Lightweight Metal Hydrides for Hydrogen Storage

DOE Award #: DE-FC3605GO15062

J.-C. Zhao (PI)

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The Ohio State University

May 12, 2011

Project ID #: ST032

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Program Overview

Timeline

- Project start date: March 2005
- Project end date: August 2011
- Percent complete: 90%

Barriers

- Right heat of formation (J)
- Absorption / desorption kinetics (E)
- Reversibility for borohydrides (D, P)

Budget

- Total Project Funding: *$4.5M*
  - DOE Share: $3.6M
  - OSU Share: $0.9M
- Funding Received for FY10
  $700K (DOE), $175K (OSU-Cost)
- Funding for FY11: $212K

Partners/Collaborations

- Members of DOE MHCoE
- Collaborations with ORNL, NIST, Caltech, UTRC, SNL, and Univ. of Utah, Univ. of Washington, and Ford.

Objectives & Relevance

Overall	Discover and develop a high capacity (> 6 wt.%) lightweight hydride capable of meeting or exceeding the 2015 DOE/FreedomCAR targets.
FY10	• Study the structure and hydrogen storage properties of AlB_4H_{11}; • Synthesize and study AlB_5H_{12} and AlB_6H_{13} for hydrogen storage property measurements; • Synthesize and study other borane compounds.
FY11	• Complete structure analysis for AlB_4H_{11} • Perform study on the absorption & desorption kinetics and catalytic effects to improve the reversibility of AlB_4H_{11}; • Complete a final report.

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This project is directly exploring materials to meet the DOE 2015 hydrogen storage targets

Approach

- Study aluminoborane compounds such as AlB_4H_{11} for hydrogen storage;
- Study the crystal structures and the decomposition mechanisms using multiple techniques such as interrupted PCT tests, NMR, IR, DSC, and residual gas analysis;
- Develop reversibility strategy from detailed mechanistic understanding of the complex desorption processes (such understanding is crucial for reversibility of all borohydrides);
- Synthesize new hydrides and complexes in collaboration with ORNL, NIST, Northwestern, JPL, Caltech, and Sandia.

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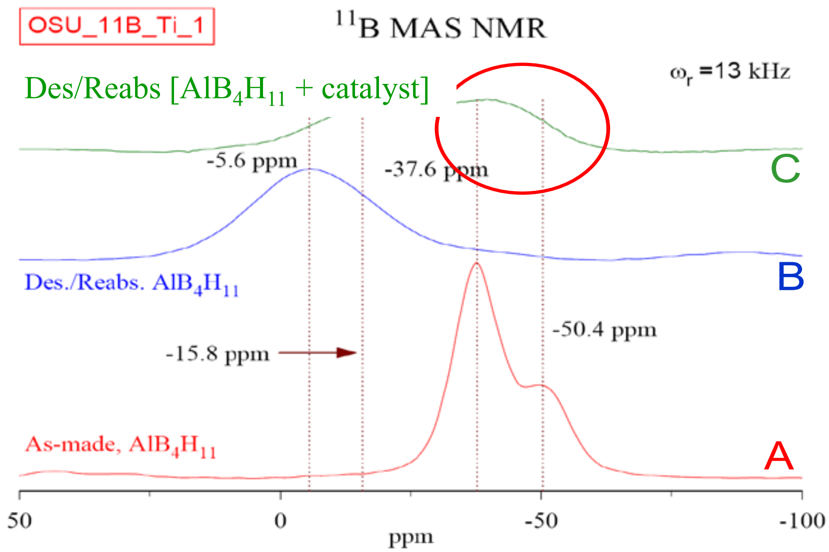
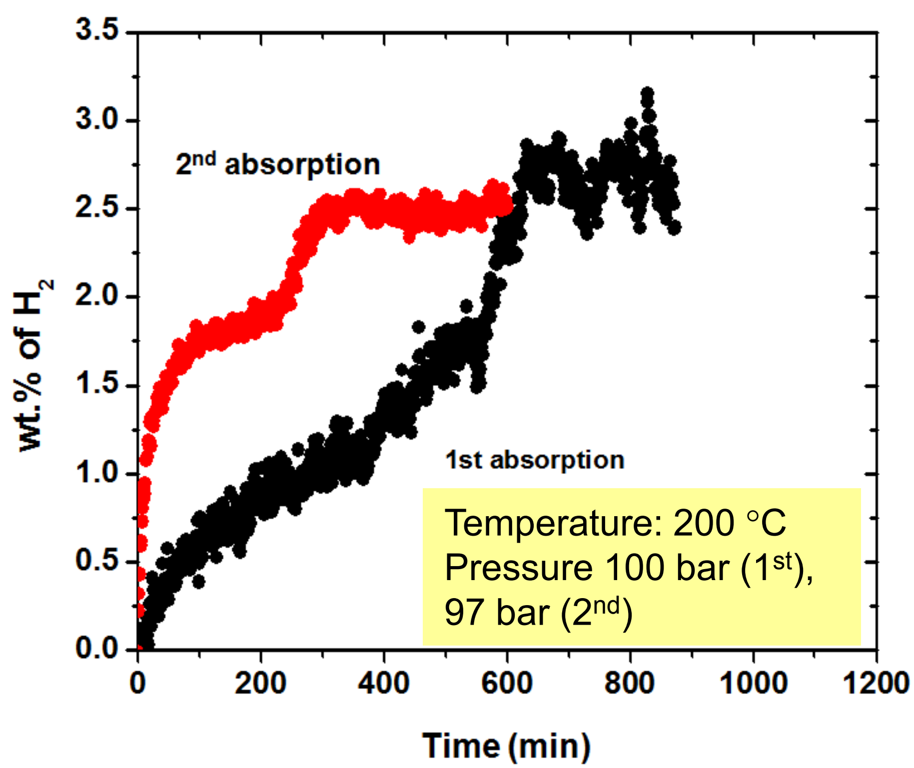
Background on AlB_4H_{11}

- Low desorption temperature (starts ~120ºC), 13.5 wt.% H_2 with small amounts of B_2H_6 (~1 vol.% gas).
- DSC shows endothermic desorption: thermodynamically reversible.
- Clearly demonstrated partial reversibility using PCT, IR and NMR at mild conditions.
- Amorphous structure with polymerization.





Structure of AlB_4H_{11}

Technical Accomplishments

amorphous and polymeric…there is nothing like it known…

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- Solution NMR
- IR
- Reactivity
- Mechanism

Prototype electrostatic ground state (PEGS) + DFT simulations

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Solid-state NMR

JPL

CALIFORNIA INSTITUTE OF TECHNOLOGY 1891

Structure of AlB_4H_{11}

Neutron vibration spectroscopy

NIST National Institute of Standards and Technology

Valence bond theory

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Mass spec

ornl OAK RIDGE NATIONAL LABORATORY

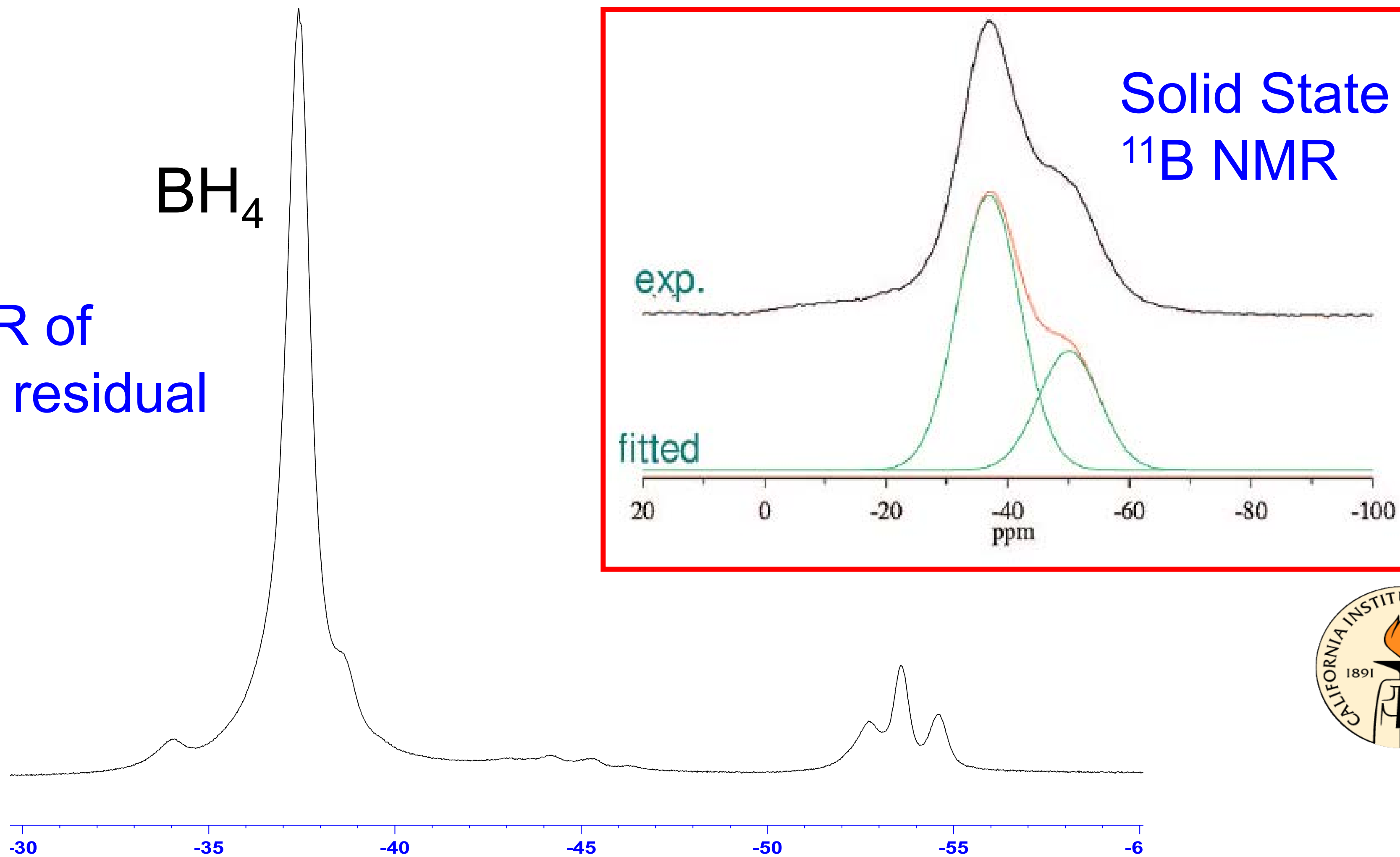
Neutron total scattering spectroscopy (NOVA) analysis

