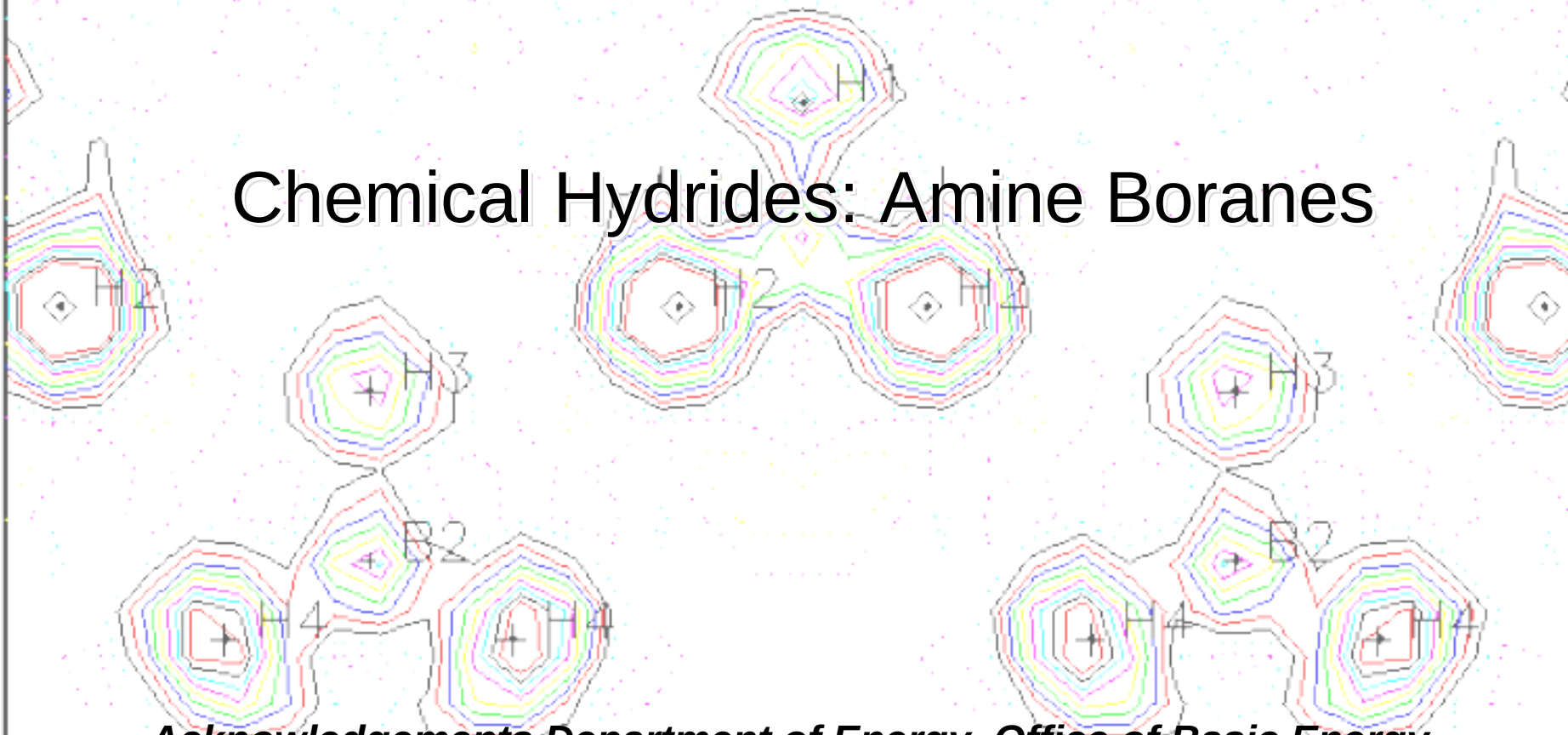
Chemical Hydrides: Amine Boranes



Acknowledgements Department of Energy, Office of Basic Energy Sciences and Energy Efficiency and Renewable Energy.

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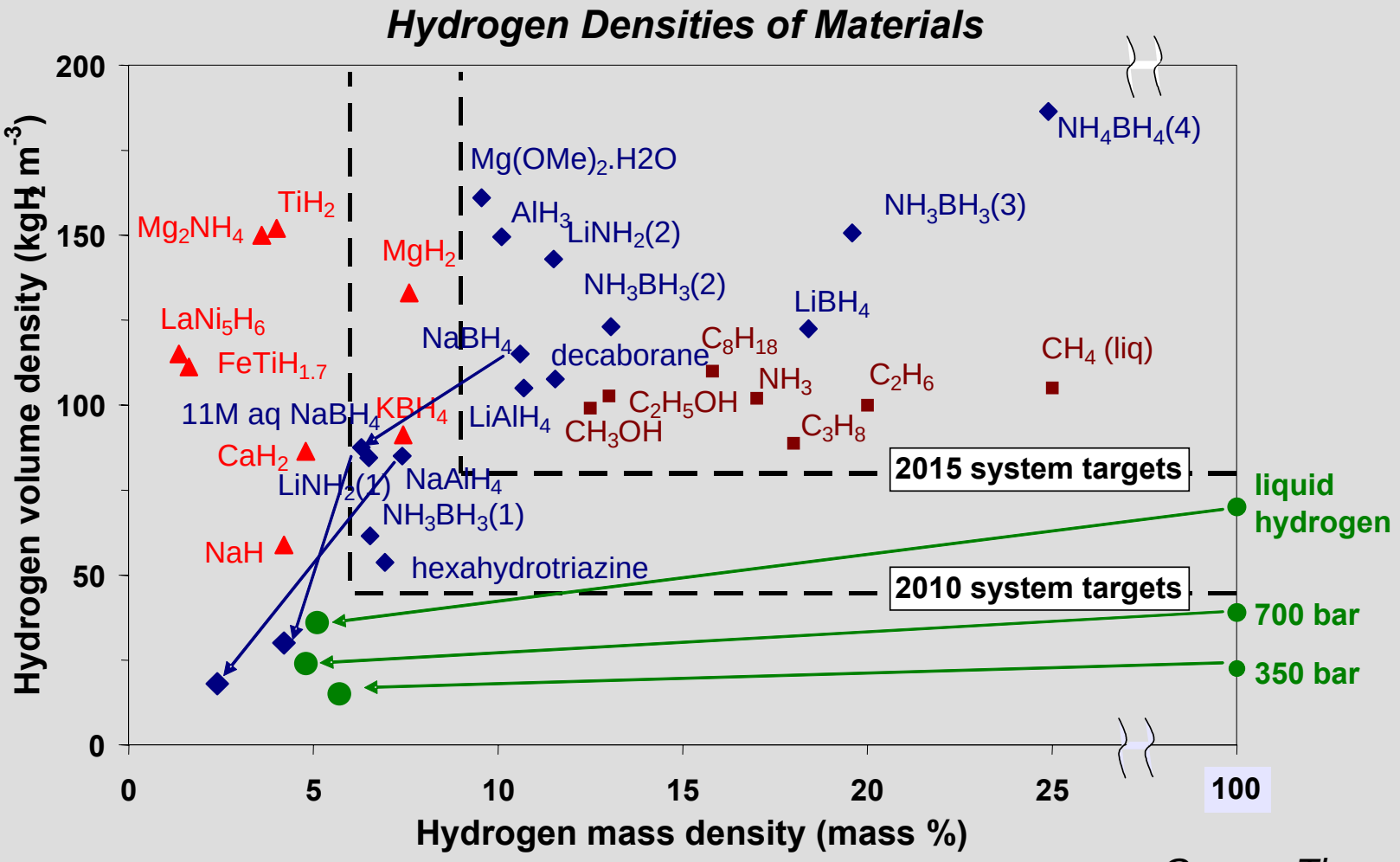
Hydrogen-rich ammonia borane (AB)



