

Triatomic and chained molecular phases of metallic hydrogen at ultra-high pressures

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Abstract

It is long believed that steadily compressed hydrogen beyond 400 GPa might undergo a transition from a proton-paired insulator to a monatomic metal, associating with dissociation of the molecules.[1, 2] A systematic investigation of dense hydrogen structures with first-principles density functional theory (DFT) electronic-structure methods, including proton zero-point motion, however, shows that no such kind of pressure-driven dissociation can be observed below 2 TPa (1 TPa=1000 GPa). A surprising rearrangement of protons into a tri-atomic phase and then into a chained molecular configuration enhances the stability of covalent bonds, and a complete transition into the metallic monatomic phase is estimated requiring at least a pressure of 5 TPa.

PACS numbers: 67.80.F-, 71.30.+h, 62.50.-p, 71.15.Nc, 64.70.-p

Keywords: metallic hydrogen, molecular crystal, ultra-high pressure, phase stability, pressurized dissociation

Having only a single electron, hydrogen is the simplest and most abundant element in the universe. It shows characteristics of both the group I alkalis and the the group VII halogens. At low pressures, hydrogen isotopes are halogenous, covalent diatomic molecules that form insulators. Yet at high pressures, it is one of the most difficult to understand. Experimentally it is known that hydrogen can exist as a low-temperature rotational crystal (phase I) on a hexagonal close-packed lattice to high pressures ($P < 110$ GPa), followed by a transition into the broken-symmetry phase II ($110 \text{ GPa} < P < 150 \text{ GPa}$) which is marked by a change to wide-angle libration and hence to a continuing incoherence of motion between different molecules, and then to phase III at about 150 GPa.[3] However, beyond the fact that protons remain paired within this pressure range, their time-average locations are to date experimentally unknown, mainly because hydrogen atoms scatter X-rays only weakly, leading to low-resolution diffraction patterns. Experimental data at higher pressures are scarce and the understanding of ultra-dense hydrogen structure is lack.

The theoretical prediction of stable crystalline structures of hydrogen is difficult because of the need to search the very large space of possible structures, and the necessity of obtaining accurate energies for each of these structures. First-principles DFT methods have proved being efficient approaches of calculating quite accurate energies, and they have provided many insights into the properties of various materials, including solid hydrogen. At present, DFT offers the highest level of theoretical description at which we can carry out searches over many possible candidate structures. Recent DFT calculations have predicted that within the static-lattice approximation, the most stable phases of paired molecular hydrogen are $P6_3/m$ (<105 GPa), $C2/c$ (105-270 GPa), $Cmca-12$ (270-385 GPa), and $Cmca$ (385-490 GPa), followed by $I4_1/amd$ monatomic phase.[4]

On the other hand, at high enough pressures where electrons are fully ionized out of the nuclei and form a uniform background, the material becomes one-component plasma. In this regime the dominated Coulomb interactions arrange the nuclei in a regular lattice called Wigner crystal, and stabilizes in a body-centered cubic (BCC) structure.[5] Unfortunately, the intermediate pressure region between this and that above 400 GPa is poorly understood and has rare investigation. Does the monatomic $I4_1/amd$ phase stabilize over a wide range of pressure or do any new phases exist before a transition into the BCC Wigner crystal phase occurs? Also it is unclear whether the proton-paired molecules dissociate and then enter a liquid state or not at zero Kelvin driven purely by compression effects.

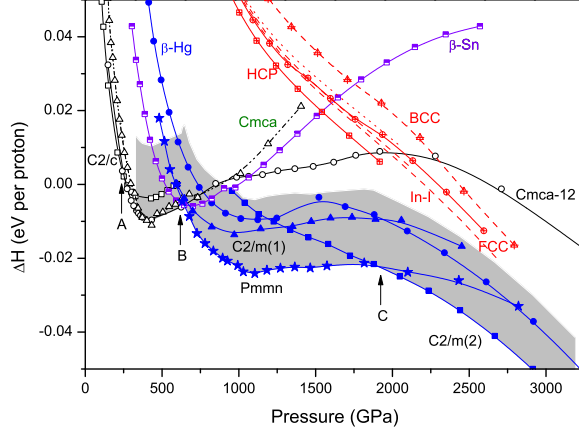


FIG. 1: (color online) Enthalpy per proton as a function of pressure with respect to the reference state. Arrows indicate the phase transitions of the ground state and the shadow region gives the maximum uncertainty due to harmonic zero-point motion of protons. Typical curves are labeled as: open square– $C2/c$, open circle– $Cmca-12$, open triangle– $Cmca$, filled star– $Pmmn$, filled square– $C2/m(2)$, filled triangle– $C2/m(1)$, filled circle– β -Hg, half-filled square– β -Sn, crossed triangle–BCC, crossed circle–FCC, and crossed square–HCP.