九州大学 KYUSHU UNIVERSITY

Structure of AlB_4H_{11}

Technical Accomplishments

^{11}B NMR of AlB_4D_{11} residual solution

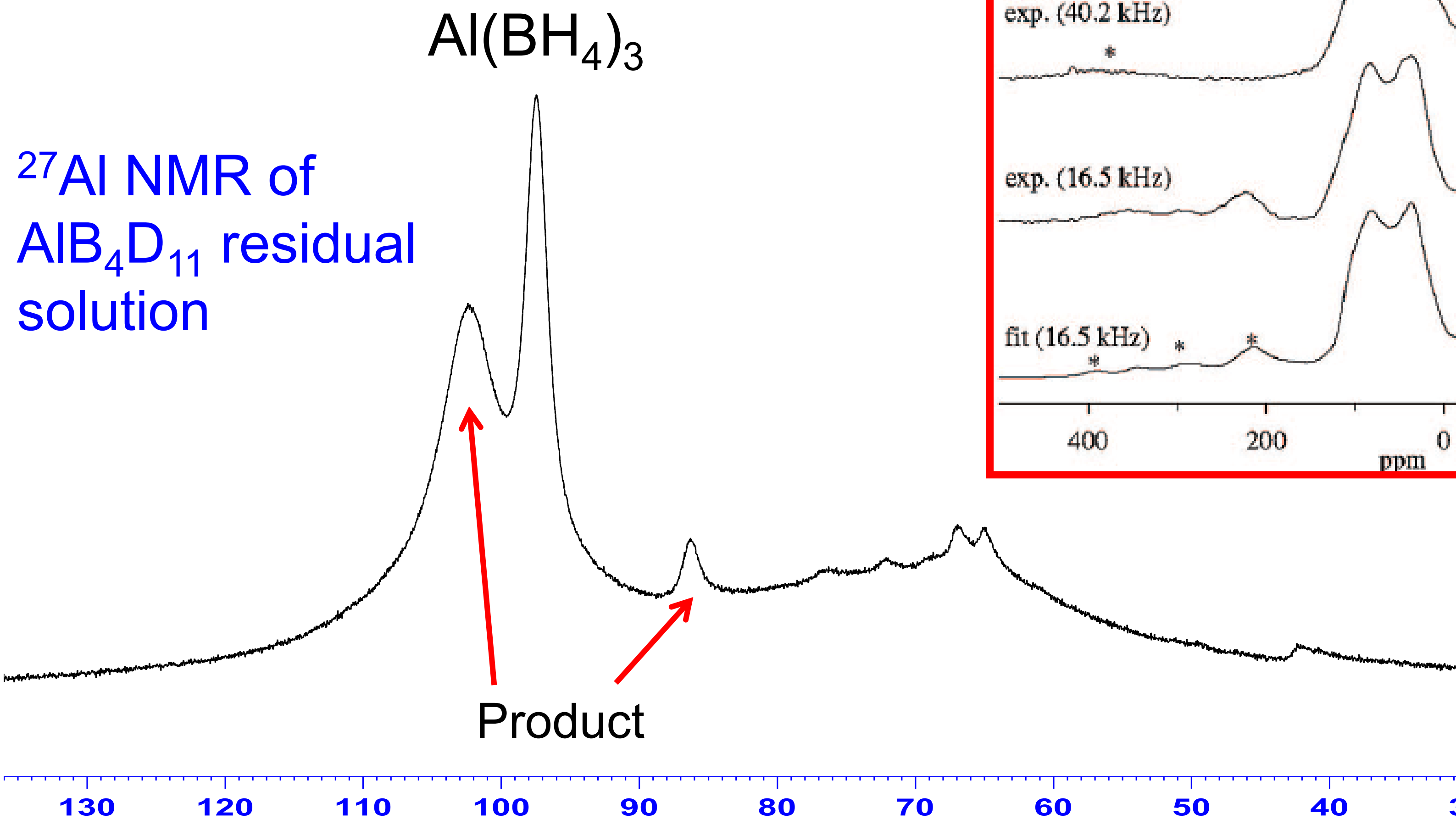


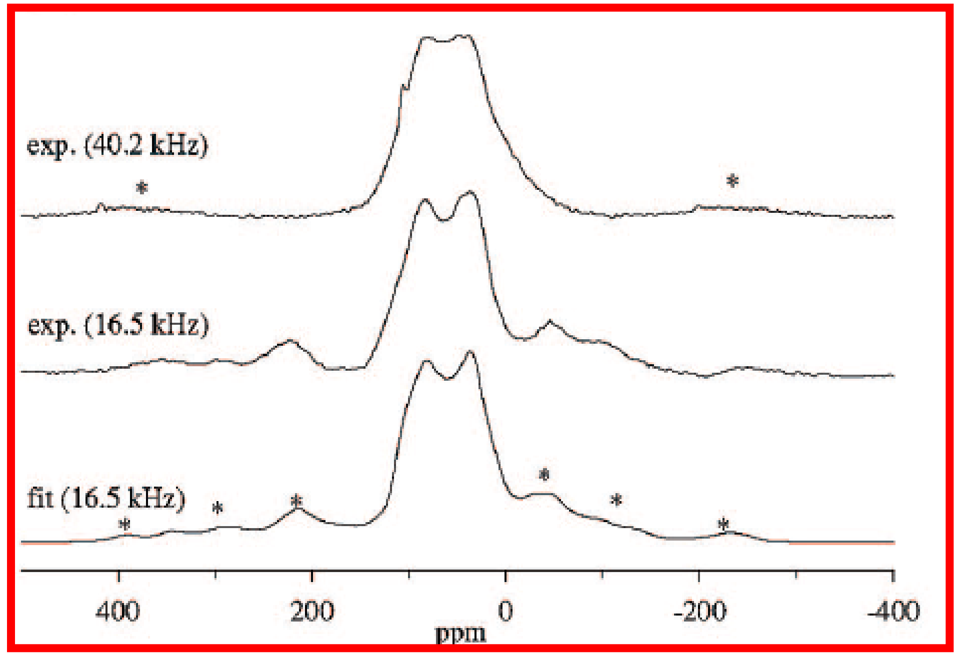
- AlB_4H_{11} not soluble in most of the solvents.
- We analyzed the residual reaction solution for structure information.
- The ^{11}B NMR from AlB_4D_{11} shows at least two different boron units.
- The ^{11}B NMR chemical shifts consistent with solid state NMR.

Structure of AlB_4H_{11}

Technical Accomplishments

^{27}Al NMR of AlB_4D_{11} residual solution





- The ^{27}Al NMR shows additional peaks in addition to that of $Al(BD_4)_3$.
- Some peaks consistent with solid-state NMR, but other peaks couldn't be explained at this point.

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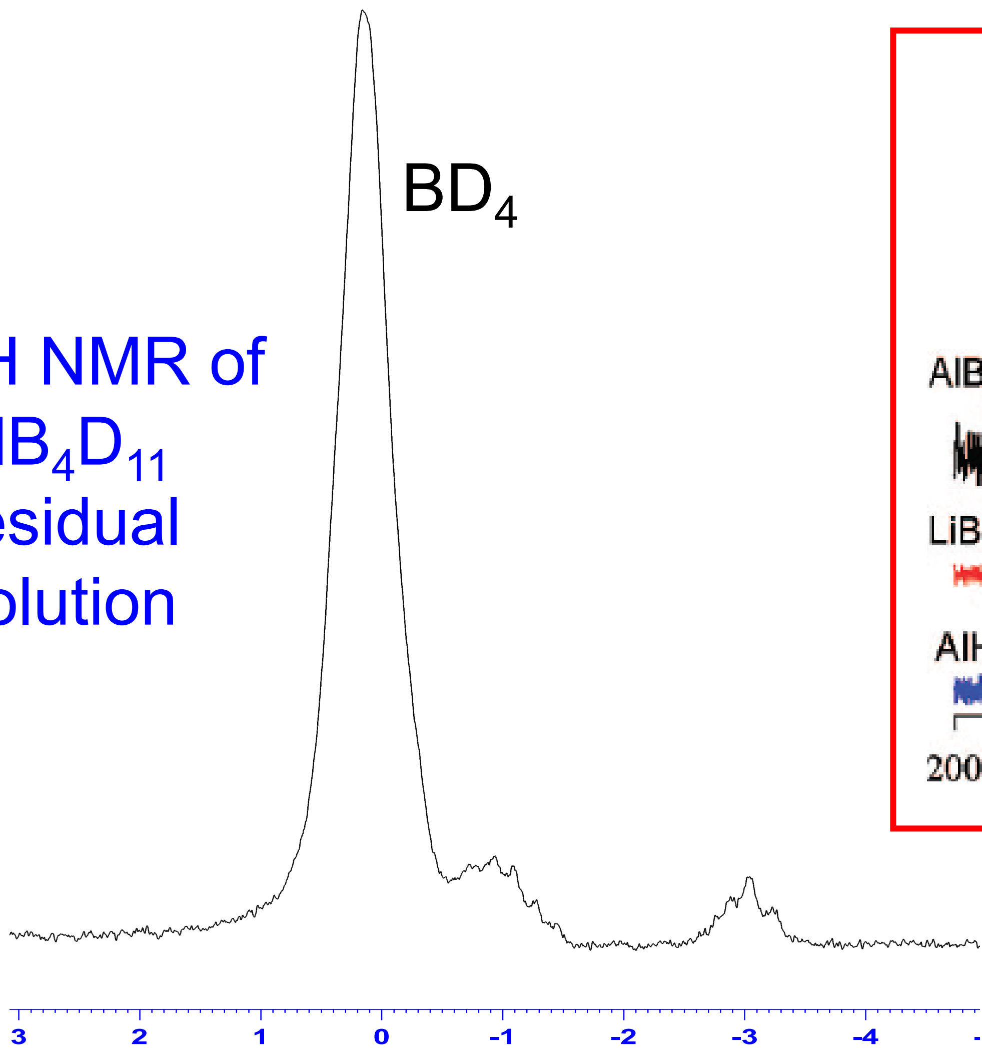
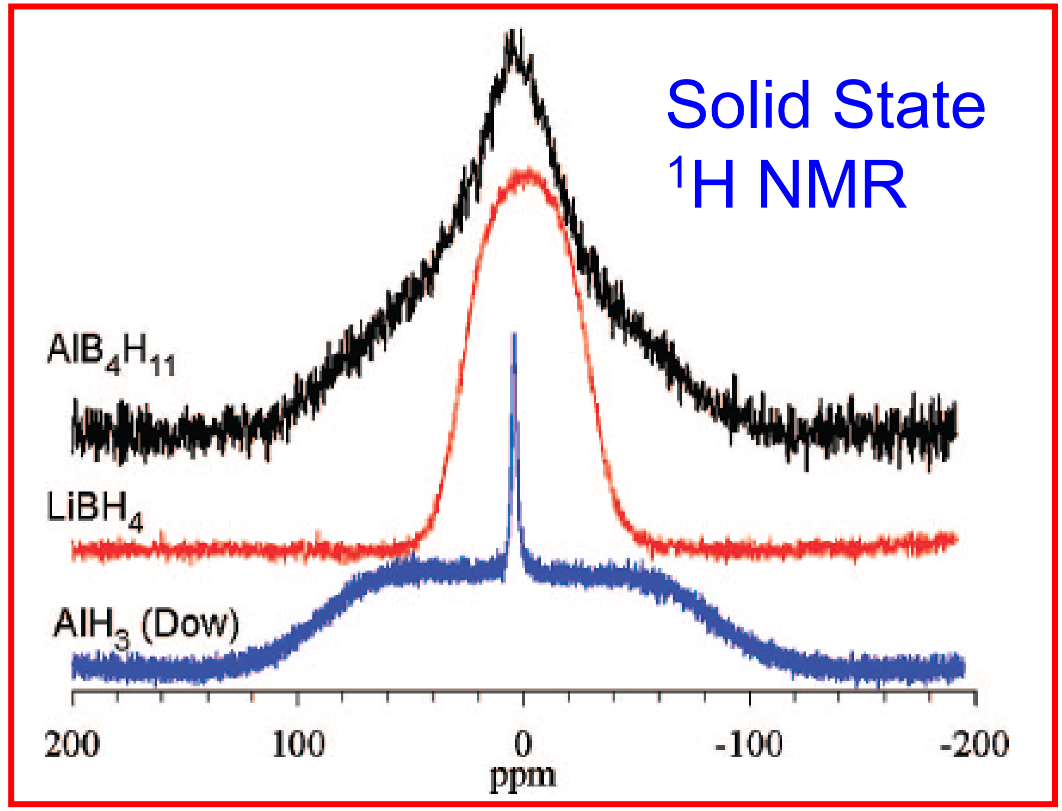
Structure of AlB_4H_{11}

Technical Accomplishments

^2H NMR of AlB_4D_{11} residual solution





- The ^2H NMR also shows additional peaks in addition to that of $Al(BD_4)_3$.
- More refined details about ^2H signals revealed by solution NMR.

Structure of AlB_4H_{11}

Technical Accomplishments

Prototype electrostatic ground state: PEGS

Majzoub & Ozolins: Phys. Rev. B 77 (2007) 104115.

- **PEGS**
  - **Hamiltonian**

$$E_{tot} = \underbrace{\sum_{i>j} \frac{Q_i Q_j}{R_{ij}}}_{\text{Coulomb}} + \underbrace{\sum_{i>j} \frac{\varepsilon_{ss}}{R_{ij}^{12}}}_{\text{Soft-sphere}}$$

Coulomb Soft-sphere

  - **Annealing Monte-Carlo**

- **PEGS+DFT procedure**

Cation / Anion group → PEGS (30 runs) → Ordered crystal structure → DFT (select) → Winner with the lowest energy !!!

AlB_4H_{11}: Al^{3+} $[BH_4]^-$, $[BH_3]^0$ $2[BH_2]^-$,

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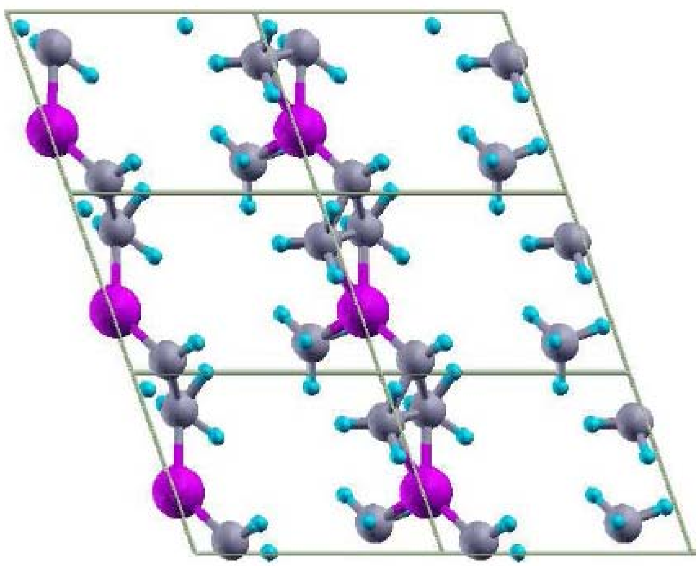
Structure of AlB_4H_{11}

Technical Accomplishments

Lowest energy structures from PEGS + DFT

Stru-3

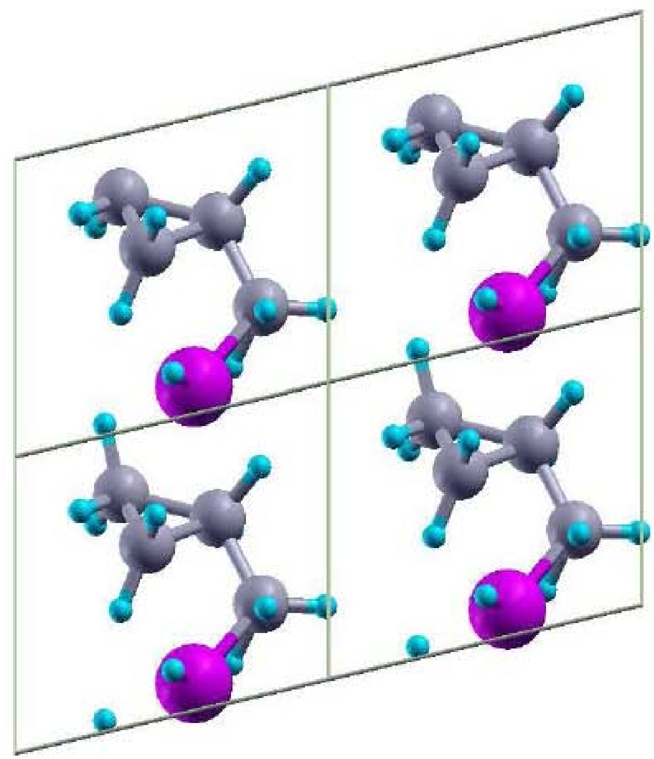


Chain:[BH4]+2[BH3]+[BH]

