

## IV.I.11 Control of Hydrogen Release and Uptake in Condensed Phases

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Contract Number: DE-AC05-76RL01830

### Motivation

Energy from renewable resources (e.g., solar and wind) are critical to a clean energy future. Methods to store renewable energy (e.g., hydrogen) are required to balance energy production with energy demand. The long-term objective of our research is to gain fundamental insight into the chemical and physical properties of hydrogen-rich materials that will provide the basis for developing new hydrogen storage systems.

### Outstanding Issues

- Molecular level interactions play an important role in the kinetics and thermodynamics of hydrogen release and uptake in condensed phases.
- How do dihydrogen bonding interactions affect the structure and dynamics of hydrogen rich molecular crystals (ammonia borane, ammonium borohydride, amido boranes)?
- What are the inherent structures of catalysts that facilitate the release of hydrogen from these inorganic materials containing both hydridic and protonic hydrogen?
- How do environmental factors such as nano-confinement modify the thermodynamics and kinetics of molecular crystals?

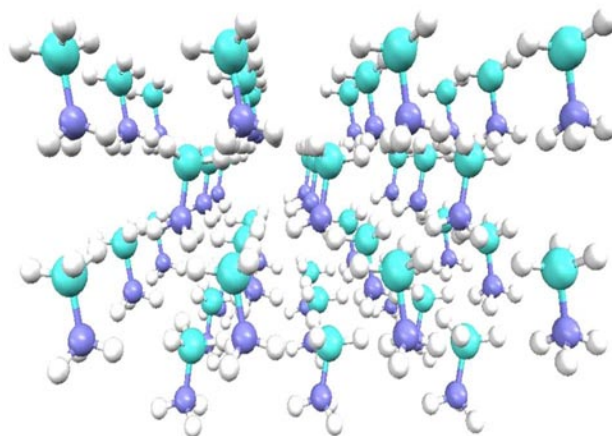
### Approach

Use experiment and theory to gain insight into mechanisms of environmental conditions, (i.e., electrostatic interactions, nano-confinement, catalysis), that provide tunable parameters to enhance kinetics and modify the thermodynamics in hydrogen-rich molecular crystals.

One critical aspect of hydrogen storage is the kinetics of hydrogen release and uptake from

materials containing ionic or covalently bound hydrogen. Specifically we are studying how the reaction environment can be used to control reactivity and selectivity of a reaction pathway. Fundamental insight into mechanisms of external parameters such as catalysis, nano-confinement, and electrostatic molecular interactions can all provide tunable mechanisms to enhance the kinetics of hydrogen release and uptake. Of special interest is the dynamics of dihydrogen bonding, the interaction between hydridic and protonic hydrogen. These electrostatic interactions between molecules affect both the structure and dynamics of hydrogen rich materials in the condensed phase. We have proposed that materials composed of both hydridic and protonic hydrogen will lead to enhanced kinetics for hydrogen release. To gain some fundamental insight into this hypothesis our group uses spectroscopic methods (NMR, Raman and Neutrons) to study the dynamics of hydrogen bonding interactions in condensed phase materials. We are also interested in catalysts that activate the release of hydrogen from materials containing both hydridic and protonic hydrogen and use in situ XAFS to directly study sub-nano metal clusters that active the release of hydrogen bonded to light elements.

At present we are studying the structure and dynamics of ammonia borane  $\text{NH}_3\text{BH}_3$ . This compound, a simple donor-acceptor complex formed by a dative bond between the non-bonding electrons on nitrogen with the empty p-orbital of borane, organizes in to a molecular crystal by virtue of (1) dipole-dipole interactions and (2) the di-hydrogen bonds formed between the protonic NH and hydridic BH groups in adjacent molecules. We believe the interactions between the hydridic and protonic hydrogen