With accurate first-principles calculations, we report here that novel states of dense hydrogen within this pressure range has been observed numerically, which is metallic but in triatomic or chained molecular configurations. This lifts the transition pressure to monatomic phases up to a much higher value than previously expected. It also suggests a continuous transition into the BCC Wigner crystal from a highly compressed chained molecular structure.

The calculations were performed with DFT as implemented in the Vienna Ab-initio Simulation Package (VASP) [6] with all-electron like projector augmented-wave [7, 8] potential and the PBE exchange-correlation functional.[9] An energy cutoff of 900 eV and more than 1500 irreducible k-points were adopted, to converge the total energy to within 3 meV per proton. We carried out extensive random searches of molecular phases at pressures up to 3 TPa, and the structures were fully relaxed to the energy minima at fixed volumes with a force tolerance of $0.1 \text{ meV}\text{\AA}^{-1}$, meanwhile computed the pressure and then the enthalpy. Structural features are estimated to be converged to better than 0.2%, and the relative energy difference between structures to within 1 meV per proton. Candidate high-pressure monatomic phases also were searched and their enthalpies were calculated, including cu-

bic structures (SC, BCC, and FCC) and their low-symmetric distortions (β -Po, β -Hg, In-I, and In-II), hexagonal (HCP and ω -Ti), diamond, and $I4_1/amd$ (β -Sn and Cs-IV) phases, respectively.[10]

The calculated enthalpy difference with respect to a reference state (defined with an enthalpy of $H = -3.985 + 0.216P^{0.55}$ eV/proton, P in unit of GPa) of the most stable phases are shown in Fig.1. Below 400 GPa, our results agree very well with previous theoretical predications: $C2/c$ is the groundstate at 100 GPa and it transforms into $Cmca$ -12 at near 270 GPa.[4] At 370 GPa, $Cmca$ overtakes slightly, but soon becomes degenerate with $Cmca$ -12, which is stable until a new phase unknown before, triatomic $Pm\bar{m}n$, becomes the most stable at 650 GPa. The groundstate then changes to $C2/m(2)$ at 1900 GPa, which keeps stable beyond 3 TPa and no other phase with lower enthalpy had been found. The main transition points are indicated by arrows in Fig.1. Point B is an intersection point of several molecular phases and the monatomic β -Sn. Previous DFT calculations with LDA approximation suggested Cs-IV being the ground state at around this pressure range.[4] However, our calculations with higher precision gave a different result: Cs-IV has an enthalpy about 70 meV/proton higher than the groundstate, almost coincides with the diamond phase (not shown). Instead it is β -Sn that has a lower enthalpy, which touches the ground at point B. But it soon becomes unfavorable, and the pressure window for this monatomic phase is as narrow as just 50 GPa.

Other simple monatomic phases, such as BCC, FCC, HCP and their distortions do not approach the ground line until 2 TPa (SC is always 50 meV higher than others and not shown here). One interesting phase is β -Hg, which caught no attention before. It enters the shadow area at 600 GPa in figure 1 and approaches to the groundstate line all the way beyond 3 TPa. Thus it might coexist with $Pm\bar{m}n$ and $C2/m$ phases over a wide range of pressure. In conventional sense it is a monatomic phase derived from BCC structure with a shorter lattice length of c vector. But for hydrogen with a pressure beyond 600 GPa the lattice length is already short enough so that establishes covalent bonds along the c direction and thus becomes a chained molecular state (see figure 2 in the supplementary materials[11]). In fact it is exactly the formation of this kind of chained molecular bonds that stabilizes the phase, which can be seen much clearly by comparing the enthalpy with that of β -Sn (no covalent bond at all), $Cmca$ (diatomic bonds), $Pm\bar{m}n$ (triatomic bonds), and $C2/m$ (molecular chains). Specifically, β -Hg constitutes only linear chains of H_2 bonds,