2[BH3]+[BH] forms a B-B circle

-68.347 eV

Stru-5

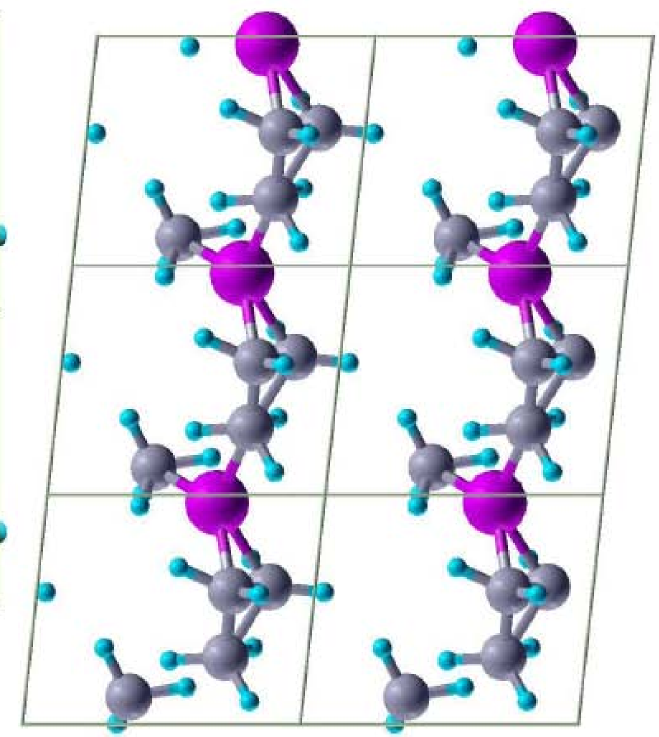


Cluster: $[AlH]+2[BH_3]+[BH_2]+[BH]$

$[BH_3]+[BH_2]+[BH]$ forms a B-B circle

-68.166 eV

Stru-6



Chain: $[BH_4]+[BH_3]+2[BH_2]$

$[BH_3]+2[BH_2]$ forms a B-B circle

-68.584 eV

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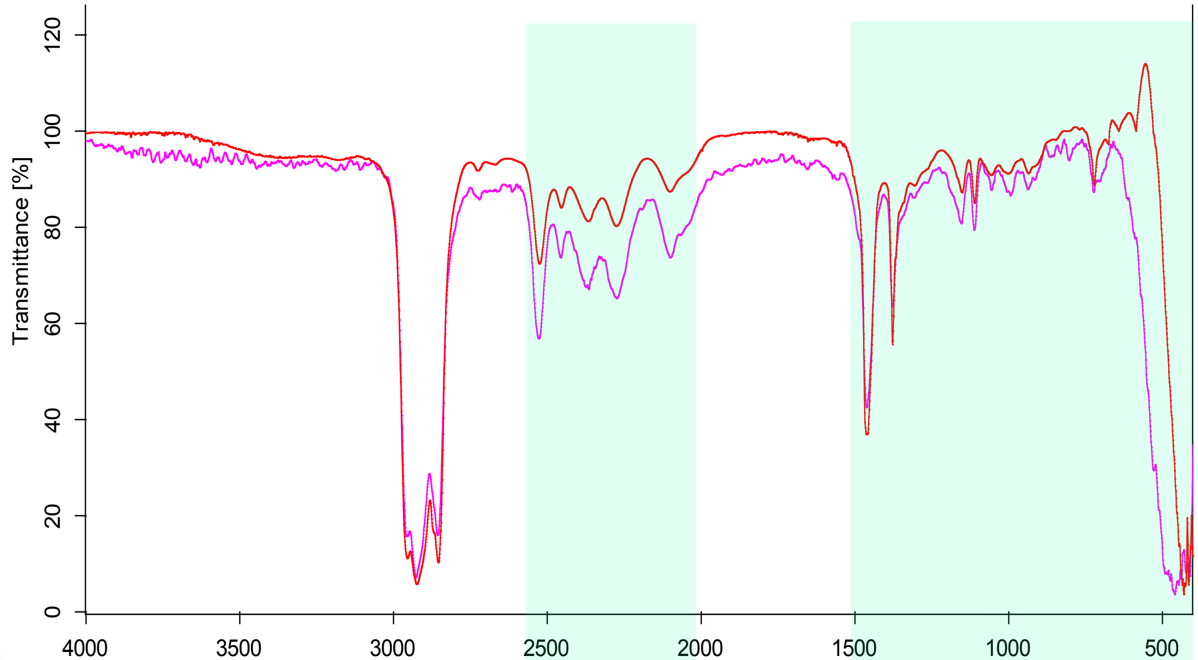
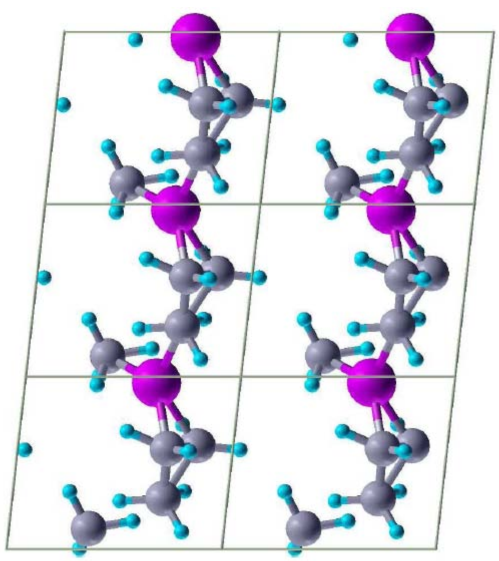
Structure of AlB_4H_{11}

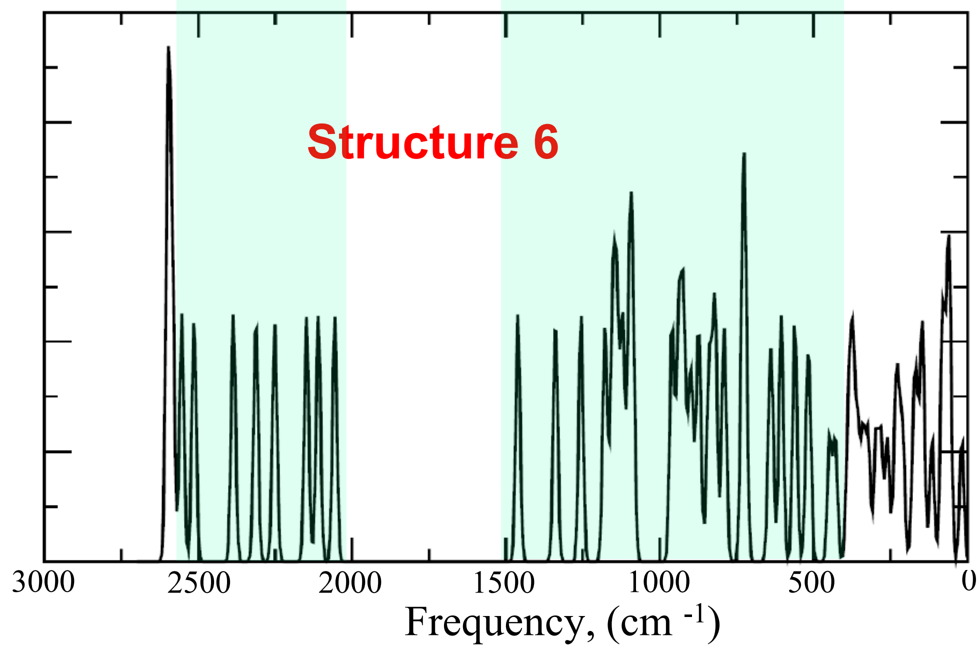
Technical Accomplishments

Expt. IR





Computed phonon density of state for structure 6



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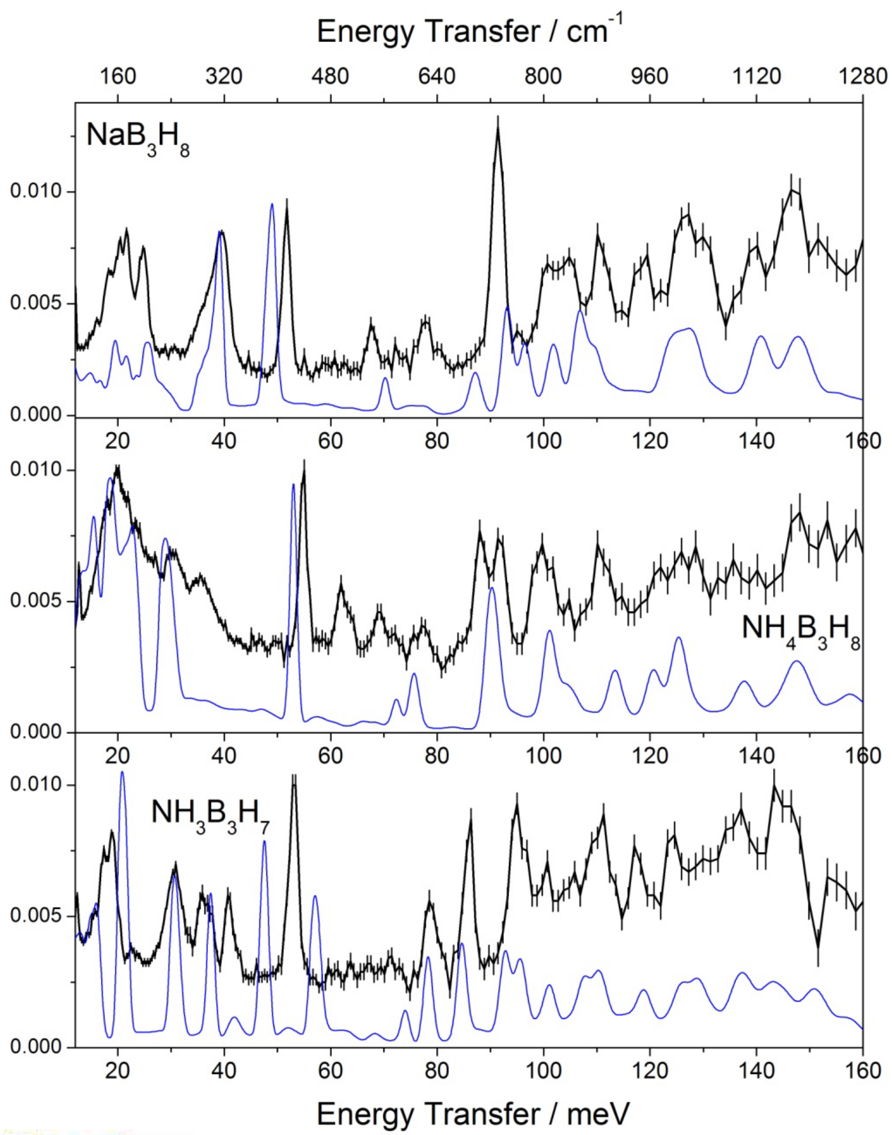
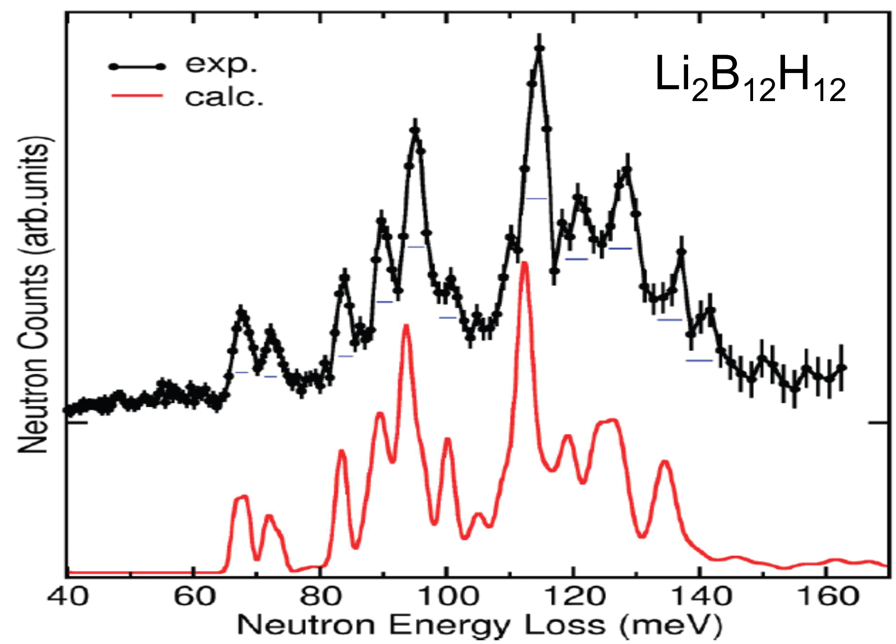
Structure of AlB_4H_{11}

Technical Accomplishments

Neutron vibration spectra: experiment vs. calculation





Benchmark:

Even for well-determined single-crystal structures, the theoretical neutron vibration spectra from DFT calculations still show appreciable deviations from experimental ones.

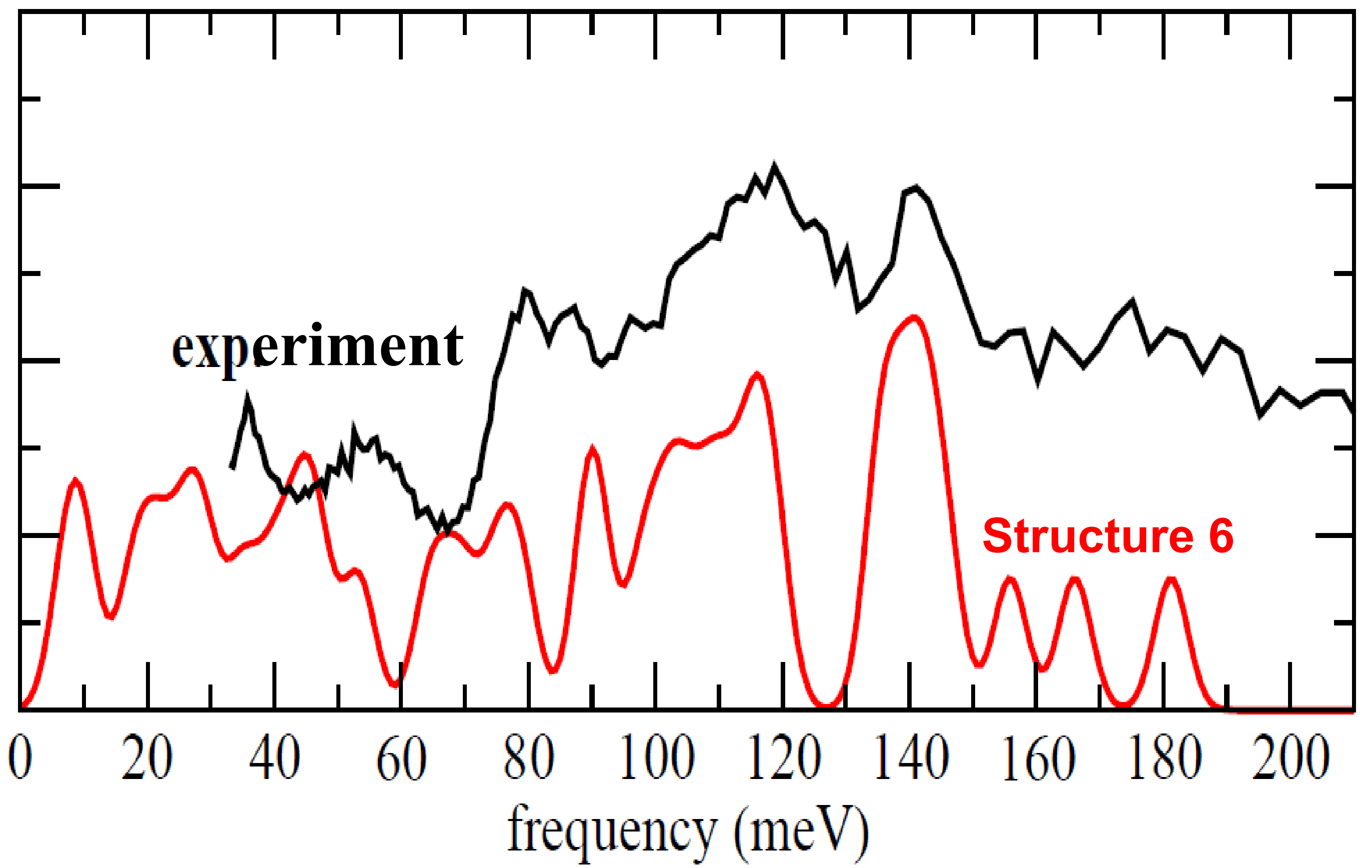
National Institute of Standards and Technology