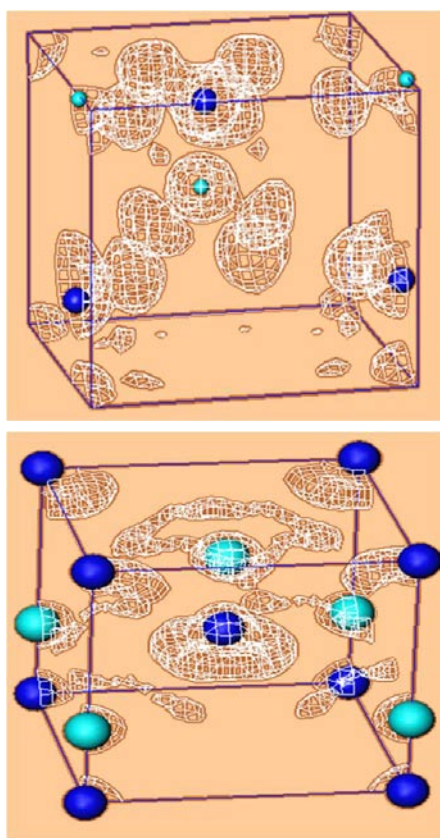
**FIGURE 1.** Orthorhombic phase (N = violet, B is turquoise, H = white) showing di-hydrogen bonding network in molecular crystal of ammonia borane.

leads to the low temperature loss of hydrogen in solid state ammonia borane.

Our group has experience in synthetic chemistry that enables us to make selectively labeled materials for spectroscopic investigations. Preparation of  $^{11}\text{B}$  enriched boron compounds enhances results from our neutron scattering work. For NMR studies we prepare  $^{15}\text{N}$  enriched materials for in situ kinetic studies. Alternatively we can selectively incorporate deuterium into the molecule to mask the neutron signal or emphasize the NMR signal. ( $\text{NH}_3\text{BH}_3$ ,  $^{15}\text{NH}_3\text{BH}_3$ ,  $^{11}\text{BH}_3\text{NH}_3$  and the corresponding deuterium labeled compounds  $\text{ND}_3\text{BH}_3$ ,  $\text{ND}_3\text{BD}_3$ ,  $\text{NH}_3\text{BD}_3$ )

#### a. Neutron Scattering Spectroscopy (in collaboration with Luke Daemen and Thomas Proffen at LANSCE)

Neutron scattering methods are ideally suited for investigation of light elements and in particular hydrogen. A variety of neutron scattering methods are well suited to study the structure and dynamics of

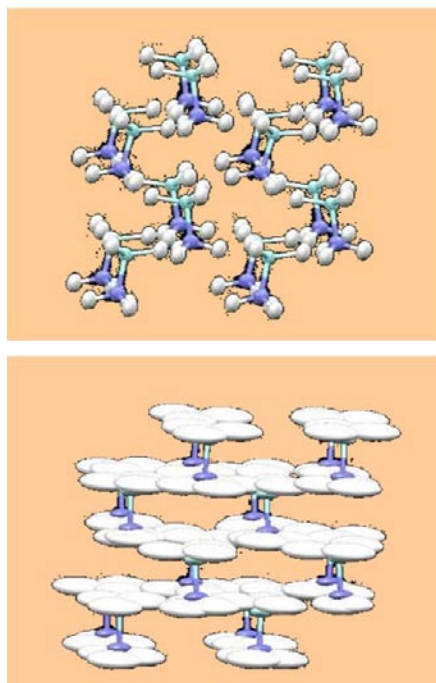


**FIGURE 2.** Experimentally measured thermal ellipsoids from neutron diffraction experiments at temperatures above and below the phase transition. The size of the ellipsoids about the B and N atoms suggests the hydrogen is substantially more mobile in low temperature phase (top) than room temperature phase (bottom).

