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Hydrogen Storage Characterization and Optimization Research Effort (HySCORE)

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Pacific Northwest National Laboratory

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Project ID: ST132

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HySCORE BERKELEY LAB NIST NREL NATIONAL RENEWABLE ENERGY LABORATORY

Overview

Timeline

Project Start: 10/1/2015

End: Project continuation determined by DOE. Currently scheduled through 9/30/18

Budget

HySCORE: $8.2M

Federal Share:

NREL: $2.6M

LBNL: $2.4M

PNNL: $2.4M

NIST: $0.8M

PNNL Funds Spent: ~$1.2M (Estimated as of 3/31/17)

Barriers

- **General:**
- A. Cost; B. Weight and Volume; C. Efficiency; E. Refueling Time
- **Reversible Solid-State Material:**
- M. Hydrogen Capacity and Reversibility;
- N. Understanding of Hydrogen Physi- and Chemi- sorption; O. Evaluation Facilities.

Partners/Collaborators

- NREL - Tom Gennett, Phil Parilla
- NIST - Craig Brown, Terry Udovic
- LBNL - Jeff Long, Martin Head-Gordon
- HyMARC - Brandon Wood, Vitalie Stavila, Lenny Klebanoff
- Hawaii – Craig Jensen
- IEA-HIA Task 32 –B Hauback, P Chen, T He, S Orimo
- AIST – Q Xu, Y Himeda, H Kawanami
- FAU Erlangen Nürnberg – K Mueller

Milestones

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6/30/2016	Perform testing on the variable pressure capability of new low temperature NMR between 1-10 bar at 273 K.	complete
9/30/2016	Measure ^{1}H NMR of physi-sorbed H_2 at temperatures between 100 and 300 K at 1 & 5 bar H_2 to show that experimental heat of adsorption is within 5 kJ/mol of reported value. (last year AMR)	complete
12/31/2017	Develop an improved computational protocol (density functional theory, DFT) and hybrid DFT/molecular mechanics MD simulations to predict enthalpy and free energy of H_2 uptake and release in complex hydride materials and calculate NMR chemical shifts of key intermediates . *(technical backup slides)*	complete
3/31/2017	Measure vapor pressure of Mg(BH4)2*THF adduct as from 300 – 373 K Calculate the binding energies of THF adducts 1-3 and use TPD-MS to measure temperature for release of THF. (accomplishments)	complete
6/30/2017	Measure ^{1}H NMR of sorption standard at 100 bar and 100 K. Assign the sorption and free hydrogen peaks and show that experimental heat of adsorption is within 10% of reported value.	on track
9/30/2017	Provide analysis and characterization of 2 samples assigned by DOE (NMR , TEM or Calorimetric) *(Collaborations)*	on track

We build upon the guidance provided by Hydrogen Storage Centers of Excellence

PNNL leverages unique capabilities to assist material developers:

- Solid-state in-situ high-pressure variable-temperature NMR (to identify key intermediates involved in the release and uptake of H_2),
- Variable pressure reaction calorimetry to experimentally determine enthalpy of H_2 addition in solid and liquid hydrogen stores (high pressure cells unique to PNNL)
- XRD and TEM for new materials characterization
- Computational chemical kinetic modeling (input for "*Soup*") and spectroscopy library (NMR, IR, Raman)

Goal of HySCORE:

- to assist materials developers to measure (and validate) critical properties and to double energy density from 25 to 50 g H_2/liter.
- to develop and enhance FCTO hydrogen storage **core characterization capabilities**
- to **validate** *new concepts* for input into predictive models that will accelerate progress of materials developers and improve approaches to onboard H_2 storage

Assisting HyMARC core team & seedling projects with materials characterization

- ST118. *Improving the Kinetics and Thermodynamics of $Mg(BH_4)_2$ for Hydrogen Storage.* LLNL, SNL. **Solid state NMR analysis of hydrogenated MgB2**.
- ST 120. *Design and Synthesis of Materials with High Capacities for Hydrogen Physisorption.* Cal Tech. **TEM analysis of metal doped high surface area carbons.**
- ST 127-130. *Hymarc consortium.* **Experimental and computational spectroscopy library (paper)**
- ST137. *Electrolyte Assisted Hydrogen Storage Reactions.* Liox Power, HRL. **Solid state and solution NMR studies of H_2 storage materials with electrolytes**
- ST 138. *Development of Magnesium Boride Etherates as Hydrogen Storage Materials*. Hawaii. **XRD analysis of boride etherates**

Dynamic connection between theory and experiment

- Use theory to guide experiment and interpret complex results
  - Predict key intermediates and products based on thermodynamics beyond E_{static} (ΔH^o and ΔG^o)

- Use experiment to benchmark and validate theory
  - NMR to follow evolution of H_2 release pathways (key intermediates and products)
  - Calorimetry to measure enthalpies of H_2 uptake and release

Progress reports illustrates how we assist materials developers

- Liquid carriers:
  - **s-Triazine $C_3N_3H_3$ (69 g H_2/liter)** – ΔH ranges from 36 – 57 kJ/mol H_2
    - Theory - Why is there such a large range of enthalpies Error bars too large to be useful, e.g., T_c varies from 20–160 °C
    - Experiment – Can we use calorimetry to measure DH to benchmark theory when there is a discrepancy . What is experimental heat of hydrogenation of triazine – calorimetry
- Complex hydrides:
  - **$Mg(BH_4)_2$ (2.5–15 wt% H_2)**
    - Theory – what intermediates and products should be targeted to enhance reversibility?
    - Theory – are there unique spectroscopic signatures for key intermediates?
    - Experiment – Can in-situ solid state NMR be used to follow the chemistry and compare additives and reaction conditions?
    - Experiment and Theory - Does a THF 'ligand' change the reaction pathways?

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Liquid Organic Hydrogen Carriers (LOHC)

What are best approaches to predict ΔH_{H2} for new LOHCs?

Air Products: target materials with ΔH_{H2} 40-55 kJ/mol for optimum reversibility (assumes ΔS_{H2} ~ 125 J/K/mol)

- Predicting ΔH_{H2} for a new LOHC – three recommendations:
  - (i) CCSD(t) or (ii) calorimetry or (iii) DFT gas phase ΔH_{H2} * scaling factor 0.9.
    - Triazine ca. 48 kJ/mol H_2 (T_c = 110 °C)
- Reaction calorimetry provides capability to determine kinetics and thermodynamics of release and uptake of H_2 in LOHCs.

- Recommendations for future work
  - Pd/C catalyst 'too good' resulting in C-N bond scission
    - Investigate oligomers of triazine to prevent formation of volatile intermediates
    - Use a more selective catalyst to activate C-H bonds (not C-N bonds)

Triazine is a liquid organic hydrogen carrier (LOHC) that has a near perfect ΔH_{H2} for reversible H_2 storage – or does it?

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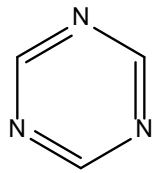
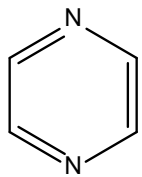
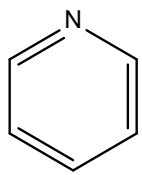
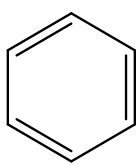
	ΔH_{H2} (kJ/mol H_2)
	36.4 to *(54.4)* *48*
	*56.5 (62.8)* *57*
	*63.6 (67.4)* *62*
	*65.3 (73.6)* *69*

Air Products *(Clot, Eisenstein, Crabtree)*
CCSD(t)
NIST data base

What level of theory is required to get 'experimental' accuracy? CCSD(t)

Do we need to account for condensed phase thermodynamics? (solvation or reactants and products)

Use calorimetry to get experimental *ΔH, in condensed phase*

Theory shows calculated enthalpy H_2 addition to triazine depends on stability of isomer

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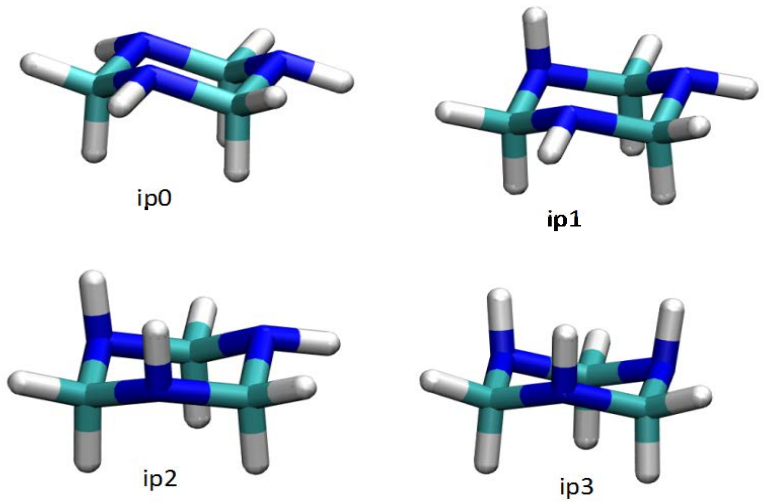

	E	Ezpc	H	ST	G
Ip0	-70.7	-35.1	-43.1	-35.6	-7.5
Ip1	-79.5	-43.5	-51.0	-35.6	-15.5
Ip2	-84.5	-48.1	-55.6	-35.6	-20.1
Ip3	-85.8	-49.0	-56.9	-36.4	-20.5

- At least 4 different isomers.
  - Ip0 is least stable (-43.1 kJ/mol)
  - ip3 is most stable (-56.9 kJ/mol)
- Ip0 could be formed on surface of heterogeneous catalyst
- What are the barriers for interconversion between isomers?

