

## IV.H.8 Novel Molecular Materials for Hydrogen Storage Applications

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### Objectives

- Discover, identify and characterize novel hydrogen-rich compounds that can be used for hydrogen storage or as agents for rehydrogenation of hydrogen storage materials at high pressures.
- Investigate high pressure routes to rehydrogenating ammonia borane and polymeric complexes of ammonia borane.
- Investigate interaction of hydrogen with metallo-organic polymers at high pressures and high temperatures to identify new *Kubas complexes* capable of high potential for hydrogen retention.

### Technical Barriers

- Understanding the structural basis of the high pressure interaction of molecular hydrogen requires using a combination of Raman and infrared spectroscopies and preferably neutron diffraction of small sub-mm<sup>3</sup> samples in high pressure diamond anvil cells.
- Developing new strategies to extract information about reaction kinetics and thermodynamics of chemical reactivities at elevated pressure-temperature conditions needs development of appropriate spectroscopy protocols as well as diamond cells that allow introduction of reactants, extraction of products and capability to initiate/arrest the chemical reaction.
- Developing strategies to metastably recover materials synthesized at high pressure – high temperature conditions.

### Abstract

The technology of using hydrogen as an environmentally clean and efficient fuel is an active research area worldwide [1-3]. The key to emergence of a viable global hydrogen economy is the availability of light weight transport and safe storage of hydrogen as a fuel. Major factors that dictate this include high volumetric and gravimetric density of the storage media, optimal thermodynamics and kinetics of hydrogenation and re-hydrogenation, ease of handling, and small environmental footprint. The effort to develop new materials and investigate their thermo-physical tunability is outpaced by the growing world energy consumption [4]. There are currently four leading methods to store hydrogen: physical means, sorbents, metal hydrides (classical and complex), and so-called chemical hydrides. At the heart of the issue is the fact that hydrogen is a gas at standard pressure and temperature and therefore low volumetric density.

On other hand, hydrogen molecules can bind to the surface of any material either through weak dispersive interactions (physisorption) or through stronger chemical bonding (chemisorption). Storage via physisorption in metal-organic or covalent-organic frameworks and activated carbons is a field that has received a lot of experimental and theoretical attention [5-9]. While both these routes to hydrogen storage show a high degree of reversibility (rehydrogenation), they suffer from poor retention and low gravimetric capacity limiting their storage capability to low temperatures (typically below 77 K) and off-board applications.

Hydrogen clathrates and molecular (van der Waal) compounds of H<sub>2</sub> and other simple molecules such as CH<sub>4</sub>, NH<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub> have been known to form under high pressures and some of them can be recovered at ambient pressure and low temperatures [10-11]. The hydrogen storage potential of such clathrates and molecular compounds has received much attention not only because of their superior gravimetric capacity (the compound CH<sub>4</sub>(H<sub>2</sub>)<sub>4</sub> has 33.4 wt% of stored hydrogen and is found stable at ambient pressure and 77 K), but potentially small environmental footprint and high degree of reversibility [12].

### Progress Report

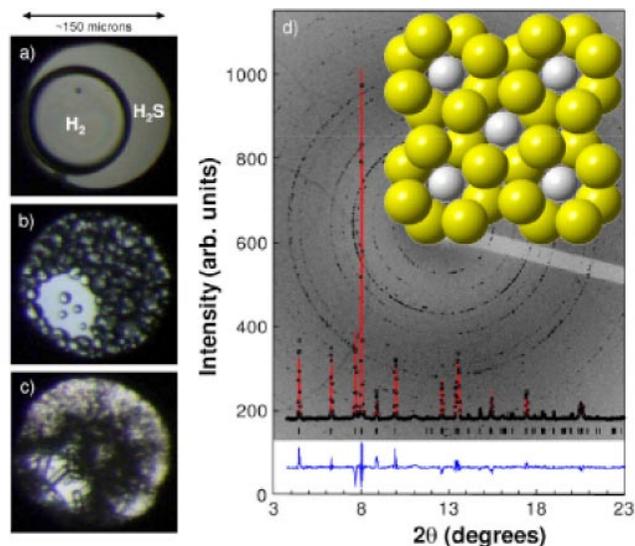
We have discovered a new structure type in the H<sub>2</sub>-H<sub>2</sub>O system at low pressure-temperature conditions. The structure of the new phase is consistent with a water framework similar to  $\alpha$ -quartz; the structure could also be related to the tetragonal clathrate phase reported previously for nitrogen and argon guests.

Raman spectroscopy and synchrotron X-ray diffraction are used to examine the high-pressure behavior of tetramethylammonium borohydride (TMAB) to 40 GPa at room temperature. The measurements reveal weak pressure-induced structural transitions around 5 and 20 GPa. Rietveld analysis and Le Bail fits of the powder diffraction data based on known structures of tetramethylammonium salts indicate that the transitions are mediated by orientational ordering of the  $\text{BH}_4^-$  tetrahedra followed by tilting of the  $(\text{CH}_3)_4\text{N}^+$  groups.

Hydrogen sulfide ( $\text{H}_2\text{S}$ ) and hydrogen ( $\text{H}_2$ ) crystallize into a ‘guest-host’ structure at 3.5 GPa and, at the initial formation pressure, the rotationally disordered component molecules exhibit weak van der Waals type interactions. With increasing pressure, hydrogen bonding develops and strengthens between neighboring  $\text{H}_2\text{S}$  molecules, reflected in a pronounced drop in S-H vibrational stretching frequency and also observed in first-principles calculations. At 17 GPa, an ordering process occurs where  $\text{H}_2\text{S}$  molecules orient themselves to maximize hydrogen bonding and  $\text{H}_2$  molecules simultaneously occupy a chemically distinct lattice site. Intermolecular forces in the  $\text{H}_2\text{S}+\text{H}_2$  system may be tuned with pressure from the weak hydrogen-bonding limit to the ordered hydrogen-bonding regime, resulting in a novel clathrate structure stabilized by cooperative interactions.