Wei Zhou & Terry Udovic

Structure of AlB_4H_{11}

Technical Accomplishments

Neutron vibration spectra: experiment vs. calculation



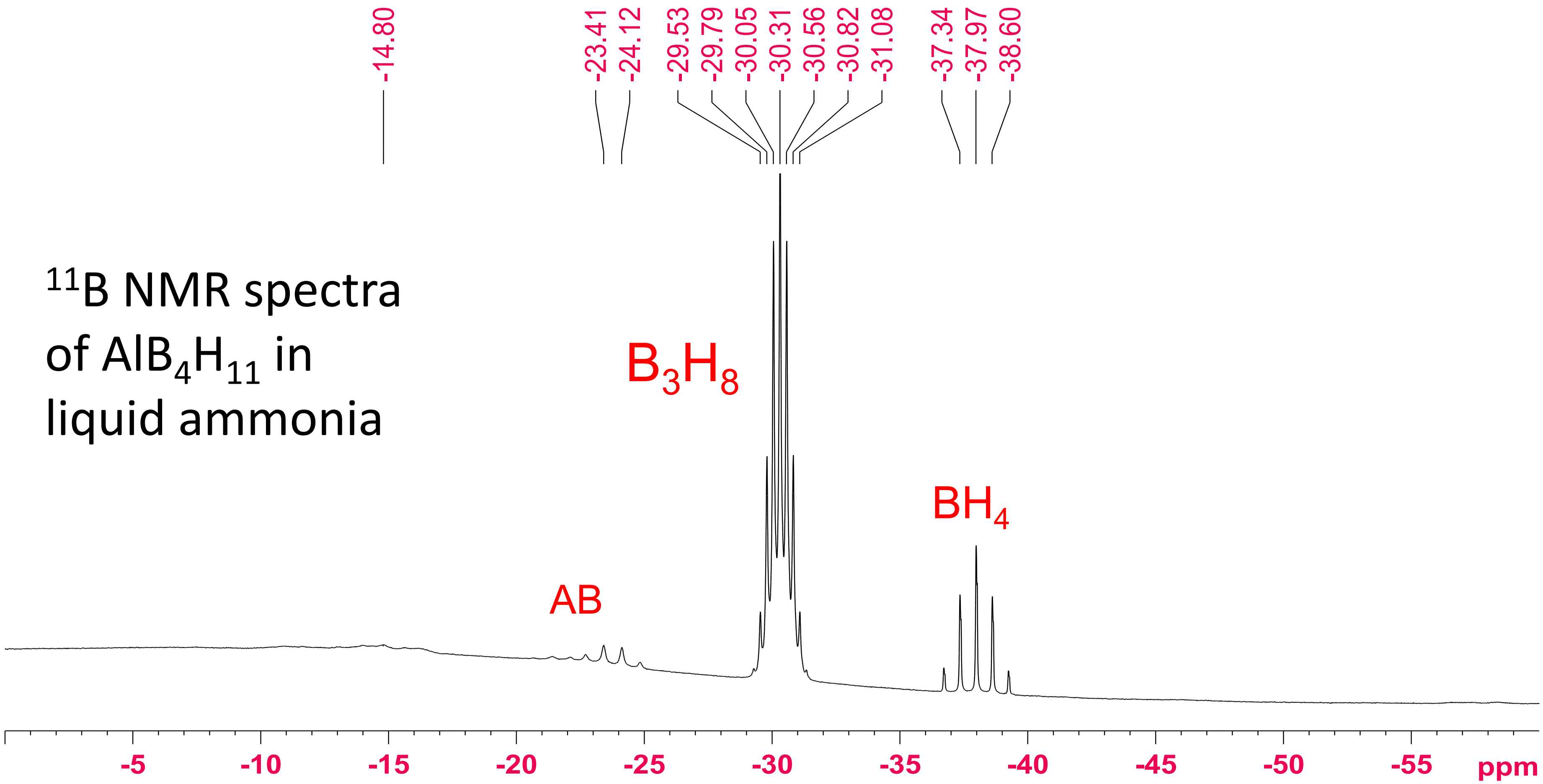
- Good overall agreement between experimental and calculated NVS of structure 6.
- We are very close to the right structure.

NIST National Institute of Standards and Technology
Wei Zhou , Terry Udovic, Kristina Verdal
Yongsheng Zhang
Yongli Wang
Chris Wolverton

Structure of AlB_4H_{11}

Technical Accomplishments

$$AlB_4H_{11}(s) + NH_3(l) \rightarrow B_3H_8^- + BH_4^-$$



^{11}B NMR spectra of AlB_4H_{11} in liquid ammonia

- The existence of B_3 unit was confirmed.
- Two different boron environments – consistent with structure 6

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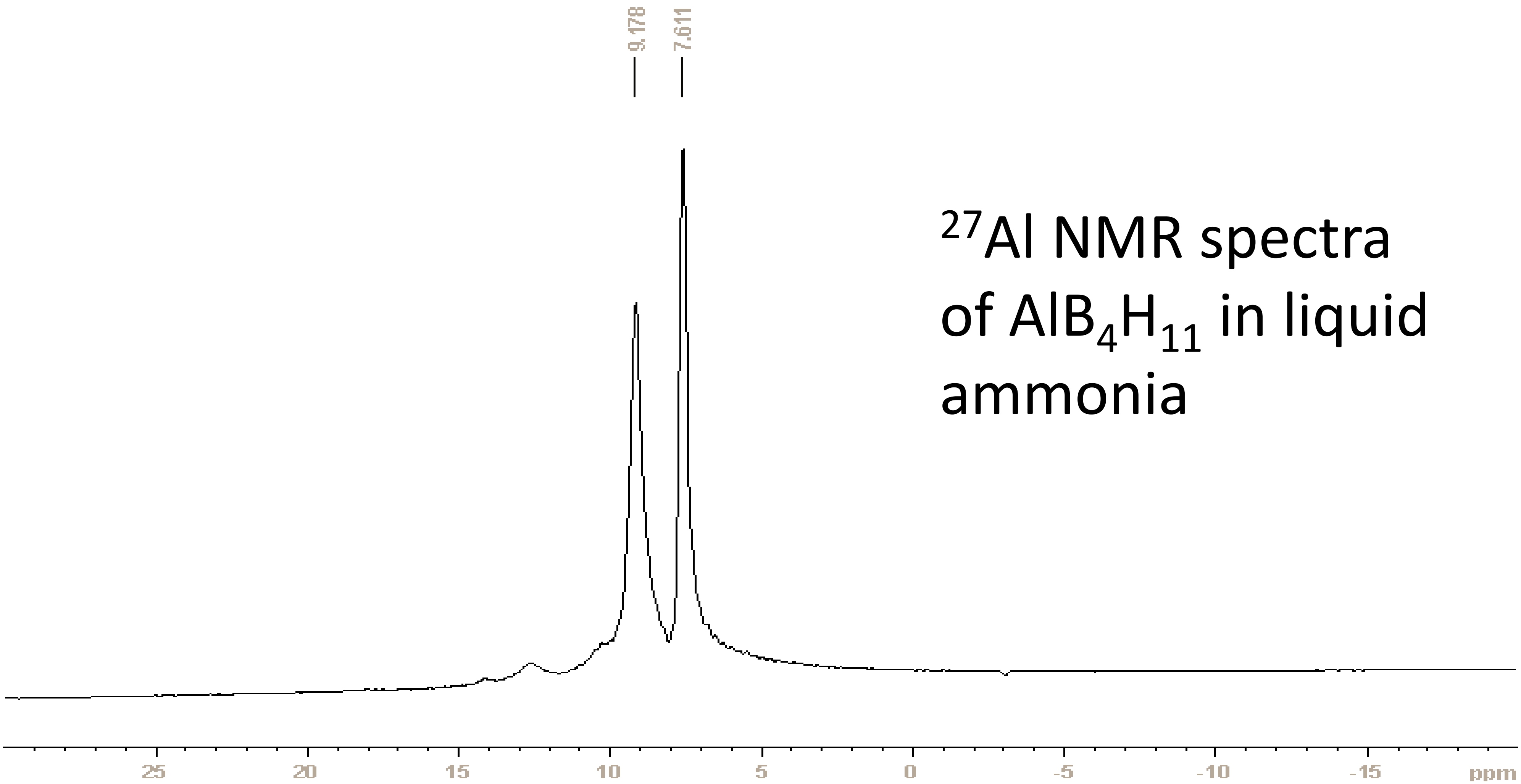
Structure of AlB_4H_{11}

Technical Accomplishments



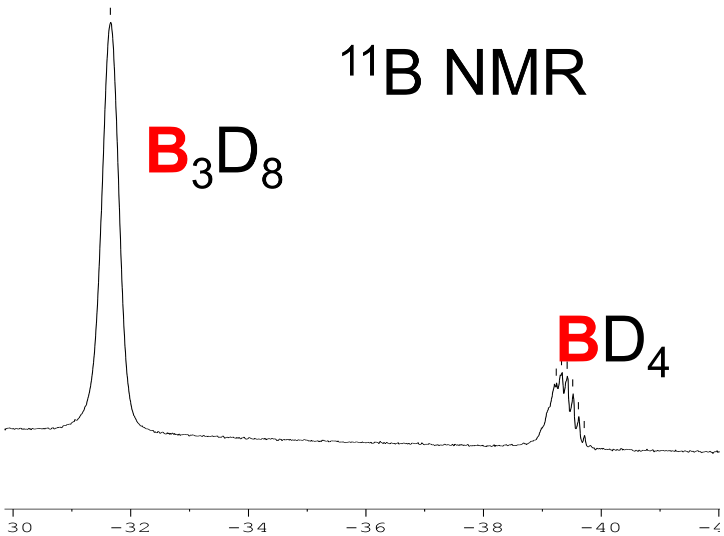
^{27}Al NMR spectra of AlB_4H_{11} in liquid ammonia

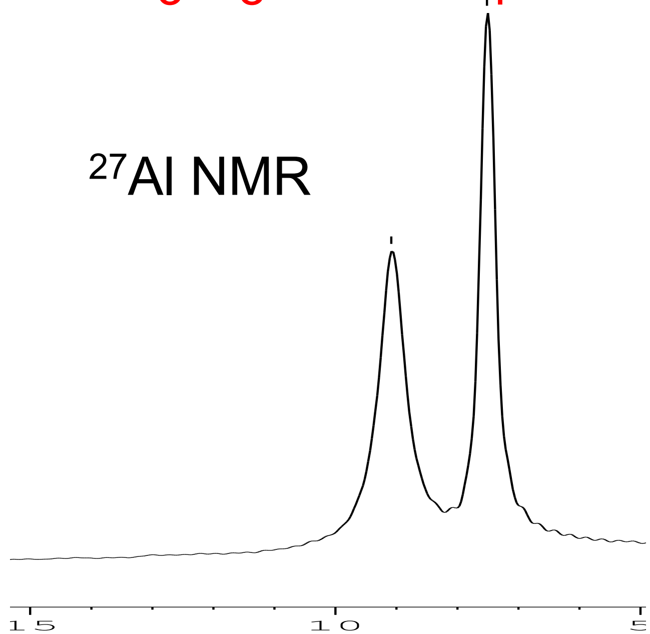
Two Al signals/environments are inconsistent with structure 6