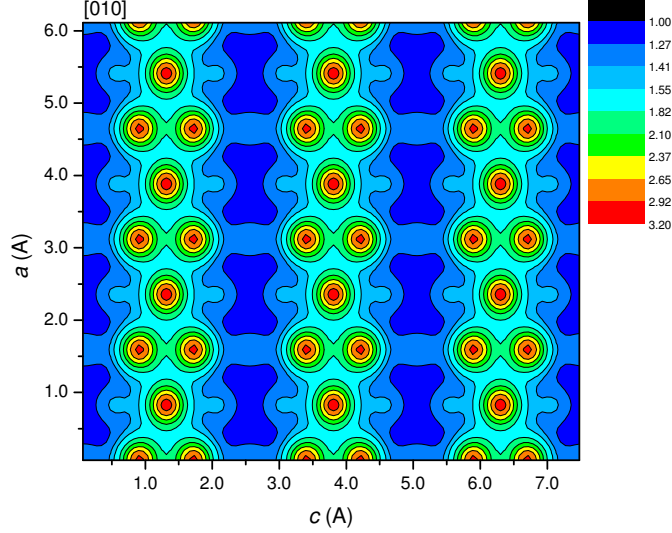


FIG. 2: (color online) Charge density of the $C2/m(2)$ phase (in tetragonal $Immm$ representation) at about 2TPa in a unit of $e\text{\AA}^{-2}$. The formation of molecular chains is evident.

whereas $C2/m$ consists of chains of H_3 clusters. $C2/m(1)$ and $C2/m(2)$ belong to the same space group $C2/m$. The only difference is in the linkage pattern and the chain orientation. Besides, $C2/m(1)$ has a shorter interchain distance and trends to form a bond network, whereas $C2/m(2)$ has more localized bonds and thus its chains are much distinct and well defined. Supplemental figure 5 and table I provide detailed structure information about these phases.[11]

Investigation reveals that these structural transitions are driven by competition between dispersion of the electron density induced by compression and the Coulomb attraction from the nuclei. The former favors metallic bonds whereas the latter tries to form covalent bonds with nearby atoms by overlapping the wavefunctions. Rearrangement of protons into triatomic and chained molecular configurations is a compromise and thus lowers the enthalpy. Point B is exactly a such kind of turning point that diatomic bonds lost competition to metallic interactions, whereas the formation of triatomic bonds helps molecular phases recapture the ground state. It then transforms to chained molecules at higher pressures. This complex behavior indicates the difficulty to ionize and dissociate hydrogen purely by compression.

Fig.2 shows the charge density of $C2/m(2)$ at about 2TPa (see supplementary materials for that of $Pmmn$ and $C2/m(1)$ phases[11]). The chains built on H_3 clusters are evident. Note that the environmental charge density is nonzero and the chains are in fact submerging

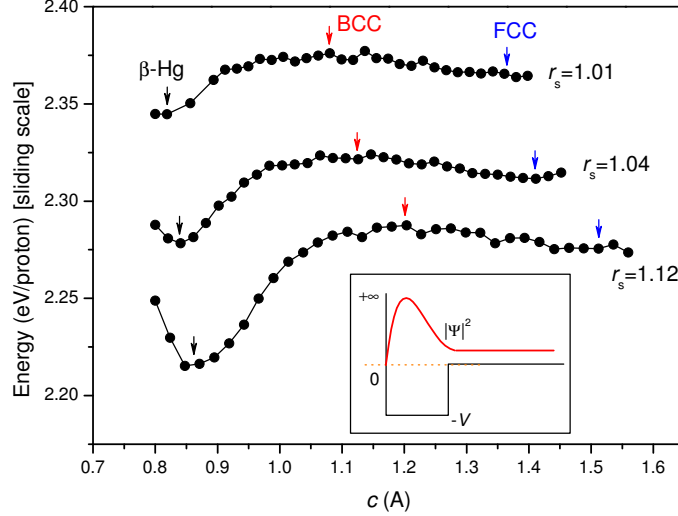


FIG. 3: (color online) Energy variation with the change of the c axial length of the β -Hg structure, which passes through FCC, BCC and β -Hg phase in sequence. Inset: a simplified half-infinite potential well that modeling the energy surface and the corresponding probability density profile.

in a sea of electrons that mediates metallic interactions. It is important to point out that although $C2/m$ and β -Hg are chained molecular crystals, they are natural conductors. We do not need to perform a band structure calculation to confirm this, since these phases have an odd number of electrons in their primitive cell, therefore there always has a half-filled band. $Pm\bar{m}n$ has 6 electrons in its primitive cell, and a detailed DFT calculation with GGA approximation showed that it is in a metallic state within its stable range of pressure. However, it is unclear whether these novel states possess the superconductivity as conjectured for monatomic metallic phases [1, 2] or not.

