the interiors of the outer planets and their satellites. The new results in the lower pressure range (<50 GPa) include the observation of new compounds (clathrates and van der Waals compounds), accurate determination of equations of state, and direct measurements of sound velocities. A key result at the highest pressures is evidence for stability of the molecular bond to ~250 GPa (at 77 K). However, the bond begins to weaken well below this pressure, and this weakening could be enhanced with increasing temperature. Experimental data also indicate a significant increase in absorption in the near infrared above 150 GPa and in the visible-near ultraviolet above 250 GPa.

INTRODUCTION

Hydrogen is the most abundant material in the solar system. As a result, the chemistry and physics of this material is crucial for numerous problems in planetary science, particularly for the outer solar system. There has been rapid growth in understanding the behavior of hydrogen and related low-Z materials at low density in the outer planets and their satellites from observational data[1]. However, there has been little direct information on the behavior at high densities, for example in deep interior conditions. For many years, the chemistry of hydrogen-rich bodies of the solar system was the subject of speculation based on extrapolations from low-pressure experiments or theoretical calculations[2].

This has changed as a result of recent breakthroughs in high-pressure experimentation, primarily static compression techniques[3]. At lower pressures (<50 GPa), for example, the equation of state of the solid (cold compression isotherms) has been accurately determined by diffraction techniques. Sound velocities have also been measured over this pressure range. Finally, an entirely new chemistry of hydrogen and other materials has been uncovered. At higher pressures — well into the megabar range (>100 GPa) — spectroscopic studies have been carried out to characterize the state of bonding of hydrogen, identify phase transitions, determine the subsolidus phase diagram, characterize optical properties (visible and infrared) and elucidate electronic properties of the material. Such conditions

correspond to densities approaching 1 g/cm^3 (at > 200 GPa). By comparison, the mean density of Jupiter and Saturn are 1.2 and 0.6 g/cm^3, respectively. At the highest pressures (250–300 GPa), such spectroscopic studies have put key bounds on the range of stability of the molecular bond (H_2). The astrophysical implications of some of these results have recently been reviewed[4].

EQUATION OF STATE

The low temperature (e.g., room-temperature) isotherm is crucial for planetary modeling because it provides an important reference for higher temperature equation of state determinations, including the density change along planetary adiabats[2]. Early work relied on interpolation between low-pressure static compression data (<2.5 GPa) and quantum statistical (Thomas-Fermi-Dirac) calculations at very high pressures (> 1 TPa). This intermediate pressure-density region includes much of the molecular envelopes of the outer planets. A number of interior models for the giant planets have been constructed[5–7]. Uncertainty in the equation of state of dense molecular hydrogen is one of the principal factors limiting their accuracy. Recently, it has been shown that through diffraction techniques, accurate equation of state data can be obtained for H_2 to very high compression at room temperature[8]. Recent x-ray diffraction results are shown in Fig. 1[9].

Fig. 1. Equation of state data for H_2 and D_2. Comparisons with potential models are made for 293 K isotherm data from x-ray diffraction (circles), shock compression data (triangles) for both deuterium (inset) and hydrogen, and a Jovian adiabat[7,17]. The long dashed line shows the 293 K isotherm determined independently from Brillouin scattering data[18].
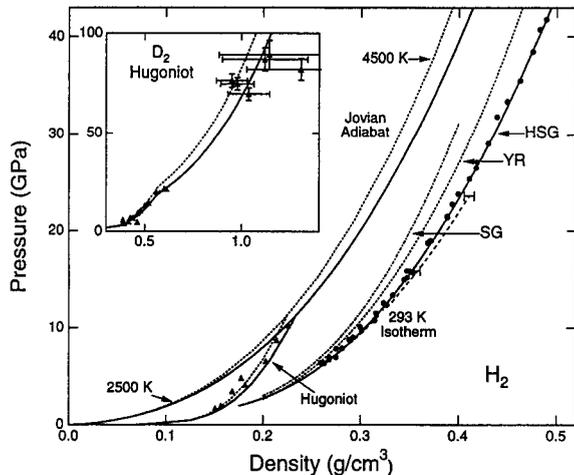
Due to their high temperatures, the interiors of the giant planets are in a fluid state. The application of shock-wave methods to hydrogen produce very high temperatures along the Hugoniot, as a result of the high compressibility of the material (Fig. 1), and thus probe the equation of state of the fluid[10] (although the temperatures along the Hugoniot do not follow planetary adiabats). Hence both static and dynamic experimental results require extrapolation for determining the

pressure-density relations under conditions appropriate to planetary interiors. For simplicity in treatment of thermal properties, these calculations are typically based on effective pair potentials. The results of calculations using a series of different pair potential models are summarized in Fig. 1. The pair potential models are based on fits to lower pressure data. Hence, the measured densities are greater than predicted from the extrapolation of lower pressure data (which is also true for other phenomenological equation-of-state models[3]).

