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Formation of H₂-rich iodine-hydrogen compounds at high pressure

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We have used synchrotron x-ray and Raman spectroscopic studies combined with molecular dynamics to investigate the I₂-H₂ system at high pressure. By laser heating the mixture at above 25 GPa we synthesized a novel molecular compound HI(H₂)₁₃, with the AB₁₃ structure type and unusually high volumetric hydrogen content. The isolation of HI molecules by (H₂)₁₃ supramolecular clusters stabilizes the compound over a remarkable pressure range from 9 to at least 130 GPa. At lower pressures and 300 K another novel compound, hydrogen diiodane H₂(HI)₂ spontaneously forms, being stable up to 12.5 GPa.

INTRODUCTION

Molecular hydrogen has been the focus of intense research for several decades, both as possible energy carrier and as a subject of fundamental studies into its behaviour under extremes of temperature and pressure [1–5]. Extreme conditions research has revealed the potential of molecular clathrates and metal-organic frameworks to act as hydrogen-storage materials, whilst the claim of high-temperature superconductivity in H₂S, has reigned the interest in dense hydrogen-bearing materials [6–9]. Another element, iodine (I₂), an archetypal diatomic molecular system, has been predicted to exhibit physical phenomena and phase transitions similar to hydrogen, but at much lower pressures. Indeed, some of these phenomena and transformations have been experimentally observed [10–12]. Therefore the high pressure behaviour of the hydrogen-iodine mixtures might reveal some new and interesting physics. For instance, structure-searching calculations have suggested that compounds of hydrogen (H₂) and iodine (I₂) with various stoichiometries could be stable at pressures above 30 GPa, with superconducting phases emerging above 100 GPa with Tc up to 18 K [13, 14].

However, experimental studies of the high-pressure behaviour of hydrogen iodide (HI) have been hindered by its intrinsic instability due to the rapid decrease of HI intermolecular distances with increasing density, and therefore the decomposition of the HI molecules at pressure [15] and to a lesser extent due to the sensitivity of HI to diagnostic techniques such as laser or x-ray beams. Recent work has shown that at room temperature in a matrix of hydrogen, HI still decomposes at 10 GPa, while cooling, further stabilises HI to about 20 GPa at 80 K [15]. Although theoretical predictions also find HI to be unstable with respect to decomposition, they predict the hydrogen-rich compounds HI(H₂)₂, H₂I and (H₂)₁₃I to be more stable, but they have not been observed experimentally [13, 14].

Herein we report on the synthesis and stability of hydrogen-iodine compounds under pressure through x-ray diffraction and Raman spectroscopy combined with laser-heating techniques and molecular dynamics calculations. At pressures above 25 GPa, laser heating the mixture of metallic iodine and molecular H₂ promotes the synthesis of supramolecular HI(H₂)₁₃ which adopts the AB₁₃ structure, known to be stable for binary hard-sphere packing with size ratios of around 0.558 [16]. This structural type is observed in a wide range of systems but never before in a molecular configuration at high pressure. The icoshedral clusters of H₂ molecules isolate the HI molecule, resulting in an extreme stability range, from 9 to at least 130 GPa. By compressing HI-H₂ mixtures, we observe the formation of another molecular compound, H₂(HI)₂, which exhibits similar stability to pure HI [15]. We note that previous theoretical structure searches identifying several H₂-HI stoichiometries have not considered such extreme H₂-contents as we report here [13, 14].

METHODS

Mixtures of HI-H₂ were synthesized in diamond-anvil cells by the direct reaction between solid I₂ and H₂. Various concentrations of I₂ were loaded in an Ar-atmosphere glovebox. High-purity (99.9%) H₂ was subsequently gas loaded at 0.2 GPa. For pressures below 50 GPa, a small chip of ruby or gold was included as a pressure calibrant and cross-checked against the equation of state of I₂ during analysis [17, 18]. For samples above 50 GPa, no additional marker was used and pressure was determined by Raman of stressed diamond edge [19]. Samples were then irradiated with 200 mW of 532 nm laser light to photodissociate I₂, which reacts vigorously with H₂ producing a mixture of liquid HI and H₂ showing clear phase
separation. Samples were left for 24 hours to equilibrate after which there was a mixture of H2 and HI, with trace amounts of I2. By varying the initial quantity of I2 we were able to control the mixture ratio of HI and H2.

