Probing hydrogen-rich molecular systems at high pressures and temperatures

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Information on the behavior of hydrogen-containing simple molecular systems at high pressures and temperatures is central to many problems in chemistry and allied sciences. The combination of increasing pressure and temperature causes a redistribution of the electronic density, and the resulting alterations in interatomic interactions give rise to changes in macroscopic properties. Experimental studies of hydrogen-rich systems under extreme conditions have advanced considerably in recent years as a result of improvements in diamond anvil cell technology in combination with resistive- and laser-heating techniques. These experimental methods are combined with spectroscopic and diffraction techniques, and the results interpreted with the aid of molecular simulations. In this *tutorial review* we discuss recent findings in hydrogen, water, and other selected hydrogen-rich systems including compounds formed from these materials. The results are examined in terms of the evolution of effective potentials and interatomic vibrational coupling, molecular dissociation and recombination, ionization and polymerization, quantum effects, and order-disorder phenomena.

I. Introduction

The atoms in simple molecular materials are strongly bonded by covalent intramolecular interactions. By definition, these are much stronger than intermolecular interactions, which usually refer to van der Waals or hydrogen bonds of hydrogen-containing materials. The closer association of the molecules that accompanies compression in general enhances intermolecular interactions. Under moderate compression, the molecules preserve their identity and materials can undergo a sequence of the phase transformations driven by various types of anisotropic forces, electronic charge redistribution from the increasing overlap of the molecular charge density, charge transfer, as well as changes in magnetic and nuclear spin-dependent interactions. These changes are often described in terms of an effective intermolecular potential, which can be a function of the physical state of the material as well. This

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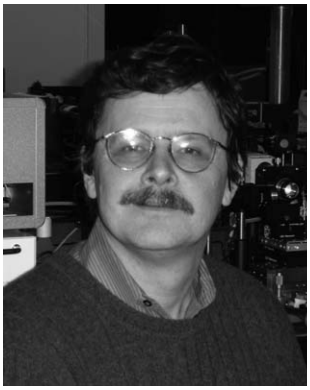

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effective potential in fact is a representation of the true many body potential that reflects the complete energy landscape of the system. At higher compressions, there can be substantial modification of the molecules themselves. Indeed, an ensemble of molecules subjected to sufficiently high pressure ultimately undergoes molecular dissociation and transformation to a non-molecular state.

Elucidating the nature of these transformations and their underlying energetics is central to chemistry and physics.[1] Until recently, detailed experimental studies of such phenomena have been restricted primarily to compression alone, *i.e.*, pressure-induced transformations at modest temperatures (*e.g.*, <300 K). On the other hand, temperature can have major and sometimes unexpected effects in molecular systems at high compressions. Here we review recent developments in the study of hydrogen-containing simple molecular materials under extreme conditions of both pressure and temperature. These systems are of fundamental interest because of their putatively simple electronic structures, low mass, and very high compressibility, which means that over an order of magnitude of densities in condensed phases can be explored. As hydrogen is the most abundant element in the cosmos, studies of such hydrogen-containing molecular systems under extreme conditions are also critically important for planetary science and astrophysics. These investigations also have implications for a broad range of problems in materials science, including hydrogen storage, new high energy density materials and the characterization of metallic hydrogen. Such systems have been difficult to study experimentally under static high *P–T* conditions and for many years have been the domain of dynamic (*e.g.*, shock-wave) techniques. However, improvements in both the ability to contain such materials and to probe their high *P–T* behavior under static conditions (Fig. 1) has provided new insights that extend and complement inferences made from transient, dynamic compression experiments. We provide examples of high *P–T* behavior in hydrogen, water, their mixtures, and other hydrogen-rich systems, focusing on how changes in intermolecular interactions give rise to changes in thermodynamic properties (*e.g.*, melting), chemical reactions, and transport properties.

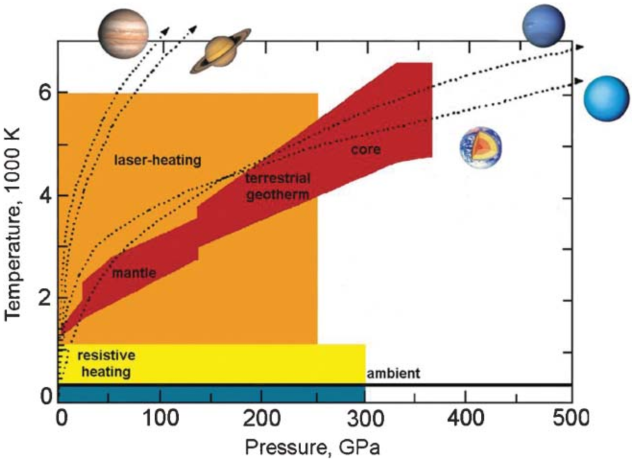

Fig. 1 *P–T* range of static compression techniques along with estimated conditions as a function of depth in various planets.

II. Experimental considerations

As a result of developments in diamond anvil cell techniques, it has become feasible to access an expanding *P–T* range under static conditions (Fig. 1). Several important improvements in this class of devices have enabled the study of molecular systems under extreme conditions. This includes more robust design of the diamond anvil cell that permits a large angular acceptance (*e.g.*, holding diamonds using conical surfaces from the sides, leaving the anvil table free for optical access); the use of diode-pumped solid state lasers, which provide more temporally and spatially stable beam for the laser heating; and the use of more sophisticated methods of sample loading for laser heating (see below).

Subjecting materials to high pressure and temperature can greatly enhance their reactivity with the gasket materials and the diamond itself. This problem substantially inhibited the studies of hydrogen, various simple acids, and alkali metals. The solution to these problems lies in finding a correct combination of the materials used for the gasket, laser coupler, pressure gauges, and thermal insulation (see below). Use of liners such as gold[2] and cubic boron nitride (c-BN)[3] has made it possible to contain chemically reactive hydrogen-containing materials. This problem is closely related to the pressure measurements in the diamond anvil cell.

