

IV.I.5 Bonding and Structures of Light Element-Hydrogen Systems under Extreme Conditions

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Progress

Since the project began last year, we have been working on a number of high pressure experimental studies on hydrogen-rich light element phases to improve our understanding of the bonding and structures in these materials and their interactions with hydrogen. Notable progress in specific Group III-VI second row element systems are as follows:

H₂O & H₂O-H₂ system: We investigated the temporal, compositional, and compressional behavior of samples of H₂-H₂O, H₂O, and D₂O after X-ray irradiation. Unlike pure H₂O ice VII, C₂ which is hydrogen-filled ice Ic, did not dissociate in the presence of X-rays until 7 GPa. We collected data on the vibrational shifts of the new H₂-O₂ compound to 70 GPa and found that the behavior diverged from pure H₂ and O₂ with increasing compression. We are collaborating with Anders Nilsson's group to look at the structure of compressed H₂O using X-ray Raman. We conducted measurements at spectroscopy at SSRL beamline 6.2 on H₂O at 0.2 GPa in March 2009.

CH₄ and CH₄-H₂ system: We have been studying the high pressure behavior of pure CH₄ which we studied up to 200 GPa. We found that CH₄ remains in a cubic structure and as an insulator up the highest pressure studied. These results were published this month in *Chem. Phys. Lett.* We have initiated molecular simulations using the random generation of initial configurations approach which has been applied successfully to multi-component molecular systems to investigate the structure of CH₄(H₂)₄. A number of lowest energy configurations were found and they are the beginning input for the DFT calculations we are currently running. We are comparing these results with high pressure X-ray diffraction data on CH₄(H₂)₄ collected in December 2008. We looked at substituting carbon for the larger silicon as a means of chemical pre-compression to stabilize the CH₄(H₂)₄ structure to lower pressure. We studied the SiH₄-H₂ binary phase diagram at high pressure and ambient temperature,

and found that unlike CH₄-H₂ which has at least four stoichiometric crystalline phases, SiH₄-H₂ forms a simple eutectic.

Boron & Boranes: We investigated changes in the bonding of decaborane (B₁₀H₁₄) in a hydrogen-rich environment at high pressure using Raman spectroscopy. We found a transition at 3 GPa and a non-negligible amount of molecular H₂ dissolved in the decaborane at high pressure. This result is submitted to *J. Chem. Phys.* We studied the X-ray Raman spectra of amorphous and crystalline boron to 5 GPa. There appears to be a transition in the amorphous boron at 5 GPa, but we need high pressure data to confirm this result.

Ammonia: We collected XRS, XRD, and Raman spectroscopy on irradiated NH₃ for both fluid and solid phases at high pressure and found complicated radiation chemistry which we are currently analyzing (Figure 1). The incident 10 keV X-rays for XRS induced dissociation of NH₃, and we observed miscibility of H₂ and N₂ in the fluid phase at lower pressure and evidence for formation of a N₂-H₂ compound at higher pressure (7-8 GPa).

Ammonia borane: We investigated changes in bonding in ammonia borane (AB), NH₃BH₃ to pressures above 20 GPa using Raman spectroscopy, and found a number of phase transitions occur in over the pressure range studied which we plan to investigate using X-ray diffraction. The vibrational modes of the NH₃ proton donor group exhibited negative pressure dependence, consistent with the behavior of conventional hydrogen

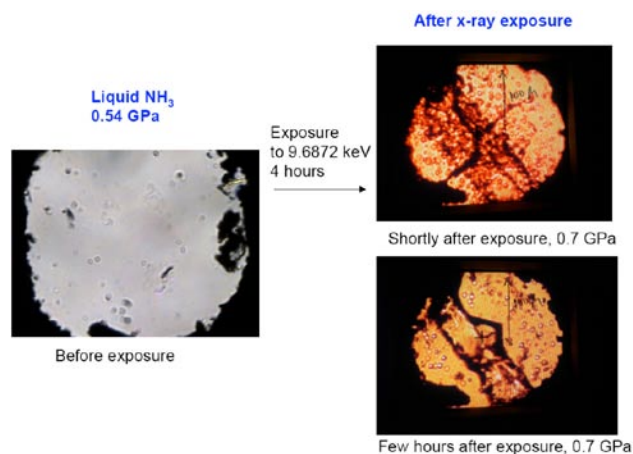


FIGURE 1. Photomicrographs of NH₃ sample in a diamond anvil cell before and after exposure to ~10 keV X-rays. The darkened/cracked region shows where the beam passed through the sample and where we observed decomposition of NH₃ into a mixture of N₂ and H₂.

bonds, while the BH_3 proton acceptor group showed a positive dependence, supporting the presence of dihydrogen bonding at high pressure. This work was published in *J. Chem. Phys.* We have also looked at AB in the presence of excess hydrogen (H_2) pressure and discovered a solid phase, $\text{AB}(\text{H}_2)_x$, where $x \sim 1.3\text{--}2$. The new AB-H₂ compound can store an estimated 8–12 wt% molecular H_2 in addition to the chemically bonded H_2 in AB. This result is in press in *PNAS*. We have collected XRD on both pure AB and $\text{AB}+\text{H}_2$ to 20 GPa to look at the structural changes during these transitions.

Publications

1. S. Wang, **W.L. Mao**, and S. Thomas Autrey, Bonding in boranes and their interaction with molecular hydrogen at extreme conditions, *J. Chem. Phys.* submitted.
2. Y. Lin, **W.L. Mao**, and H-k. Mao, Storage of molecular hydrogen in a novel ammonia borane compound at high pressure, *Proc. Natl. Acad. Sci.* in press.
3. L. Sun, W. Yi, L. Wang, J. Shu, S. Sinogeikin, Y. Meng, G. Shen, L. Bai, Y. Li, J. Liu, H-k. Mao, **W.L. Mao**, X-ray diffraction studies and equation of state of methane at 200 GPa, *Chem. Phys. Lett.* **473**, 72-74, 2009.
4. Y. Lin, V. Dozd, J. Chen, L. Daemen, and **W.L. Mao**, Raman spectroscopy study of ammonia borane at high pressure, *J. Chem. Phys.* **129**, 234509, 2008.

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