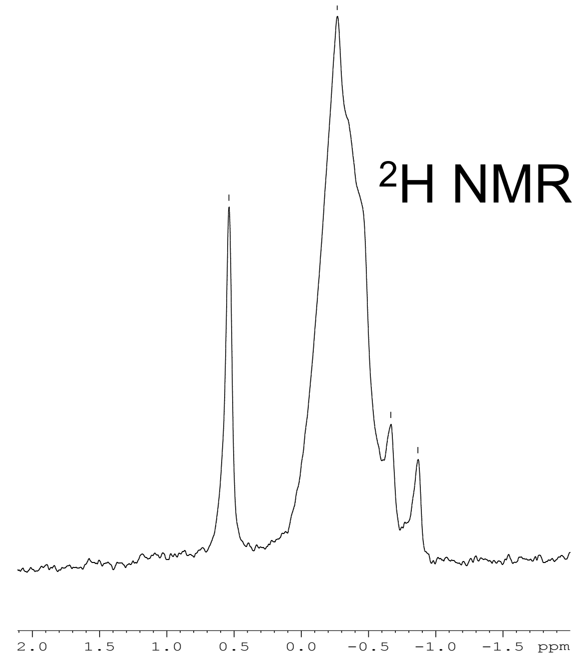
Structure of AlB_4H_{11}

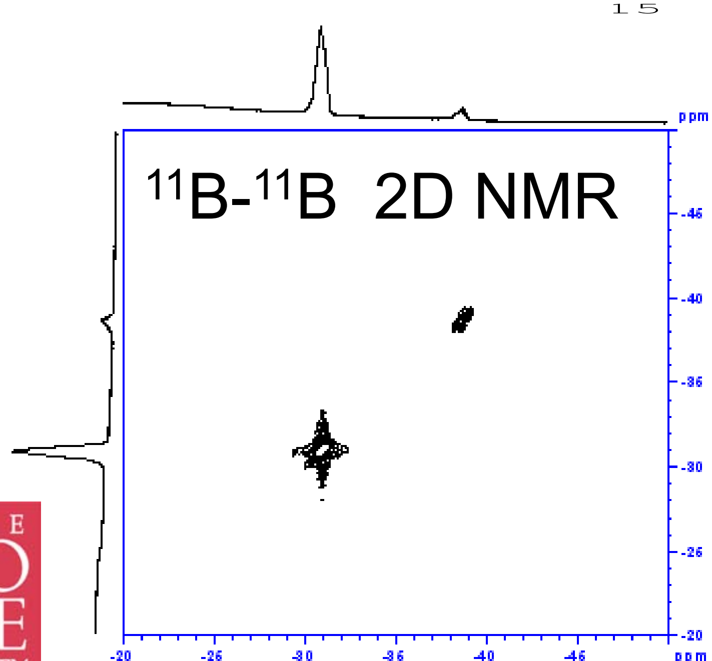
Technical Accomplishments

$AlB_4D_{11}(s) + NH_3(l) \rightarrow B_3D_8^- + BD_4^-$

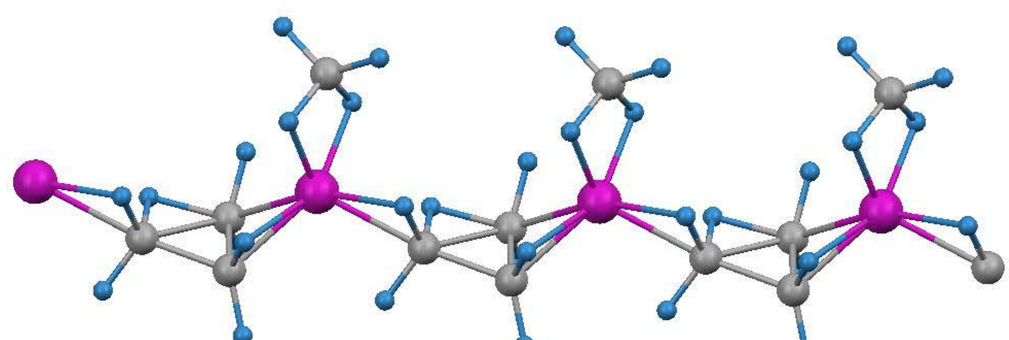






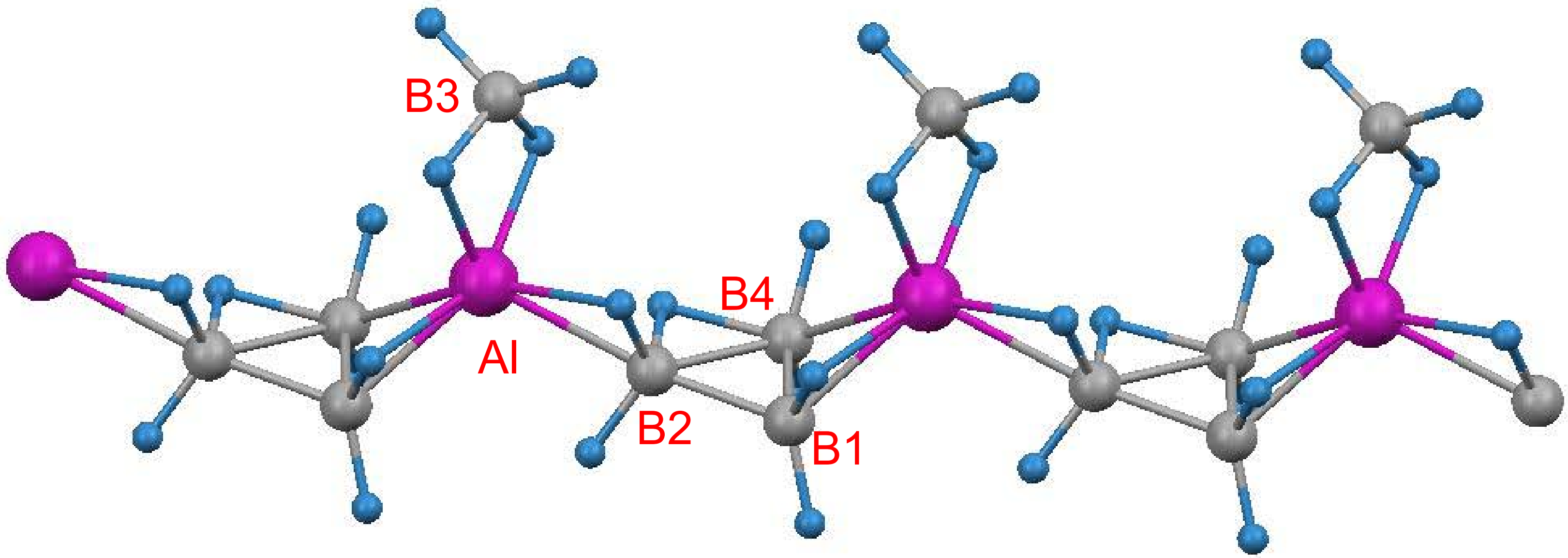


- 2D NMR indicates that the two boron units/groups are not correlated.
- Consistent with structure 6



Structure of AlB_4H_{11}

Technical Accomplishments



Surround B2: 5 bonds, B2-Al, 3x B2-H, B2-B1-B4;

The total valence electron number in each unsymmetrical unit:

$$3\ (Al) + 4 \times 3\ (B) + 11 \times 1(H) = 26$$

The bond numbers in each unsymmetrical unit:

7 normal bonds (2x B3-H_t, Al-B2, B2-H_t, B1-H_t, 2 x B4-H_t)

7 three center-two electron bonds (2x Al-H_b-B3, Al-B4-B1, Al-H_b-B1, Al-H_b-B2, B2-H_b-B4, B1-B2-B4).

So 14 bonds need 28 electrons but only 26 electrons are available.

Valence bond analysis shows that Structure 6 needs improvement.

Structure of AlB_4H_{11}

Technical Accomplishments

- Two types of boron environments (BH_4 and a triangular B-B-B unit) are clearly identified from both solution NMR and solid state NMR as well as PEGS+DFT calculations.
- We are very confident that the boron units in AlB_4H_{11} are already clearly identified.
- Structure 6 needs modification to incorporate two Al environments.
- Bond valence analysis also suggests that structure 6 needs modification.
- A new set of PEGS + DFT calculations was performed at Northwestern based on the above information and produced a new two formula unit structure (denoted as 2fu_structure, ~ 400 meV lower energy than structure 6)

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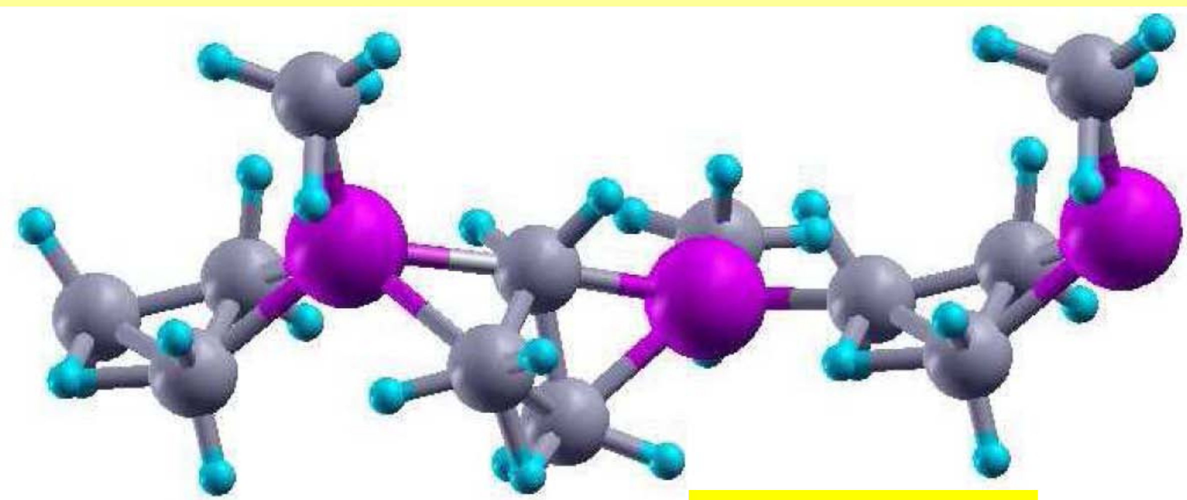
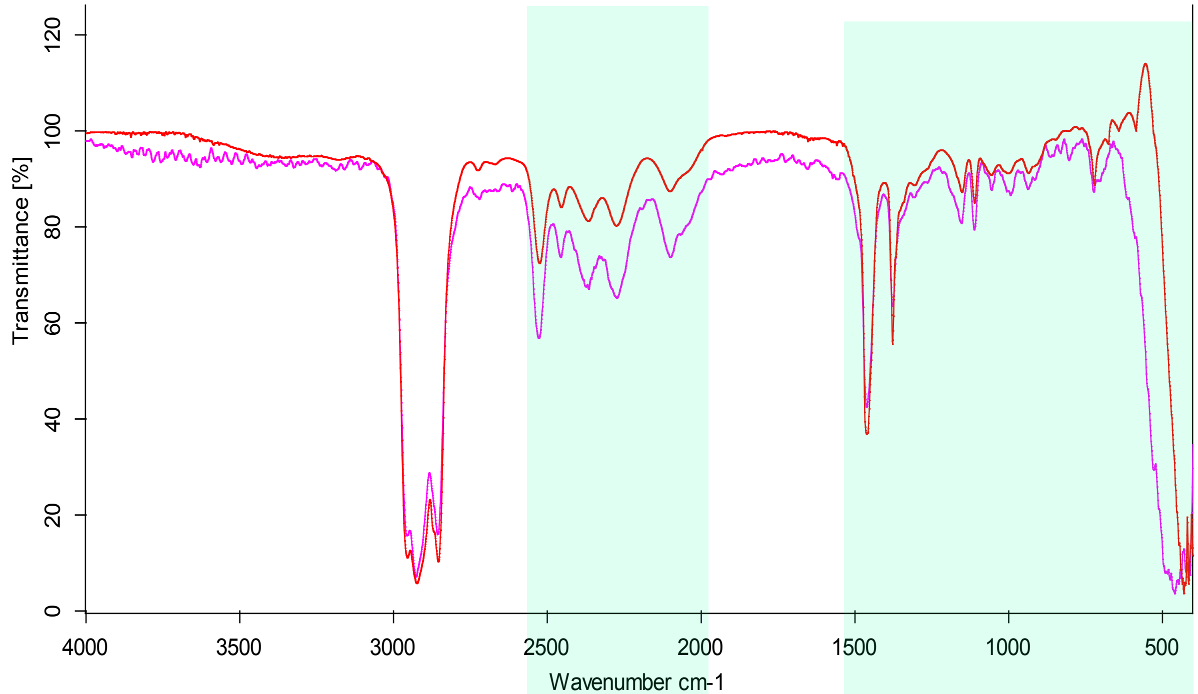
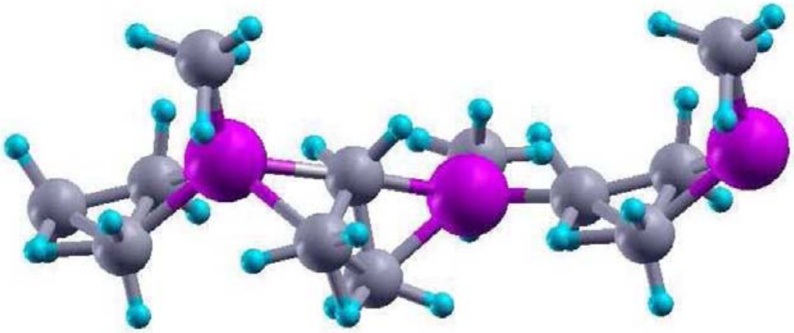