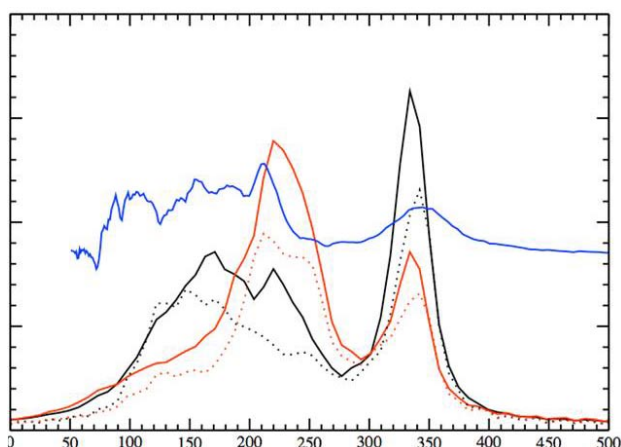
molecular crystalline ammonia borane. Neutron powder diffraction (NPDF) can be used to obtain structure as a function of environment (temperature, pressure, nano confinement) and to yield specific location of hydrogen atoms. Inelastic incoherent neutron scattering (IINS) provides low temperature vibrational spectra to study chemical bonding and dynamics, including hydrogen bond dynamics. The spectrum is also a useful fingerprint to identify ammonia-borane and the effect on the solid of chemical environment.

**Neutron Powder Diffraction (NPDF).** Diffraction patterns at different temperatures, above and below the 220 K phase transition have been collected on the Neutron Powder Diffractometer, NPDF – a high-resolution total scattering powder diffractometer at LANSCE. At 175 K, the axes of ammonia-borane molecules are nearly aligned with the c-axis of the unit cell and the adjacent  $-\text{BH}_3$  and  $-\text{NH}_3$  groups are not quite coplanar. There are 6 total hydrogen bonding interactions per molecule providing a calculated cohesive energy of 76-90 kJ/mol, however, the rotational barrier of the  $-\text{BH}_3$  and  $-\text{NH}_3$  groups are surprisingly low indicative of very dynamic motion.

**Incoherent Inelastic Neutron Scattering. (IINS).** We used the filter difference spectrometer (FDS) at LANSCE to collect low frequency vibrational spectra of three ammonia-borane isotopomers:  $\text{NH}_3^{11}\text{BH}_3$ ,  $\text{ND}_3^{11}\text{BH}_3$ , and  $\text{NH}_3^{11}\text{BD}_3$ . Isotopic substitution takes advantage of the large incoherent scattering cross section



**FIGURE 3.** Calculated thermal ellipsoids for the same structures. There are weaker interactions between the hydrogens in the room temperature phase of AB is likely the discrepancy for the structure and dynamics.



**FIGURE 4.** Comparison of the low frequency ( $\text{cm}^{-1}$ ) torsional modes in the vibrational spectrum of ammonia-borane,  $\text{NH}_3^{11}\text{BH}_3$  obtained from experimental and MD simulation (CP2K dynamics). The blue line is experimental (IINS) and the red line is the simulated spectra focused on the  $\text{NH}_3$  side of the molecule and the black line is the simulated spectra focused on the  $\text{BH}_3$  side of the molecule.

of hydrogen (compared to deuterium) to facilitate vibrational mode assignment. The low frequency portion of the vibrational spectrum of ammonia-borane is shown in Figure 4. The relatively broad band at  $350\text{ cm}^{-1}$  is the torsional mode of the molecule in which  $\text{NH}_3$  and  $\text{BH}_3$  rotate about the B-N axis with opposite phases. This mode is not IR- or Raman-active. The  $350\text{ cm}^{-1}$  band in the experimental vibrational spectrum is somewhat broader than the internal modes and much broader than the external modes below  $250\text{ cm}^{-1}$ . Preliminary MaxEnt analysis suggests that this band maybe comprises two bands at slightly different frequencies. Computational work is in progress to develop models to help understand the fundamental properties of hydrogen bonding interactions in ammonia borane.

