
Basic Research for the Hydrogen Fuel Initiative: Control of Hydrogen Release and Uptake in Condensed Phases

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Program Scope

This research effort will result in knowledge that will provide the basis for development of new materials that release and absorb hydrogen at moderate temperatures and pressures. New theoretical and experimental tools to investigate hydrogen-rich materials will be developed. The proposed work specifically addresses the focus area “Novel Materials for Hydrogen Storage” and peripherally “Design of Catalysts at the Nanoscale” of the Hydrogen Fuel Initiative. These fundamental studies will provide a strong basis for support of DOE’s EERE Centers of Excellence in hydrogen storage.

The long-term objective of the proposed research is to develop knowledge about hydrogen-rich materials that will provide the basis for developing new hydrogen storage systems. We contend that: (i) hydrogen can be stored reversibly in materials with alternating electron-rich and electron-poor sites, (ii) thermally reversible hydrogen storage can be accomplished with chemical hydrides based on the B,N,C elements, and (iii) nanoscale effects and interfacial interactions can enhance kinetics and modify thermodynamics of hydrogen release and uptake.

Structure and bonding in the NBH materials

- How do the properties of the B—N, N—H, and B—H bonds change in the NH_xBH_x series ($x=0-4$)?
- How do the proton and hydride affinities of the N and B sites, respectively, evolve in this series?
- How do the properties of the di-H bonds; i.e., $\text{N—H}^{\delta+} \cdots \delta^- \text{H—B}$, evolve in this series?
- What is the directionality of di-H bonds?
- What is the interplay of perturbation components, such as electrostatics, induction, dispersion, and valence repulsion, in di-H bonds?
- How important are cooperative (non-additive) effects?
- Is a dihydrogen bond a precursor to molecular hydrogen formation?
- How do substitutions on the B and/or N atoms affect properties of the B—N, N—H, B—H, and di-H bonds?

Thermodynamics and kinetics of hydrogen release and uptake

- Can the stability of NBHs be analyzed in terms of proton and hydride affinity of electron-rich and electron-poor sites, respectively, and long-range intermolecular interactions?
- What is the mechanism for H_2 release and uptake from NBH materials?
- What are reaction pathways and barriers for the two distinct steps of hydrogen release, nucleation and growth?

- How do the substitutions on B and/or N atoms affect the mechanism, barriers, and thermodynamics of hydrogen release and uptake?
- What is the role of quantum effects in dynamics of molecular and atomic hydrogen?
- Will alloying of NBH materials with carbon or other, light, main-group elements lead to HRMs with desirable thermodynamics of hydrogen release and uptake?

Interfacial chemistry and catalysis

- How do interfaces with various supports affect the kinetics, thermodynamics, and selectivity of reversible hydrogenation?
- Are the nucleation and growth steps the same in neat NBH and NBH deposited in a nanoporous scaffold?
- How do nanocatalysts immobilized on the support and/or dispersed in bulk of the NBH materials affect kinetics of hydrogen release? Are the nucleation and growth steps the same as in neat NBH?
- Can we use neutron scattering, EXAFS, and NMR techniques to investigate catalytic activation of hydrogen in the solid state?

Recent Progress

Neutron vibrational studies of di-hydrogen bonding: The low frequency region of the inelastic neutron scattering (INS) spectrum collected at 15 K is shown in Figure 1 for $\text{H}_3\text{N}^{11}\text{BH}_3$, $\text{D}_3\text{N}^{11}\text{BH}_3$, and $\text{H}_3\text{N}^{11}\text{BD}_3$. Specific isotopic labeling of the hydridic and protic positions has allowed for study of the soft dihydrogen vibrational modes.

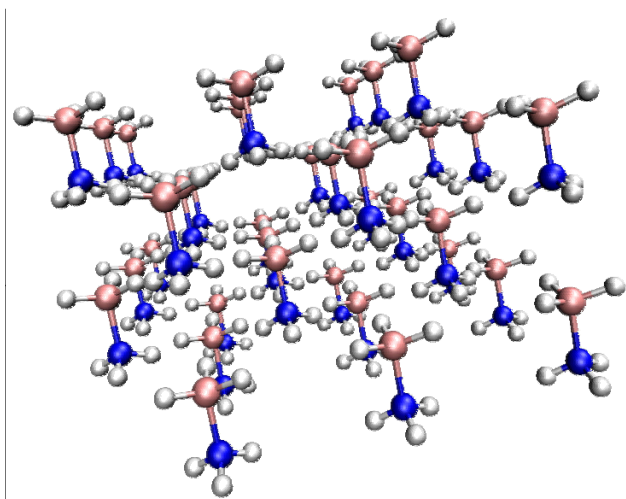


Figure 1. Orthorhombic phase of ammonia borane illustrating extended network of intermolecular dihydrogen bonding between adjacent BH—HN.