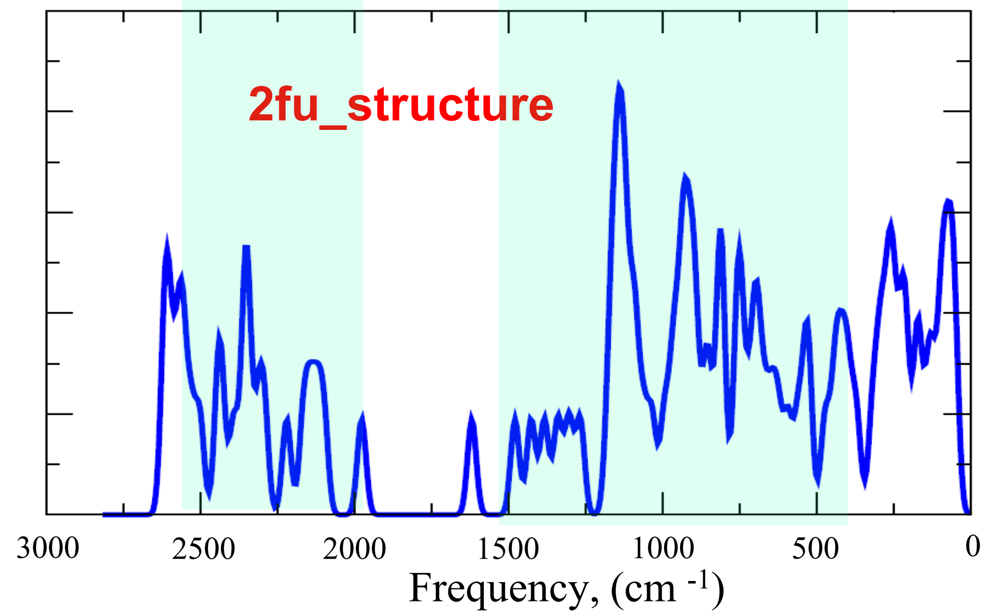
2fu_structure

Structure of AlB_4H_{11}

Expt. IR







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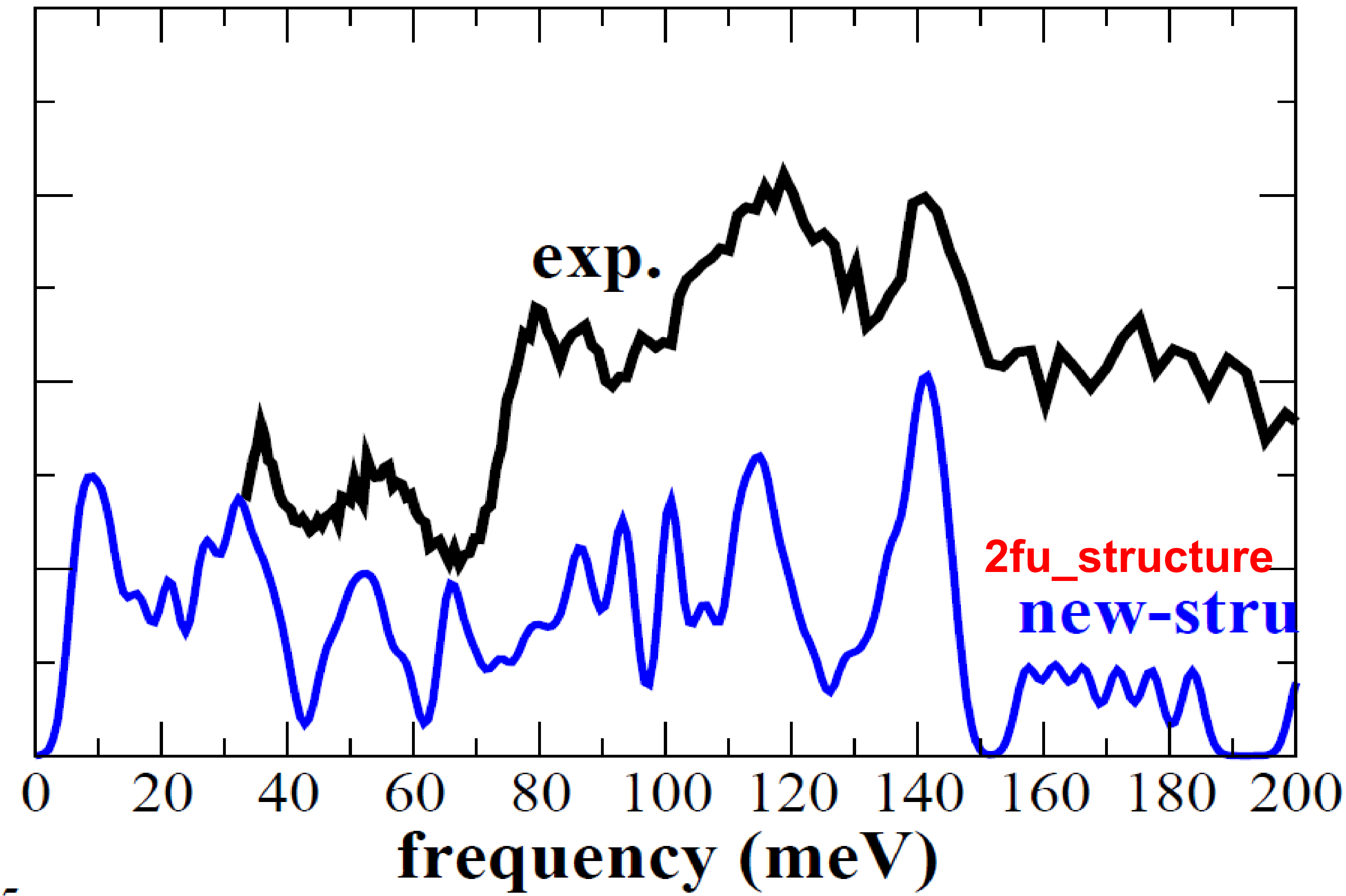
Computed phonon density of state for the 2fu_structure

Structure of AlB_4H_{11}

Technical Accomplishments

Neutron vibration spectra: experiment vs. calculation



- Good overall agreement between experimental and calculated NVS of 2fu_structure.

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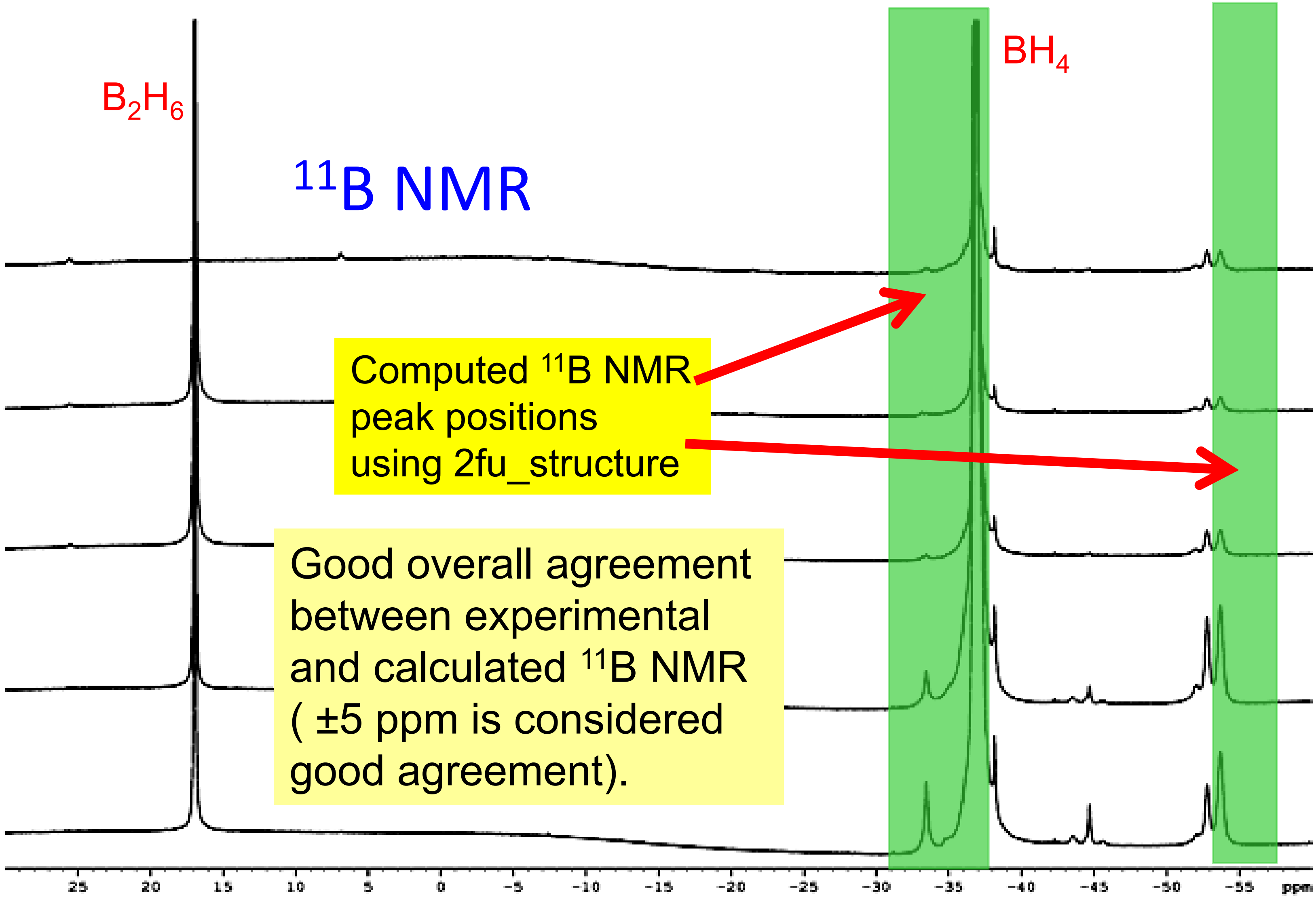
Structure of AlB_4H_{11}

Technical Accomplishments



Good overall agreement between experimental and calculated ^{11}B NMR (±5 ppm is considered good agreement).

Xiaoguang Bao

Yongsheng Zhang
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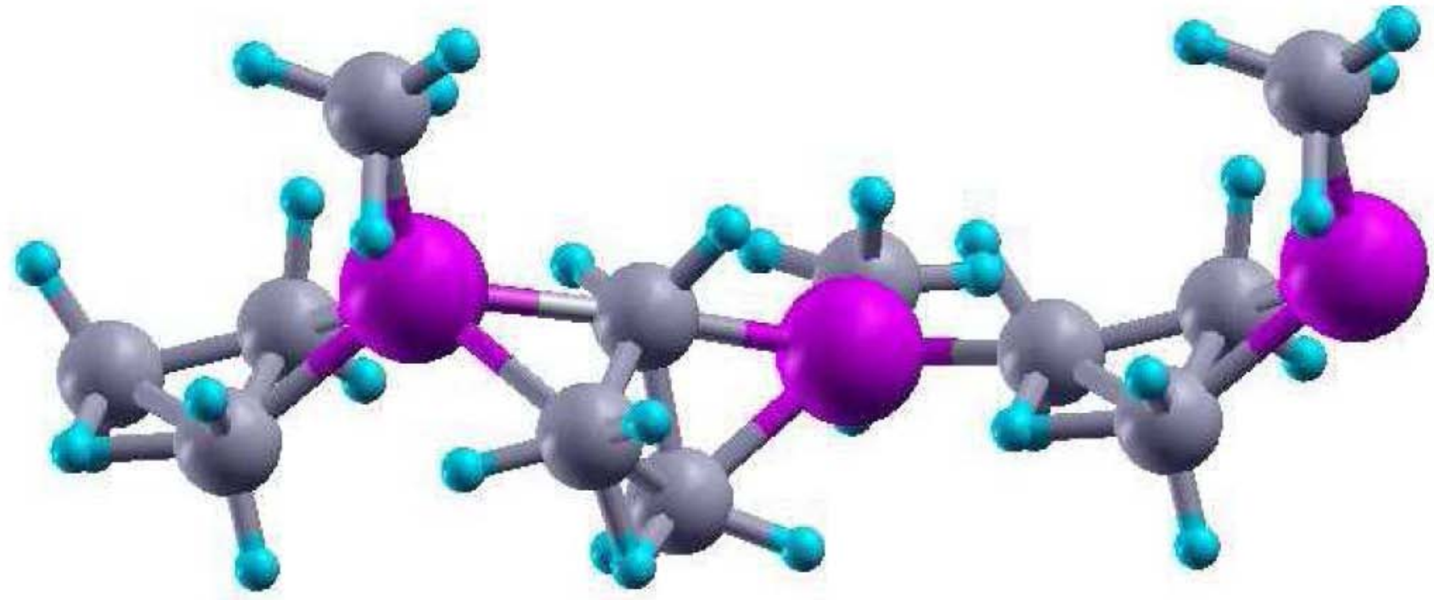
Structure of AlB_4H_{11}

Technical Accomplishments



Brief Summary of AlB_4H_{11} Structure Analysis:

- We are very confident that the two boron units (BH_4 and a triangular B-B-B unit) in AlB_4H_{11} are already clearly identified.
- The new 2fu_structure has two Al environments.
- AlB_4D_{11} made for NOVA analysis which will provide radial atom distribution information for structure refinement.
- We probably got the right structure or are very close the right structure.

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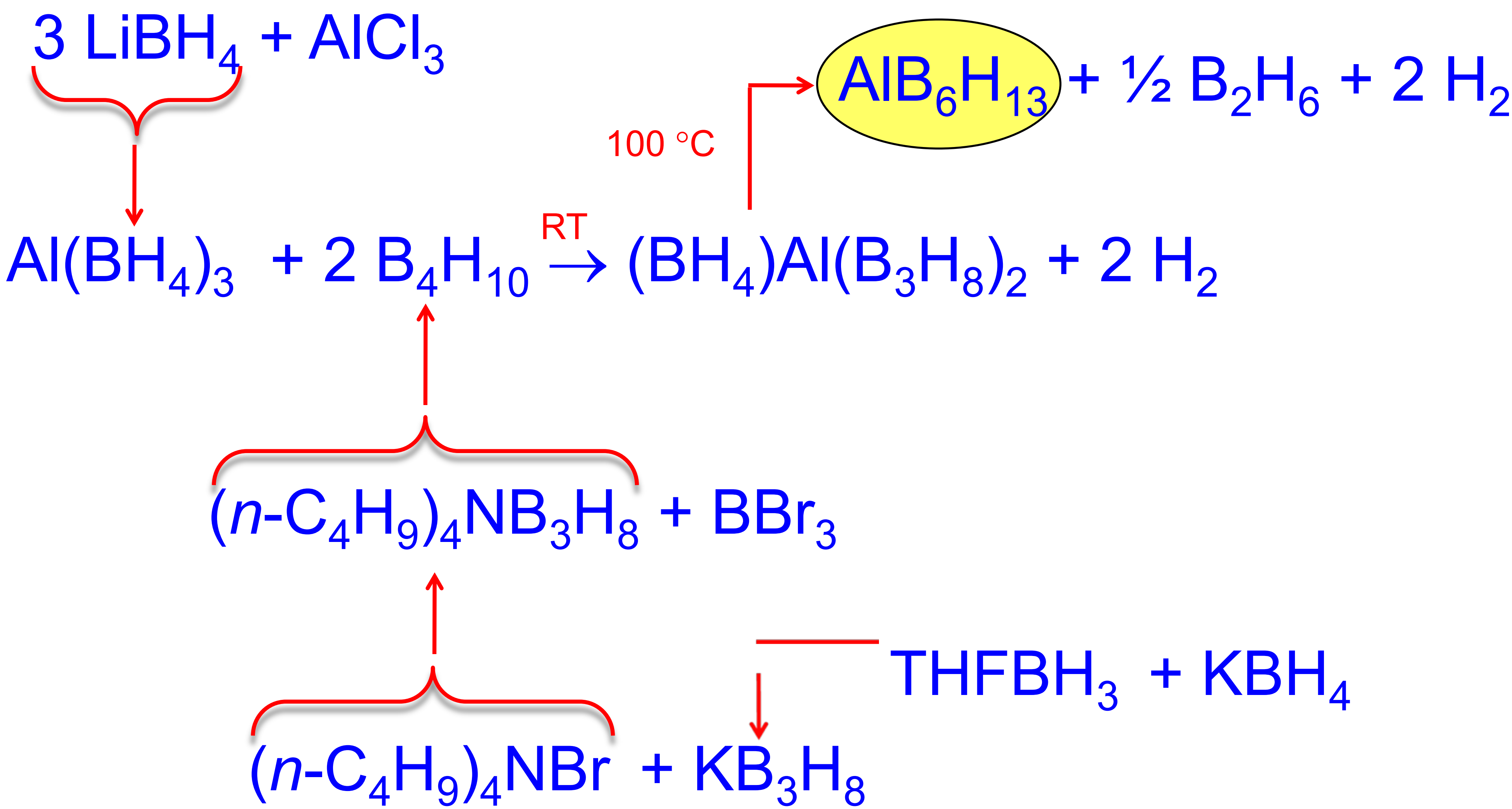
AlB_6H_{13} 12.5 wt.% H