Bojana Ginovska

Barrier to isomerization is low enough to form most stable isomer even at room temperature

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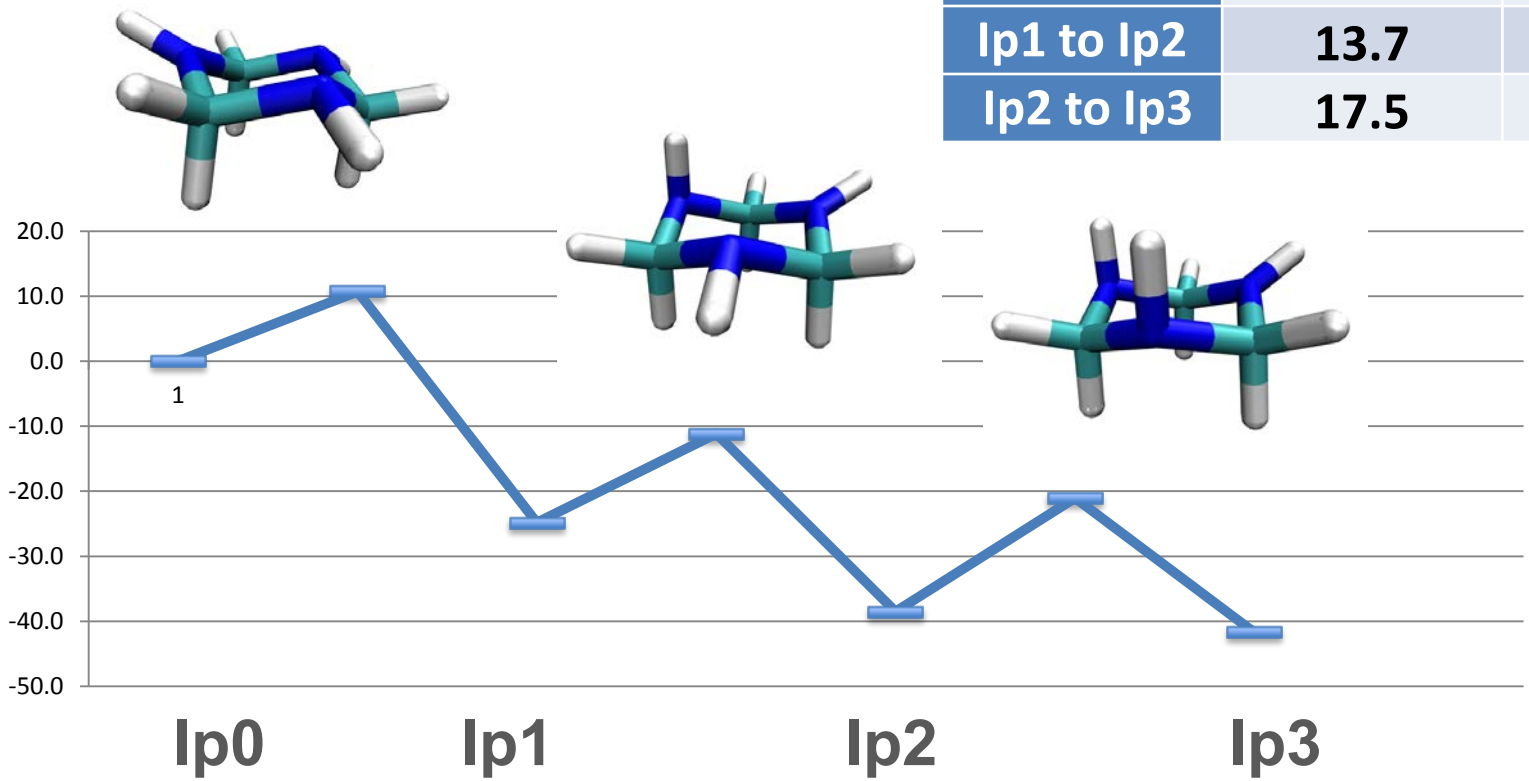
Transition states for inversion reactions of $C_3N_3H_9$:

	ΔH	*ΔG*
reactant	kJ/mol	kJ/mol
Ip0 to Ip1	10.7	11
Ip1 to Ip2	13.7	14
Ip2 to Ip3	17.5	17.7



Solvation does not significantly stabilize LOHCs

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Reaction (H_2 uptake)	thermochemistry per H_2 ΔH_s (ΔH_g)	ΔG_s (ΔG_g)
▶ $C_3N_3H_3+3H_2 \Leftrightarrow C_3N_3H_9$	-58.4(-56.9)	-22.1(-20.5)
▶ $C_3N_3H_9+3H_2 \Leftrightarrow 3CH_3NH_2$	-50.0(-50.9)	-53.7(-54.5)
Ring opening		
▶ $C_3N_3H_3+6H_2 \Leftrightarrow 3CH_3NH_2$	-108.0(-107.8)	-76.6(-74.1)

- **solvation correction probably unnecessary, gas phase calculation sufficient. Check to see if D3 (dispersion correction) better than D2.**
- **Ring opening destabilizes perhydro-triazine**

Triazine products unstable so demonstrated capability to measure *ΔH* with pyrazine (diazine)

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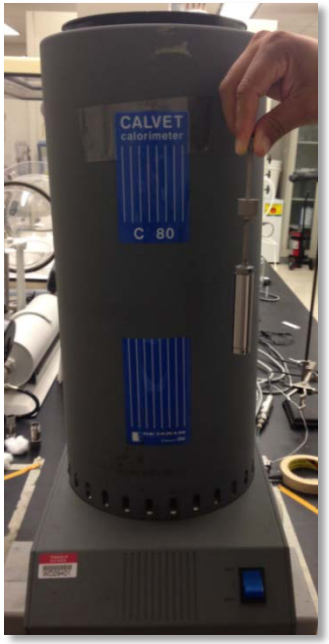

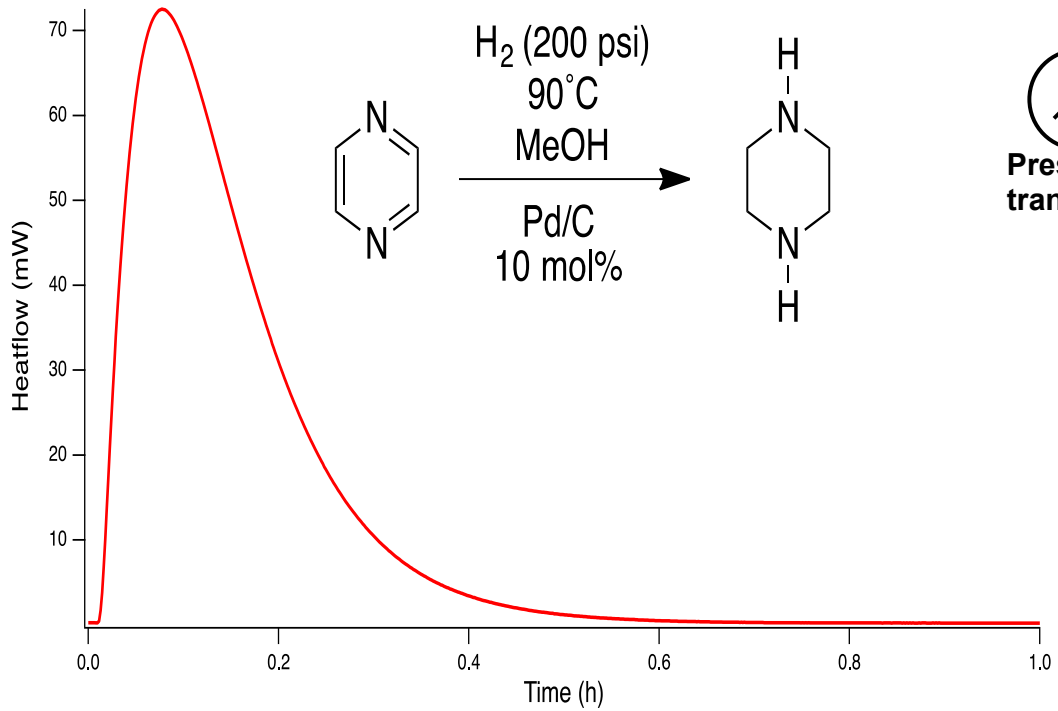

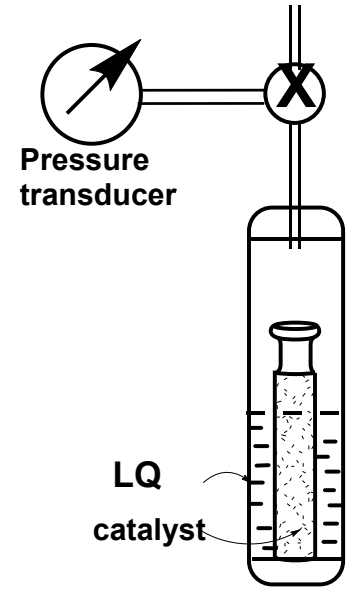

ΔH_{exp} = -64(4) kJ/mol H_2 (this work)
ΔH_{DFT} = -56 to -63 kJ/mol H_2

Note heat is measured as function of time so we can compare rates of different catalysts

Liquid carriers – reaction calorimetry provides capability to benchmark theory (thermodynamics)

Lessons Learned

- to get accurate prediction of ΔH_{H2} it is critical *to* Identify all the isomers
- Solvent corrected DFT (continuum model) shows solvation has little affect on calculated ΔH_{H2} gas phase calculations sufficient with scalar.
- Scaling factor needed for (D2) DFT. Is D3 better?