SOUND VELOCITY

Seismic observations of the giant planets offer the promise of radically improving our understanding of the interior structure of these bodies, much as helioseismology has opened a new window into the solar interior. Significant theoretical progress in understanding Jovian oscillations has been reported[11]. Observational programs based on impact sources[12] and ring perturbations[13] have been discussed, and in the case of the former, carried out during the impacts of Shoemaker-Levy 9 into Jupiter in July, 1994. Other ground-based searches for low-degree global oscillations have been conducted[14,15] and the first successful observations reported[15]. The observations are intriguing because the observed fundamental frequency differs strongly from that predicted from current interior models[5-7]. Direct measurement of sound velocities in planetary materials at elevated pressure are needed to better understand the seismic response of Jupiter and other gaseous planets.

During the past several years, we have developed techniques for measuring sound velocity in planetary materials, including single crystals, polycrystals, and fluids, to very high pressures. This represents an extension over our previous methods[16] in the following way: (1) single crystals grown and full anisotropy of the sound velocities determined; (2) technique combined with single-crystal synchrotron x-ray diffraction to determine the orientation of the single crystal; (3) higher sensitivity in the measurement (6-pass tandem Fabry-Perot spectrometer); (4) improved diamond anvil cells to access wider $P - T$ range. In recent work, the new technique has been applied to determine the compressional and shear wave velocities of single-crystal hydrogen to 24 GPa at room temperature[17,18]. From such measurements, the single-crystal elastic moduli were determined[18]. Together with Debye theory, the thermodynamic properties of H_2 — including the Grüneisen constant — were calculated.

Figure 2 shows the hydrodynamic or bulk sound velocities for a polycrystalline aggregate obtained from the measurements by averaging over the elastic constants[17]. We also compare the results of thermodynamic perturbation calculations for the fluid phase using several effective pair potentials. As found from x-ray diffraction work, there is a need for softening the equation of state at higher pressures relative to that predicted from pair potentials fit to lower pressure data. The improved potential (HSG) was used to calculate the fundamental oscillation frequency of Jupiter under a wide range of conditions The frequency of the fundamental mode is given by $v_0 = [\int_0^R dr/v(r)]^{-1}$, where R is the radius of the planet

and v(r) is the sound speed. The analysis indicates that the reported frequency is inconsistent with that expected given our current knowledge of the physical properties of the constituents of Jupiter, assuming existing compositional models[17]. Hence, either there is a need for a significant revision of current interior models or the reported observations are incorrect. This is also in agreement with recent analysis based on shock-wave measurements for pure hydrogen[19].

Fig. 2. Sound velocity of hydrogen as a function of pressure. The filled symbols are experimental data[17]. Lines show potential model calculations as in Fig. 1. The vertical line shows the 293 K fluid-solid phase boundary for H_2. The inset shows experimental fluid phase data for hydrogen (solid symbols and full line) and helium (full line). Open symbols are for a equimolar mixture of hydrogen and helium, and the dashed line shows the calculated sound velocities in the mixture[17].
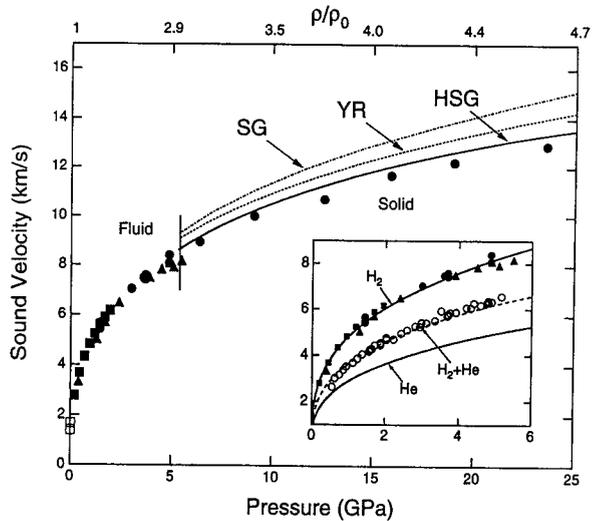
VIBRATIONAL SPECTROSCOPY