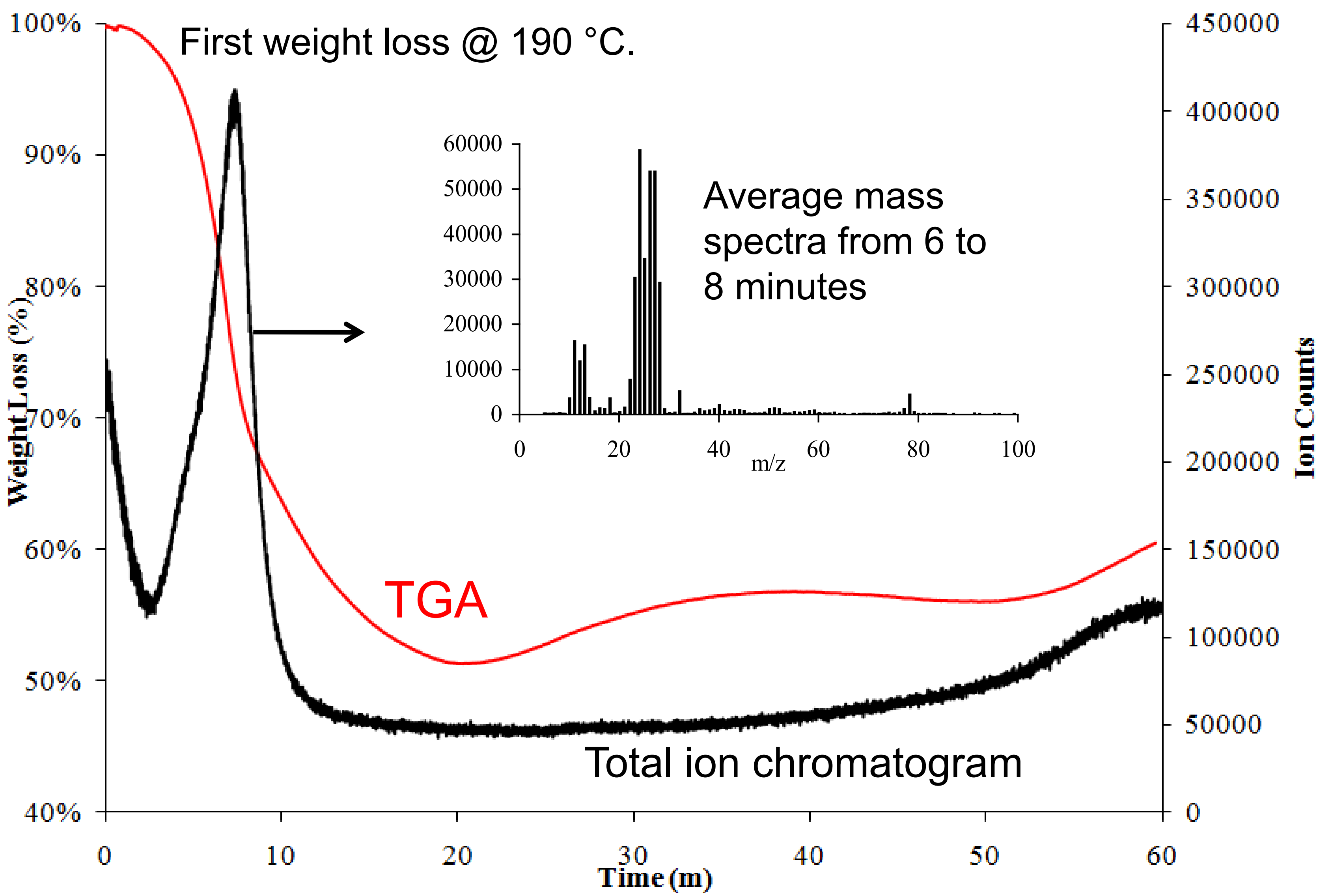
Technical Accomplishments



IR consistent with values reported by Himpsl & Bond

AlB_6H_{13}

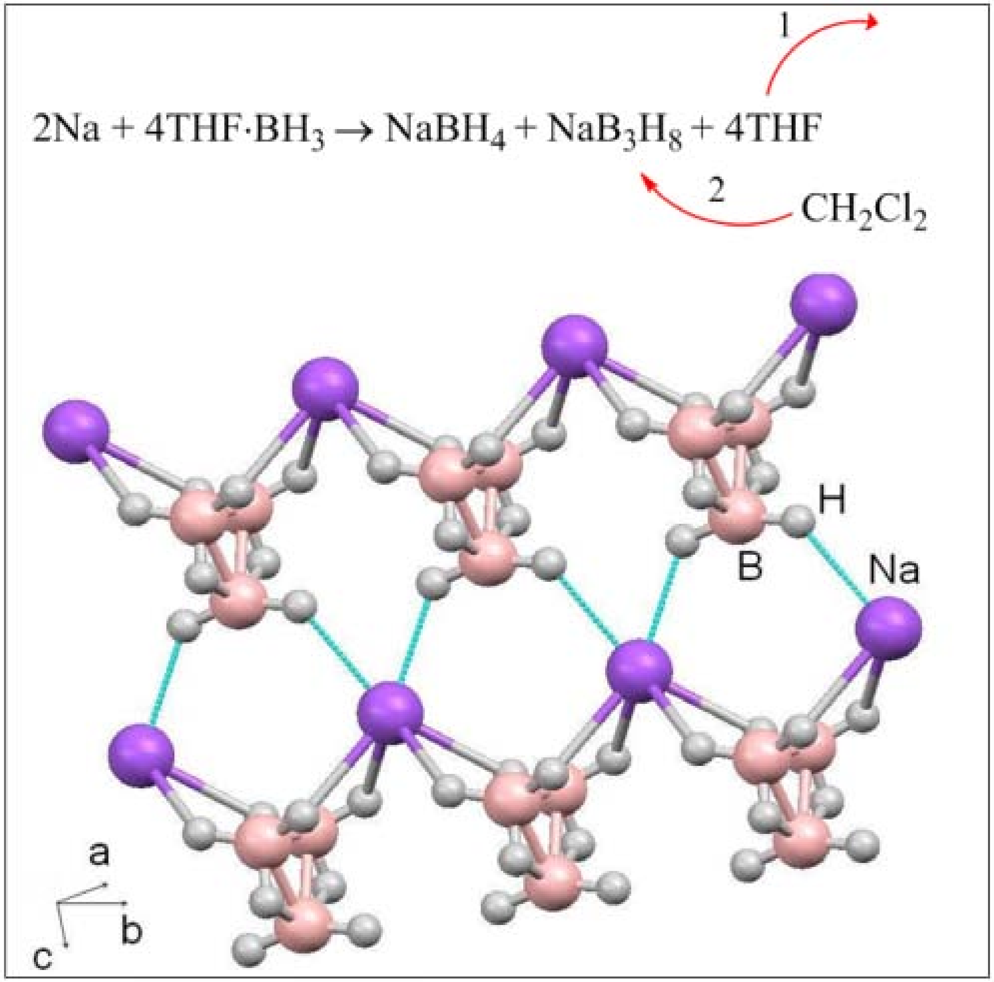
Technical Accomplishments

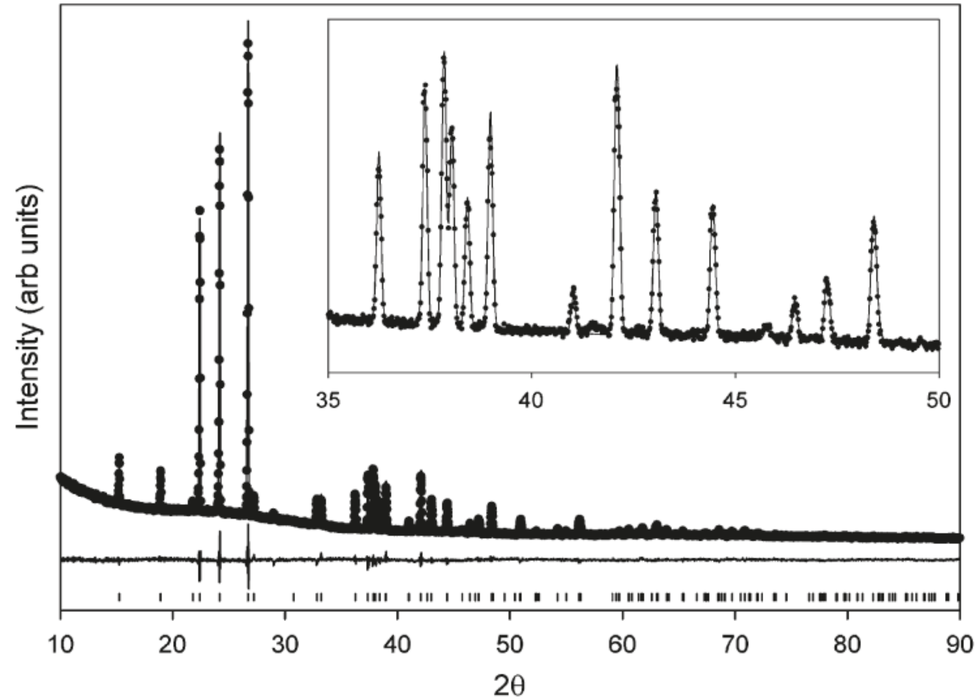


Large amount of B_2H_6 formation during desorption makes AlB_6H_{13} unsuitable for hydrogen storage

NaB_3H_8 – 12.6 wt.% H

Technical Accomplishments

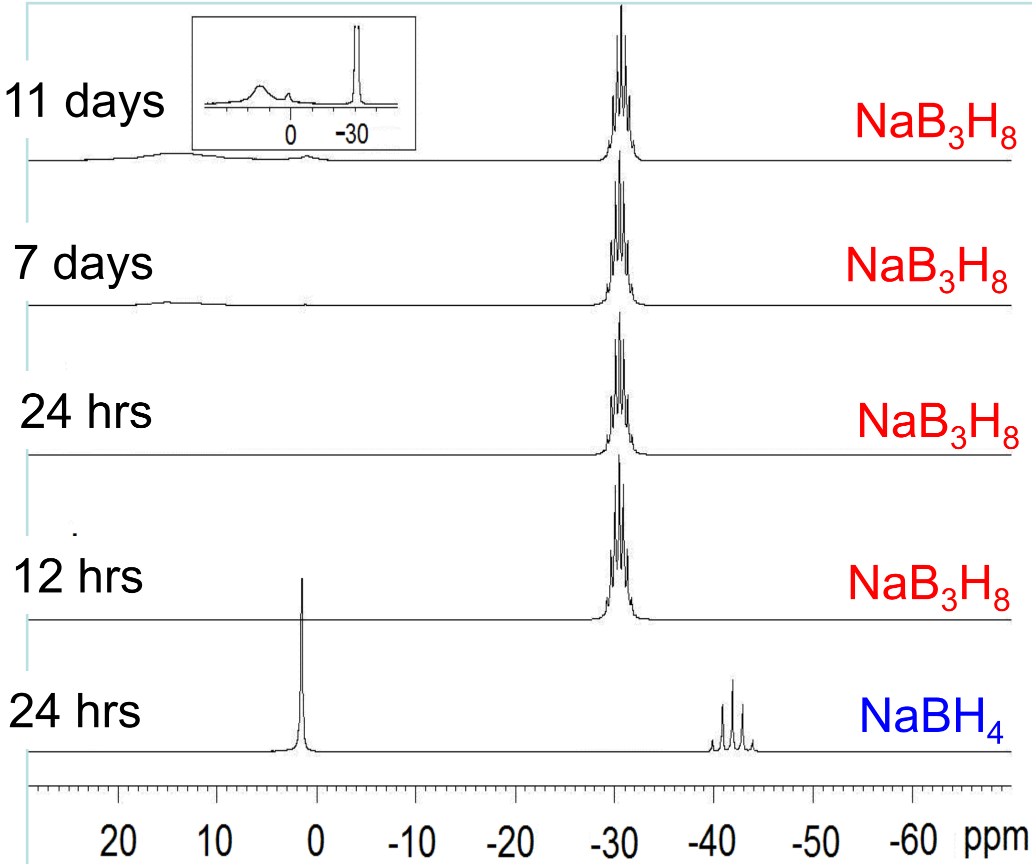




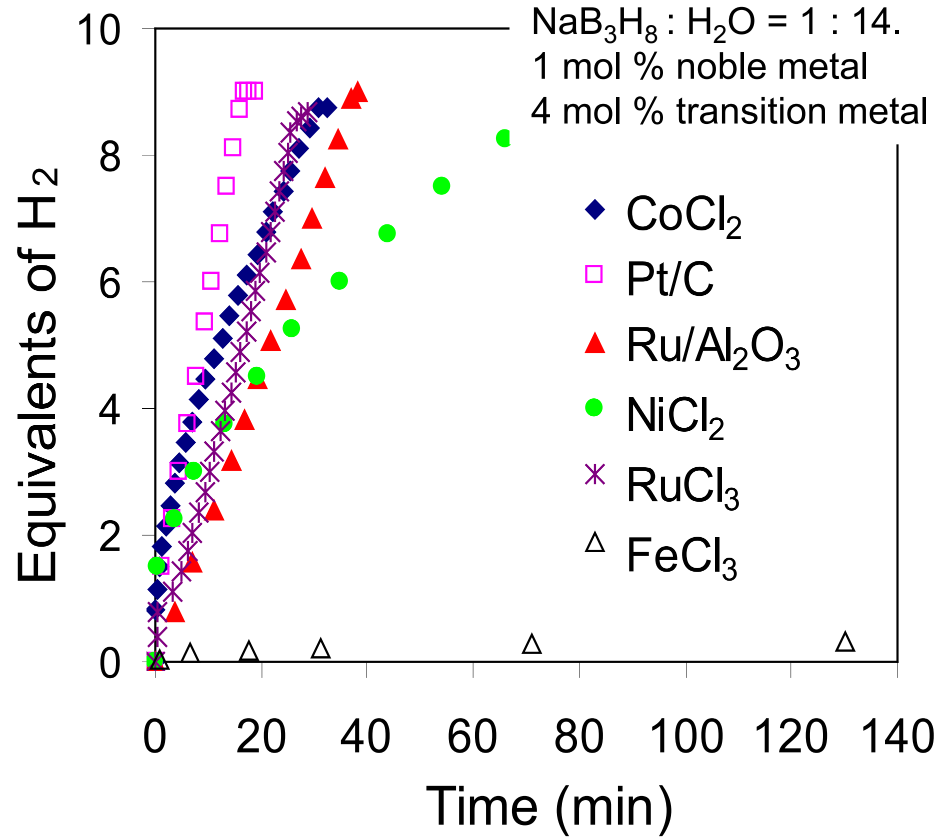
- Safe (B_2H_6 and BF_3 free) synthesis developed for unsolvated NaB_3H_8.
- Thermal decomposition gives of a significant amount of borane species.
- Unsuited for reversible onboard hydrogen storage.
- Structure identified (*Pmmm*).