George Thomas

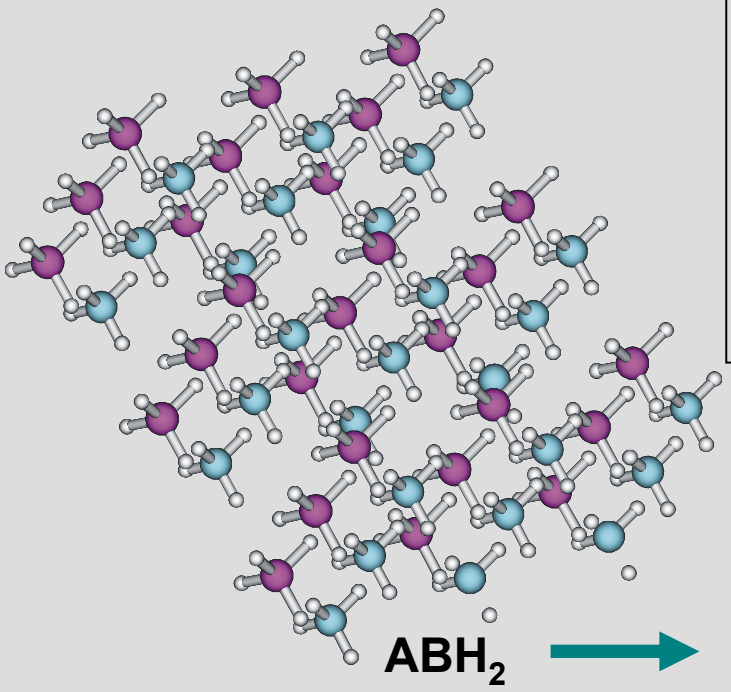
NH_xBH_x Store hydrogen (>6 wt%/step)

	Wt% H_2	T (K)
$NH_4BH_4 \rightarrow NH_3BH_3 + H_2$	6.1	<300
$NH_3BH_3 \rightarrow (NH_2BH_2)_n + H_2$	6.5	<375
$(NH_2BH_2)_n \rightarrow (NHBH)_n + H_2$	6.9	>375
$(NHBH)_n \rightarrow BN + H_2$	7.3	>>800

Two sequential steps > 12 wt% hydrogen!

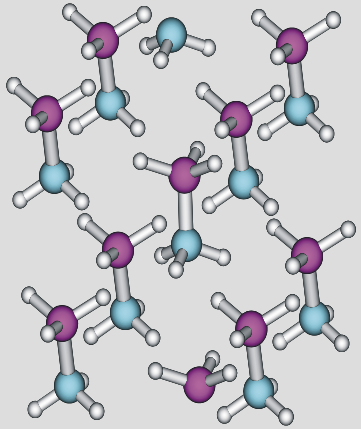
Solid state chemistry: thermodynamics and kinetics of hydrogen release?

Thermodynamics

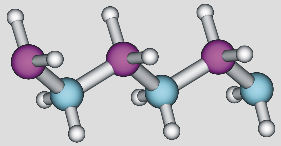


ABH_2

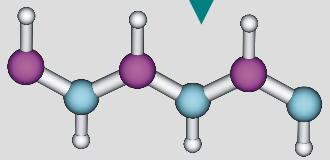
Reactants	Products	ΔE (kJ/mol)
$NH_4BH_4(s)$	$\rightarrow NH_3BH_3(s) + H_2$	-10
$NH_3BH_3(s)$	$\rightarrow (NH_2BH_2)_n + H_2$	+37
$(NH_2BH_2)_n$	$\rightarrow (NHBH)_n + nH_2$	-13
$(NHBH)_n$	$\rightarrow BN(s) + nH_2$	-38



AB+ H_2



PAB+ H_2



PIB+ H_2

$ABH_2 = NH_4BH_4$
$AB = NH_3BH_3$
$PAB = (NH_2BH_2)_n$
$PIB = (NHBH)_n$

$BH_4 + 4H_2O \rightarrow B(OH)_4 + 4H_2$
$\Delta H = -250$ kJ/mol

Approaches

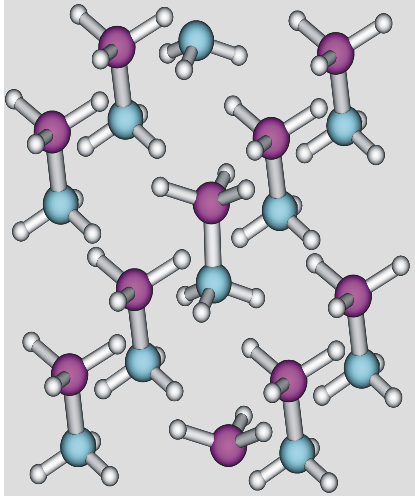
- Scanning calorimetry combined with mass detection and gravimetric analysis
  - Thermodynamics of hydrogen loss
  - Kinetics and insight into mechanism of H-release
- NMR and Raman spectroscopy
  - Solid state to study phase transitions and molecular dynamics
  - Variable temperature for in-situ kinetic investigations
- Neutron spectroscopy
  - QENS (for dynamics of H motion)
  - INS (structural properties)