A major outstanding problem in planetary science is the pressure of the theoretically predicted molecular dissociation transition in hydrogen. The classic question considered here concerns the transition in the low temperature limit (i.e, to the Wigner-Huntington monatomic state[20]), first predicted to be as low as 25 GPa. Raman, and infrared spectroscopy have provided crucial experimental constraints on the transition. The Raman measurements indicate that the molecular bond is stable to at least ∼250 GPa (at liquid nitrogen temperatures and below)[21,22]. The measurements reveal that the frequency of the intramolecular vibration observed in both Raman scattering and infrared absorption decreases with increasing pressure, indicating that the molecular bond is becoming destabilized with increasing density. The critical pressure at which the frequency decrease is observed differs in Raman and infrared as a result of intramolecular vibrational coupling, which increases dramatically with pressure (Fig. 3)[3,23]. Thus, the results indicate that in addition there is increase in intramolecular interactions such as

charge transfer. Measurements conducted to date above 250-300 GPa by Raman scattering have failed to observe the signature of the molecular bond. The loss of the Raman signal suggests dissociation, but this remains speculative because of technical difficulties associated with the Raman measurement.

Moreover, Raman and infrared vibrational spectroscopic measurements reveal a rich phase diagram for the solid at megabar pressures. These measurements involve principally the observation of discontinuities in the vibrational frequency across phase transitions. A generalized phase diagram for deuterium, showing $P - T - v$ along with proposed invariant points p_i in the system, is presented in Fig. 4. Three phases persist to megabar pressures (> 100 GPa)[3]: phase I, the rotationally disordered lower pressure phase with the hcp structure; phase II, the low-temperature intermediate phase, and phase III, which is stable above 150 GPa. The latter is characterized by a large discontinuity in the Raman and IR vibrons[21,24,25], a dramatic increase of the infrared vibron oscillator strength[25,26], and sharp decrease of the vibron discontinuity at a possible invariant point p_2[27,28]. In studies over a narrow temperature range, the I-II phase line has been extended to megabar pressures and found to intersect the phase III boundary at a triple point p_1[3,27−29]. Although these results pertain directly to the solid in a lower temperature domain, the results are important for planetary applications because they show the properties of the material at such pressures (100-300 GPa) differ markedly from those at lower pressures.
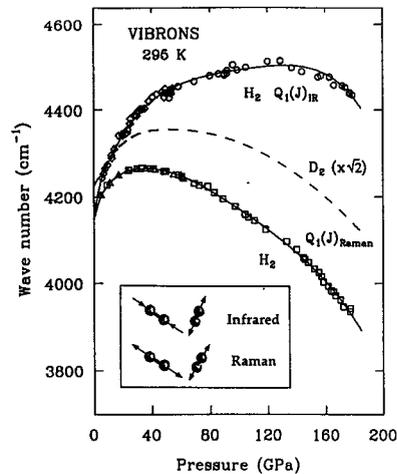
Fig. 3. Pressure dependence of the Raman and infrared intramolecular modes (vibrons) in solid hydrogen at room temperature.

OPTICAL PROPERTIES

Recently it has been proposed that radiative layers may exist near the surfaces of Jupiter, Saturn, and Uranus at temperatures of $\sim$2000 K[30]. If true, the interiors of these bodies would not be fully convective and their interior structure may be quite different from what is generally assumed. For example, interior

temperatures would be significantly lower than predicted by completely convective models[31], although the effect is not likely to resolve discrepances in seismic observations[17]. Among the significant uncertainties in determining the opacity of the giant planets is the effect of pressure on the collision-induced absorption in the H_2-He system[30]. Determination of infrared absorption is therefore crucial for models of radiative heat transfer and optical opacity as a function of depth within the planets. In the isolated molecule, the internal stretching mode is dipole-forbidden but becomes weakly allowed by collision-induced processes, an effect which increases with increasing density[32]. Similar induced processes occur in the dense solid, but with the added constraint imposed by crystalline symmetry. Mid- to near-infrared absorption measurements have been conducted as a function of pressure. The first set of measurements to very high pressure was a study to 54 GPa at room temperature using diamond-cell techniques and a conventional Fourier-Transform spectrometer[33]. This study included measurements in the fluid state (i.e., to 5.4 GPa). More recently, the development of high-pressure synchrotron infrared spectroscopy has permitted such measurements to be extended to above 200 GPa[23,25].