In situ laser heating was carried out on mixtures of solid I2 and H2 in diamond-anvil cells at pressures of at least 20 GPa. Samples for X-ray diffraction data collection were then compressed to 20 GPa and 33 GPa respectively before irradiation with up to 50 W of 1064 nm laser light. We estimate temperatures to be less than 1000 K as no black-body radiation was detectable from the sample during heating. These pressures were chosen to determine if the molecular dissociation of I2, occurring between 23.2 GPa and 30.4 GPa, influenced the reactivity of I2. These pressures are also high enough to ensure the full decomposition of HI and (HI)2H2 into their constituent elements [15].

Samples were characterized by microfocused X-ray diffraction and Raman spectroscopy. X-ray diffraction data were collected at beamlines BL10XU, SPring-8, Japan and 16-ID-B, Advanced Photon Source, USA using incident energies of ca. 30 keV. Two-dimensional image-plate data were integrated with DIOPTAS[20] to yield intensity vs. 2θ plots. Le Bail profile refinement was carried out in JANA2006[21], refinement of the crystal structure was carried out against \( |F^2| \) with the SHELXL refinement package [22]. X-ray diffraction and Raman spectroscopy measurements prior to laser heating indicate the cell contained pure I2, H2, and the Au pressure marker.

Molecular dynamics calculations were done using Density Functional Theory and the CASTEP program[23] with PBE exchange-correlation, on-the-fly iodine pseudopotential. For the detailed description of the experimental and theoretical methods used in this study see Supplemental Materials [24].

RESULTS AND DISCUSSION

At low pressures (0.2-0.5 GPa) H2 and I2 react spontaneously. Once synthesized, HI is very unstable on compression and decomposes by ~10 GPa at 300 K [15]. On further compression to 60 GPa at 300 K, there is no further reaction between I2 and H2. High-temperature laser heating has been shown to be an effective way to synthesize high-pressure compounds with unusual stoichiometries [25, 26]. By performing in situ laser-heating x-ray diffraction measurements at pressures of ≥24 GPa we observe the appearance of relatively weak but well-defined diffraction lines in addition to those from iodine (Fig. 1). Interestingly these lines appear only upon quenching to
The diffraction lines could be readily indexed to a primitive cubic unit cell \( (a = 5.080(1) \text{ Å} \) at 25 GPa). Initial analysis of the diffraction data indicated a single, strong, electron-density peak corresponding to HI, arranged in a primitive cubic lattice. The spacing between HI molecules \( (\text{i.e. unit-cell length } a) \) was clearly much larger than the combined radii of HI, suggesting the presence of additional H\(_2\) molecules.

Raman spectroscopic measurements confirmed two distinct molecular species in the compound having two characteristic intramolecular vibrational modes (vibrons): one mode at ca. 2300 cm\(^{-1}\) due to HI molecules, and one peak due to H\(_2\) molecules at approximately 4220 cm\(^{-1}\) (at 20 GPa, see Fig. 2(a)). Measuring the vibrational modes as a function of pressure shows that both vibrons exhibit a turnover in frequency, with maxima at a pressure of 25 GPa. Both vibrational modes are observable up to 60 GPa, the highest pressure achieved in the Raman study, and show considerable broadening and reduction in intensity with increasing pressure ([24] Fig. S1). We were not able to discern any distinctive modes in the low-frequency regime due to the strong Raman bands from the unreacted iodine. On decompression at 300 K, the compound is found to be stable to 9 GPa, below which there is the simultaneous disappearance of the corresponding vibrational modes and diffraction lines, leaving signals from only I\(_2\) and H\(_2\).

To estimate the stoichiometry of this compound, we compare the experimentally determined volume per formula unit with that calculated for various compositions derived from atomic equation-of-state for I\(_2\) [11, 27] and H\(_2\) [28]. As can be seen in Fig. 1, a composition of HI(H\(_2\))\(_{13}\) results in a close fit to the observed equation of state. Structures with composition AB\(_{13}\) have been observed in a number of systems: from intermetallic compounds to binary colloidal crystals and Brazilian gem opals [29–31]. Two forms of AB\(_{13}\) structure are known, and differ by the arrangement of B spheres, which may form icosahedra or cuboctahedra around a central B sphere with corresponding space-group symmetries \( \text{Fm} \overline{3}\text{c} \) and \( \text{Pm} \text{3} \text{m} \) [31]. Hydrogen is a poor scatterer of x-rays ruling out direct determination of the H\(_2\) arrangement by x-ray diffraction methods. To distinguish between the two packing types we have performed molecular dynamics (MD) density-functional theory calculations at 300 K and 30 GPa. Fig. 3(a) shows an instantaneous snapshot and averaged atomic positions over 5 ps. At this pressure H\(_2\) and HI molecules exhibit extensive rotational disorder but are stable and do not undergo proton transfer. The average positions from the simulation clearly shows H\(_2\) molecules adopting an icosahedral distribution as found in the \( \text{Fm} \overline{3}\text{c} \) polymorph (cf. Fig. 3(a)). Fivefold symmetry is incompatible with translational symmetry, so in the derived crystal structure alternate icosahedra are rotated 90° relative to each other resulting in a cubic structure containing eight (H\(_2\))\(_{13}\) units.

