IV.I.4 Novel Molecular Materials for Hydrogen Storage Applications

P.I. Russell J. Hemley
Geophysical Laboratory,
Carnegie Institution of Washington

Contract Number: DE-FG02-06ER43280
Date of submission: 4/24/2009.
Covering the period 4/01/08 – 4/01/09.

Accomplishments:

1. Ammonia Borane - Rehydrogenation and Complexation at high P-T

Hydrogen interactions with NH\textsubscript{3}BH\textsubscript{3} and its thermal residues have been investigated at pressures up to 10 GPa using in situ Raman spectroscopy in a Diamond Anvil Cell. At room temperature, pressure-induced complexation in the NH\textsubscript{3}BH\textsubscript{3}-H\textsubscript{2} system has been observed at 6.7 and 10 GPa. The formation of these complexes is accompanied by the appearance of vibrational modes shifted to a lower frequency at 5.7 GPa and to higher frequency at 10 GPa, relative to that observed in pure H\textsubscript{2}. In comparison to pure NH\textsubscript{3}BH\textsubscript{3}, there are no noticeable changes to the internal modes of NH\textsubscript{3} and BH\textsubscript{3} functional groups in these complexes suggesting a close structural relationship to the corresponding high pressure phase of pure NH\textsubscript{3}BH\textsubscript{3}. A likely origin of these intermolecular interactions is due to H\textsubscript{2} molecules that are stabilized by the dihydrogen bonding network in NH\textsubscript{3}BH\textsubscript{3}. In another set of experiments conducted with thermal residues of NH\textsubscript{3}BH\textsubscript{3}, i.e., polymeric aminoborane [-\textsubscript{2}(NH\textsubscript{3}BH\textsubscript{3})] \textsubscript{3} and polymeric iminoborane [-\textsubscript{2}(NHBH)\textsubscript{x}], it was found that H\textsubscript{2} preferentially complexed with these residues. The complexation was observed at pressures as low as 2 GPa at room temperature evidenced by the appearance of a broad low frequency H\textsubscript{2} stretching mode. Pressure-quenched complexes exist metastably at ambient conditions. This study has identified novel B-N-H complexes and established a complexation-based approach of hydrogen reuptake by chemical hydrides that could be extended to light metal complex hydrides as well.

2. Hydrogenation Studies in COF-102

The structural rigidity and behavior of COF-102 under pressure was explored using three different pressure media – silicone oil, Ar and H\textsubscript{2} by following the compressibility and deviation from cubic symmetry. The powder X-ray diffraction experiments performed at the 16-ID-B beamline on samples of COF-102 supplied by the Yaghi group showed remarkable incompressibility in H\textsubscript{2} while the structure collapsed quickly at pressures below 1 GPa in other media. Using the data obtained from Ar and H\textsubscript{2} media, we estimate the amount of H\textsubscript{2} that can be packed into this material at high pressures and conclude that as much as 12 wt% of hydrogen storage can be effected using pressure. We also performed low temperature release experiments while monitoring the volume of the unit cell. The cell volume changes associated with H\textsubscript{2} release is observed to occur step-wise and complete at 59 K. Comparing the IR measurements on COF samples with and without H\textsubscript{2} indicates that there could be multiple sites of H\textsubscript{2} molecular adsorptions within the framework consistent with this observation of stepwise release. The H\textsubscript{2} vibron shows a decrease in frequency in comparison to that observed in pure H\textsubscript{2} and also shows a higher IR activity indicative of interaction between the framework and the adsorbed molecules rather than a purely pressure-induced packing.

3. Studies on the Silane-Hydrogen Binary System

Under high pressure conditions, methane (CH\textsubscript{4}) was previously shown to form at least four stoichiometric van der Waals compounds with hydrogen (H\textsubscript{2}). Recently, we have made significant progress in investigating interactions between molecular hydrogen and other group IVa covalent hydrides. We have demonstrated the formation of a novel compound of silane (SiH\textsubscript{4}) and H\textsubscript{2} that displays markedly stronger intermolecular interaction than previously reported compounds. Vibrational spectroscopy of the new compound has revealed large H\textsubscript{2} binding energies that tend towards a “Kubas-like” state with pressure. These pressure induced interactions may be helpful in the design of novel storage materials with larger H\textsubscript{2} binding interaction.