Fig. 4. Generalized phase diagram for deuterium in the megabar pressure range based on Raman scattering measurements.
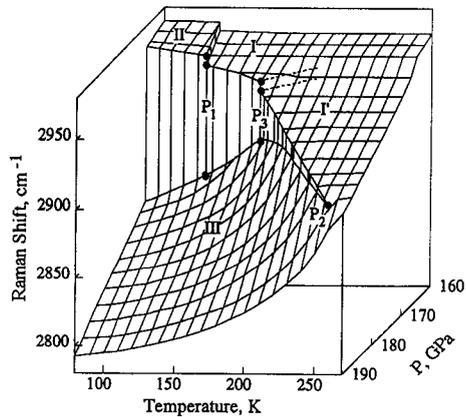
Measurements have been conducted as a function of temperature between 77 and 300 K over this pressure range. In the fluid and solid phase (phase I) the intensity in the region of the H-H stretching fundamental (vibron) increases with increasing density ρ as ρ^2, or as $1/r^6$ where r is the average intermolecular separation. This is a larger increase than is found in lower pressure calculations of collision-induced absorption, which is based on low density gas-phase data[32]. Moreover, recent experiments reveal a marked increase in absorption in the high-pressure solid phase (phase III), which is stable above 150 GPa[25], as discussed above. The pressure or density dependence of the band gap of hydrogen is the central question associated with the electronic properties of the material in the molecular state[3]. There is now strong experimental evidence for a decrease in the band gap of hydrogen under pressure. Measurements of the dispersion of the refractive

index at lower pressures can be used to determine an effective oscillator frequency which tracks the band edge (see, Ref. 3). These measurements (for the solid) are in excellent agreement with shock-wave electrical conductivity measurements as well as theoretical calculations (beyond the local density approximation)[3,34,35]. In addition, there is evidence for direct observation of absorption at visible wavelengths at the highest pressures reached in static experiments on hydrogen ($\sim$300 GPa)[22].

HYDROGEN CHEMISTRY

The gaseous planets are multicomponent systems, and it is generally assumed that these systems can be modeled using only end-member properties. This assumption has not been tested under conditions relevant to the interiors of these bodies, and the properties of mixtures of planetary materials are just beginning to be studied. One of the most exciting results of this field is the discovery of new high-pressure compounds involving hydrogen and other low-Z elements or simple molecular materials, in particular in the C-H-O-N system. Thus, there is a strong indication of compound formation in the cooler regions of the large planets and surfaces of the satellites. Although the deeper interiors of the Jovian planets are thought to consist primarily of fluids due to the high temperatures that prevail, the chemical interactions which drive compound formation should influence phenomena in this higher temperature regime as well (e.g., fluid-fluid separation). The properties of mixtures of He, H_2O, NH_3, CH_4, and H_2 are of critical importance for progress on a variety of issues relating to planetary interiors[36]. In particular, recent studies of Saturn's moon Titan suggest that its interior may contain complex mixtures of methane, ammonia, and water, including a possible methane clathrate hydrate[37].

In the small number of mixtures studied to date, compound formation has been the rule rather than the exception. The behavior was first observed in the N_2-He system, where evidence for $He(N_2)_{11}$ was found[38]. For hydrogen mixtures, one of the most interesting studied has been the H_2-H_2O system, where two new clathrates have been discovered (Fig. 5)[39,40]. The higher pressure one is stable to at least 60 GPa. Studies of the Ar-H_2 system reveal evidence for $Ar(H_2)_2$; spectroscopic studies suggest unusual optical and electronic behavior above 170 GPa[41]. More recent work has revealed evidence for new compounds in the H_2-CH_4[42] and H_2-O_2[43] systems. A particularly important system is H_2-He. No compound formation has yet been documented in this system[44]; moreover, recent work indicates no measurable solubility of He in H_2 above 100 GPa ($<$300 K)[45]. Compound formation has also been observed in related low-Z systems[46,47].

