

High capacity molecular hydrogen storage in novel crystalline solids

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Abstract

A number of hydrogen-rich van der Waals compounds have recently been discovered and hold promise for improving hydrogen storage technology, but the structure and nature of the intermolecular interactions in many of these materials is unknown. We have determined the previously unknown structure of $\text{CH}_4(\text{H}_2)_4$ using a novel combined theoretical and experimental approach. This material contains the largest amount of hydrogen of any known compound (33.4 wt%). $\text{CH}_4(\text{H}_2)_4$ was found to have an orthorhombic methane substructure with two different sites for H_2 molecules which interact strongly as single entities with the two nearest methane molecules. Interactions of the hydrogen molecules with the methane sublattice in $\text{CH}_4(\text{H}_2)_4$ allows the hydrogen molecules to be packed with higher density than solid hydrogen at its normal freezing point, indicating a novel increased interaction in $\text{CH}_4(\text{H}_2)_4$. This finding provides insight into understanding intermolecular interactions in hydrogen-dense environments has implications for designing high capacity hydrogen storage materials.

Introduction

Replacing fossil fuels with hydrogen as an energy carrier has potential for significantly reducing greenhouse gas emissions from transportation applications at the point of use. One of the major hurdles to realizing a hydrogen economy is finding a practical on-board hydrogen storage material. The material must satisfy a number of requirements which include (but are not limited to): high hydrogen content (by mass and volume), near ambient synthesis, storage, and release conditions, environmentally friendly by-products, reasonable cost, etc. Major effort has been devoted to finding a suitable solution, and a wide variety of methods and materials have been investigated. However, none of the current approaches meets all the requirements mentioned above.

The objective of our exploratory proposal was to study novel crystalline phases with a high capacity for molecular hydrogen storage over varying pressures and temperatures using both an experimental and theoretical approach. Synthesizing novel materials in extreme environments (e.g. pressure, temperature, radiation fluxes) may seem like an impractical approach for finding materials which will be used at ambient conditions, but nature already provides us with an excellent example, diamond, whose stability field is at high pressure and temperature, but whose metastable field extends down to the ambient conditions. Knowledge about this high pressure phase of carbon led to the development of synthesis techniques to mimic its creation (high pressure-temperature methods) which drive the billion dollar diamond abrasives industry. More ingenious, understanding the sp^3 bonding of diamond enabled the design of a new synthesis pathway which uses sp^3 bonded carbon in a methane plasma as a starting material for chemical vapor deposition growth of diamond in a near vacuum environment; high pressure is no longer required.

For this exploratory proposal we used a closely coupled experimental and theoretical approach for investigating hydrogen-rich systems. We investigated the novel structures with high hydrogen storage with the plan to then demonstrate pathways for synthesizing these phases at practical conditions. The goal of this one year project is to identify and characterize a few promising crystalline solids which store a high-capacity of molecular hydrogen and then stabilize these materials to near ambient conditions by addition of chemical promoters. We decided to start with tetrahydrogen-methane ($\text{CH}_4(\text{H}_2)_4$), which contains 33.4 wt% molecular hydrogen (not including the hydrogen in methane), but whose crystal structure had not yet been identified, so how it stores so much molecular hydrogen is poorly understood.

Background

Extreme environments provide us a much broader field to search for phases with desirable properties. Studying hydrogen-rich systems is still a research area in its infancy, but which has yielded the discovery of exciting new phases with high storage capacity (Figure 1) [Mao and Mao, 2004].