Combination of experiment & theory to gain fundamental understanding of chemical & physical properties of AB

Ammonia borane isoelectronic with ethane

	NH_3BH_3	CH_3CH_3
MW	30.81	30.07
Mp[°C]	124	-183
M[D]	5.2	0
bonding	N->B dative	C-C covalent
R[A]	1.58 (1.62)	1.53
kg H_2/kg	191	2.1
kg H_2/liter	143	1.3

Background crystalline NH_3BH_3



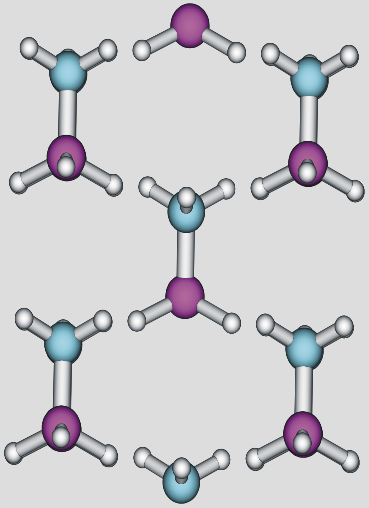
- Synthesis (Shore and Parry in 1955)
- AB in equilibrium with diammoniate of diborane

$$2NH_3BH_3 \leftrightarrow [NH_3BH_2NH_3][\ BH_4]$$

- $NH_3BH_3 \rightarrow H_2 +$ *polyaminoborane* at < 370 K. $\Delta H_{rxn} = -20$ kJ/mol (Wolf et al. 2000)

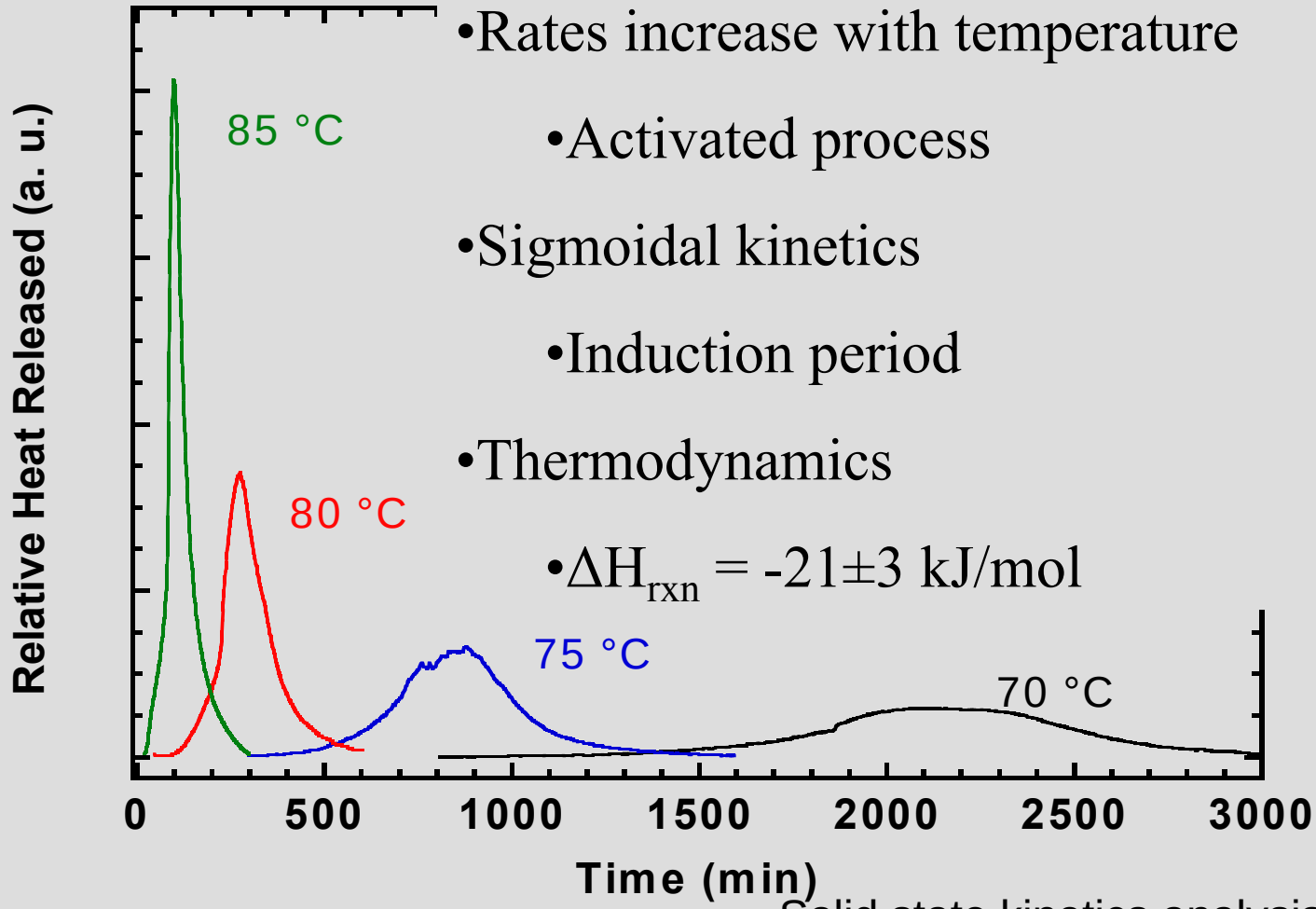
•First order-disorder phase transition at 225 K, the low T structure is orthorhombic, the high T tetragonal (Reynhardt & Hoon)

•Electrostatic bonding between $(N)H^+$ and $(B)H^-$ (dihydrogen bond) (Crabtree et al. 1999)