The reactivity of hydrogen with other materials such as silicates, oxides, and metals at very high pressure is important for constraining the amount of hydrogen in planetary cores and rocky layers. The structure, stability, and physical properties of high-pressure hydrous silicates and oxides, and their relevance to terrestrial planetary interiors, are examined elsewhere in this volume. Here, we note that

recent work has documented the formation and stability of metal hydrides to very high pressures. In particular, Fe-H has been shown to be stable to pressures approaching the megabar range (at room temperature)[48]. Moreover, there is strong evidence that hydrogen reacts and forms stable dense hydrides with nominally inert metals such as rhenium at high pressures (e.g., > 10 GPa)[49]. Such work suggests that hydrogen could exist in substantial quantities in planetary cores, and that hydrides could have formed in the early stages of planetary evolution. The presence of hydrogen (as well as other light elements) significantly depresses melting relations (e.g., Ref. 50) and this could have a profound effect on the thermal state of planetary interiors.

Fig. 5. Crystal structure of the high-pressure H_2-H_2O clathrate (idealized proton-ordered form)[39].
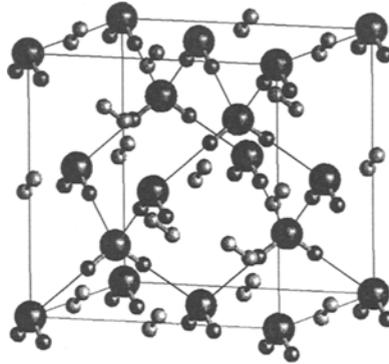
HIGHER $P - T$ BEHAVIOR

Most static compression studies of planetary materials have been performed at lower temperatures (≤ 300 K) than those relevant for planetary interiors. One question therefore is what is the temperature effect on phase transitions in hydrogen? For example, the I-III phase boundary has a positive slope, but has not been explored above room temperature[27]. There is also the question of metallization in the molecular phase associated with band-overlap (in a band picture) or the convergence of a mobility edges (in a disordered system having no well defined bands). This will lead to metallic conductivity in the molecular state in the limit of $T \to 0$ K. Both of these are in general consistent with the decrease in band gap obtained from recent experiments. Thermal excitation of electrons at temperatures that prevail within the molecular layer of the large planets is expected to give rise to a conducting fluid prior to both formal gap closure and dissociation. The new data on mixtures leads to the possibility that impurity ionization could also play an important role; i.e., pressure- and temperature-induced ionization of soluble components (such as H_2O, NH_3, and O_2) could contribute conducting electrons from impurity bands into the gap prior to gap closure.

The thermal effects on the Wigner-Huntington transition require examination. In particular, recent theoretical work predicts the existence of a plasma

phase transition[51]. Hence, experimental checks on this transition, and establishing its possible connection, in both a thermodynamic and structural sense, to the low-temperature Wigner-Huntington transition remain to be explored. Thermally induced dissociation, and concomitant density increase, at high $P - T$ conditions was suggested several years ago[52] on the basis of the decrease in the intramolecular stretching frequency with pressure documented for hydrogen and by analogy to proposed behavior of shocked nitrogen[53]. This would further enhance the electrical conductivity at shallower depths. Interestingly, recent high-temperature quantum simulations predict rapid exchange of atoms between molecules in the fluid state at pressures below those at which the molecules fully dissociate (150 GPa)[54]. Recent measurements and analyses of shock-temperatures have been interpreted in terms of a continuous dissociation transition in the high-density fluid state[19]. This conclusion is based on the low temperatures measured relative to those predicted from effective pair potential calculations. Such a conclusion is complicated, however, by uncertainties associated with fitting pair potentials appropriate to the high-density fluid state; recent work has shown that pair potentials that most accurately describe the x-ray and sound velocity measurements for the solid also predict lower shock temperatures along the Hugoniot (i.e., without invoking dissociation)[17]. Nevertheless, such a continuous increase in conductivity with depth cannot be ruled out, and needs to be examined within current interior models (i.e., influence on magnetic fields).

CONCLUSIONS

The results of recent static high-pressure experiments thus provide a growing experimental database for understanding the composition, chemistry, global processes, and evolution of the outer planets and their satellites. The dominant themes emerging from this work are the new phenomena in hydrogen ranging from lower pressure phenomena from pressures of < 1 GPa to the 300 GPa range. As a result, a great deal of new information has been obtained which is relevant to planetary surfaces and atmospheres, including the observation of new compounds (clathrates and van der Waals compounds), highly accurate determination of equations of state, and direct measurements on sound velocities under pressure. However, a complete microscopic description based on accurate many-body potentials and applicable over a wide $P - T$ range is not yet in hand. The challenge for future work will be the direct determination of physical and chemical properties of hydrogen and related systems at combined high $P - T$ conditions.

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