Many of the materials that are typically used as the optical pressure sensors at high temperature (*e.g.*, strontium tetraborate[4]) are not stable in corrosive environments such as acids or water. Their use under such conditions can be arranged by making a second very small cavity for the sensors only.[4] Unfortunately, this method increases the uncertainty in the determination of pressure at high temperature since pressures in both cavities may differ, while making very thin walls between cavities is challenging. Another problem with fluorescence gauges such as ruby, Sm:YAG and $SrBO_4$ is a substantial decrease of the signal (and its broadening) with temperature, so none of these materials can be used above 1000 K. Use of chemically stable Raman gauges (*e.g.*, c-BN) provides an alternative.[5] In any case, pressure sensors at high temperatures need to be calibrated by cross-checking with other known gauges, since the use of ambient pressure temperature dependences of the property used for calibration at high pressures may not be sufficiently accurate (see Ref. 6).

Uniform heating of molecular materials in diamond cells at very high temperatures has been a challenging task. Externally heated cells restrict the accessible temperature range to approximately <1000 K. Also, the chemical reactivity and pressure calibration problems discussed above are more severe with external heating in comparison to laser heating. Conversely, the drawback of laser heated cells is the very large temperature gradients and the necessity to use metallic couplers placed in the sample cavity, making the requirements of measuring techniques much more stringent as compared to measurements made at ambient conditions.

Successful configurations of the sample chamber employ noble metal laser couplers, with a central hole of ~10 μm diameter, placed in the gasket cavity.[7] Fig. 2 shows a sample configuration with a 40 × 40 × 10 μm^3 Ir plate. This hole forms a sample cavity that ensures radially symmetric heating

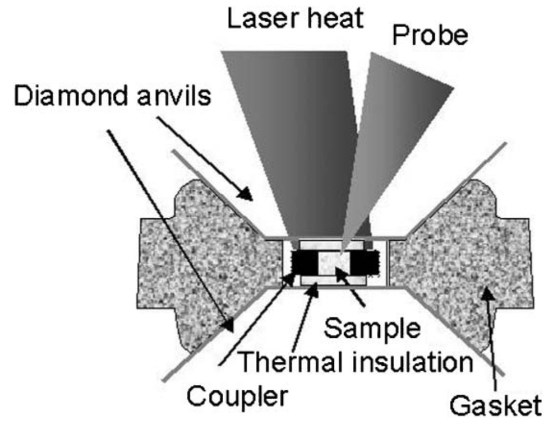

Fig. 2 Sample configuration in a laser heated diamond anvil cell for studying molecular systems at high pressures and temperatures.

and allows probing the entire sample in the axial direction to increase the signal. In order to further reduce thermal gradients, the sample can be thermally insulated from the diamond anvils by introducing thin plates made of appropriate material (*e.g.*, alumina) of ~5 μm thickness. This sample arrangement has proven to work for *in situ* studies by Raman spectroscopy and X-ray diffraction up to 3000 K (*e.g.*, Ref. 5). Temperature determination still remains a problem since there is a large gradient from the surface of the coupler (which is being effectively heated) and the central part of the sample, while the whole sample area is normally probed. The radiation emitted by the coupler is analyzed radiometrically to give the sample temperature; in general this measurement gives an upper bound. Measurements of the Stokes and anti-Stokes vibrational excitations by Raman scattering[7,8] provide an independent determination of the sample temperature; however, this measurement can underestimate temperature when there are large temperature gradients across the sample, since the cooler part of the sample makes a negligible contribution to the anti-Stokes signal. When the solid sample is imbedded in the coupler or when the coupler itself is examined, the two methods give consistent results.

When the sample is laser heated, its pressure in general changes. Part of this change is due to the stress relaxation of the sample and the pressure medium. This contribution can be minimized by performing a preheating that releases stresses; the subsequent heating circles are usually reproducible and can be used for measurements. There can be an additional pressure drift (often reproducible) due to relaxation of the diamond cell. These changes can be difficult to eliminate and/or calculate because they depend on the properties of the sample, pressure medium, and apparatus; thus, ideally the pressure at high temperature must be measured *in situ*. The choice of pressure sensors under these conditions and the reliability of their calibration are crucial for quantitative measurements.

III. High *P*–*T* hydrogen

Understanding the stable configuration of an ensemble of electrons and protons at a given pressure and temperature is central to our understanding of matter. Under conditions that are most familiar, this collection of particles forms a gas of hydrogen molecules. Indeed, the covalent bond of H_2, with its bond-length of 0.74 A, bond strength of 4.5 eV, and 14 bound states has been the test-bed of chemical theory since the advent of modern quantum mechanics (Fig. 3).[9–11]

The effect of pressure is ultimately to destabilize molecular bonding and to drive the system to a state with itinerate electrons (*i.e.*, metallic). This change, or sequence of changes, occurs because the system has lower free energy in denser structures. This energy change arises from the reduction in kinetic energy of electrons that move from being localized in bonds to itinerate in the denser phase. Hydrogen in an electrically conducting state exists in nature in the form of a *fluid* in the interiors of giant planets such as Jupiter, but it has not yet been created and characterized in static compression experiments in the laboratory. Moreover, the dense metallic (*e.g.*, atomic) *solid* phase has yet to be found experimentally. Consequently, a number of important questions remain to be answered. These include the nature of the metallic state (molecular or nonmolecular), the phase of the metal (solid or fluid), the existence of a maximum in the melting curve of the molecular solid, and the electronic properties of the fluid near the conjectured melting maximum (nonmetal or metal).

The state and stability of molecules are readily probed by vibrational spectroscopy. The vibrational properties of hydrogen and its heavy isotope, deuterium depend critically on the rotational quantum number of the molecule determined by the rotational quantum number *J*. The latter in turn is coupled to the total molecular nuclear spin number *I*: since molecular hydrogen and deuterium have indistinguishable nucleons, the molecules are classified as *para* and *ortho*, depending on whether the rotational wave functions is symmetric with respect to the permutation of the nuclei. This classification is of great importance (especially at lower pressures), since *ortho*–*para* transitions are forbidden for isolated molecules.[11]

Vibrational transitions (called vibrons) are the internal molecular stretching vibrations and they are split into a multiplet, because vibrational transitions with different rotational quantum numbers have different frequencies. When molecules are associated in a crystal, this vibrational transition gives rise to a vibrational band due to intermolecular coupling.