NaB_3H_8 – 12.6 wt.% H

Technical Accomplishments



^{11}B NMR spectra of water solution



- > 50 % $NaBH_4$ hydrolysed over a day
- < 10 % NaB_3H_8 hydrolysed over a week.

- Hydrolysis produces high (10.5) wt.% pure H_2.
- High solubility and good stability in H_2O.
- Cobalt-based catalyst effective for hydrolysis.
- Better than $NaBH_4$ (7.5 wt.% H) and NH_3BH_3 (5.1 wt.% H) for hydrolysis (solubility in water considered).

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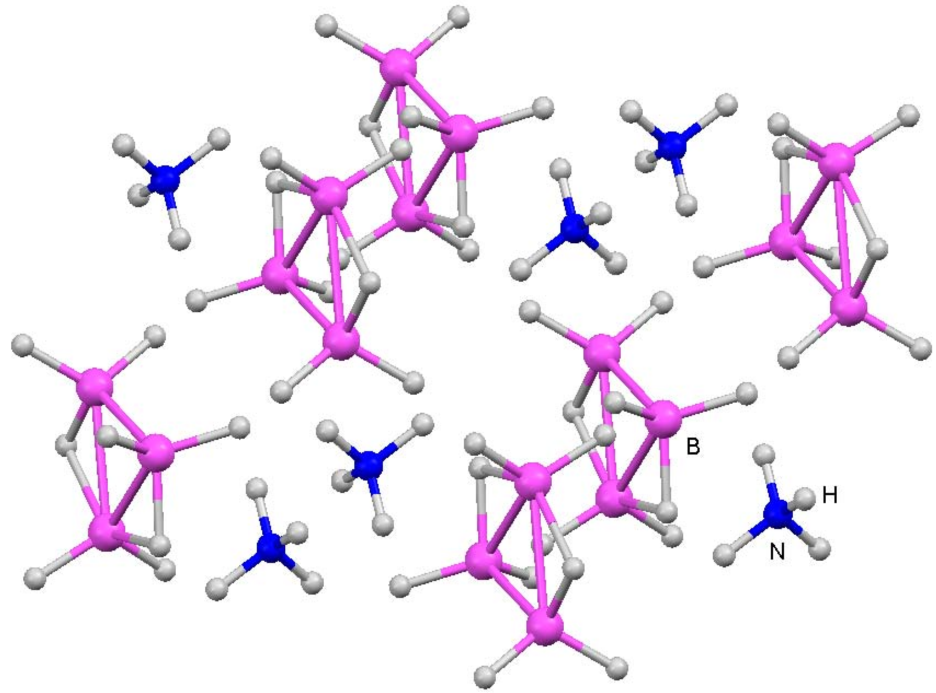
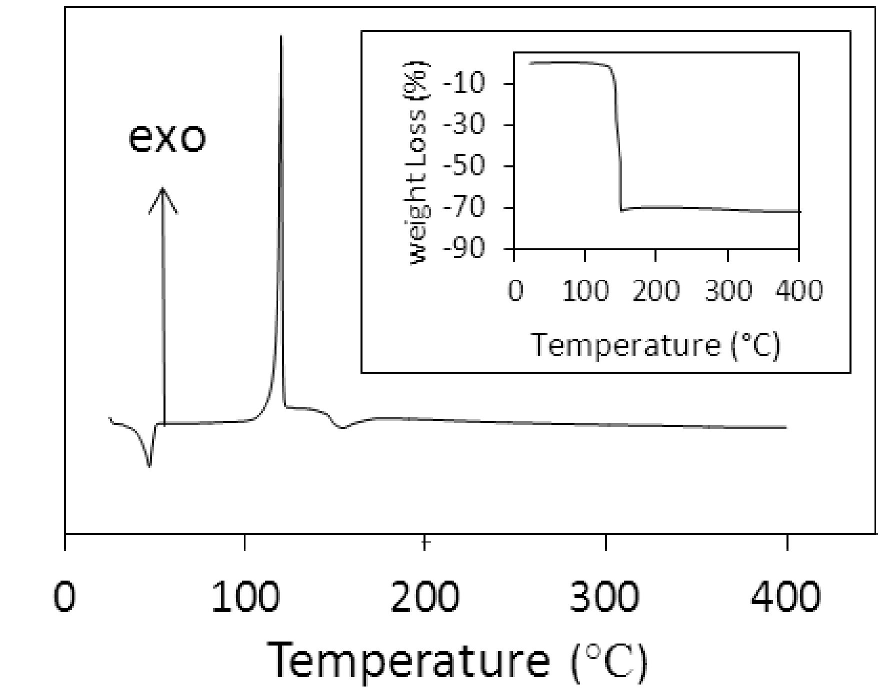
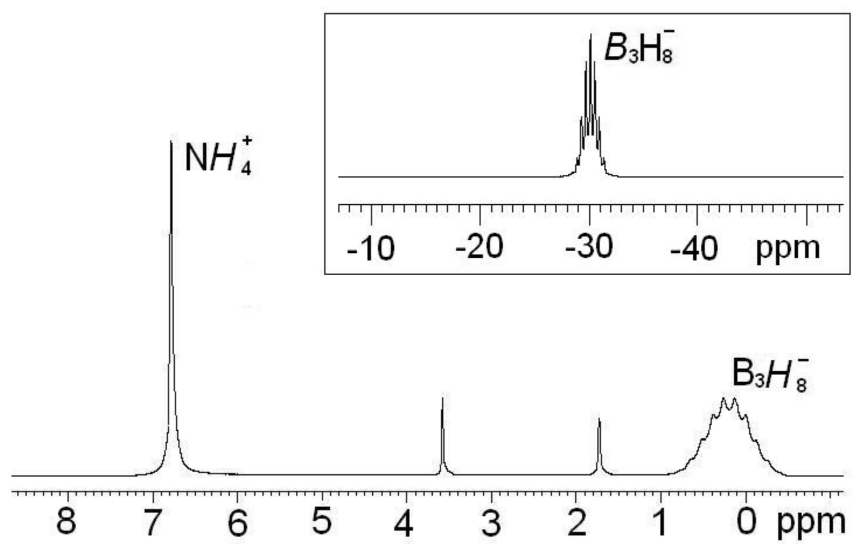
$NH_4B_3H_8$ – 20.5 wt.% H

Technical Accomplishments

$$NH_4Cl + NaB_3H_8 \rightarrow NH_4B_3H_8 + NaCl$$







- Thermal decomposition exothermic – not suited for onboard reversible storage.
- Thermal decomposition gives of a significant amount of borane species.

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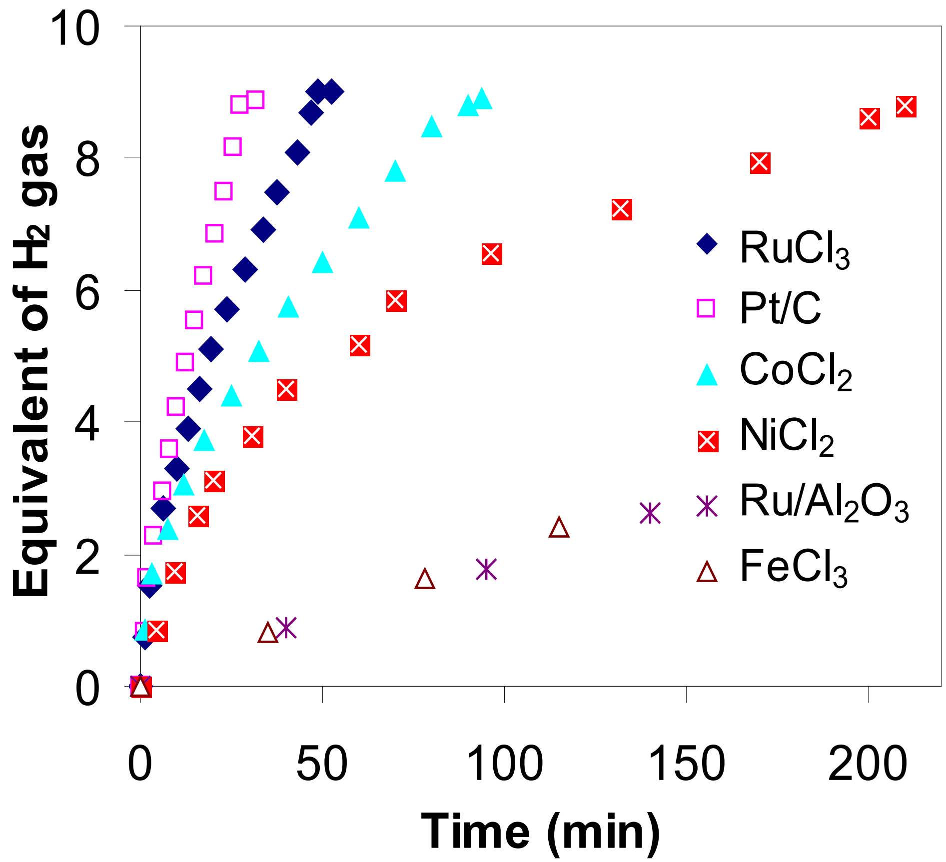
$NH_4B_3H_8$ – 20.5 wt.% H

Technical Accomplishments



1 mol % noble metal
4 mol % transition metal

- Hydrolysis produces high (7.5 wt.%) pure H_2.
- High solubility and good stability in H_2O.
- Cobalt-based catalyst effective for hydrolysis.
- Better than $NaBH_4$ and NH_3BH_3 for hydrolysis.

$$NH_4B_3H_8(s) + 6H_2O(l) \xrightarrow{\text{cat.}} NH_4^+(aq) + 3BO_2^-(aq) + 2H^+(aq) + 9H_2(g)$$

7.5 wt.% H (including H_2O weight)

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Summary

- **AlB_4H_{11}** (13.5 wt.% H):
  - We mounted a multi-pronged structure analysis of AlB_4H_{11} in close collaboration with Northwestern and NIST using solution NMR, solid state NMR, IR, neutron vibration analysis, chemical analysis, bond valence analysis, and PEGS+DFT simulations.
  - Two boron units (BH_4 and a triangular B-B-B unit) in AlB_4H_{11} are already clearly identified from both solution NMR and solid state NMR as well as PEGS+DFT calculations; and solution ^{27}Al NMR suggests two Al environments.
  - We think we got the correct structure or we are very close to get the correct structure.
  - AlB_4D_{11} is made for NOVA analysis which will provide radial atom distribution information for structure analysis.

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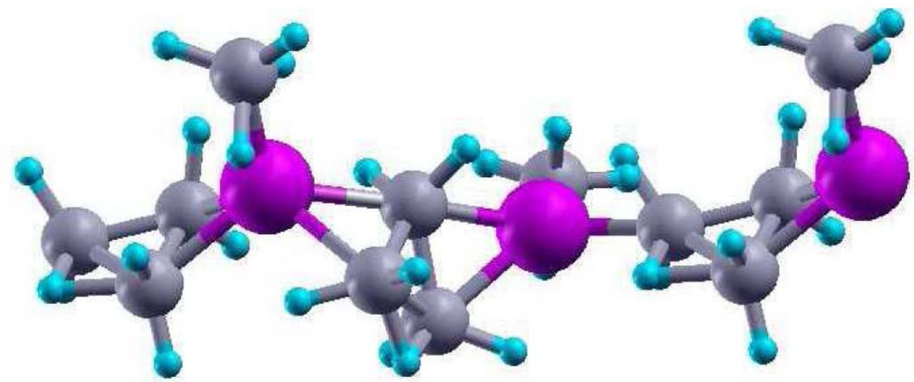

Summary (continued)

- **AlB_4H_{11}** (continued):
  - We performed catalyst screening for AlB_4H_{11}, but found no effective catalysts so far.
  - Structure information will provide more insights into hydrogen interaction mechanisms and clues for catalyst exploration.
- **AlB_6H_{13}**:
  - We finally synthesized this compound for the first time since the 1981 Himpsl and Bond paper.
  - IR consistent with Himpsl and Bond data
  - DSC similar to that of AlB_4H_{11}.
  - Large amount of B_2H_6 found by TGA-MS.
  - Probably not a good candidate for reversible hydrogen storage.

Summary (continued)

- **NaB_3H_8** :
  - Safe (B_2H_6 and BF_3 free) synthesis developed for NaB_3H_8.
  - Thermal desorption gives of large amount of borane species.
  - Unsuited for reversible onboard hydrogen storage.
  - Hydrolysis produces high wt.% (10.5) pure H_2, Better than $NaBH_4$ (7.5 wt.% H) and NH_3BH_3 (5.1 wt.% H)
  - High solubility and good stability in H_2O.
  - Cobalt-based catalyst effective for hydrolysis.
- **$NH_4B_3H_8$** :
  - Thermal decomposition exothermic and gives of a significant amount of borane species – not suited for reversible H_2 storage.
  - Hydrolysis produces high wt.% (7.5 wt.%) pure H_2.
  - High solubility and good stability in H_2O.
  - Cobalt-based catalyst effective for hydrolysis.
  - Better than $NaBH_4$ and NH_3BH_3 for hydrolysis.

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Future Work

FY11

- Compete the structure identification of AlB_4H_{11}.
- Based on structural information, study the hydrogen absorption and desorption mechanisms.
- Based on structure and mechanisms, perform screening of catalysts for improved reversibility.
- Provide property data to DOE Hydrogen Storage Engineering Center.
- Write a final report.

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Collaborations

- Strong collaborations among OSU, Northwestern and NIST are crucial for the identification of the AlB_4H_{11} structure.
- ORNL and OSU collaborate on synthesis and characterization of both AlB_4B_{11} and AlB6H13. Samples were analyzed at OSU, ORNL, JPL and Caltech for hydrogen desorption and structures (via NMR).
- AlB_4H_{11} synthesized at OSU was sent to NIST for neutron analysis.
- $Mg(BH_4)_2$ and $Li_2B_{12}H_{12}$ synthesized at OSU was provided to UTRC and HRL for nano-framework encapsulations.
- $Mg(BH_4)_2$ synthesized at OSU was sent to University of Washington for solid state NMR analysis and to NIST for TEM analysis.
- Several compounds synthesized at OSU were sent to Sandia for analysis using STMBS (simultaneous thermogravimetric modulated beam mass spectrometry).
- $(NH_4)_2B_{12}H_{12}$ synthesized at OSU was sent to Ford for further study.
- Initiated collaboration with Kyushu University for NOVA analysis of AlB_4D_{11}.

A close collaboration among OSU, Northwestern, NIST and ORNL led to the progress.

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