**FIG. 2.** Representative Raman spectra and vibrational mode positions of HI(H\(_2\))\(_{13}\) and H\(_2\)(HI)\(_2\). a) Representative Raman spectra from a sample containing HI(H\(_2\))\(_{13}\) and pure H\(_2\) on compression and decompression. b) Vibrational frequencies vs. pressure of HI (light blue squares), H\(_2\)(HI)\(_2\) (dark blue circles), HI(H\(_2\))\(_{13}\) (green diamonds) and H\(_2\) (black triangles) at 300 K. Filled symbols represent data on compression, whilst open symbols represent data collected on decompression c) Representative Raman spectra of the HI-H\(_2\)-I\(_2\) mixture (light blue), formation of H\(_2\)(HI)\(_2\) at 3.9 GPa (dark blue) and its subsequent decomposition with pressure (black).
in the \( Fm\bar{3}c \) conventional cell (Fig. 3(b)).

![Diagram of molecular dynamics trajectories and structural model of H\( \text{(H}_2\text{)}_{13} \).](image)

(a) Average positions MD and H\( \text{(H}_2\text{)}_{13} \) crystal structure

(b) \( \text{(H}_2\text{)}_{13} \) unit cell

**FIG. 3.** Molecular dynamic trajectories and structural model of H\( \text{(H}_2\text{)}_{13} \). (a) Time-averaged mean positions of selected atoms from the MD trajectory viewed along (110). The mean position of either atom in a rotating diatomic molecule is at the molecular centre - even though the atom is never actually there. Consequently the \( \text{H}_2 \) molecules comprise two superimposed spheres, and only the iodine is visible for the HI molecules. (b) \( \text{(H}_2\text{)}_{13} \) crystal structure with the orientation of icosahedral clusters highlighted with ‘bonds’ between \( \text{H}_2 \) positions to guide the eye.

A single HI vibron is in agreement with one unique HI molecular environment. The appearance of the vibron is consistent with rotational disorder as in HI phase I [15, 32]. As shown in Fig. 3 there are two unique \( \text{H}_2 \) molecular environments present in the \( AB_{13} \) structure (see Ref. [24]). But we are unable to distinguish in Raman between these modes within the icosahedra. This mode is markedly red-shifted compared with pure \( \text{H}_2 \), and has different frequency behaviour and broadening with pressure (see [24] Fig. S1), which mirrors that of the HI vibron extremely closely. The similarities in the behaviour of the two modes, suggests strong intermolecular coupling between HI and \( \text{H}_2 \). In the MD calculations we observe that the nearest approach between non-bonded H-atoms involves the hydrogen in HI. Radial-distribution functions for \( \text{H}_2 \) molecules (see [24] Fig. S2) also indicate the icosahedral symmetry adopted by the clusters and furthermore confirm that the \( \text{(H}_2\text{)}_{13} \) supramolecular units are well-separated and act as individual objects in the crystal structure. Changes in the average H\( \text{-H} \) bond distance with pressure (see [24] Fig. S3) shows no turnover in frequency as is observed for pure \( \text{H}_2 \) over the same range, indicating marked changes in \( \text{H}_2 \) vibrational behaviour in agreement with the strong intermolecular coupling observed in Raman.

