

Synthesis of H₂-rich molecular compounds by laser heating at high pressures

As hydrogen has an exceptional energy density by weight, finding new methods for capturing hydrogen in a dense state has been subject to intense investigation for decades. High-pressure techniques have revealed the potential of molecular clathrates and metal-organic frameworks to act as desirable hydrogen-storage materials, and the claim of high-temperature superconductivity in H₂S has reignited the interest in dense hydrogen-bearing materials [1]. For instance, recent structure-searching calculations predicted that compounds of hydrogen (H₂) and iodine (I₂) with various stoichiometries could be stable at pressures above 30 gigapascals (GPa), with emergent superconducting phases above 100 GPa [2].

Studying this system experimentally is however far more challenging as hydrogen iodide (HI) is unstable and readily decomposes upon exposure to laser or X-ray radiation. Early work on HI at high pressures claimed the existence of an insulator-to-metallic transition at 50 GPa. However, work by our group has shown that at room temperature HI decomposes above 10 GPa, returning to its constituent elements [3]. However, this apparent instability of HI, could ultimately lead to the formation of new H-I compounds at higher pressure and/or temperature. Theoretical simulations predict the possible formation of numerous new hydrogen-rich configurations; HI(H₂)₂, H₂I, and (H₂)₂I, none of which were experimentally observed.

The synthesis of new H₂-I₂ compounds was explored using high-pressure X-ray diffraction at SPRing-8 BL10XU, combined with *in situ* laser heating and Raman spectroscopy [4]. Mixtures of HI-H₂ were synthesized in diamond-anvil cells by direct reaction between solid I₂ and dense fluid H₂. After loading, samples were then irradiated with green laser light (532 nm) to photodissociate I₂, which reacts vigorously with the surrounding fluid H₂ media, resulting in a mixture of liquid HI and H₂. Through varying the initial quantity of I₂, we were able to control the mixture ratio of HI and H₂. Samples were then compressed to approximately 30 GPa before irradiation with up to 50 W of 1064 nm laser light.

As seen in Fig. 1, laser-heating leads to the appearance of relatively weak, but well-defined diffraction lines, in addition to those from iodine. 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 was clearly much larger than the combined radii of HI, suggesting the presence

of additional H₂ molecules, however they cannot be observed by X-ray diffraction.

In order to estimate the stoichiometry of this compound, the volume-per-formula-unit was compared with various compositions from the summation of the atomic equations of state for I₂ and H₂ which suggested the surprising composition of HI(H₂)₁₃. Structures with this AB₁₃ composition have been observed in a number of systems: from intermetallic compounds to binary colloidal crystals and Brazilian gem opals. Two forms of AB₁₃ structure are known and differ by the arrangement of their B spheres. To distinguish between the two packing types we performed molecular dynamics (MD) density functional theory calculations at 300 K and 30 GPa. The average positions from the simulation clearly show H₂ molecules adopting an icosahedral (H₂)₁₃ distribution as found in the *Fm* $\bar{3}$ *c* polymorph (Fig. 2).

Through Raman spectroscopic studies (Fig. 3), a single HI vibrational mode is observed in agreement with one unique HI molecular environment from our assigned structure. The (H₂)₁₃ intramolecular vibrational mode is red-shifted compared with that of

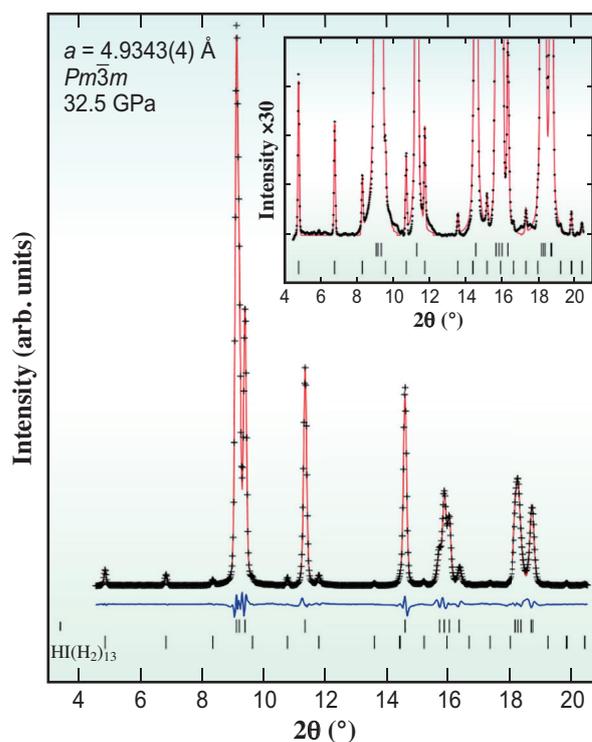
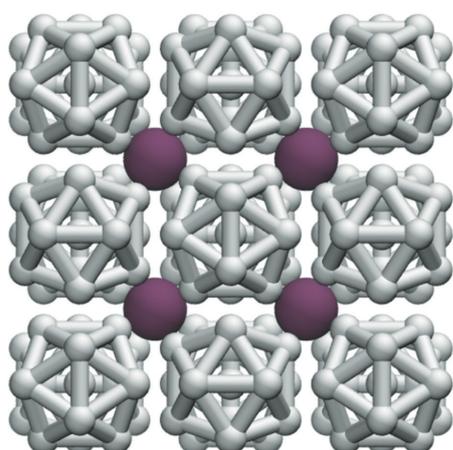