Success will be using calorimetry to optimize catalysis (kinetics)

Complex hydrides: $Mg(BH_4)_2$ and solvates of $Mg(BH_4)_2$

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What is optimum range of ΔH^o_{H2} for $Mg(BH_4)_2$? (need to know ΔS^o_{H2})

- Calc. ΔS^o_{H2} (ΔH^o_{H2} ΔG^o_{H2}) for $B_3H_8^-$, $B_2H_6^{2-}$, $B_3H_6^{3-}$, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$.
  - ΔS_{H2} ca. 90±10 J/K/mol (so ΔH_{H2} should range from 30- 45 kJ/mol)
    - ΔH_{H2} **$B_3H_8^-$**. Too large: not sufficiently stable to make without additives to stabilize
    - ΔH_{H2} **$B_{12}H_{12}^{2-}$**. Too small: more stable than BH_4 will need extremely high pressure to regenerate
    - ΔH_{H2} $B_3H_6^{3-}$ & **$B_{10}H_{10}^{2-}$** (7.5 and 8.2 wt% H_2.) Just right:

- Develop *in-situ* ^{11}B NMR approach to follow evolution of B with different additives
- Calculated ^{11}B NMR for $B_3H_8^-$, $B_2H_6^{2-}$, $B_3H_6^{3-}$, $B_{10}H_{10}^{2-}$.
  - Observe $B_{10}H_{10}^{2-}$ as major product in THF*$Mg(BH_4)_2$.
  - Observe -48 ppm peak – might be $B_3H_6^{3-}$?

Complex hydrides: $Mg(BH_4)_2$ and solvates of $Mg(BH_4)_2$

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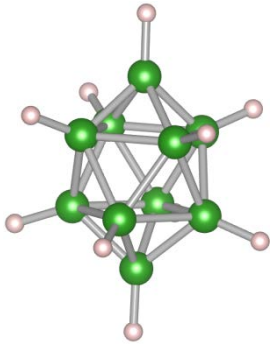
Does THF enhance selectivity to form $MgB_{10}H_{10}$?

- Yes - Validated THF solvate of $Mg(BH_4)_2$ forms $MgB_{10}H_{10}$ with high selectivity at lower temperatures
  - Selectivity
    - No THF: $[MgB_{10}H_{10}]$ / $[MgB_{12}H_{12}]$ ~ 1
    - With THF: $[MgB_{10}H_{10}]$ / $[MgB_{12}H_{12}]$ >30/1.
  - Reactivity
    - Without THF: $Mg(BH_4)_2$ conv to $[MgB_{10}H_{10}]$ ca. <1% (180 °C 24 h)
    - With THF: $Mg(BH_4)_2$ conv to $[MgB_{10}H_{10}]$ ca. 60% (180 °C 24 h)
    - Conversion to B10H10 may be limited by equilibrium (ΔHo ca. 39 kJ/mol)



- Recommendations for future research: Foundational studies to understand how additives control selectivity of H_2 release pathways

Do THF adducts of $Mg(BH_4)_2$ enhance both reactivity and selectivity?

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Reaction	ΔE (ΔG) (kJ/mol H_2)	wt% H_2
1. $3Mg(BH_4)_2 \Leftrightarrow Mg(B_3H_8)_2 + 2MgH_2 + 2H_2$	176(124)	2.5
2. $3Mg(BH_4)_2 \Leftrightarrow Mg_3(B_3H_6)_2 + 6H_2$	53 (9.7)	7.5
3. $5Mg(BH_4)_2 \Leftrightarrow Mg(B_{10}H_{10}) + 4\ MgH_2 + 11H_2$	59 (10.2)	8.2
4. $6Mg(BH_4)_2 \Leftrightarrow Mg(B_{12}H_{12}) + 5\ MgH_2 + 12H_2$	48 (-4)	8.1

(I) Characterization of key intermediates $B_3H_8^-$ vs $B_2H_6^{3-}$

Theory predicts $B_2H_6^{3-}$ but experiment shows $B_3H_8^-$. Work to understand the discrepancy between experiment and theory (see technical backup slides)

(II) Validation that additives modify reaction pathways

(THF makes reaction 3 most favorable)

If true, how much THF is required to control selectivity?

Craig Jensen

Chemical additives change the reaction pathway for H_2 release from $Mg(BH_4)_2$

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Approaches

- Chemical: Bond to complex, e.g., Mg cation (tunable binding energy)
- *Physical : Ball mill additive into mixture*

Effects

- Kinetic
  - Chemical effect: non-innocent ligands (lower barrier for H2 activation)
  - *Materials effect: Physical change phase, defects, grain boundaries*
- Thermodynamic
  - Stabilize starting material and/or products
  - Stabilize intermediates, (favor one competing pathway over another)

THF binds to Mg and is a 'chemical additive approach'
THF 'solvates' of Mg to differentiate with solvents
e.g., 1:1 stoichiometry not excess solvent

Accomplishment

Theory suggests that *chemical additive* can be a sound approach, i.e., not volatile, binds to Mg^{2+}

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in kJ/mol	E	Ezpe	H	G
Mg(BH4)2+THF -> Mg(BH4)2*THF	-92	-86	-85	-38
Mg(BH4)2*THF+THF -> Mg(BH4)2*THF2	-67	-61	-60	-11
Mg(BH4)2*THF2+THF -> Mg(BH4)2*THF3	-29	-23	-23	30
MgB12H12+THF -> Mg(B12H12)2*1THF	-197	-188	-189	-139
Mg(B12H12)2*1THF+THF -> Mg(B12H12)2*2THF	-124	-116	-113	-72
Mg(B12H12)2*2THF+THF -> Mg(B12H12)2*3THF	-100	-87	-87	-29

- First THF binds very strong, last THF binds very weak $THF_1 > THF_2 > THF_3$
- THF binds more tightly to Mg in $MgB_{12}H_{12}$ then Mg in $Mg(BH_4)_2$

This is important to insure THF 'sticks' to Mg during the reaction

Accomplishment

TGA/DSC experiment confirms calculations that first THF binds stronger than 3rd THF

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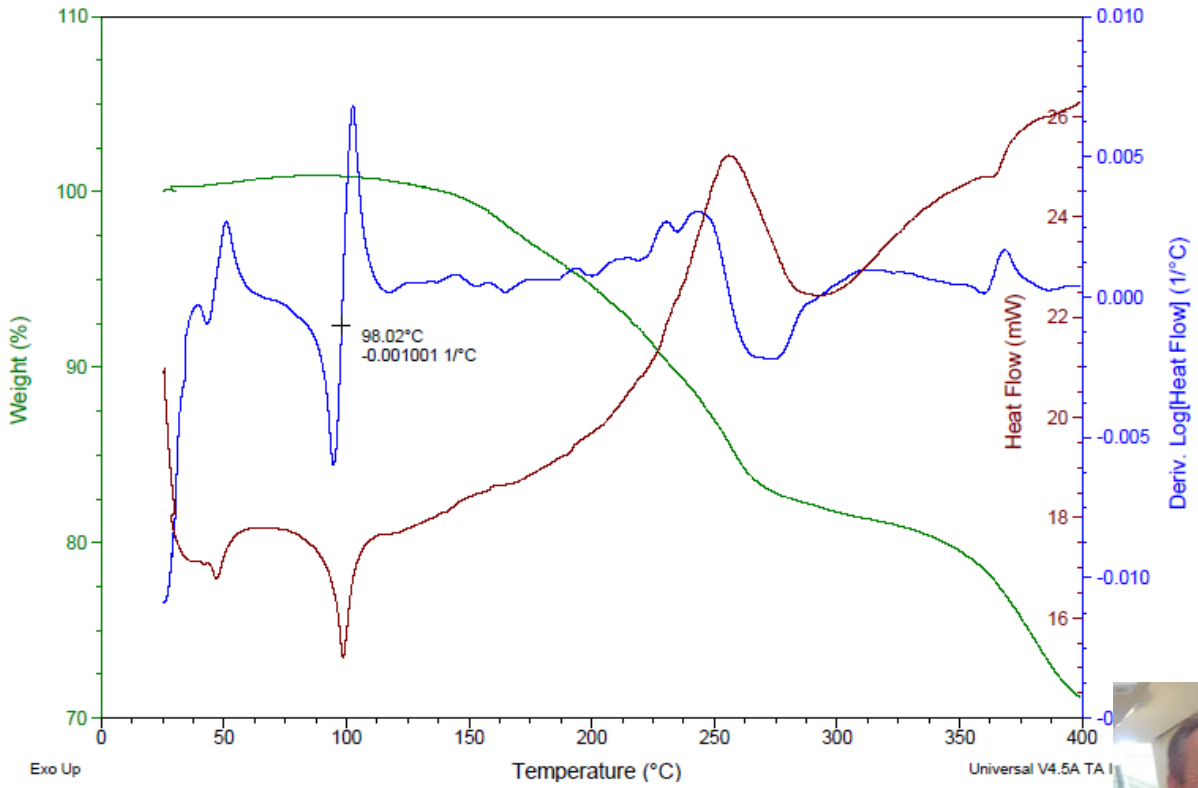
- **0.5THF*$Mg(BH_4)_2$**
- loss of 0.5THF ca. 40 % wt loss.
- Need to heat over 200 °C to release THF (Et_2O comes off at 150 ° C)
- See phase change at 95 °C
- See other 'volatiles' that are from prep of $Mg(BH_4)_2$. E.g. NEt_3, Me_2S, Et_2O.