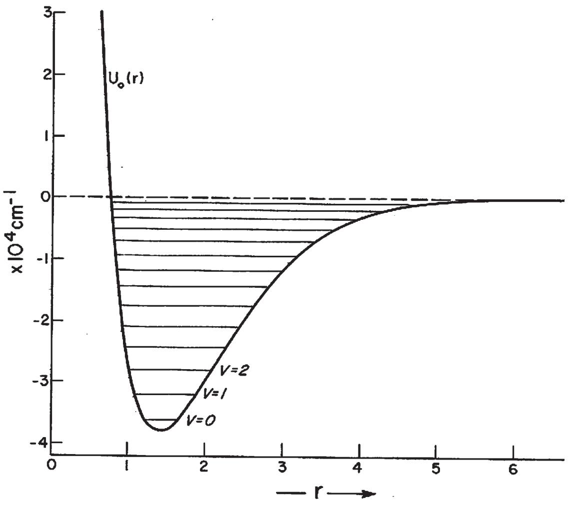

Fig. 3 Intramolecular potential for the isolated hydrogen molecule.[11]

The band structure depends on the physical arrangement of the molecules in the crystal and on intermolecular bonding. In a simplest nearest neighbor approximation in the hcp structure (phase I of hydrogen), the bandwidth is $8\varepsilon'$, where ε' is the parameter that characterizes the vibrational coupling.[11] In general, the selection rules are $\Delta v = \pm 1$ and $\Delta J = \pm 0,1$, where v and J are the vibrational and rotational quantum numbers, respectively. In the ordered crystal, the corresponding transitions are called vibrons, which can be observed in Raman scattering and direct optical processes (absorption and reflectivity) in the infrared (IR) spectral range [called $Q_1(J)_{\mathrm{Raman}}$ and $Q_1(J)_{\mathrm{IR}}$], where Q corresponds to $\Delta J = 0$]. While this terminology strictly applies to the ordered crystal, the term vibron has become more widely applied to the internal stretching modes of simple molecular systems. The frequencies of the Brillouin-zone center vibrons are split by $8\varepsilon'$; thus, the intermolecular coupling can be determined by measurement of both the Raman and IR excitations or by dissolving the molecule in a matrix (*e.g.*, Ref. 12), although it must be noted that in the latter case the frequencies probe an intermolecular potential perturbed by the surrounding medium.

Another important class of excitations of hydrogen molecules are the pure rotational transitions between the levels with different rotational quantum number, J. Those transitions depend crucially on the spin state of the molecule (*ortho–para* distinction, see above). The rotational energies of diatomic molecules are primarily dependent on the rotational constant $B = h/(4\pi)^2 cI$, where I is the rotational moment of inertia. Translational vibrations of molecules complete the picture of the elementary vibrational excitations in hydrogen.

Studies of the vibrational properties of hydrogen at high pressure continue to be central to our understanding of the system at very high density. Hydrogen becomes a solid under pressure (5.5 GPa) or when cooling down (14 K) forming phase I, which consists of disordered orientationally freely rotating molecules forming a hexagonal closed packed crystal lattice. A number of new discoveries and unexpected observations have been made in recent years. They include the observation of the vibron turn over, the identification of the broken-symmetry phase (breakdown of the spherical $J = 0$ state) and orientational ordering of the molecules (phase II), the discovery of a large IR vibron activity in phase III, the observations of invariant points on the phase diagram of hydrogen and deuterium (*e.g.*, triple points between phases I, II and liquid), and the observations of absorption of visible light at the very highest pressures (see Refs 12–15 and references therein). Though the focus of this paper is on the high P–T properties, we point out that there have been new developments in studies at low temperature, for example, using combined X-ray and neutron diffraction techniques.[16]

Measurements to the ~300 GPa range indicate that the molecules are still intact at room temperature and below (Fig. 4). Extrapolation of the equation of state of hydrogen, which has been measured to 120 GPa,[17] indicates that the system is >12-fold compressed at these pressures. The vibron linewidth increases above 200 GPa,’[13,15] and this broadening can be distinguished from that related to nonhydrostatic stress components in the sample because the low frequency libron bands remain much narrower.[18] Assuming a homogeneous linewidth, the excited state (T_1) lifetime is 30 fs at 250 GPa,

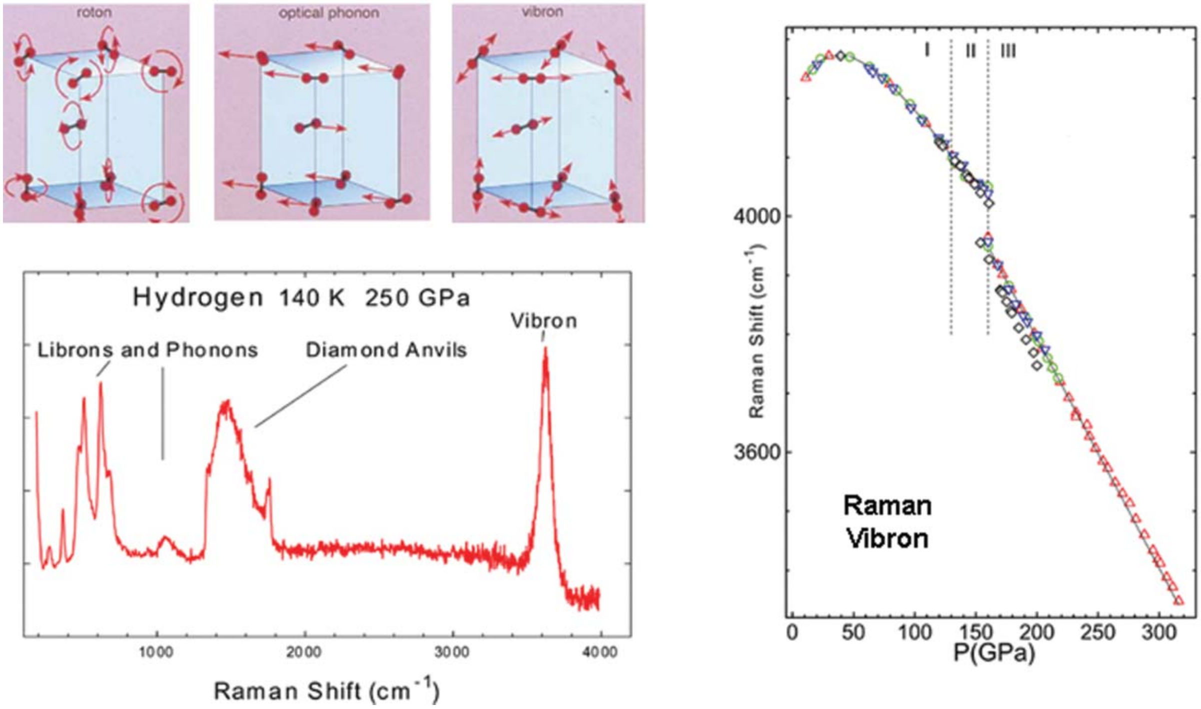

Fig. 4 Vibrational excitations of hydrogen. Top: principal excitations in the hcp structure. Lower left: Raman spectrum at 250 GPa and 140 K; note the free rotations have become restricted to give rise to complex librons at low frequency.[15] Right: Pressure dependence of the Raman vibron frequency through the I–II–III transitions at low temperature (adapted from Ref. 13, which should be consulted for further details).