The zero point (ZP) motion contribution of protons to the energy and enthalpy can be taken into account within quasi-harmonic approximation. It does not change the relative stability of molecular phases very much. However, for highly compressed monatomic phases, this treatment is inaccurate because of the strong anharmonic effects.[12] Thus this ZP contribution only provides the uncertainty information of the phase stability that predicted by static lattice calculations, rather than the relative stability between monatomic and molecular states. It is estimated that the total error in enthalpy difference due to harmonic ZP contribution is less than 20 meV per proton for molecular phases (the shadow area shown in Fig.1). Thus we have to treat all phases within this area in Fig.1 as degenerated with this approximation.

Within DFT formalism it is difficult to conduct a quantitative calculation on anharmonic ZP effects. However, this problem still can be addressed in a qualitative but insightful way. To illustrate the physics encountered here we computed a portion of the energy surface that cross-cuts through the transition path from FCC to β -Hg at a constant density. Namely, change the length c of the β -Hg structure while adjusting a and b accordingly at a fixed density with r_s equaling 1.12 (~ 1 TPa), 1.04 (~ 1.5 TPa), and 1.01 (~ 2 TPa), respectively (see Fig.3. The enthalpy surface is quite similar, as can be perceived from Fig.1.) Here the dimensionless parameter r_s is defined as the radius of a sphere which encloses on the average one electron in a unit of the Bohr radius.[5] The obtained energy surface is approximation free, except those already introduced in the standard DFT formalism. ZP effects are thus described by the movement of particles on this potential surface (in a mean field of electrons). The surfaces as shown in Fig.3 are not necessarily the flattest ones (namely, with the largest anharmonicity), but they are typical enough for providing a qualitative picture of the physics we considered here. It is easy to find out that the harmonic approximation is completely failed for monatomic phases: no potential well can even be defined for them. The flatness of the energy surface perfectly reveals the origination of the unusual large anharmonic effects in monatomic phases observed in QMC calculations.[12] Having such a flat energy surface, the material should be in liquid state even at zero temperature.

The ZP energy of molecular hydrogen in harmonic approximation is about 0.13 eV per proton, rising to about 0.42 eV per proton at 2 TPa. This value is, however, inaccurate due to the flattening of the potential well. On the other hand, the harmonic ZP root mean square displacement (rMSD) gives a typical value of 0.2 Å for the β -Hg phase, which characterizes a typical ZP motion range for protons. Thus at a pressure of 1 TPa the ZP motion should be confined within the potential well for the case shown in Fig.3. But it is comparable with the well width at 1.5 TPa, and exceeds it at 2 TPa, where monatomic phases might appear. In a view point of quantum mechanics, the ZP motion in monatomic phases could melt the lattice, disperse the nuclei spatially, and modify the periodic potential in which the Bloch waves of electrons propagate. This quantum behavior of the lattice grid can be described approximately by a plane wave function $e^{ik \cdot R}$ when the change of the lattice parameter R leads to only a flat energy variation, as shown in Fig.3 (where the wavefunction $e^{ik \cdot R}$ describes a specific pattern of the collective motion that evolves the lattice vectors along the assigned transition path.) Thus a possible phase equilibria between chained molecular

and monatomic phases driven by ZP motion can be modeled phenomenologically by an effective particle moving in a half-infinite potential well (the inset of Fig.3). When the ZP energy is less than a critical value, bound states are developed in the well and the chained molecular structures are stable. When the ZPE is greater than the threshold, however, bound states disappear and monatomic phases have nonzero probability to exist. Using the model of a simple half-infinite potential well, this is manifested by satisfying a condition of $8MVx^2 \geq \pi^2\hbar^2$ where $x(V)$ is the potential width(depth), which confirms the existence of a bound state below 1.5 TPa for the case shown in Fig.3. Even when no bound state exists, phase cancelation between reflected waves from the potential well also makes chained molecular phases a high possibility to appear, as the probability density profile in the inset shown. Here we considered only one motion pattern and only β -Hg phase. For the ground state phases of $Pmmn$ and $C2/m(2)$, since their transition path to monatomic phases is unknown, it is difficult to construct a meaningful energy surface as Fig.3. However, we can qualitatively estimate the well depth by adding the corresponding enthalpy difference to that of β -Hg. The obtained results predict that monatomic phases would not appear below 2 TPa. At higher pressures, the potential wells become shallow enough and ZP motion could expel protons dispersively out into liquid monatomic phases and the atoms would then flow back, thus establishes a quantum dynamical equilibrium between the two states.