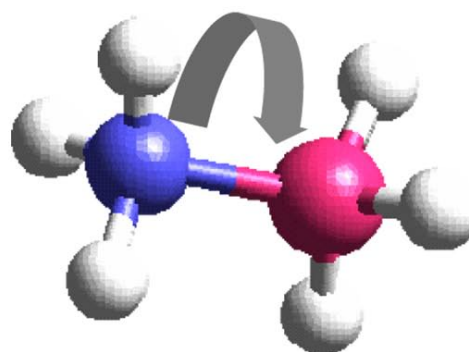
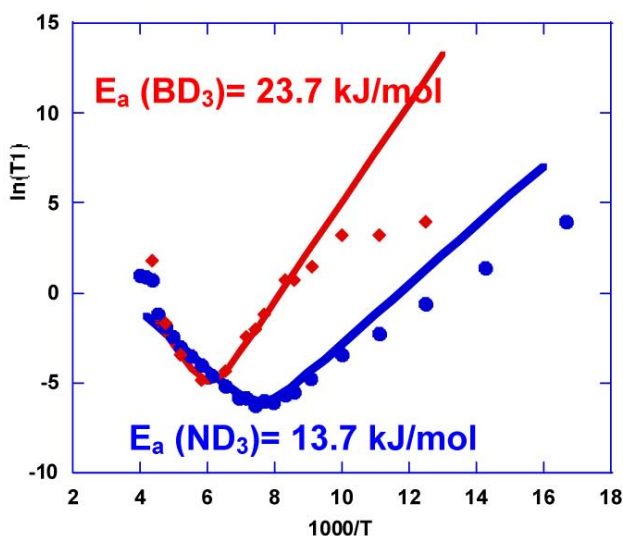
## b. NMR Spectroscopy

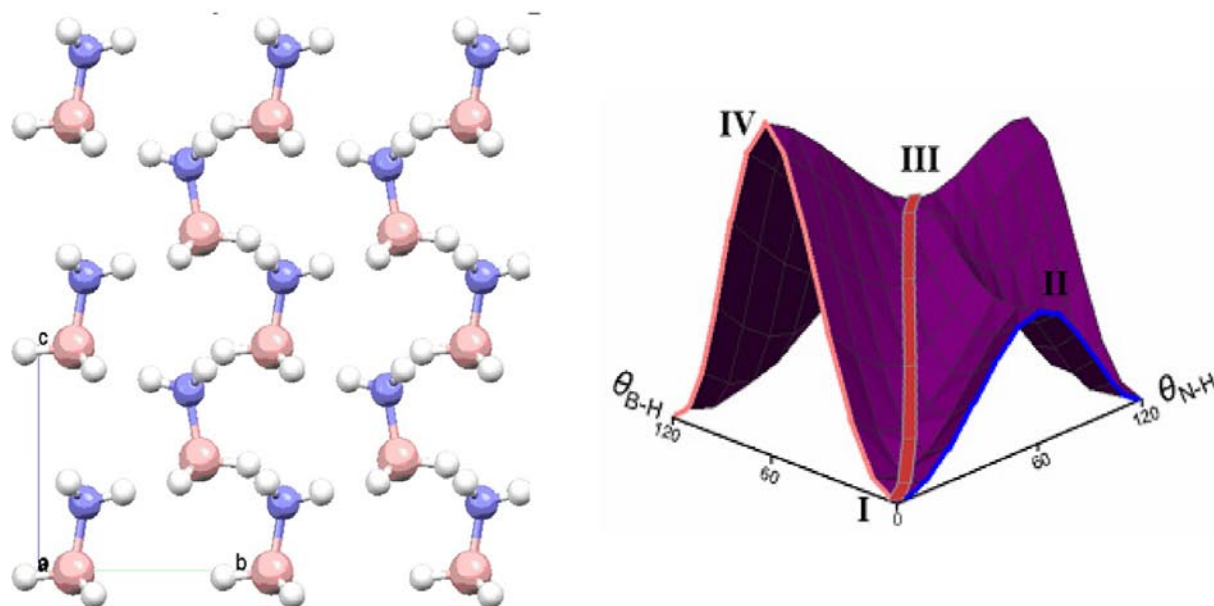
We are using  $2\text{H } ^2\text{H}$  NMR to probe the rotational dynamics in solid phase ammonia borane ( $\text{NH}_3\text{BH}_3$ ). Both the  $^2\text{H}$  line-shape and  $^2\text{H}$  spin-lattice relaxation rate ( $T_1^{-1}$ ) exhibited strong anomalies around 220 K. The analysis of  $T_1^{-1}$  using the Bloembergen-Purcell and Pound (BPP) model showed that the motional correlation time,  $\tau$ , increased from about 1 ps to 100 ps while the corresponding Arrhenius activation energy increased from 6 to 13.4 kJ/mol for the  $\text{NH}_3$  rotor motion.  $^2\text{H } T_1^{-1}$  measurements were obtained for  $-\text{ND}_3$  and  $-\text{BD}_3$  rotor motion over the temperature range from 220 K to 80 K. At higher temperatures ( $>100\text{ K}$ ) the rotational barrier for  $-\text{ND}_3$  (13.7 kJ/mol) was consistent with the barrier  $-\text{NH}_3$  rotation, however at lower temperatures there appears to be an anomaly in the experimental observations. A change in the rotational dynamics could be due to the change in structure as observed by NPDF.