decreasing to 300 fs at 50 GPa and 3 ps in the zero-pressure, low-temperature solid. The anharmonicity of the intramolecular potential at very high pressures implied by these results remains to be determined, and additional experimental and theoretical studies are needed to ascertain the extent of proton exchange (*e.g.*, as in water discussed below), charge transfer or other phenomena.

Experimental studies of hydrogen under simultaneous high pressures and temperatures have been challenging due to difficulties in containing hydrogen, which are related to its very high chemical reactivity and ability to penetrate into very small cracks and escape, as well as its very high compressibility. Using a nonmetallic gasket to help seal the hydrogen, Gregoryanz *et al.*[3] measured Raman spectra to explore melting and the possibility of subsolidus transitions. A strong curvature in the melting line was observed, consistent with lower pressure observations[2] (Fig. 5). The measurements also showed that H_2 is stable at simultaneous high pressures and temperatures explored, *e.g.*, to 1100 K at 70 GPa and at least 800 K at 150 GPa. The strong pressure dependence of the negative frequency shift with temperature $(d\nu/dT)_P$ contains information on the temperature dependence of the intermolecular coupling terms as well as intrinsic anharmonicity. Additional measurements of the IR vibrons at high temperatures and pressures are important to fully constrain the anharmonicity in the hot dense material.

First-principles theoretical calculations predict that the regime of molecular dissociation in hydrogen can be reached at ~150 GPa and high temperatures.[19,20] These calculations predict that this is related to a maximum in the melting line near 100 GPa of the solid molecular hydrogen in phase I, inferred experimentally[2,3] and calculated from first principles.[20] The higher density of the liquid relative to the solid above the predicted melting line maximum could arise from partial dissociation of the molecules in the fluid or from softening of intramolecular interactions due to charge transfer. Bonev *et al.*[20] suggest the latter without metallization. How this relates to the softening and broadening of the vibron above 100 GPa remains to be explored.[3]

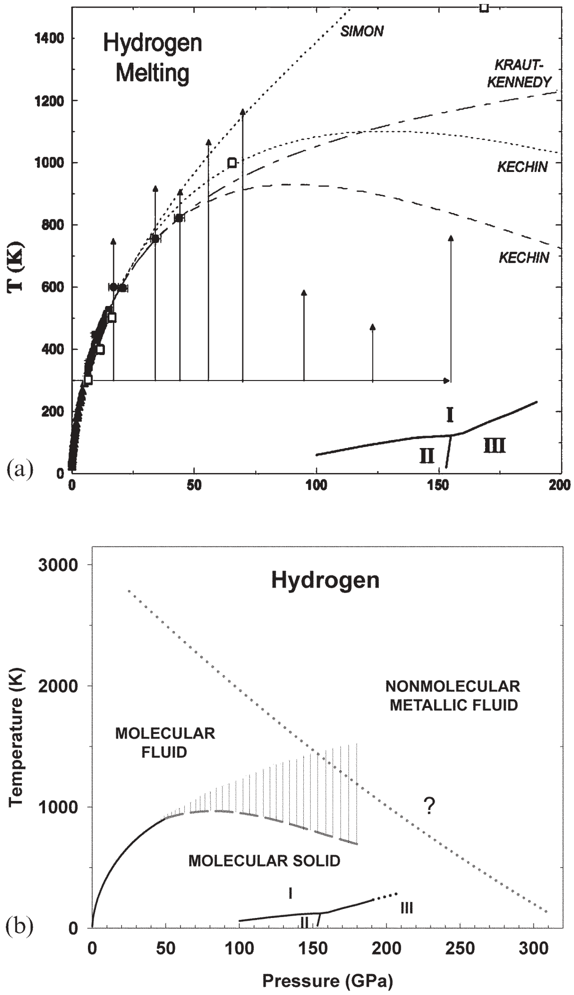

Fig. 5 Phase diagram of hydrogen. a) Region explored directly by high *P*–*T* Raman scattering.[3] The solid symbols are static compression data and the arrows indicate representative *P*–*T* paths followed in the experiment; the open squares are predictions from classical simulations.[43] Various extrapolated melting laws fit to experimental data are shown, including the two recent Kechin law analyses,[2,3] along with the I–II–III solid–solid phase boundaries.[12] b) Schematic phase diagram of hydrogen at higher *P*–*T* conditions.