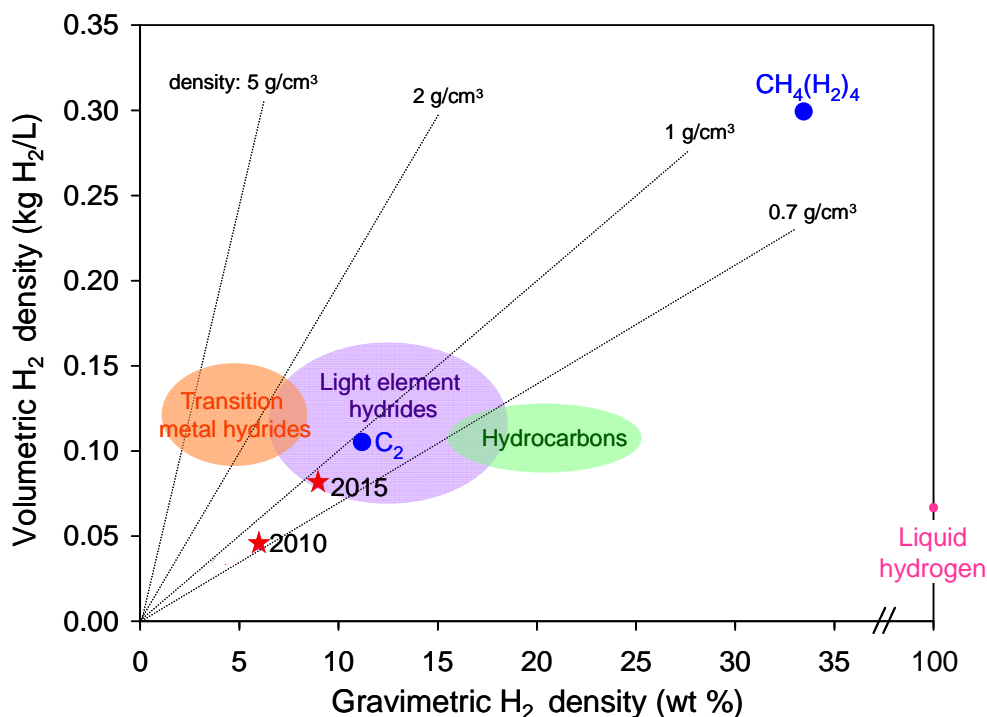


Figure 1. Hydrogen storage capacity for a hydrogen-methane molecular compound ($\text{CH}_4(\text{H}_2)_4$) and a hydrogen hydrate (C_2) plotted as volumetric and gravimetric density. Overall density of each material is shown by dotted lines. Comparison for general region where transition metal hydrides (orange), light element hydrides (purple), and hydrocarbons (green) generally plot. Red stars show DOE technical targets for year 2010 and 2015 for an on-board hydrogen storage system. These targets are for the entire system (i.e. includes any tanks, refrigeration system, etc.). Adapted from [Mao et al., 2007].

Currently only a limited number of hydrogen-rich binary systems have been explored, and basically no ternary systems have been studied, but with the discovery of promising hydrogen-rich phases in the CH₄-H₂ and H₂O-H₂ systems, in the past three years this research area has taken off. Understanding the structure of these materials allows us to then develop methods for synthesizing them at practical conditions. A proof of concept is the discovery of a new hydrogen rich molecular solid, H₂(H₂O)₂, and the subsequent determination of its structure [Mao *et al.*, 2002] directed researchers to a method of stabilizing the material by the addition of a promoter molecule, in this case tetrahydrofuran, which allowed synthesis of the hydrogen hydrate at 50 bars and 280 K (compared to 3000 bars without the chemical promoter) [Florusse *et al.*, 2004]. This demonstrates that once we have determined the structure of the hydrogen storing phase, we can then develop a method for stabilizing the structure to practical conditions.

Results

In determining the structure of CH₄(H₂)₄ we used a combined theoretical and experimental approach. Our molecular modeling method made use of a multiple initial configurations approach with four stages: generation of initial random configurations, geometry optimization using classical molecular models, geometry optimization using ReaxFF and geometry optimization using ab initio density functional theory (DFT). For the classical force field, the most favorable structure was orthorhombic and had an average cell volume of 370 Å³; an orthorhombic structure was always obtained, even when asymmetric cell angle ranges (e.g., 55° - 95° and 85° - 125°) were used, demonstrating that this result is robust. Given that classical force fields are typically overly repulsive in nature, it was expected that the cell volume calculated using the more accurate ReaxFF and DFT methods would be lower. Indeed, both the ReaxFF calculations and the DFT calculations resulted in a cell volume of 332 Å³, the DFT results verifying the vastly computationally cheaper ReaxFF results.

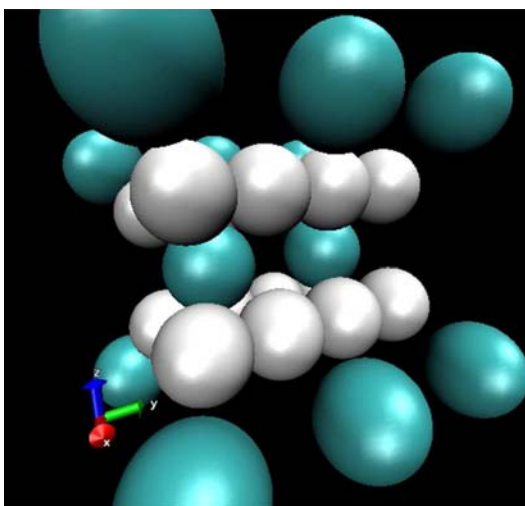


Figure 2. Schematic diagram of the crystal structure of CH₄(H₂)₄ determined from molecular simulations and DFT calculations. The blue spheres represent CH₄ molecules, whereas the white spheres represent H₂ molecules.

Figure 2 shows one of the favored structures for $\text{CH}_4(\text{H}_2)_4$ calculated from DFT. The 4 CH_4 molecules and the 16 H_2 molecules fit into an orthorhombic cell ($\alpha = \beta = \gamma = 90^\circ$) with side lengths $a = 6.872 \text{ \AA}$, $b = 7.342 \text{ \AA}$ and $c = 6.608 \text{ \AA}$, which results in a cell volume of 332 \AA^3 and a density of 479 kg/m^3 ; this is close to the expected density of 484 kg/m^3 . The simulation box, in fact, contains two unit cells along the b direction, each containing 2 CH_4 molecules and 8 H_2 molecules.