This transition confirms previous investigations that ZP motion of protons eventually favors isotropic structures over low-symmetry geometries at high pressures,[12, 13] with the difference that here the symmetric structure is in a liquid phase rather than a solid state. The transition pressure is also higher than that predicted by QMC calculations.[12] It is understandable since in that QMC calculations strong constraints had been applied by assuming ideal crystalline lattices and a proton wave function that was constructed by a product of Gaussian orbitals centered on lattice sites. This obviously overestimated ZP effects and was incapable of describing possible atomic liquid phase.

A liquid state of hydrogen at zero temperature is physically interesting [14–16] and might be a two-component superconductor for the protons and electrons, as well as a superfluid.[17] Above discussion cannot conclude whether the equilibrium is a solid molecular-liquid monatomic coexistence or a liquid-liquid mixture. Pressure driven melting at zero temperature requires ZP motion to destabilize the structure. For rigid chained molecular state, this also implies a destruction of the intra-molecule covalent bonds. Thus a 0 K liquid state

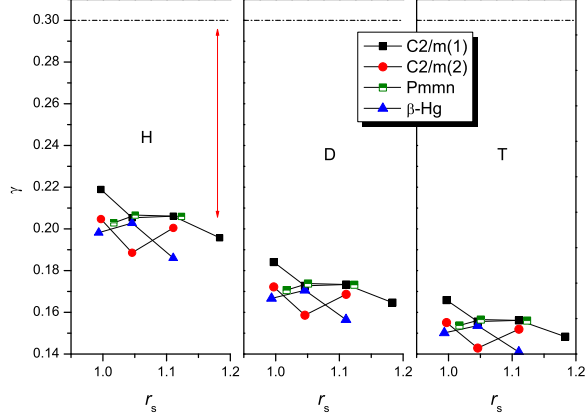


FIG. 4: (color online) The Lindemann ratio with respect to the next nearest neighbors as a function of density for hydrogen, deuterium, and tritium, respectively.

of molecular chains is unlikely. The Lindemann ratio γ of the ZP motion rMSD with respect to the next nearest protons (siting on the other chains) also suggests a solid state of molecular chains, as shown in Fig.4. For a quantum state, a value of γ less than 0.3 seems cannot lead to melting [12, 18]. The γ with respect to the bond-connected protons is also less than 0.25, indicates the stability of molecular bonds against compression (and ZP) driven dissociation.

To summarize, we have carried out extensive calculations on structure stability of molecular and monatomic phases of dense hydrogen up to 3 TPa. A new ground state line beyond 400 GPa has been found, which differs drastically from the expectation that monatomic phases are favored under these pressures. It also diminishes the possibility to observe pure monatomic phase in experiments at low temperatures in the near future. A triatomic molecular state becomes favored when diatomic molecular phases lost competition to monatomic β -Sn at about 650 GPa. The ground state then shifts to a metallic chained molecular configuration at 1.9 TPa. This chained phase is stable up to a very high pressure, and might equilibrate with liquid monatomic phase after 2 TPa driven by ZP motion of protons that favors isotropic structures.

Extrapolation suggests that β -Hg becomes the most stable phase over $C2/m(2)$ at about 5 TPa. It will continuously transform into BCC Wigner crystal when the lattice vectors a and b are compressed close to twofold of the Bohr radius where the electrons would be completely ionized out to form an even background and the system enters one-component plasma regime. Thus triatomic and chained molecular phases bridge the familiar extremes

of low-pressure diatomic crystals and high-pressure Wigner crystals. Between them it is unlikely that there is any new monatomic phase to appear. The near degenerated molecular phases over a wide range of pressure, especially near the point B, indicates the melting temperature of dense hydrogen is very low.

As isotopes of hydrogen, the deuterium and tritium have almost the same electronic behavior. The only difference is that due to their heavier ionic mass, the ZP effects are much smaller. Therefore the uncertainty in the harmonic approximation should be narrower, the stability of the chained molecular crystals should get enhanced, and the equilibrium with monatomic phases should take place at a higher pressure than for hydrogen.

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