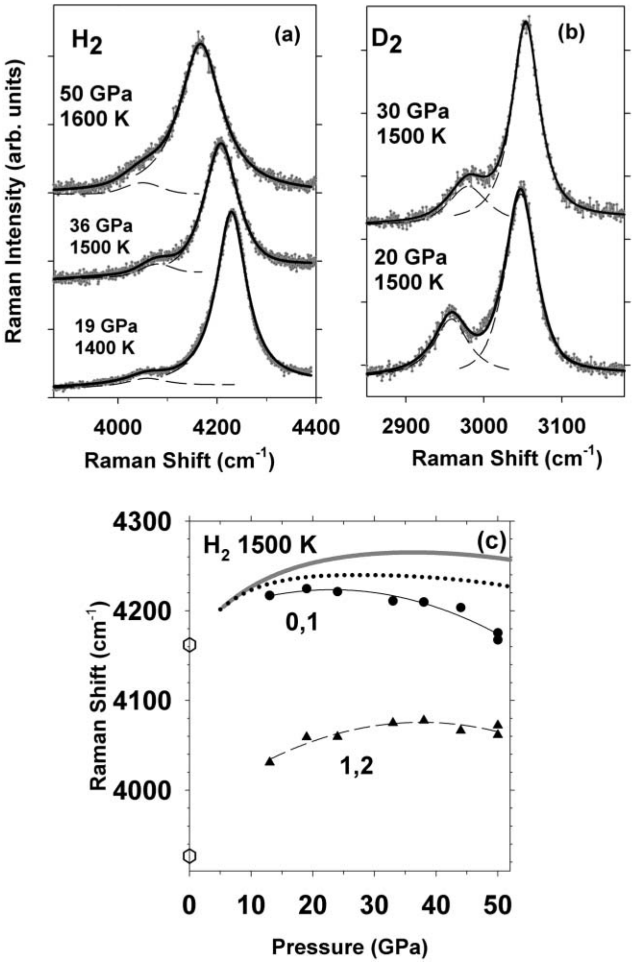

Fig. 6 Top: High *P*–*T* Raman spectra of H_2 and D_2. Lower: Vibrational frequency shifts for the 0–1 and 1–2 vibron excitations[21] (see Fig. 3).

As a start on exploring molecular stability of compressed hydrogen at higher temperatures, Goncharov and Crowhurst[21] probed the intramolecular stretching mode by simultaneous Raman scattering and laser heating. They used hydrogen in the form of small vesicles surrounded by water and metal and formed by chemical reaction of water with Al metal in the laser heated diamond cell. The sample obtained by this technique was laser heated to 1500 K (small pieces of Ir and unreacted Al served as laser couplers in some experiments), determined by fitting the thermal radiation spectrum and verified from the Stokes/anti-Stokes intensity ratio, and the relative intensity of a hot band, a vibrational transition from the excited vibrational level (Fig. 6). This transition is shifted to lower energies due to anharmonicity of the intramolecular potential. Measurements carried out to 50 GPa indicate that the anharmonicity of the intramolecular potential probed spectroscopically decreases initially with pressure. Similar results were found for N_2, which dissociates under high pressure.[21] Experiments to higher pressures and theoretical calculations will be able to track the full evolution of the intramolecular potential to more extreme conditions.

IV. H_2O at high *P–T* conditions

For hydrogen, the nature of bonding in water is synonymous with the development of our most fundamental concepts of chemical bonding.[22] In particular, the distinct macroscopic properties of water have challenged our understanding of bonding in associated liquids, and specifically the nature of its hydrogen bonds that link the hydrogen atoms of one water molecule to the oxygen atoms of neighboring water molecules. At low and modest pressures, the molecules in the common forms of solid water form a network that obeys Pauling's ice rules, which require each molecule to be oriented in such a way that it participates in the formation of four hydrogen bonds. The hydrogen atom in this arrangement is located in a nearly straight line connecting the oxygen atoms of two different water molecules. In the high-density regime, two interpenetrating diamond sublattices (*i.e.*, ice I_c) in the tetrahedral arrangement form a structure called ice VII. At higher pressures (above ~50 GPa), the protons begin to tunnel between oxygen atoms and eventually take the midway position between two neighboring oxygen sites, a situation referred to as hydrogen bond symmetrization. Ice in this form (ice X) is not molecular and can be viewed as an ionic material (Fig. 7).

The microscopic changes in the atomic configuration described above result in a pronounced modification of the interatomic forces. Materials such as water with strong hydrogen bonding offer a unique possibility to study the transformation from a molecular to nonmolecular structure in a continuous manner by tuning the pressure. These changes can be efficiently probed by detecting vibrational excitations corresponding to intra- and intermolecular motions. Vibrational spectroscopy[23] and first-principles calculations[24] show that the O–H intramolecular stretching mode dramatically softens and broadens under compression, which corresponds to a lengthening of the intramolecular O–H distance. At the transition to the symmetric hydrogen-bonded phase, the fundamental O–H stretching band is overdamped (broader than the frequency), and it appears again in the IR above the transition. Theoretical calculations of the Raman spectra[25] indicate the appearance of a new excitation corresponding to the oxygen atom vibration in the bcc lattice while the hydrogen

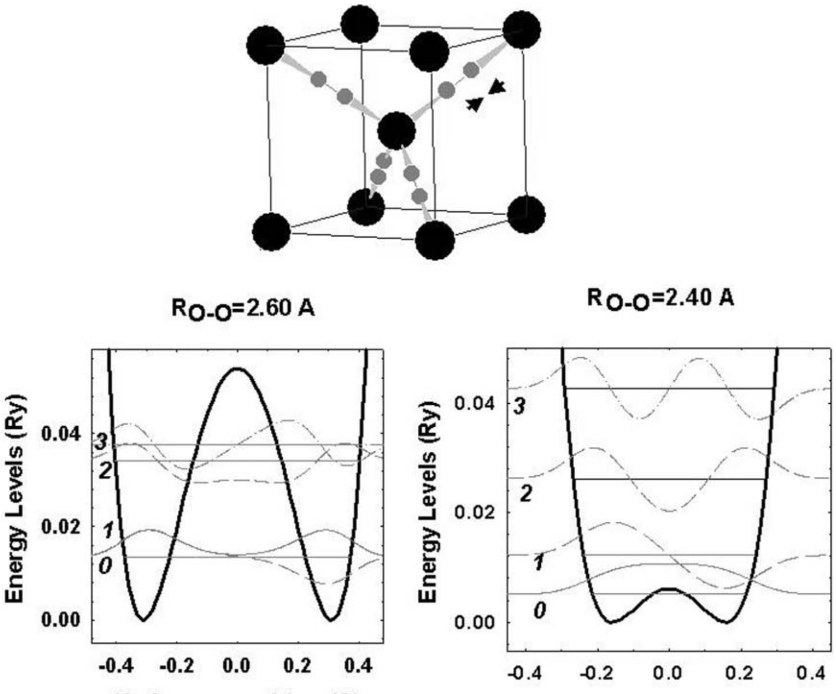

Fig. 7 Top: 'Split hydrogen atom' representation of the vibrational motion (tunneling) between the two equivalent sites in the ice X structure. Bottom: Effective double well potentials associated with this motion at two different pressures (O–O distances).