In an attempt to predict the change to these vibrational modes with deuteration, we have mapped the N-H...B-H unit involved in dihydrogen bonding to a traditional model of hydrogen bonding. A proton acceptor, proton donor and proton are required for conventional hydrogen bonding. In the case of ammonia borane which has both protic and hydridic hydrogens, we have made the assumption that the proton acceptor includes the

entire (B-H) unit. The nitrogen atom is then the traditional proton donor. Under these constraints, deuteration of the hydridic hydrogen has a weaker effect on the vibrational frequency based solely on the reduced mass change (see Table 1). This model underestimates the softening which results from deuteration of the (B-H) unit, but does predict observed weaker vibrations. Deuteration of the protic positions again results in less energetic vibrations; however, the observed change is far less dramatic than predicted by this model. One explanation may be due to the molecular arrangement in the solid state. The protons are oriented between two hydridic positions of an adjacent molecule. Hydrogen bonding is therefore a cooperative

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process which involves more than one proton, proton donor, and proton acceptor. This model does predict a weakening on the dihydrogen vibrational energy upon deuteration as observed in the INS spectra.

Our experimental results are compared with various levels of theory for the perprotonated ammonia borane as well as with expected shifts in the vibrational frequency due to isotopic labeling. Experimental and calculated vibrational positions

are tabulated in Table 1. Semi-empirical MP2/aug-cc-VDZ results of the ammonia borane dimer are for each isotopomer reveals the relative changes in the soft modes. Clearly the vibrational frequencies for the dimer are not equivalent to those in the bulk; however, trends in the soft mode frequency changes due to isotopic substitution are

consistent with observed INS results. The dihydrogen symmetric stretching mode (A_g) at 204 cm^{-1} for $\text{H}_3\text{N}^{11}\text{BH}_3$ is relatively stable upon H/D substitution. Further, the bend (A_u) at 93 cm^{-1} and the rocking modes at 150 cm^{-1} (A_g) and 242 cm^{-1} (B_u) for $\text{H}_3\text{N}^{11}\text{BH}_3$ are relatively stable. The other low energy vibrations are assigned to rotational and lattice modes.

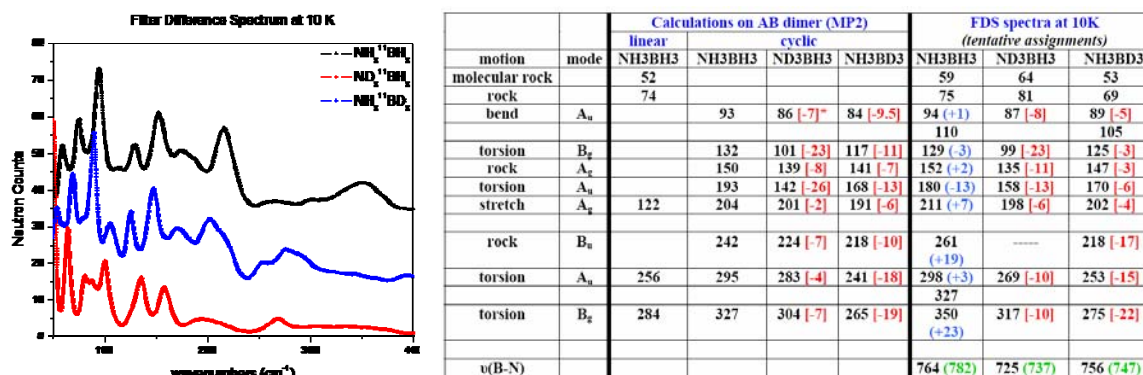


Figure 2. Neutron vibrational spectrum was obtained for three isotopomers of ammonia borane at 15 K to gain insight into the nature of dihydrogen bonding in the solid state. Linear dimer is solid state structure, cyclic dimer is gas phase structure.

Publications.

In-situ XAFS and NMR Study of Rhodium Catalyzed Dehydrogenation of Dimethylamine Borane. Y Chen, JL Fulton, JC Linehan, T Autrey, J. Am. Chem. Soc. 127, 3254, 2005.

Dynamics of Ammonia Borane Using Neutron Scattering. CM Brown, TL Jacques, NJ Hess, LL Daemen, E. Mamontov, JC Linehan, AC Stowe, and T Autrey, accepted Physica B, 2006.