< 1 THF binds tightly to Mg and lowers T for H_2 release. Results depend on source of $Mg(BH_4)_2$ (and THF) when observing volatile components

Tom Gennett

In-situ solid state ^{11}B NMR can be used to follow evolution of amorphous intermediates during H_2 release from $[Mg(BH_4)_2$ *THF adducts

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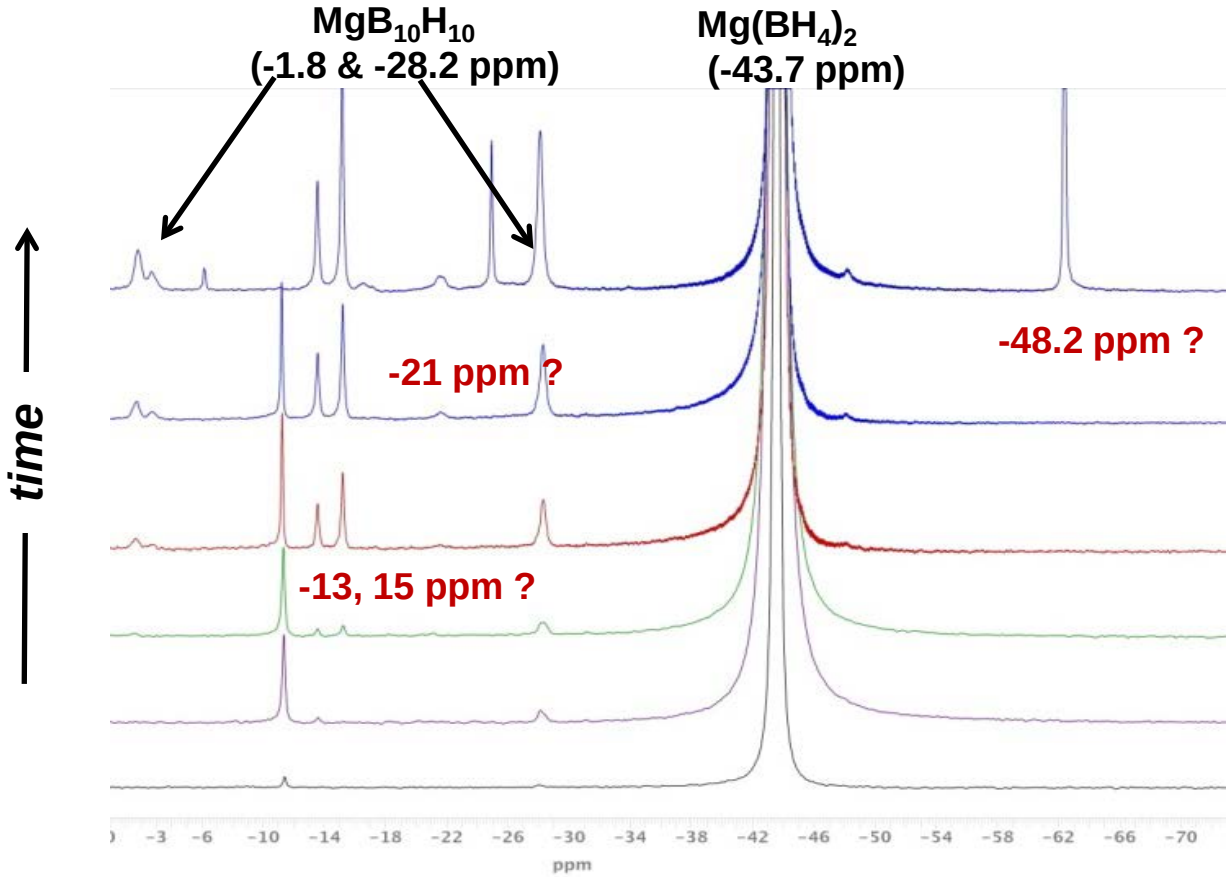
Marina Chong



- Unknown peak(s) at -13, -15, -21 and -48.2 ppm –
  - is -48.2 ppm $Mg_3(B_3H_6)_2$?
  - -13 starts and -15 catches up and passes

$B_{10}H_{10}$ appears to grow in from beginning

Summary Solvates work – not yet perfect. ≤1:1 THF/Mg decreases temperature for H_2 release and changes product selectivity

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Lessons learned

- THF enhances reactivity and selectivity
- THF better adduct then Et2O, TG, Diglyme, DMSO, TEA, & pyridine, binds tighter and less side reactions
- Need <1THF:Mg to prevent VOC. E.g., 0.5 THF (6.1 wt% H_2)
- *New concept: Solvates induce low temperature phase change to enhance diffusion rates and enable low temperature H_2 release*

success will be when we understand how solvates enhance selectivity – then we can make them better.

Future work

With Hawaii to complete additives study

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Phuong Nguyen, Sunil Shrestha and Craig Jensen

Do chemical additives stabilize or destabilize H_2 uptake and release from $Mg(BH_4)_2$?

Preliminary results for $B_{12}H_{12}$ suggest 'destabilization'

Measure ΔH for regen of $THF*Mg(BH_4)_2$ from reducing $THF_3Mg(B_3H_8)_2$ using calorimetry. (experimentally benchmarking)

Determine if the observed reversible dehydrogenation of Mg-borohydride to Mg-boranes can be extended to $THF*Mg(BH_4)_2 \Leftrightarrow THF*MgB_{10}H_{10}$

compare glyme and MeTHF to THF for reactivity and selectivity

Make $Mg_3(B_3H_6)_2$ by authentic pathway. Does it convert to BH_4 – if so 'design' additive to make it from $Mg(BH_4)_2$

With HyMARC to model the *soup*. The *soup* is a model that accounts for both chemical and physical phenomena

Any proposed future work is subject to change based on funding levels

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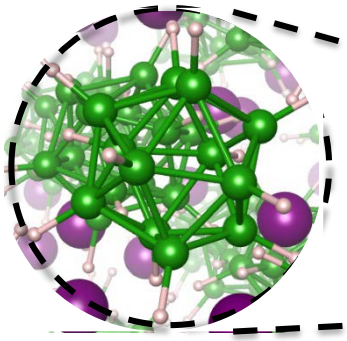
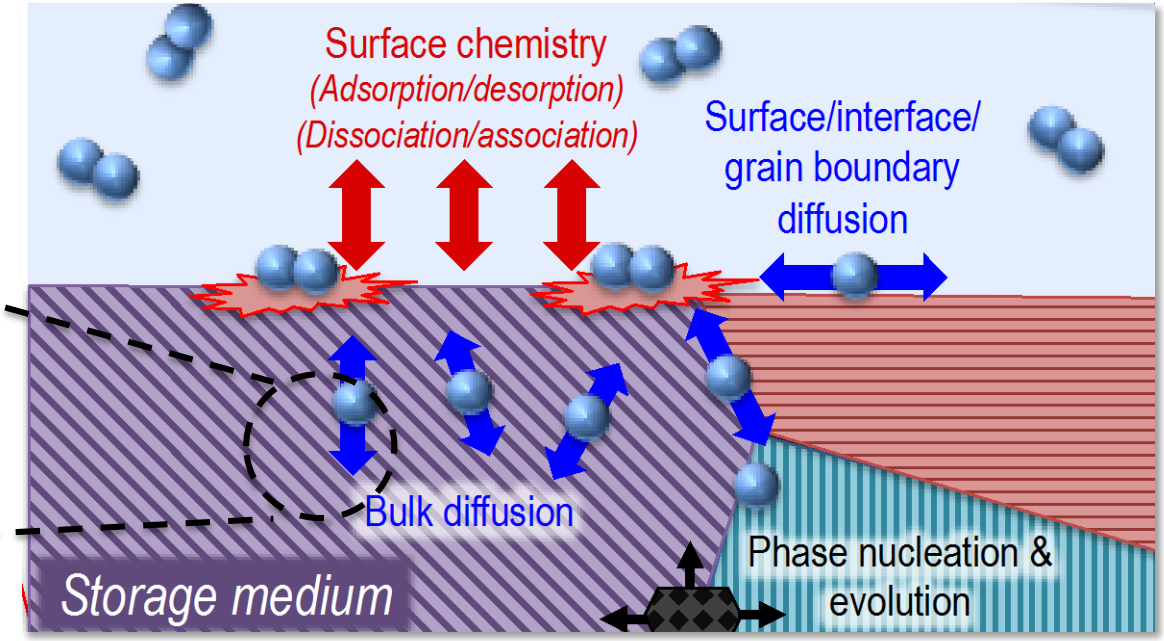
Predictive model accounting for both chemical and physical effects. Tae Wook Heo, Shinyoung Kang, Brandon Wood, Iffat Nayyar, Bojana Ginovska