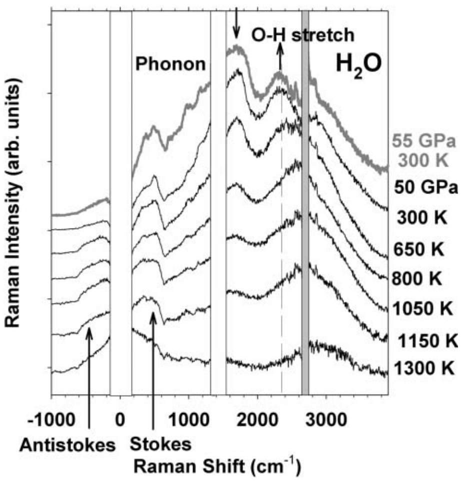

Fig. 8 Low frequency high *P–T* Raman spectra of H_2O.[28]

atoms take the centrosymmetric position at the mid-point between oxygen pairs, so they become Raman-inactive.

Subsequent theoretical calculations for ice VII have suggested additional phenomena. An intermediate regime has been predicted in which the proton tunnels between two potential wells, but the probability of finding it has a single wide maximum located between them.[26] In this regime, the ice rules are transiently, but systematically, violated. The vibrational spectra in the dynamically disordered phase (of ice VII) are very broad because of the breakdown of the wave vector conservation selection rules. A superionic phase of water with a stability field below the melting line, has been predicted theoretically.[27] In this phase, the oxygen atoms form a regular bcc lattice and the protons are very mobile, with the diffusion coefficient exceeding 10^{-4} cm^2 s^{-1}.

The behavior of H_2O at high *P–T* conditions has been examined by resistive and laser-heating techniques.[28,29] The Raman spectra of ice show a dramatic decrease of the hydrogen bond strength (from the increase of the O–H stretching in frequency), and an abrupt change of the shape of the translational mode, which has been interpreted as an indication of melting (Fig. 8). Moreover, this translational mode broadens at lower temperatures in a way very similar to that observed at the transition to the dynamically disordered phase at 53 GPa. An abrupt change of slope of the melting line near 40 GPa and 1000 K is observed (Fig. 9).[28,29] The change of slope indicates high entropy, and the 'refractory' nature of non-molecular ice X. The high melting temperature suggest the possibility of pressure-induced freezing of H_2O inside planets despite their high thermal gradients (Fig. 9). The extent to which this is due to proton mobility in a superionic phase remains to be determined. The predicted superionic regime and dynamically disordered ice VII have the same symmetry and the difference is likely determined by a character of the proton mobility (the proton is localized between two oxygen atoms or is capable of diffusing through the lattice). No electrical conductivity has been found in ice at room temperature to 100 GPa.[30] Moreover, spectroscopic measurements to 63 GPa at 400 K show a decrease of the proton diffusion with pressure.[31] Higher temperature proton diffusion and electrical conductivity measurements are necessary to further understand this system.

First-principles molecular dynamics simulations show a substantial increase of mobility of oxygen and hydrogen atoms in the fluid with increasing pressure.[32] Above approximately 20 GPa, the results of calculations show that the ice rules are violated and OH^- and H_3O^+ species form. Further compression leads to freezing of the oxygen sublattice, and almost at the

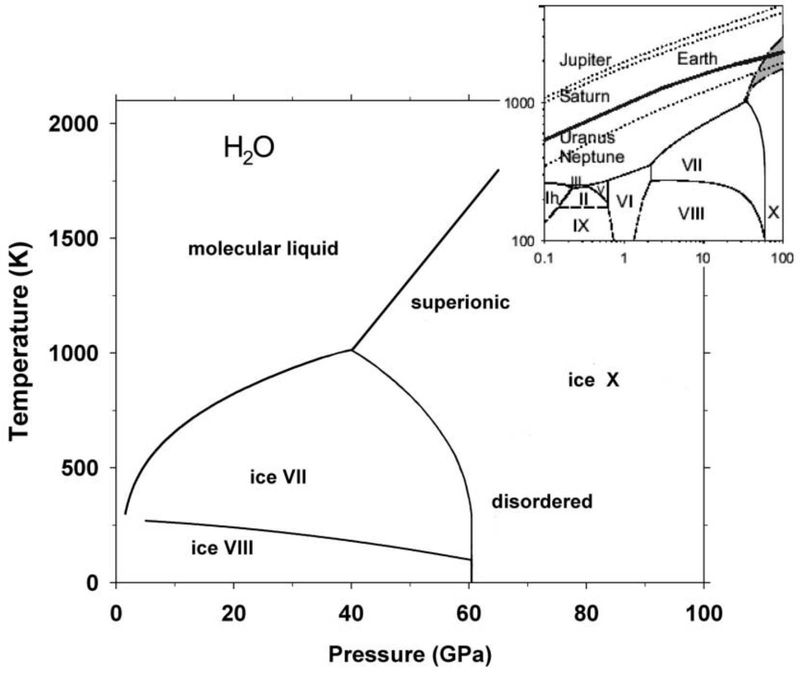

Fig. 9 Schematic high *P–T* phase diagram of H_2O to megabar pressures.[28,29] The inset shows the diagram over an expanded range that includes lower *P–T* phases as well as planetary interior conditions.

same time, the lifetime of H_2O molecule becomes so short that it becomes less than the vibrational period of the O–H stretch (~10 fs). Raman observations show an almost total disappearance of the O–H stretch, in agreement with these simulations. An interesting prediction of theory is the formation of an extensive bond network, consisting entirely of partially covalent O–H bonds, which makes water at 2000 K and 100 GPa analogous to ice X with symmetric hydrogen bonds.[32]

In addition to the evidence for combined pressure and temperature-induced dissociation of H_2O, previous work has shown evidence for elemental recombination to form O_2, with loss of hydrogen.[29] Recent experiments demonstrate that ice VII can be cleaved under pressure to form both H_2 and O_2 on exposure to X-ray irradiation above 10 keV.[33] These studies point to the need for detailed study of the hydrogen–oxygen binary phase diagram at extreme *P–T* conditions, a problem of first rank in astrophysics as well as chemistry and physics.