Preliminary calculations (on a cluster of 8 ammonia boranes) performed for the 175 K structure at the DFT level of theory shows great correlation with the rotational barriers determined by NMR  $T_1^{-1}$  experiments.

## c. XAFS Spectroscopy (APS)

We have been interested in developing an understanding of catalytic activation of hydrogen release from amine boranes using a combination of *operando* XAFS and NMR techniques. Operando spectroscopy permits the direct observation of key intermediates under reacting conditions, i.e., at reaction pressure and temperature, to gain insight into catalytic processes. Operando X-ray absorption fine structure (XAFS) spectroscopy has enabled us to identify and characterize a four Rh atom cluster that is a critical species involved in the catalytically-induced release of  $\text{H}_2$  from amine





**FIGURE 5.** DFT calculated barrier for rotation of  $-\text{NH}_3$  (pathway II, 13.1 kJ/mol),  $-\text{BH}_3$  (pathway IV, 30.7 kJ/mol) and whole molecule rotation  $\text{NH}_3\text{BH}_3$  (pathway III, 22.4 kJ/mol) at 175 K. Our calculations confirm the higher rotational barrier for  $\text{BH}_3$  compared to  $\text{NH}_3$  as observed by experiment ( $^2\text{H}$  NMR  $T_1^{-1}$  and QENS). The ground state structure is stabilized by di-hydrogen bonding, however there is greater repulsion between the H-atoms in  $\text{BH}_3$  rotational plane.

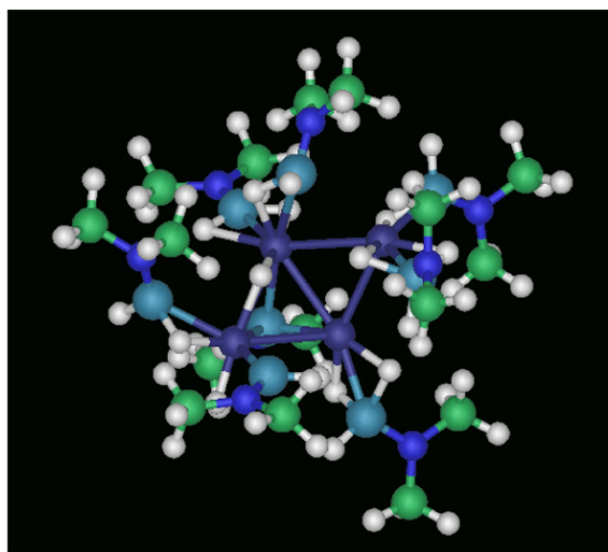
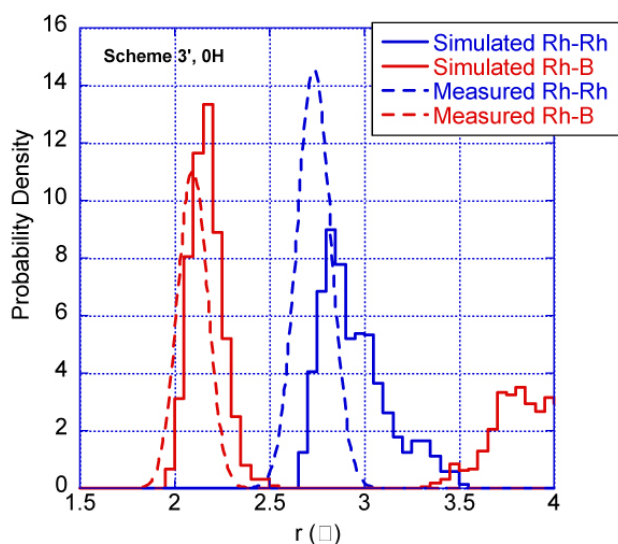
boranes. These results demonstrate that metallic nanoparticles are not directly involved in the catalyzed release of  $\text{H}_2$ . These are important findings that will enable the design of concepts to control transformations in a multitude of related catalytic processes. XAFS spectroscopy shows that the predominate rhodium species formed under the catalysis conditions is a  $\text{Rh}_4$  cluster (diameter of approximately 0.3 nm) rather than a 2 nm-diameter Rh nanoparticle. Knowledge of the Rh structures provides key insights into the catalysis species and the mechanism of the formation of hydrogen from amine borane compounds.