Bond chemistry





Graphic courtesy of Vitalie Stavila

Future work

With NREL, LBNL and NIST to investigate physi-sorption

Any proposed future work is subject to change based on funding levels

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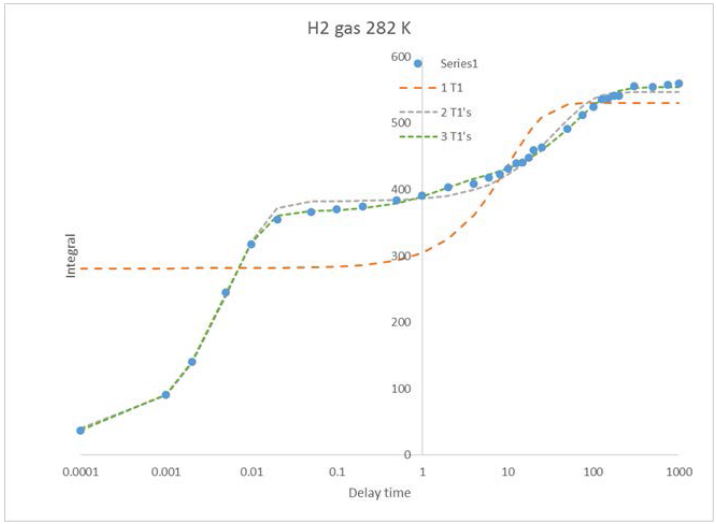
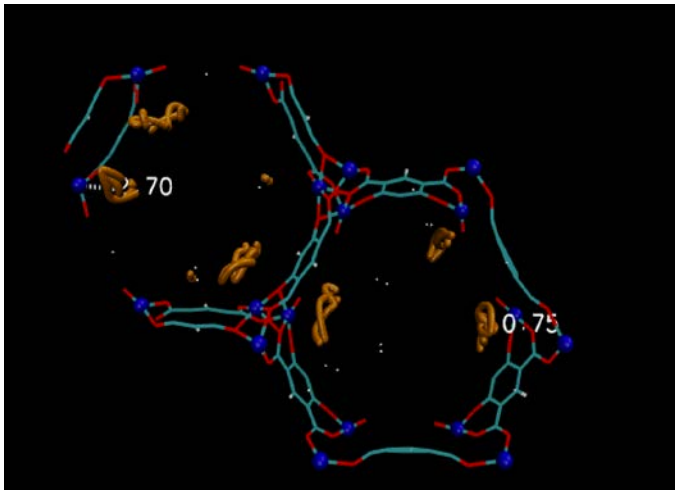
Investigate dynamics of H_2 interactions with metal centers to better model low temperature (30-100 K) ^{1}H NMR

- Able to get binding energies from T_1 measurements (not so simple to measure change in intensity)
- Demonstrate multiply H_2's per metal center





Preliminary results CP2K using DFT showing dynamics of H_2 at 75 K. Orange spaghetti plot are H_2 within 3.5 Å of cobalt cation in dobdc illustrates H_2 rotation on 1000 ps time scale. Longer simulation times will give insight into translational motion

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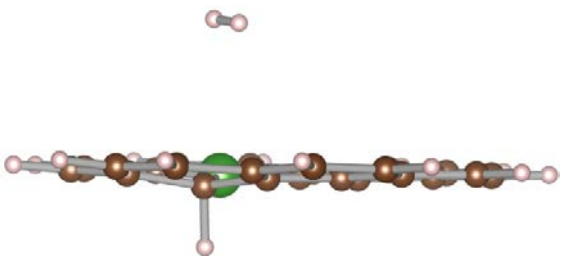
With NREL, LBNL and NIST to investigate physi-sorption

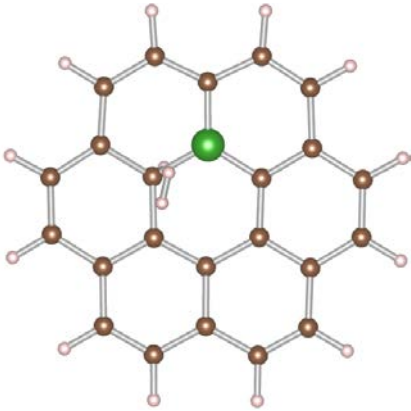
Investigate the binding energies of H_2 to B and N doped carbons

- Use theory to guide synthesis - initial results w/ gas phase, moving to periodic systems (graphene's)
- Use chemistry to place B and N in known structures
- Use ^{11}B NMR to identify sp^2 vs. sp^3 boron and B-B vs. B-C bonding.

Iffat Nayyar

System	Nomenclature	Binding Energy (KJ/mol H_2)
$C_{24}H_{12}$	C	-6.2
$BC_{23}H_{13}$	B	-7.6
$NC_{23}H_{13}$	N	-6.7
$B_2C_{22}H_{12}$	BB ortho	-6.6
	BB meta	-5.9
	BB para	-5.6
$B_2C_{22}H_{12}$	BN ortho	-6.8
	BN meta	-7.4
	BN para	-6.9
$B_3N_3C_{16}H_{12}$	BN cyclic	-5.5





Report with descriptors to correlate binding energy (e.g., charge, bond order, symmetry, defects.

Acknowledgements

Department of Energy Office or Energy Efficiency and Renewable Energy
Fuel Cell Technology Office

Pacific Northwest National Laboratory is operated by Battelle for the US Department of Energy

Reviewers: Thank you for the constructive feedback! Specific comments are address in reviewer only slides

Technical backup slides

Publications

- Zhangpeng Li, Xinchun Yang, Nobuko Tsumori, Zheng Liu, Yuichiro Himeda, Tom Autrey and Qiang Xu. Tandem Nitrogen Functionalization of Porous Carbon: Toward Immobilizing Highly Active Palladium Nanoclusters for Dehydrogenation of Formic Acid. ACS Catalysis **2017** Accepted.
- Zachary Giustra, Gang Chen, Monica Vasiliu, Abhi Karkamkar, Tom Autrey, David Dixon, Shih-Yuan Liu. A Comparison of Hydrogen Release Kinetics from 5- and 6- Membered 1,2-BN-Cycloalkanes. J. Am. Chem. Soc. **2017**. Accepted.
- Kriston Brooks, Mark Bowden, Abhi Karkamkar, Sean Whittemore, Tom Autrey. Coupling of Exothermic/Endothermic Reactions for Hydrogen Release of Carbon-Boron-Nitrogen Containing Materials. **2016** (J Power Sources 324, 170-178) DOI:10/1016/j.powsour.2016.05.067.
- Sean M. Whittemore, Mark Bowden, Abhi Karkamkar, Kshitij Parab, Doinita Neiner, Tom Autrey, Jacob S. A. Ishibashi, Gang Chen, Shih-Yuan Liu, David Dixon. Blending materials composed of Boron, Nitrogen and Carbon to transform approaches to Liquid Hydrogen Stores. *Dalton Trans* 45(14) 6196-6203, **2016** (special issue on main group chemistry) DOI: 10.1039/c5dt04276c
- Elsa Callini, Zuleyha Özlem, Kocabas Atakli, Bjørn C. Hauback, Shin-ichi Orimo, Craig Jensen, Martin Dornheim, David Grant, Young Whan Cho, Ping Chen, Bjørgvin Hjörvarsson, Petra de Jongh, Claudia Weidenthaler, Marcello Baricco, Mark Paskevicius, Torben R. Jensen, Mark E. Bowden, Thomas S. Autrey, Andreas Züttel. Complex and liquid hydrides for energy storage. *Applied Physics A*. 122(4) **2016**. invited review. DOI: 10.1007/s00339-016-9881-5.

Future work

Working with international experts to optimize properties of LOHC

Karsten Mueller (Germany FAU Erlangen Nurnberg) TEA to compare LOHCs. (ASF July-Sept 2017)

Yuichi Himeda and Hajima Kawanami (Japan AIST) Catalysts for H_2 release in LOHCs

Teng He (China DICP) (ASF April 2017 – March 2018) **Optimizing catalysts for H_2** uptake and release in LOHCs (calorimetry)

Extracurricular writing projects

Hydrogen Storage Systems for Energy Applications: Materials Development and Characterization. Editors Bob Bowman and Karl Gross. (Elsevier) Complex Hydrides Thermodynamic and Kinetic Challenges and Strategies with Vitalie Stavila, Kriston Brooks and Teng He.

Hydrogen storage in small molecules. Editors Thomas Zeller and Robert Langer. (DeGruyter). Dehydrogenation of ammonia borane and related compounds and Recovery strategies with Mark Bowden

Chemistry consideration in H_2 release and uptake in $Mg(BH_4)_2$. Chemical Communications Feature Article (RSC) with Craig Jensen and Marina Chong

With NIST for NVS to measure similarities and differences between solvated and unsolvated $Mg(BH_4)_2$

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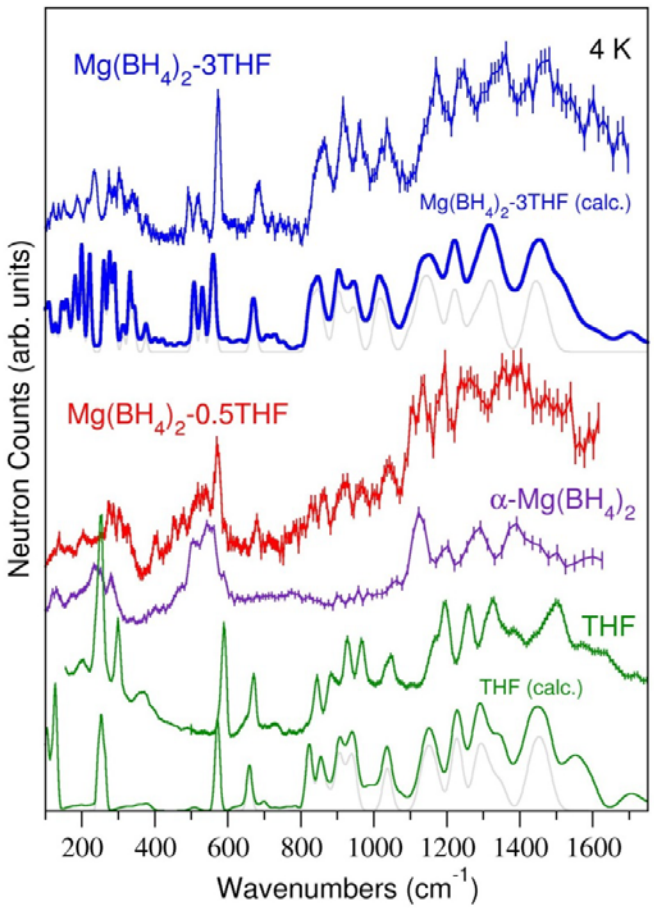

Spectroscopic studies will provide clues to differences between solvated and unsolvated complex hydrides
IR, Raman, NVS

Preliminary results from Neutron vibrational spectroscopy (Terry and Mira). Will repeat with ^{11}B labelled $Mg(BH_4)_2$ curtesy of NREL.