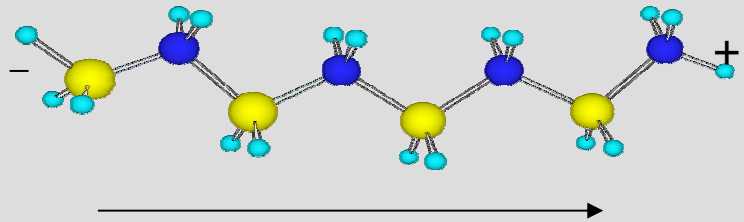
Thermal decomposition of solid AB

$$NH_3BH_3(s) \rightarrow (NH_2BH_2)(s) + H_2$$

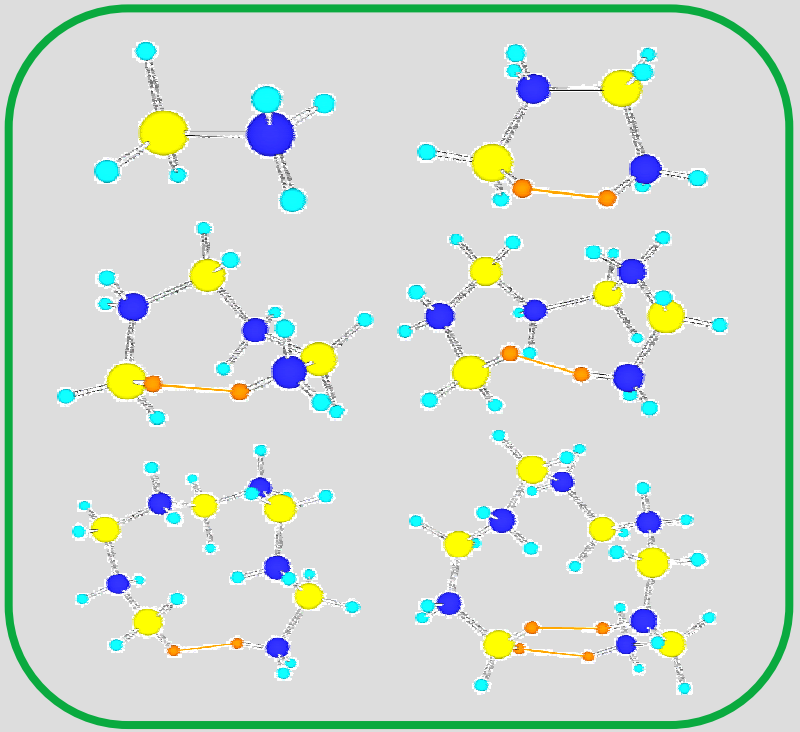


- Rates increase with temperature
  - Activated process
- Sigmoidal kinetics
  - Induction period
- Thermodynamics
  - $\Delta H_{rxn} = -21 \pm 3$ kJ/mol

Stabilizing polymerization



Large dipole moment → instability

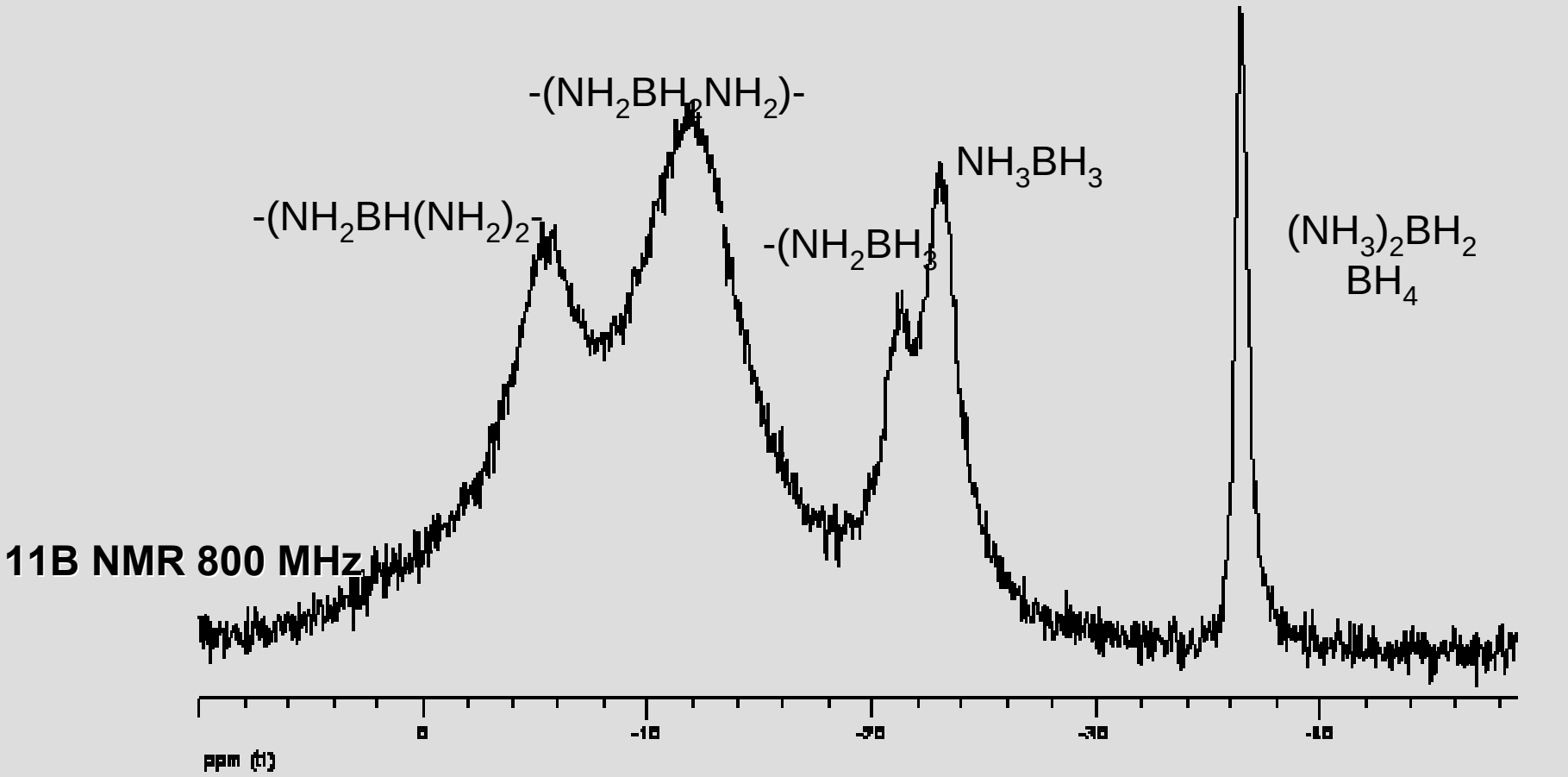


Relieving instability

- Coiling of oligomers → cyclization
- Branching of oligomers

Simulated annealing reveals "coiled" or "cyclic" structure of oligomers, stabilized by dihydrogen bonds – precursors to observed cyclic products