4. Xe\textsubscript{4}(H\textsubscript{2})\textsubscript{21} – A New Hydrogen-Rich Molecular Compound

Single crystal X-ray diffraction and optical spectroscopy measurements reveal the formation of a number of stable compounds in the Xe-H\textsubscript{2} binary system. At 4.8 GPa, a unique, hydrogen-rich, trigonal structure forms that can be viewed as a tripled solid hydrogen lattice modulated by layers of Xe, which in turn consists of xenon dimers. The structural refinements, based on new single crystal diffraction techniques, also provide clear evidence for pressure-induced changes in electron density associated with the formation of bonding states between xenon atoms and hydrogen molecules. Raman and infrared spectroscopy measurements reveal complex
interactions in this hydrogen-rich, van der Waals solid that is stable to pressures as high as 255 GPa.

5. Hydrogen Storage Studies in Crown Ethers

Crown ethers that form the backbone of supramolecular synthesis have been predicted to complex with H$_2$ molecules via the lone pair oxygens. There has been considerable interest in harnessing this interaction as well as the ability of crown ethers to form polymeric, transition metal-ion complexes to design new hydrogen storage materials. We have investigated the complexation of 12-crown-4; 15-crown-5 and 18-crown-6 with hydrogen at pressures up to 20 GPa and temperatures up to 600 K. In situ Raman and IR spectroscopy measurements indicate modulation of the C-O-C and H-H vibrational frequencies at pressures above 1.2 GPa indicative of active complexation. Surprisingly, larger pore size is observed to decrease complexation as observed from comparison of the pressures dependencies of vibrational frequencies in Ar, Ne and H$_2$ media. Low temperature release experiments in 15-crown-5 show that hydrogen is released in a single step at 160 K and can be efficiently replaced into the system at pressures as low as 0.2 GPa and 500 K.

6. Search for New Compounds in H$_2$-H$_2$O System

The H$_2$ – H$_2$O system shows several stoichiometric compounds which may have potential for H$_2$ storage. Three high H$_2$ content compounds are currently known: sII clathrate (3.8 wt% H$_2$), filled ice C1 clathrate (1.8 wt% H$_2$), and filled ice C2 clathrate (10.1 wt% H$_2$). Exploration of new portions of the phase diagram may yield novel high energy content compounds. Recently, we made spectroscopic observations upon cooling samples of C1 and C2 clathrate indicating structural changes within the clathrate framework. As the samples were cooled, new features in both the rotational and vibrational spectra of H$_2$ suggest the presence of novel water environments hosting the H$_2$ molecules. These results may indicate a new low temperature clathrate structure which may have hydrogen storage implications.

Papers Published/Submitted

1. Pressure-Induced bonding and compound formation in Xenon and Hydrogen
   Maddury Somayazulu, Przemyslaw Dera,

   Alexander F Goncharov, Stephen A Gramsch,
   Peter Liermann, Wenge Yang, Zhenxian Liu,

2. A Novel Compound Composed of Molecular Silane and Hydrogen

3. Pressure-induced complexation in NH$_3$BH$_3$-H$_2$

4. Hydrogen interaction with crown ethers at high pressures

5. Inelastic neutron scattering spectroscopy of tetrahydrofuran, hydrogen clathrate

6. Hydrogen storage under pressure in COF-102

Research Personnel supported by this grant at the Geophysical Laboratory

Research Scientists:

(1) Maddury Somayazulu (2 months)
(2) Changzheng Zha (2 months)
(3) Qi Liang (1 month)

Postdoctoral Fellows:

(1) Weinberger, Michelle (100%)
(2) Chellappa, Raja (100%)
(3) Janolin, Pierre-Eymeric (2 months)

Technical Staff:

(1) Krasnicki, Szczesny (6 months)
(2) Lai, Joseph (2 months)
(3) Yu, Thomas (7 months)