THF additive to $Mg(BH_4)_2$ favors formation of $MgB_{10}H_{10}$ (how much is needed)?

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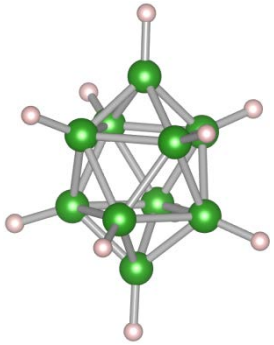
$$5Mg(BH_4)_2{\cdot}(THF)x \Leftrightarrow MgB_{10}H_{10}{\cdot}(THF)x + 4MgH_2 + 11H_2$$



- Work backwards (again). Assume 3 THF's bind to Mg cation and work backward, 0.6 THF is maximum to avoid making volatile THF in products.

THF/Mg	wt%H2
0	8.16%
0.25	7.00%
0.5	6.12%
1	4.89%
2	3.49%
3	2.72%

- Will selectivity $B_{10}H_{10}/B_{12}H_{12}$ change with THF content?

- $MgB_{10}H_{10}{\cdot}3THF + 4MgH_2 + 11H_2 \rightarrow 5Mg(BH_4)_2{\cdot}0.6THF$ 6 wt% H_2

- Assumes THF binds strongly to Mg, is this a good assumption?

Background: Calculated thermodynamic predictions of key intermediates.

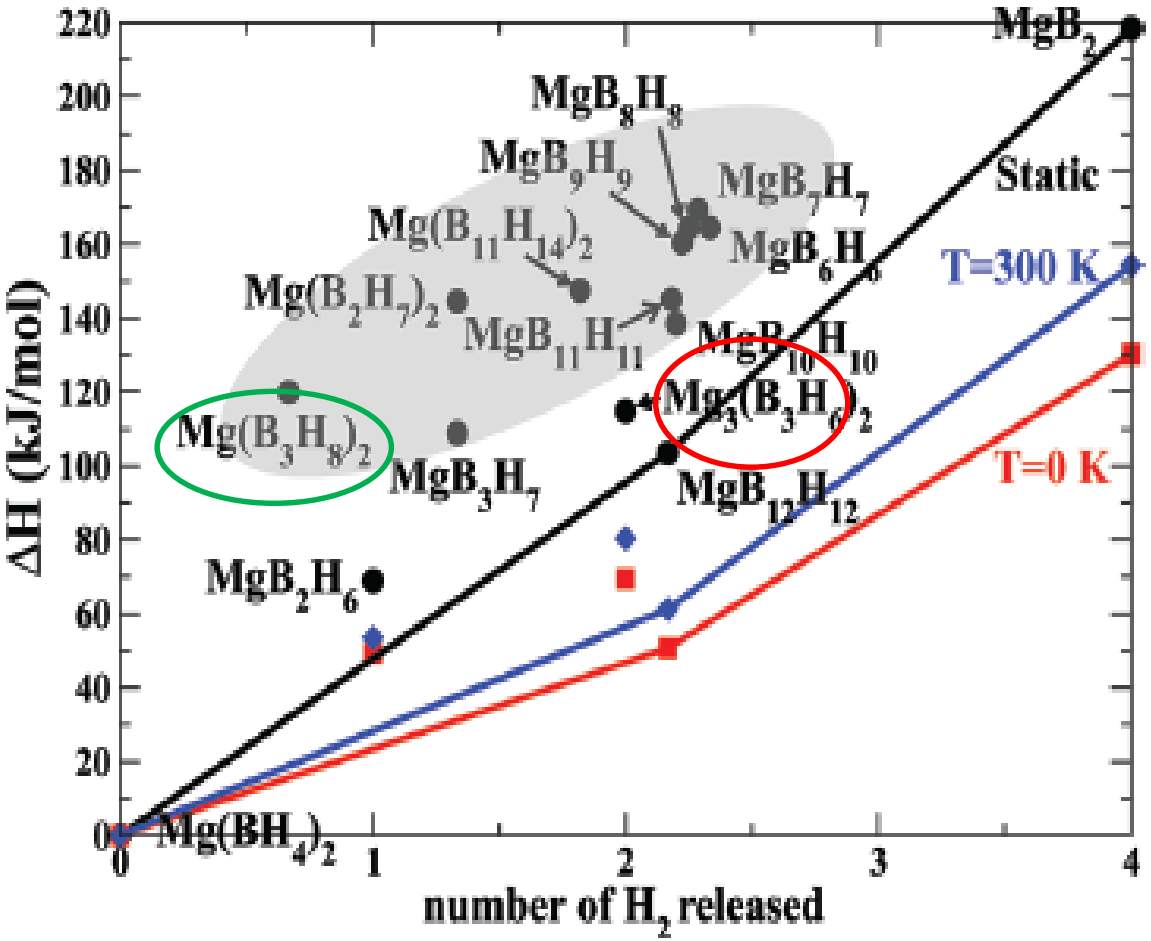
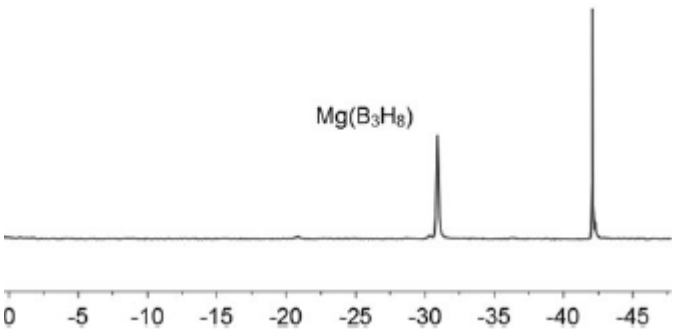


Figure from J. Phys. Chem. C 2012, 116, 10522

A. Can we understand the discrepancy between experiment and theory for **$Mg(B_3H_8)_2$** ?



B. Theory suggests that we should form **$Mg_3(B_3H_6)_2$**

C. Experiment and theory are at complete odds

Progress: Calculating ΔG to compare with experiment. Can we rely on calculated E_{static} to predict experiment?

Iffat Nayyar

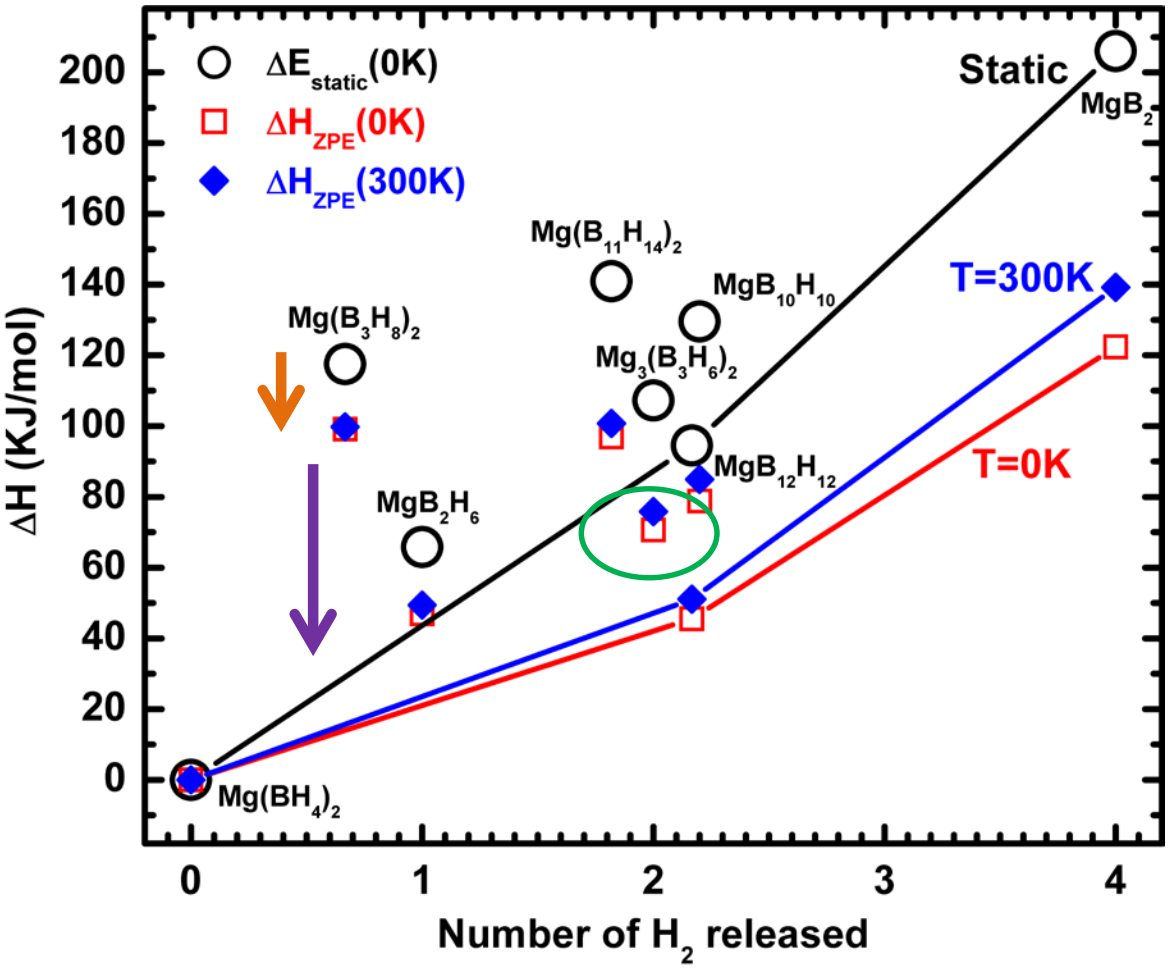
- ***At least 4 steps needed to compare direct with experiment:***