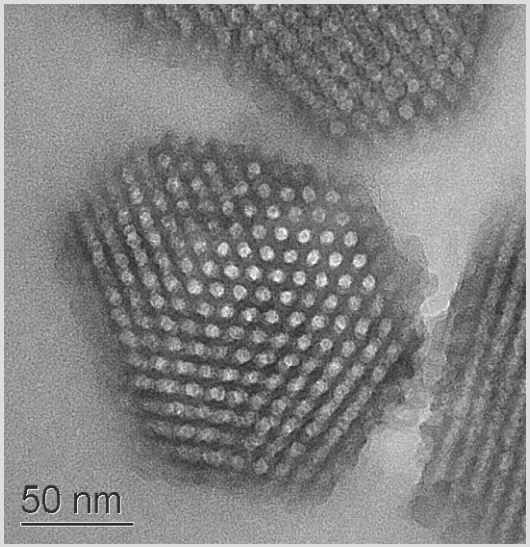
Ammonia borane decomposition



Complex mixture of cyclic, branched polymeric products

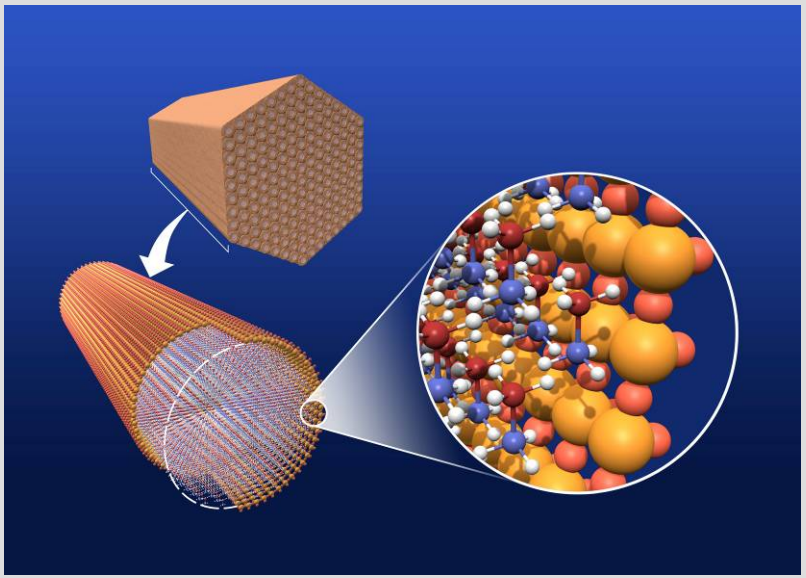
Nano-phase ammonia borane

Use mesoporous silica (SBA-15) as a scaffold. The 6-7 nm wide channels will *hold* Ammonia Borane (NH_3BH_3) in the nano-phase. Should also preserve nanophase.



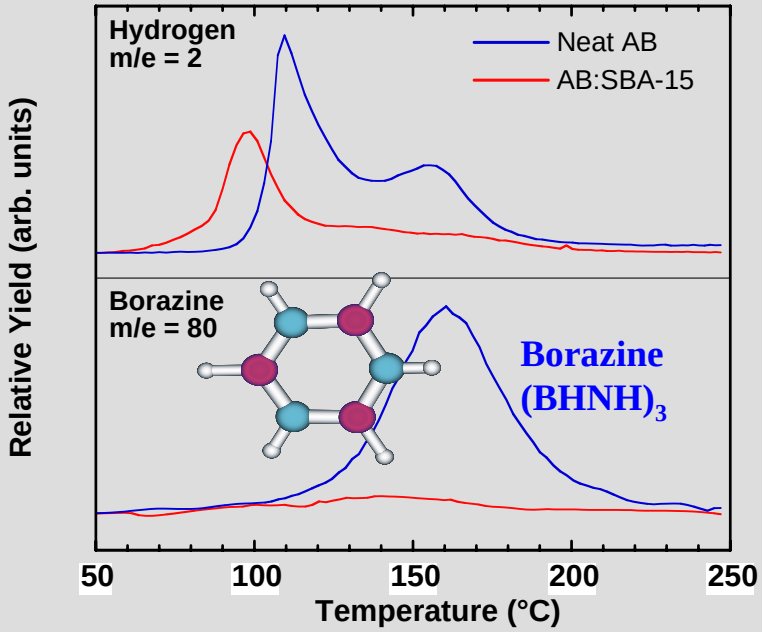
NH_3BH_3

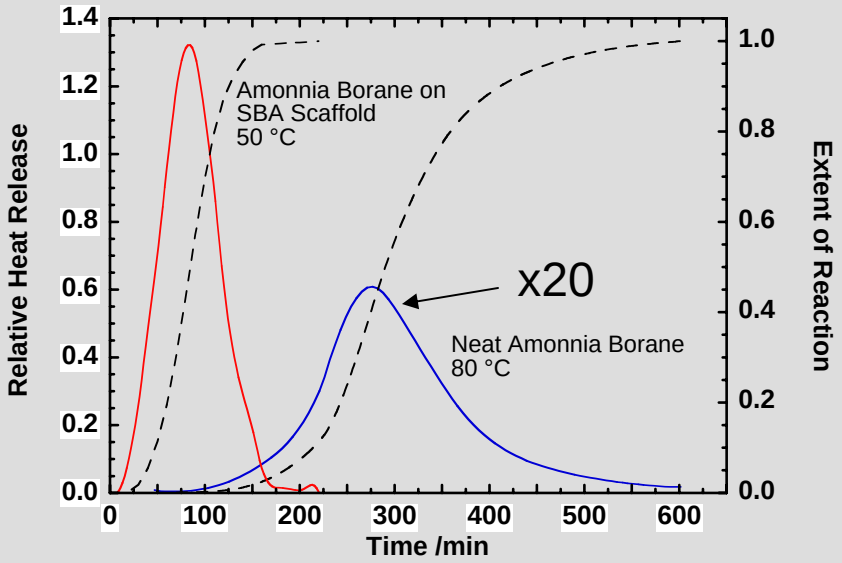
Add saturated solution of NH_3BH_3 to SBA-15