V. Other hydrogen-rich systems

Early static compression experiments have established that simple hydrocarbons subjected to high temperatures above 15 GPa break down to form diamond (see Ref. 1). Shock-wave compression experiments on methane showed a large increase in density along the Hugoniot at these pressures that were interpreted in terms of the breakdown transition.[34] These observations suggested that diamond and possibly related refractory high-density, low-*Z* materials may form the cores of large planets. Later first-principles calculations have predicted that methane condenses to form heavier hydrocarbons (*i.e.*, ethane); that is, prior to the presumed complete dissociation into the elements.[35] Infrared measurements establish that methane can persist to pressures well above a megabar on compression at 300 K[36] (Fig. 10). In contrast, laser heating of methane at pressures below 15 GPa results in breakdown of the material[37] (see also Ref. 38). Raman measurements reveal the presence of higher hydrocarbons and the formation of free hydrogen.

Additional phenomena are exhibited by formic acid (HCOOH), which shows complex behavior to 50 GPa that reflects the heterogeneous nature of the intra- and intermolecular bonds in the material.[39,38] At high temperatures and moderate pressures (<10 GPa) melting and chemical decomposition compete with a crossover at 6 GPa. Different chemical paths include the formation of CO_2, H_2O and CO, as well as the formation of a quenchable polymer to ambient conditions polymer. In contrast, formic acid experiences a two-stage polymerization under high pressures at 300 K. The first stage (at 20 GPa) is related to a formation of the symmetric hydrogen bonds and it is fully reversible. In the second stage (near 40 GPa), formic acid transforms to an amorphous polymer with large hysteresis on decompression. This effect is attributed to three-dimensional polymerization with a formation of interchain bonds.

High-pressure studies continue to document a rich high-pressure chemistry in mixtures of various simple molecular materials, including both solid-solution behavior and new compound formation. At high pressure, hydrogen forms a series of crystalline molecular compounds with methane, including the intriguing $(H_2)_4CH_4$ which contains the largest weight percent of hydrogen of any known compound.[40] Recent powder neutron diffraction studies of $H_2(H_2O)_2$, which crystallizes as a cubic structure II clathrate, reveal an unusual temperature dependent order–disorder transition in the component $(H_2)_4$ clusters in the structure.[41] Studies of these systems also provide information on the evolution of covalent interactions in van der Waals and hydrogen-bonded systems over a broad range of *P–T* conditions. These studies also provide direct information on the stability fields of these new compounds important for materials science and planetary science and may also open new paths to bond-breaking of the component molecules. This work should help to establish the role of impurities in shaping a donor or acceptor band and promoting a conducting state in pressurized hydrogen-bearing systems[42] and possible 'quantum' sublattice melting of the hydrogens that may parallel the behavior discussed above for

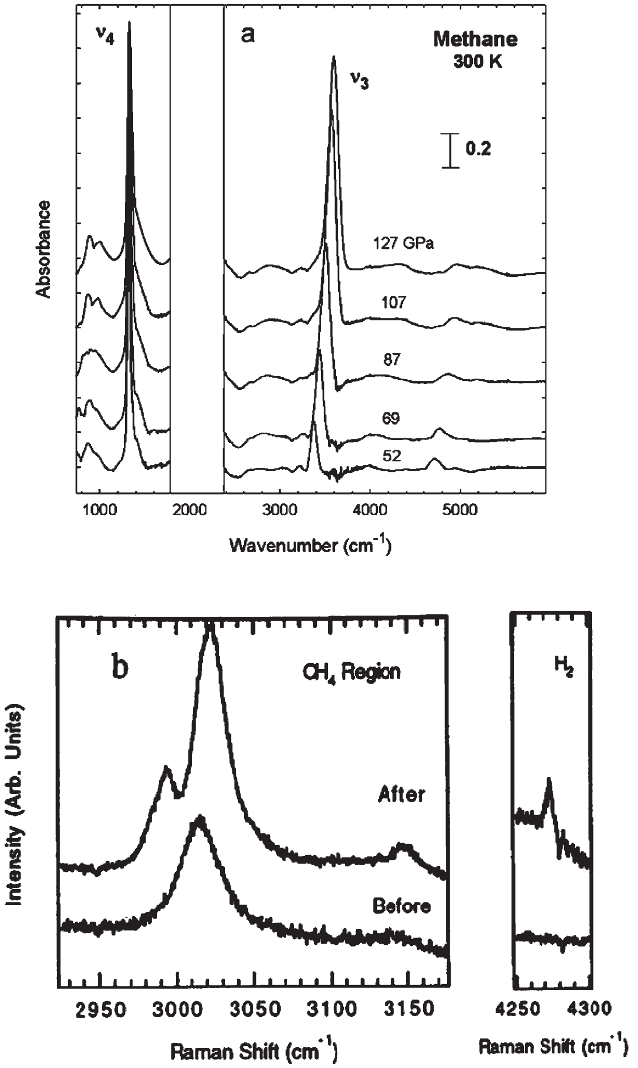

Fig. 10 High-pressure behavior of methane. (a) Synchrotron infrared measurements at 300 K.[34] (b) Raman measurements at 15 GPa before and after heating with a CO_2 laser, showing the dissociation of methane to form higher hydrocarbons together with the evolution of molecular hydrogen.[37]

H_2O. Extending these studies to high pressure and temperature will be important for developing improved understanding of the electrical conductivities of dense hydrogen-rich layers in giant (and super-giant) planets.

VI. Conclusions

Improvements in diamond anvil cell technology in combination with resistive- and laser-heating techniques have made possible a broad range of new experimental studies of hydrogen-rich systems under extreme pressures and temperatures. Spectroscopic and diffraction experiments carried out with these P–T generation methods provide new constraints on fundamental understanding of the component interatomic and intermolecular interactions over a broad range of conditions. Recent findings can be understood in terms of the evolution of effective potentials and interatomic vibrational coupling. However, these approaches are still incomplete and require full many-body treatments of the true interactions. Continued studies of compounds formed from these simple molecular materials are leading to new insights into pressure effects on molecular dissociation and polymerization as well as intriguing information on quantum properties associated with low-Z systems and how these couple with electronic structure.