Another possible route to the synthesis of iodine-hydrogen compounds is by the compression of HI and \( \text{H}_2 \), rather than \( \text{I}_2 \) and \( \text{H}_2 \). Mixtures of HI and \( \text{H}_2 \) were prepared at 0.2 GPa, where we observe clear phase separation between HI and \( \text{H}_2 \). On compression above 0.3 GPa we observe the crystallization of HI phase I in the sample, which becomes grainy in texture [15]. At a pressure of 3.5 GPa, we observe the formation of large crystal grains as solid HI reacts with surrounding fluid \( \text{H}_2 \). Diffraction peaks corresponding to the newly formed compound, hydrogen diiodane \( \text{(H}_2\text{(HI)}_2) \), could be indexed to a body-centered tetragonal unit cell \( a = 7.8626(6) \) \( \text{Å}, c = 6.5757(8) \) \( \text{Å} \) at 5 GPa. A complete systematic-absence analysis was not possible due to peak overlap with \( \text{I}_2 \). However, the analogous \( \text{H}_2\text{(H}_2\text{S)}_2 \) and \( \text{H}_2\text{(CH}_4\text{)}_2 \) compounds adopt space group \( I4/mcm \), and subsequent refinement in this space group results in a good fits to the data with no unexplained peaks \( (wR_p = 2.39\%) \) [33, 34]. In this structure, rotationally disordered HI molecules form alternating layers perpendicular to the c axis with \( \text{H}_2 \) molecules occupying vacancies between these layers.

**Figure 2(c)** shows the Raman spectra of hydrogen diiodane on compression. Below 3.5 GPa, only the vibrons of \( \text{H}_2 \) and HI phase I are observed. On compression to 3.5 GPa there is the appearance of a second \( \text{H}_2 \) vibron, 90 cm\(^{-1}\) lower in frequency than that of the pure species. This mode softens with pressure, the opposite of pure molecular \( \text{H}_2 \) which hardens in this pressure regime. The HI vibrational mode broadens slightly at the formation pressures, however this was previously determined to be a transition to a phase \( \text{I}' \) in pure HI [15]. A combination of weak hydrogen bonding and decomposition means that, unlike \( \text{H}_2\text{(H}_2\text{S)}_2 \), \( \text{H}_2\text{(HI)}_2 \) does not undergo a \( H \)-ordering transition under compression, but instead decomposes at slightly higher pressure (12.5 GPa) than pure HI (10 GPa) [15, 33].

We observe diffraction peaks from HI\( \text{(H}_2\text{)}_{13} \) (Raman vibrational modes were observed up to 58 GPa) over a remarkably large pressure range, from 9 GPa on decomposition to 130 GPa on compression. The structural information obtained can provide some indication as to the origin of this stability \( \text{versus} \) HI and \( \text{H}_2\text{(HI)}_2 \). Amongst the hydrogen halides only HBr and HI have been experimentally proven to decompose into their constituent elements [15, 35]. Molecular dynamics simulations of this process in HBr indicate that intermolecular distances reduce under compression leading to the spontaneous for-
Isolation atomic equations of state for stoichiometry H\textsubscript{2}\textsuperscript{13} shows good agreement with values calculated from the corresponding atomic equations of state of I\textsubscript{2}\textsuperscript{12} and H\textsubscript{2}\textsuperscript{28}. Volume-per-formula unit (V/Z) as a function of pressure shows good agreement with values calculated from the atomic equations of state for stoichiometry H\textsubscript{2}(HI)\textsubscript{2}, supporting the result of the refinement. Crystal structure of H\textsubscript{2}(HI)\textsubscript{2}, layers of HI molecules are space along c by the insertion of H\textsubscript{2}. HI molecules represented by purple spheres, H\textsubscript{2} molecules by white spheres.

Triadecadihydrogen iodane has an unprecedented 93 mol-% H\textsubscript{2} content. Amongst molecular hydrogen-storage materials, HI(H\textsubscript{2})\textsubscript{13} shows a relatively high weight-percent H\textsubscript{2} content, 17.7\%, which compares favorably to other materials such as H\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2} (5.3 H\textsubscript{2} wt %), H\textsubscript{2}(H\textsubscript{2}O) (11.2 H\textsubscript{2} wt %)\textsuperscript{40} and Xe(H\textsubscript{2})\textsubscript{8} (10.9 H\textsubscript{2} wt %)\textsuperscript{37}, although it falls short of the record 33.4 wt % found in (H\textsubscript{2})\textsubscript{4}CH\textsubscript{4}\textsuperscript{40}. The formation of HI(H\textsubscript{2})\textsubscript{13} also poses an interesting question as to whether such a structure could be stable for other molecules that satisfy the size ratio compatible with the (H\textsubscript{2})\textsubscript{13} supramolecular building block. Interestingly Xe, isoelectronic to HI, has also been shown to form van der Waals compounds with H\textsubscript{2}, it may be possible that higher H\textsubscript{2}-content structures could be stable in that system\textsuperscript{37}. This observation of an AB\textsubscript{13} structure containing molecular hydrogen might initiate the search for molecules capable of forming such a hydrogen-rich stoichiometry at close to ambient pressures.

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