Fig. 1. High-pressure X-ray diffraction pattern collected from a laser-heated mixture of H₂ and I₂ at 32.5 GPa ($\lambda = 0.4141 \text{ \AA}$) collected at BL10XU.



HI(H₂)₁₃ unit cell

Fig. 2. HI(H₂)₁₃ crystal structure with the orientation of icosahedral clusters highlighted with “bonds” between H₂ positions to guide the eye.

pure H₂ and its pressure-evolution mirrors that of the HI vibrational mode. The similarities in the behavior of the two modes suggest strong intermolecular coupling between HI and H₂. In the MD calculations we observe that the nearest approach between non-bonded H atoms involves the hydrogen in HI. Radial-distribution functions for H₂ molecules also indicate the icosahedral symmetry adopted by the clusters and furthermore confirm that the (H₂)₁₃ clusters are well separated and act as individual objects in the crystal structure.

We observed diffraction peaks from HI(H₂)₁₃ over a remarkably large pressure range, from 9 GPa on decompression to 130 GPa on compression. Amongst the hydrogen halides only HBr and HI have been experimentally proven to decompose into their constituent elements. Decomposition occurs when intermolecular distances are short enough to lead to the spontaneous formation of H₂ molecules. In HI(H₂)₁₃, HI molecules are widely dispersed amongst (H₂)₁₃ clusters and this hinders the decomposition mechanism, stabilizing the compound by more than an order of magnitude. This remarkable change in stability makes HI(H₂)₁₃ among the most stable bimolecular compounds at high pressures, comparable to Xe(N₂)₂ and Xe(H₂)₈, which are stable up to 180 and 255 GPa, respectively.

Among molecular hydrogen storage materials, HI(H₂)₁₃ shows a relatively high weight-percent H₂ content, 17.7%, which compares favorably to other materials such as H₂(H₂O)₂ (5.3 H₂ wt%), H₂(H₂O) (11.2 H₂ wt%), and Xe(H₂)₈ (10.9 H₂ wt%), although it falls short of the record 33.4 wt% found in (H₂)₄CH₄. The formation of HI(H₂)₁₃ also poses an interesting question as to whether this structure type could be

stable for other molecules that satisfy the geometric size ratio compatible with the (H₂)₁₃ supramolecular building block. In a subsequent molecular dynamics study we demonstrated the stability of a number of so-far unobserved AB₁₃ compounds, including the hydrogen halides and the noble gas xenon [5]. Further experimental studies will test these predictions in the search for more hydrogen-rich compounds.

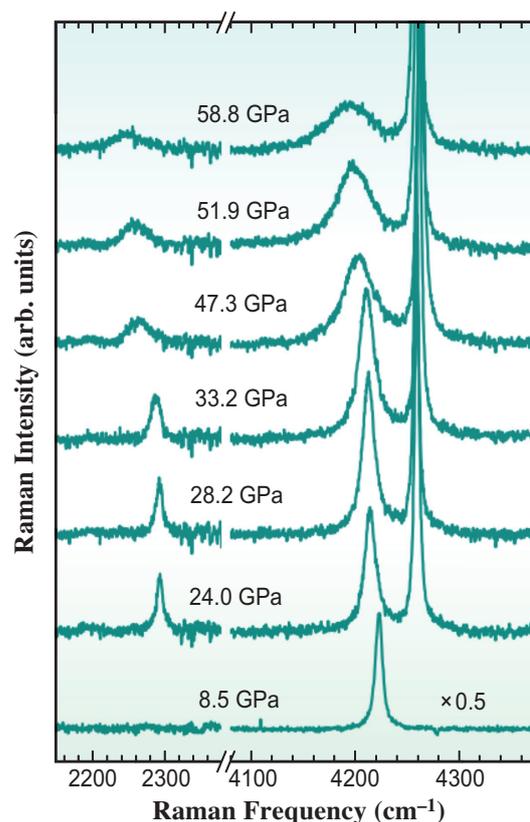


Fig. 3. Raman spectra of HI(H₂)₁₃.

Jack Binns*, Philip Dalladay-Simpson and Ross Howie

Center for High Pressure Science and Technology
Advanced Research, Shanghai, China

*Email: jack.binns@hpstar.ac.cn

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