The methane substructure of $\text{CH}_4(\text{H}_2)_4$ was also investigated experimentally at high pressure and low temperature using X-ray diffraction (XRD). A nominally 4:1 fluid mixture of hydrogen and methane (80.6 mol% and 19.4 mol%, respectively) was loaded into a symmetric diamond anvil cell using a gas-loading system at 200 MPa. After the sample was clamp-sealed in the gasket at 2.2 GPa, the DAC was removed from the gas vessel, and the pressure was further increased to 3.5 GPa. Angle-dispersive XRD data were taken at beamline 16-IDB of the High Pressure Collaborative Access Team (HPCAT), Advanced Photon Source (APS), Argonne National Laboratory (ANL).

Refinement of hydrogen positions from XRD spectra depends on the availability of reliable intensity data, which was challenging because of the weak interaction of hydrogen with X-rays and the coarse crystallinity of the sample. The XRD spectra for $\text{CH}_4(\text{H}_2)_4$ were composed of numerous large spots, as opposed to smooth Debye rings. While this renders the intensities obtained using this method unusable for refinement of atomic positions, the peak positions were used to constrain the unit cell symmetry for comparison with our theoretical calculations. The most likely candidates were the orthorhombic space groups $\text{Cmc}21$, $\text{Ccc}2$, $\text{Amm}2$, and $\text{Ama}2$.

Discussion

The calculations predict that the H_2 molecules are located between the center and the corner CH_4 molecules of the unit cell. Moreover, the calculations show that the bond axis of the H_2 molecules does not directly point towards the hydrogens of methane, but can not resolve between orientations where the hydrogen molecules are directed away from the C-H bonds. Different H_2 orientations would result in a different chemical environment for the CH_4 molecules at the center and the corner of the unit cell. This is consistent with the previous observations from Raman spectroscopy of two distinct hydrogen sites.

Interactions of the hydrogen molecules with their two nearest methane molecules allow the hydrogen molecules to be spaced very closely. In the calculated structure the average intermolecular distance between the different H_2 molecules is 3.30 \AA , which is smaller than those in solid hydrogen at the normal freezing point (3.78 \AA). Increased intermolecular interactions is thus found in $\text{CH}_4(\text{H}_2)_4$ as was observed previously in hydrogen clathrate hydrates, with the important difference that in this case the hydrogen molecules do not form clusters and their intermolecular interactions are mediated by the methane sublattice. Moreover, it is likely that other hydrogen-rich materials at high density will show a wide range of novel bonding. This implies that bonding can be tuned by increasing pressure in hydrogen-rich dense environments. The combined approach presented here can also be applied broadly to design optimized hydrogen storage materials with high storage capacity. First, new hydrogen-rich phases at high pressure can be discovered, followed by stabilizing these phases to lower pressures on the basis of an

understanding of the structure and interactions. For example, after the structure of the $\text{H}_2(\text{H}_2\text{O})_2$ clathrate was determined, it was found that the clathrate structure could be stabilized by the addition of a third compound: a promoter which reduced the pressure necessary to synthesize the clathrate at 280 K from 300 MPa down to 5 MPa.

Conclusions

The goal for this one-year exploratory proposal was to establish the efficacy and potential of our approach for finding practical high-capacity hydrogen storage materials which can be used at practical conditions. In the test case of $\text{CH}_4(\text{H}_2)_4$, our calculations indicate that the structure of this very hydrogen-rich compound is orthorhombic with methane molecules at the corners and unit cell center. Independent high pressure DAC experimental results are consistent the theoretically predicted structure. This work demonstrates that this theoretical approach can be used to elucidate the bonding and structure of hydrogen-rich phases under a wide range of conditions, which provides direction for understanding the intermolecular interactions in these materials. In this way, the influence of pressure, temperature and composition on the structure and interactions of a variety of hydrogen-rich phases can be explored more efficiently and effectively. An option for lowering the required pressure is the addition of a species to increase the interaction with hydrogen; for example, recent theoretical work suggests that the addition of Li to metal-organic frameworks could improve hydrogen binding. Another possibility is to modify the structure of $\text{CH}_4(\text{H}_2)_4$ into an inclusion compound by addition of a cage-former (e.g. H_2O or an alcohol). We are testing these approaches and also exploring the rich $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$ ternary system and other hydrogen rich binaries (e.g. ammonia borane (NH_3BH_3) and silane (SiH_4) in the presence of additional molecular H_2) using the integrated experimental and theoretical approach. We plan to continue study these materials during the no-cost extension period which will run until the end of October 2010.

Publications

Kroon, M. C., H. Docherty, P. T. Cummings, C. J. Peters, G.-J. Witkamp, and W. L. Mao. Novel Interactions in Hydrogen-Rich van der Waals Compound $\text{CH}_4(\text{H}_2)_4$, JACS, submitted.

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