  (i) E_{static} → (ii) ΔH(0K) → (iii) ΔH^o → (iv) ΔG^o

  - **Challenge – no experimental crystal structure for $Mg(B_3H_8)_2$ so best guess is to start with PEGS/DFT structure**
  - **Are we missing some critical 'extra' entropy in the borane clusters?**

Reaction Path	Supercell Size	ΔE_{static} (T=0K)		ΔH_{ZPE} (T=0K)		ΔH_{ZPE} (T=300K)		ΔG_{ZPE} (T=300K)	ΔS (T=300K)		T_c	
		(KJ/mol H_2)							(J/mol H_2 K)		(°C)	
			Lit[a]		Lit[a]		Lit[a]			Lit[a]		Lit[a]
$Mg(BH_4)_2 \rightarrow 1/3\ Mg(B_3H_8)_2 + 2/3\ MgH_2 + 2/3\ H_2$	1	176.3	180	148.7	-	147.9	-	128.2	65.5	-	1983	
	4	176.3		148.7		149.7		124.2	84.9		1489	
$Mg(BH_4)_2 \rightarrow 1/3\ Mg_3(B_3H_6)_2 + 2\ H_2$	4	53.6	57.4	35.3	34.7	37.9	40.2	9.7	94.3	108	129	99
$Mg(BH_4)_2 \rightarrow 1/5\ MgB_{10}H_{10} + 4/5\ MgH_2 + 11/5\ H_2$	2	58.9	63	35.8	-	38.6	-	10.2	94.6	-	135	
	4	58.9		35.8		38.6		10.2	94.9		134	
$Mg(BH_4)_2 \rightarrow 1/11\ Mg(B_{11}H_{14})_2 + 10/11\ MgH_2 + 20/11\ H_2$	1	77.5	81.1	53.3		55.4	-	28.5	89.8	-	344	
	2	77.5		53.3		55.4		28.5	89.9		343	
$Mg(BH_4)_2 \rightarrow MgB_2H_6 + H_2$	4	65.8	68.9	46.9	49.3	49.4	53.5	21.5	92.9	97.2	259	277
$Mg(BH_4)_2 \rightarrow MgB_2 + 4\ H_2$	1	51.5	54.6	30.6	32.6	34.8	38.6	3.6	95.9	111.5	90	73
$Mg(BH_4)_2 \rightarrow 1/6\ MgB_{12}H_{12} + 5/6\ MgH_2 + 13/6\ H_2$	2	43.6	47.8	21	23.4	23.57	28.3	-4.4	93.3	105.3	-21	-5

Progress: Accounting for (ii) zpe and (iii) thermal corrections <u>only</u> lowers *ΔH* by 20-30 kJ/mol H_2



A. Even if the wrong polymorph is predicted by PEGS/DFT? Might be able to get another 40 kJ/mol – but we need to find another 100 kJ/mol

B. $B_3H_6^{3-}$ sure looks appealing from thermodynamics – can you get there 'kinetically'?

Progress: When not available in the literature return to theory to calculate NMR chemical shift

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^{11}B Solid State NMR Chemical Shift δ (ppm)			
	$(\sigma_S)_{The}$	$(\delta_S)_{The} = (\sigma_S - \sigma_R)_{The} + (\delta_R)_{Exp}$	$(\delta_S)_{Exp}$
$Mg(BH_4)_2$	27.5	-42.2	-41
$Mg(BH_4)_2$ α	27.6	-42.1	-40.8
$Mg(BH_4)_2 . 3THF$	30.3	-39.4	-43.2
$Mg(B_3H_8)_2$	39.1	-30.6	-30.3
$Mg_3(B_3H_6)_2$	22.5	-47.2	unknown
$MgB_{10}H_{10}$	73.3	3.6	-1.8
	45.9	-23.8	-28.2
$Mg(B_{11}H_{14})_2$	57.2	-12.5	-12.5
	54.2	-15.6	-14.9
MgB_2H_6	24.9	-44.8	
MgB_2	122.4	52.6	97
$MgB_{12}H_{12}$	56.7	-13	-15

- **NMR chemical shifts agree with experiment**
- Chemical shielding sensitive to
  - Valence electrons descried by plane waves
  - Size of core represented by PAW psuedopotentials
- **Allow interpretation of new resonances**
- To our knowledge these are some of the first calculated NMR spectra in the solid state