Previous efforts had focused on the  $\text{NH}_3\text{BH}_3/\text{H}_2$  system and its polymeric analogs which were found to form van der Waals compounds at elevated pressures. In order to address questions regarding rehydrogenation of spent BN materials, compounds of the series  $\text{NR}_x\text{H}_{(3-x)}\text{BH}_3$  were analyzed using gas phase G3MP2 calculations previously shown to reproduce BN and BH bond forming reactions to within 1.0 and 1.8 kcal/mol, respectively.  $\text{Me}_2\text{NHBH}_3$  was down selected from the series due to the inability of the compound to lose multiple equivalents of  $\text{H}_2$  and the modest enthalpy associated with the hydrogen release reaction as compared to other compounds of the series.  $\text{Me}_2\text{NHBH}_3/\text{H}_2$  mixtures were found to hydrogenate ethylene and carbon dioxide at room temperature and pressures above 0.5 GPa. Control cells with no  $\text{Me}_2\text{NHBH}_3$  showed no reaction after several weeks. The reaction with  $\text{CO}_2$  was found to consistently produce  $\text{CH}_4$  as the only product, but due to the multiple phases present, rates of the reaction have difficult to measure.

As a continuation of our high pressure studies of metal-rich hydrides, we continued to pursue synthesis, characterization and high pressure studies on this unique class of hydrides. The structural behavior of  $\text{Na}_2\text{ReH}_9$  and  $\text{K}_2\text{ReH}_9$  at high pressure was studied using in situ Raman spectroscopic and X-ray diffraction studies at high-pressure. The measurements reveal new phase transformation above 9 GPa and 18 GPa for both  $\text{Na}_2\text{ReH}_9$  and  $\text{K}_2\text{ReH}_9$  due to compression. The deuterated analogues have been synthesized and characterized. These samples were used to



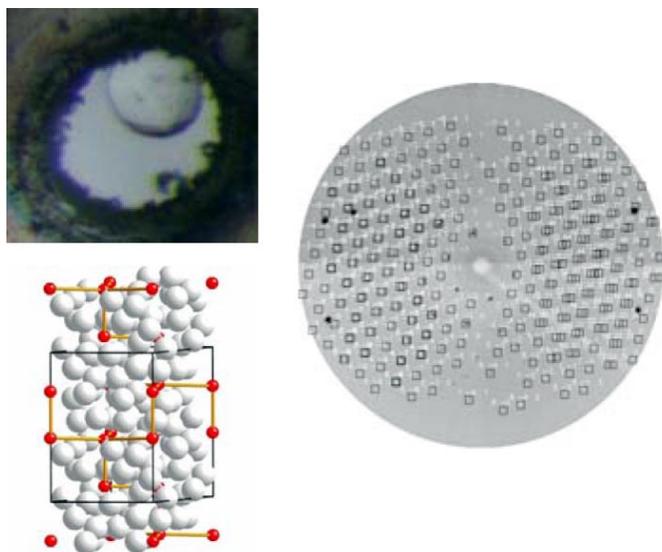
**FIGURE 1** (color online). Photomicrographs of  $\text{H}_2 + \text{H}_2\text{S}$  mixtures at room temperature: (a) 0.2 GPa: fluid  $\text{H}_2$  and liquid  $\text{H}_2\text{S}$ ; (b) 1.0 GPa; fluid  $\text{H}_2$  and solid  $\text{H}_2\text{S}$  phase I; (c) 3.5 GPa: fluid  $\text{H}_2$  and compound. Dark areas result from light scattering off grain boundaries and dissipated with time. (d) Experimental diffraction pattern ( $\lambda = 0.40548 \text{ \AA}$ ) at 4.5 GPa (points) and Rietveld profile refinement (red line). Difference is shown as lower blue trace,  $R_{wp} = 3.52\%$ . The background shows the two-dimensional diffraction image, and the crystal structure, normal to the  $c$ -axis, is provided as the inset; yellow and white spheres represent disordered  $\text{H}_2\text{S}$  and  $\text{H}_2$  molecules, respectively.

obtain in situ diffraction patterns at high pressures using the Paris-Edinburgh cell at SNS.

The solid phase that occurs at 4.2 GPa and 300 K in the Xe- $\text{H}_2$  system has been identified as  $\text{Xe}(\text{H}_2)_{24}$ . The stoichiometry has been deduced from a determination of the overall xenon stoichiometry based on direct method solution of the crystal structure. The volume of the unit cell and the known molar volume of xenon at this pressure is then used to determine the lower bound on the hydrogen stoichiometry. Refinement of crystal structure indicates higher hydrogen content based on the fact that the xenon site occupancy is lower than unity for one of the three sites. Raman spectroscopy and X-ray diffraction studies show that this phase can be retrieved at 90 K and at atmospheric pressure.

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**FIGURE 2.** Photomicrograph of  $\text{Xe}(\text{H}_2)_{24}$  in a diamond cell. The diffraction pattern could be indexed to a hexagonal unit cell and the structure of the xenon sublattice is shown in red. The hydrogen molecules are shown in gray.

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### Publication list (selected) acknowledging the DOE grant or contract

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