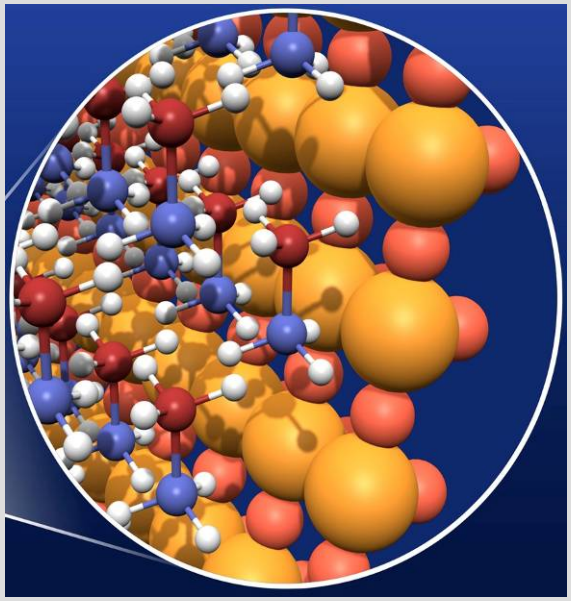


Ammonia borane infiltrated

Change in Reactivity and Selectivity







Ammonia borane in SBA-15

<u>Scaffolds</u>:

enhance rates of H_2 release

enhance purity of H_2 (little borazine)

change in thermodynamics

Angew. Chem. Int. Ed. **2005**, 44, 3578.

Fundamental Science Questions

$$NH_3BH_3 \rightarrow (NH_2BH_2)_n + H_2 \quad + \quad ? \qquad <100\ ^\circ C$$

How is H_2 formed from solid AB?

Is the mechanism intra or intermolecular?

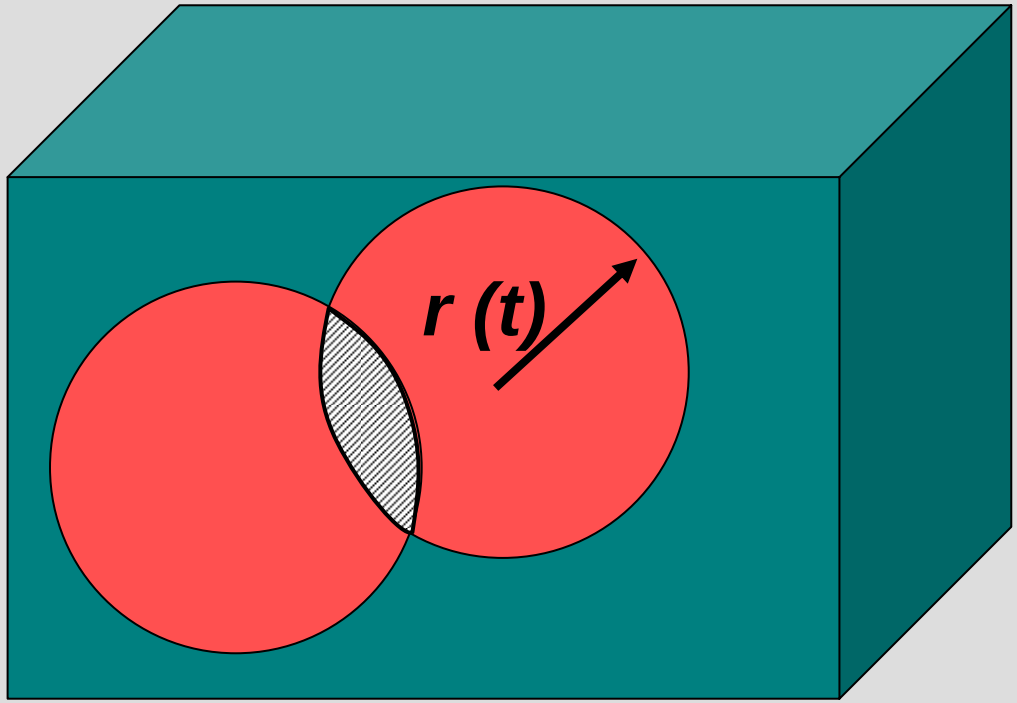
What is the activation barrier?

Can we change it with catalysis, (*other*)

Can we control the decomposition pathways?