Progress: In-situ ^{11}B MAS NMR following hydrogenation of $Mg(B_3H_8)_2$

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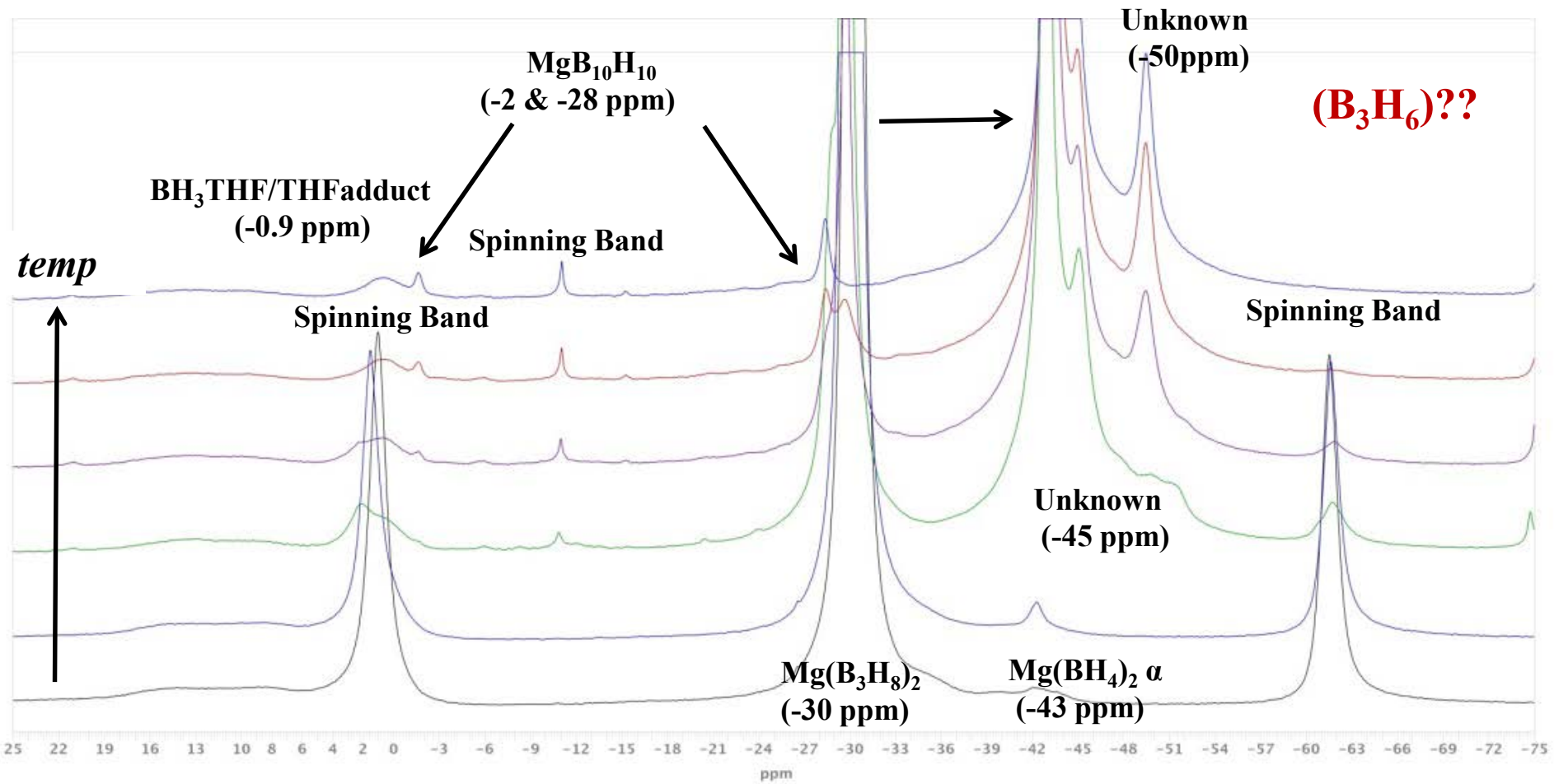
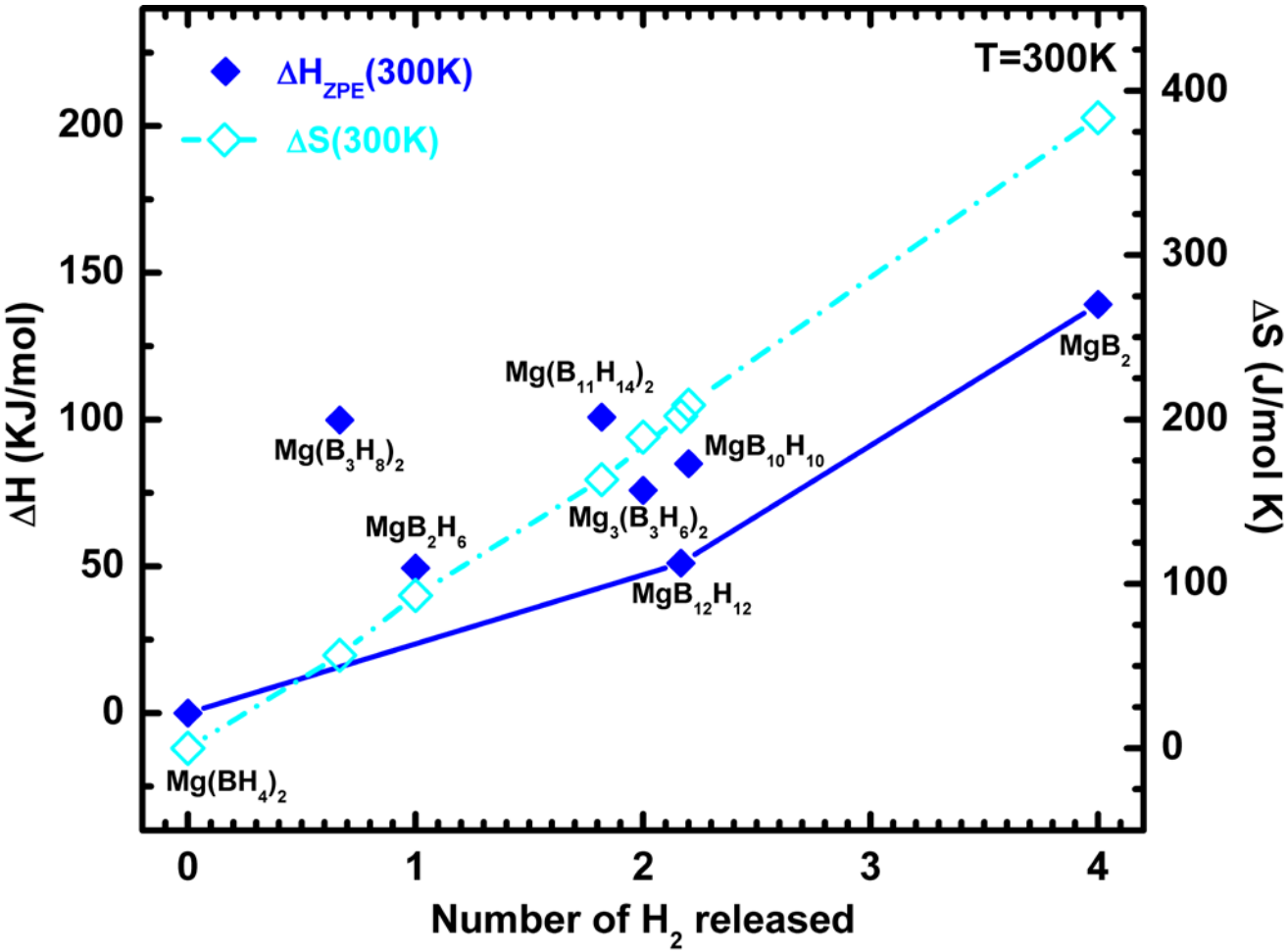


^{11}B NMR [$Mg(B_3H_8)_2$. 4THF + MgH_2 , 20 - 200 ºC Hydrogenation

HySCORE BERKELEY LAB NIST NREL NATIONAL RENEWABLE ENERGY LABORATORY

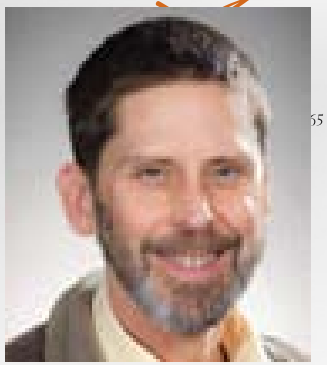
Progress: Harmonic approximation does not suggest any special entropy component for $Mg(B_3H_8)_2$.



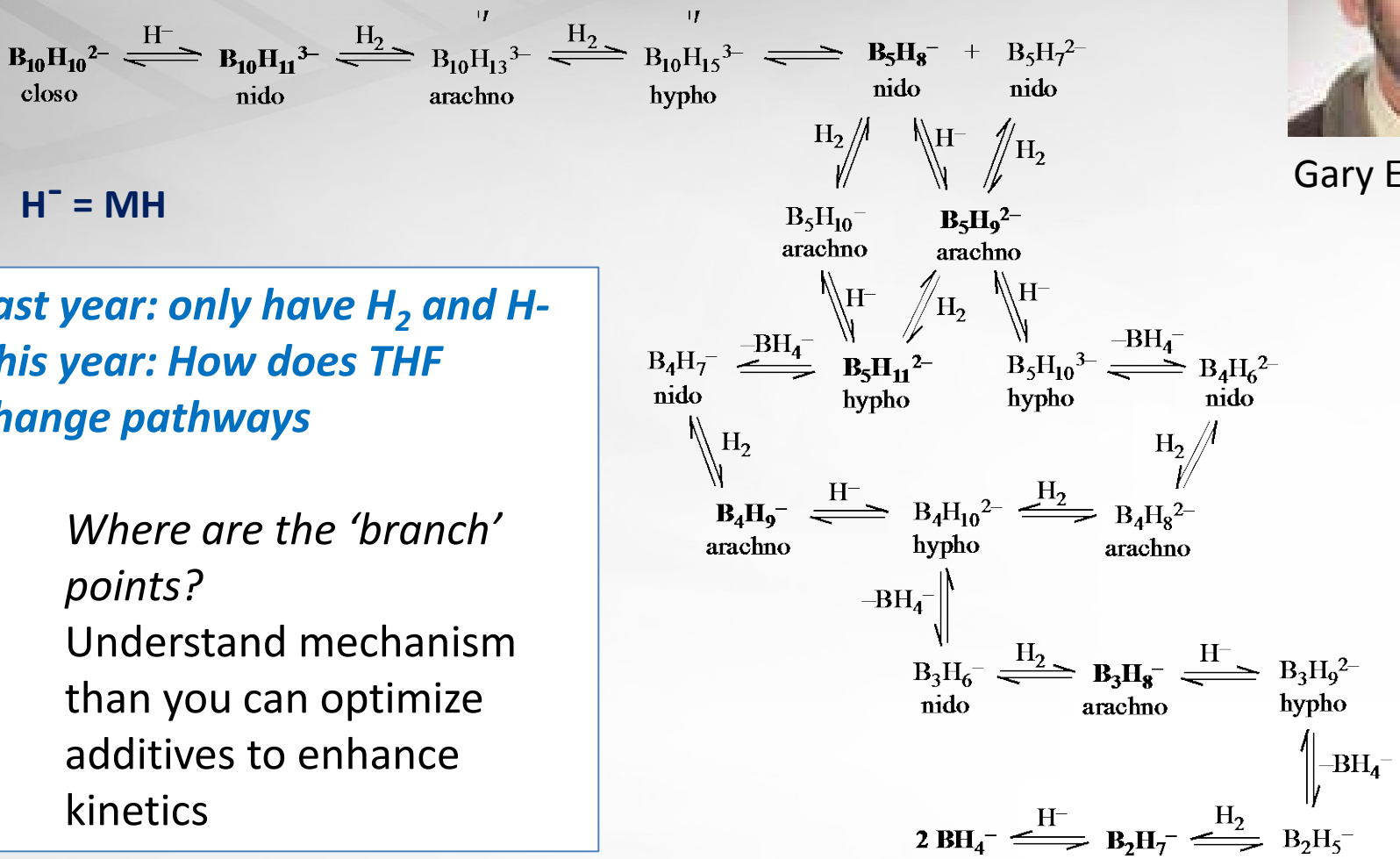
Entropy 'loss' consistently ~ 90 J/K/mol H_2

Is the harmonic approximation still missing something important?

How does THF change the reaction pathway from ($B_{12}H_{12}$ + $B_{10}H_{10}$) to $B_{10}H_{10}$ only?



Gary Edvenson



H^- = MH

Last year: only have H_2 and H-
This year: How does THF change pathways

- *Where are the 'branch' points?*
- Understand mechanism than you can optimize additives to enhance kinetics