### Publications (2007-2009)

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characterization of the tetragonal-to-orthorhombic phase transformation in ammonia borane. *J. Phys Chem. C.* **2009**, *113*, 5872.

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5. Shawn M. Kathmann, Vencislav Parvanov, Gregory K. Schenter, Ashley C. Stowe, Luc L. Daemen, Monika Hartl, John Linehan, Nancy J. Hess, Abhi Karkamkar and Tom Autrey. Experimental and Computational Studies on Collective Hydrogen Dynamics in Ammonia Borane: Incoherent Inelastic Neutron Scattering. *J. Chem Phys.* **2009**, *130* 024507.
6. David J. Heldebrant, Abhi Karkamkar, John C. Linehan, Tom Autrey. Synthesis of Ammonia Borane for Hydrogen Storage Applications. *Energy and Environmental Science*, **2008**, DOI: 10.1039/b808865a.
7. Nancy J. Hess, Michael R. Hartman, Craig M. Brown, Eugene Mamontov, Abhijeet Karkamkar, David J. Heldebrant, Luc L. Daemen, Tom Autrey. Quasielastic neutron scattering experiments of orthorhombic ammonia borane. *Chem. Phys. Lett.* **2008**, doi:10.1016.
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**FIGURE 6.** Comparison of simulated and experimental XAFS spectra of rhodium species formed from the catalyst precursor Rh(cod)chloride and dimethylamine borane. Structure on the bottom is obtained by molecular dynamics simulations and shows the potential resting state of the active Rh(4) cluster. Each Rh atom has two boron ligands.

9. Herman Cho, Wendy J. Shaw, Vencislav Parvanov, Gregory K. Schenter, Abhijeet Karkamkar, Nancy J. Hess, Chris Mundy, Shawn Kathmann, Jessie Sears, Andrew Lipton, Paul Ellis, Tom Autrey. Molecular Structure and Dynamics in the Low Temperature (Orthorhombic) Phase of NH<sub>3</sub>BH<sub>3</sub>. *J. Phys. Chem. A*, **2008**, *112*, 4277.

10. Nancy J. Hess, Vencislav M. Parvanov, Mark E. Bowden, Chris Mundy, Shawn Kathmann, Greg Schenter, Tom Autrey. Spectroscopic studies of single crystal NH<sub>3</sub>BH<sub>3</sub> as a Function of temperature from 88 to 330 K. *J. Chem. Phys.* **2008**, *128*, 034508.

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12. Ashley C. Stowe, Wendy J. Shaw, John C. Linehan, Benjamin Schmid and Tom Autrey. In situ solid state <sup>11</sup>B MAS-NMR studies of the thermal decomposition of ammonia borane: mechanistic studies of the hydrogen release pathways from a solid state hydrogen storage material. *Phys. Chem. Chem. Phys.*, **2007**, *15*, 1831. DOI: 10.1039/b617781f.

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