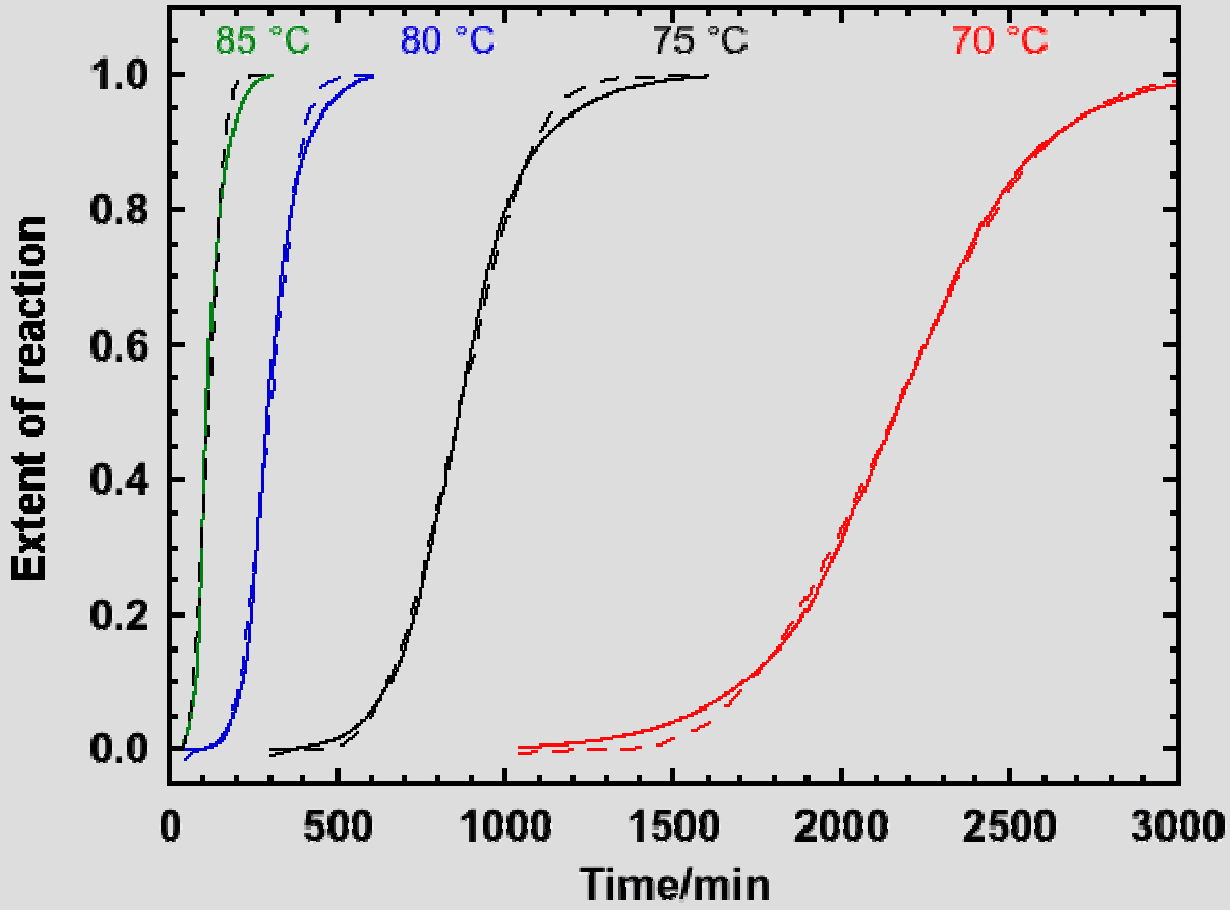
Need approaches to study solid state kinetics

Phase transformation kinetics



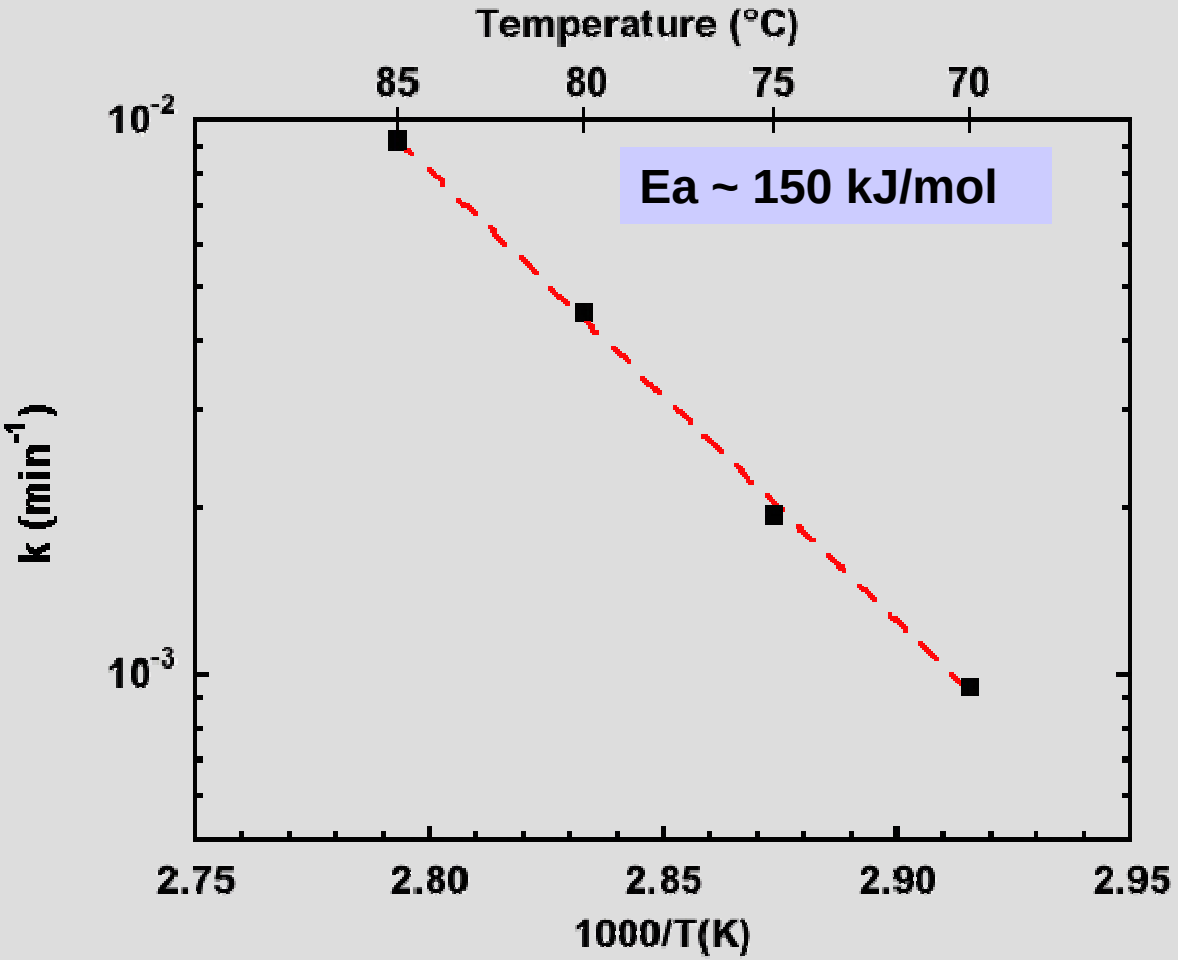
Avrami Equation $X_{Crystal} = 1 - \exp(-(kt)^n)$

Avrami rate as function of T (70-85 C)



$$X_{reaction} = 1 - \exp(-(kt)^3)$$

Arrhenius analysis of k(Avrami) vs. temperature



Activation barrier for H_2 formation from solid state ammonia borane is ca. 150 kJ/mol.