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References

1 R. J. Hemley, *Annu. Rev. Phys. Chem.*, 2000, **51**, 763.
2 F. Datchi, P. Loubeyre and R. LeToullec, *Phys. Rev. B*, 2000, **61**, 6535.
3 E. Gregoryanz, A. F. Goncharov, K. Matsuishi, H. K. Mao and R. J. Hemley, *Phys. Rev. Lett.*, 2003, **90**(17), 175701.
4 F. Datchi, R. LeToullec and P. Loubeyre, *J. Appl. Phys.*, 1997, **81**, 3333.
5 A. F. Goncharov, J. C. Crowhurst, J. K. Dewhurst and S. Sharma, *Phys. Rev. B*, 2005, **72**, 100104.
6 A. F. Goncharov, J. M. Zaug, J. C. Crowhurst and E. Gregoryanz, *J. Appl. Phys.*, 2005, **97**, 094917.
7 J. F. Lin, M. Santoro, V. V. Struzhkin, H. K. Mao and R. J. Hemley, *Rev. Sci. Instrum.*, 2004, **75**, 3302.
8 A. F. Goncharov and J. C. Crowhurst, *Rev. Sci. Instrum.*, 2005, **76**, 063905.
9 W. Heitler and F. London, *Z. Phys.*, 1927, **44**, 455.
10 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1935.
11 J. Van Kranendonk, *Solid Hydrogen*, Plenum, New York, 1983.
12 H. K. Mao and R. J. Hemley, *Rev. Mod. Phys.*, 1994, **66**, 671.
13 P. Loubeyre, F. Occelli and R. LeToullec, *Nature*, 2002, **416**, 613.
14 R. J. Hemley and H. K. Mao, *J. Low Temp. Phys.*, 2001, **122**, 331.
15 A. F. Goncharov, E. Gregoryanz, R. J. Hemley and H. K. Mao, *Proc. Natl. Acad. Sci. U. S. A.*, 2001, **98**, 14234.
16 I. N. Goncharenko and P. Loubeyre, *Nature*, 2005, **435**, 1206.
17 P. Loubeyre, R. LeToullec, D. Häusermann, M. Hanfland, R. J. Hemley, H. K. Mao and L. W. Finger, *Nature*, 1996, **383**, 702.
18 A. F. Goncharov, R. J. Hemley, H. K. Mao and J. Shu, *Phys. Rev. Lett.*, 1998, **80**, 101.
19 D. Hohl, V. Natoli, D. M. Ceperley and R. M. Martin, *Phys. Rev. Lett.*, 1993, **71**, 541; S. Scandolo, *Proc. Natl. Acad. Sci. U. S. A.*, 2003, **100**, 3051.
20 S. Bonev, E. Schwegler, T. Ogitsu and G. Galli, *Nature*, 2004, **431**, 670.
21 A. F. Goncharov and J. C. Crowhurst, *Phys. Rev. Lett.*, 2006, **96**, 055504.
22 J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1933, **1**, 515; L. Pauling, *J. Am. Chem. Soc.*, 1935, **57**, 2680.
23 A. F. Goncharov, V. V. Struzhkin, M. Somayazulu, R. J. Hemley and H. K. Mao, *Science*, 1996, **273**, 218; K. Aoki, H. Yamawaki, M. Sakashita and H. Fujihisa, *Phys. Rev. B*, 1996, **54**, 15673.
24 M. Bernasconi, P. L. Silvestrelli and M. Parrinello, *Phys. Rev. Lett.*, 1998, **81**(6), 1235.
25 A. Putrino and M. Parrinello, *Phys. Rev. Lett.*, 2002, **88**, 176401.
26 M. Benoit, A. H. Romero and D. Marx, *Phys. Rev. Lett.*, 2002, **89**, 145501.
27 C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tosatti, M. Bernasconi and M. Parrinello, *Science*, 1999, **283**, 44.
28 A. F. Goncharov, N. Goldman, L. E. Fried, J. C. Crowhurst, I. F. W. Kuo, C. J. Mundy and J. M. Zaug, *Phys. Rev. Lett.*, 2005, **94**, 125508.
29 J. F. Lin, E. Gregoryanz, V. V. Struzhkin, M. Somayazulu, H. K. Mao and R. J. Hemley, *Geophys. Res. Lett.*, 2005, **32**, L11306.
30 R. J. Hemley, M. I. Eremets and H. K. Mao, in *Frontiers of High Pressure Research II:*, ed. H. D. Hochheimer, B. Kuchta, P. K. Dorhout, and J. L. Yarger, Kluwer, Amsterdam, 2002, pp. 201.
31 E. Katoh, H. Yamawaki, H. Fujihisa, M. Sakashita and A. Aoki, *Science*, 2002, **295**, 1264.
32 N. Goldman, L. E. Fried, I. F. W. Kuo and C. J. Mundy, *Phys. Rev. Lett.*, 2005, **94**, 217801.
33 W. L. Mao, H. K. Mao, Y. Meng, P. Eng, M. Y. Hu, P. Chow, J. Shu and R. J. Hemley, *Science* to be published.
34 W. J. Nellis, F. H. Ree, M. van Thiel and A. C. Mitchell, *J. Chem. Phys.*, 1981, **75**, 3055.
35 F. Ancilotto, G. L. Chiarotti, S. Scandolo and E. Tosatti, *Science*, 1997, **275**, 1288.
36 A. F. Goncharov, J. Badro, Z. Liu, H. K. Mao and R. J. Hemley, to be published.
37 T. Schindelback, M. Somayazulu, R. J. Hemley and H. K. Mao, *MRS 1997 Fall Meet. Prog*, 1997, 583.
38 L. R. Benedetti, J. H. Nguyen, W. A. Caldwell, H. Liu, M. Kruger and R. Jeanloz, *Science*, 1999, **286**, 100.
39 A. F. Goncharov, M. R. Manaa, J. M. Zaug, R. H. Gee, L. E. Fried and W. B. Montgomery, *Phys. Rev. Lett.*, 2005, **94**, 065505.
40 W. L. Mao, V. V. Struzhkin, H. K. Mao and R. J. Hemley, *Chem. Phys. Lett.*, 2005, **402**, 66.
41 K. A. Lokshin, Y. Zhao, D. He, W. L. Mao, H. K. Mao, R. J. Hemley, M. V. Lovanov and M. Greenblatt, *Phys. Rev. Lett.*, 2004, **93**, 125503.
42 N. W. Ashcroft, *Phys. Rev. Lett.*, 2004, **92**, 187002.
43 M. Ross, F. R. Ree and D. A. Young, *J. Chem. Phys.*, 1983, **79**, 1487.