Kinetic model for hydrogen formation

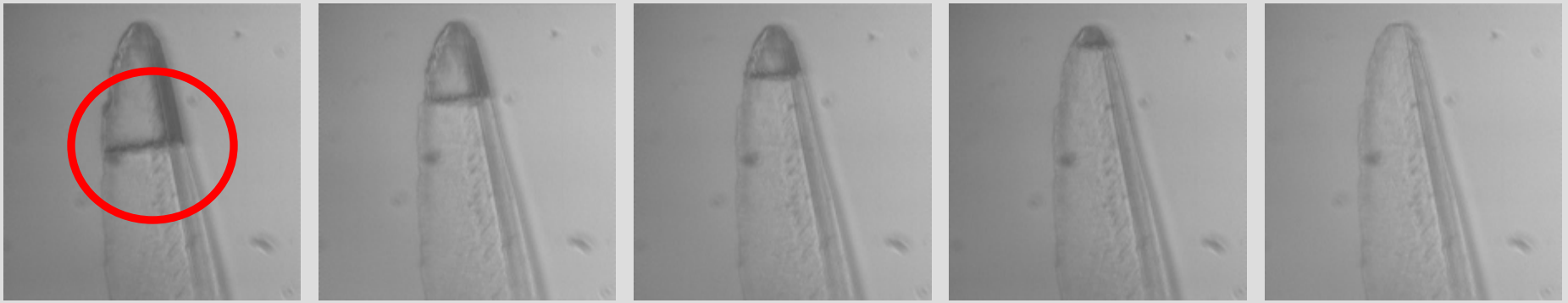
Sigmoidal kinetic behavior

Induction, Nucleation & Growth

- Induction:
  - Rate limiting. How to decrease (scaffold)?
- Nucleation:
  - Physical or Chemical Change
- Growth:
  - hydrogen formation
  - How do you modify pathways, change thermodynamics?

Induction, nucleation, growth

Optical microscope studies



Time 0
75C → 100C

7 min

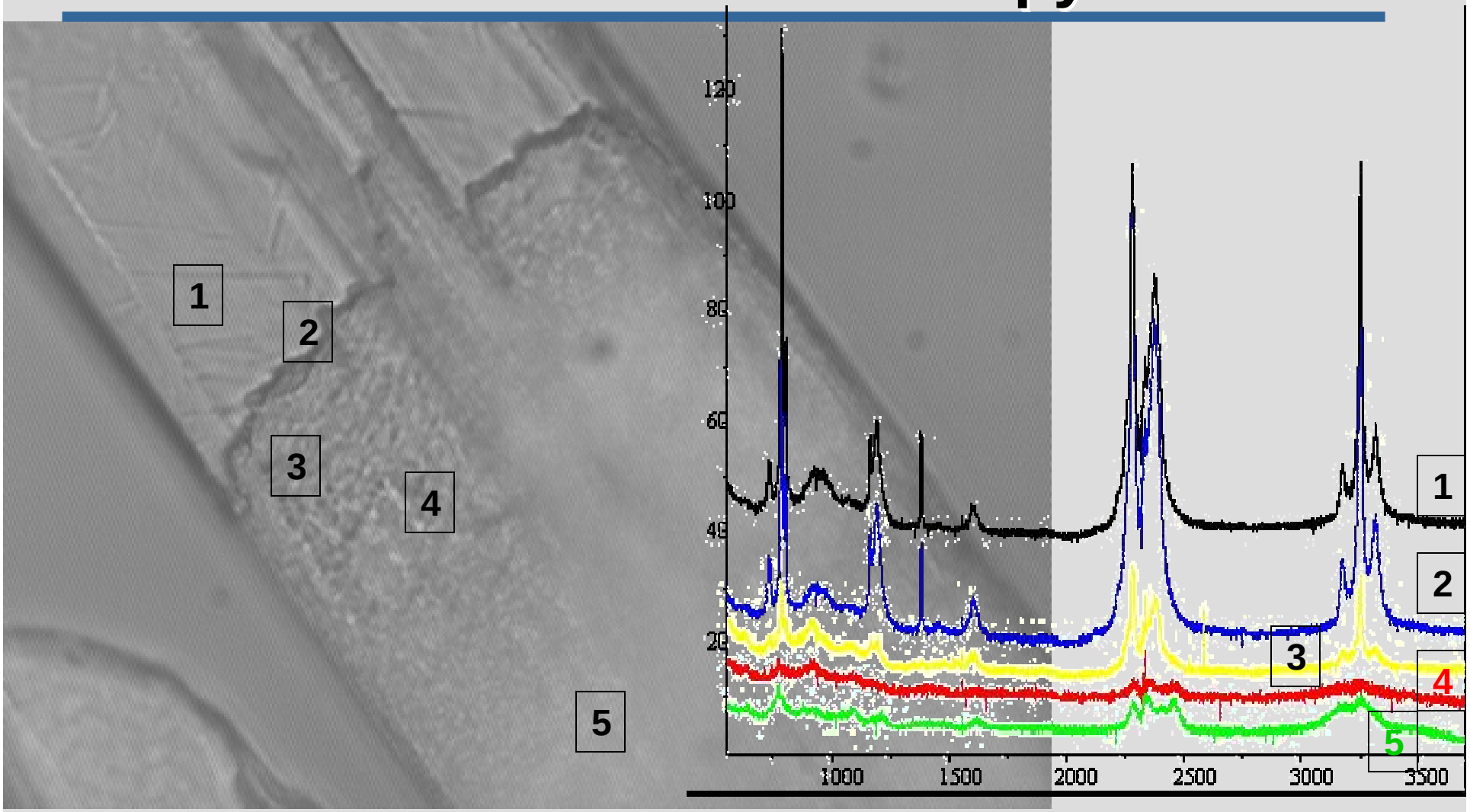
10 min

13 min

14 min

Crystal of AB (~0.1 mm)

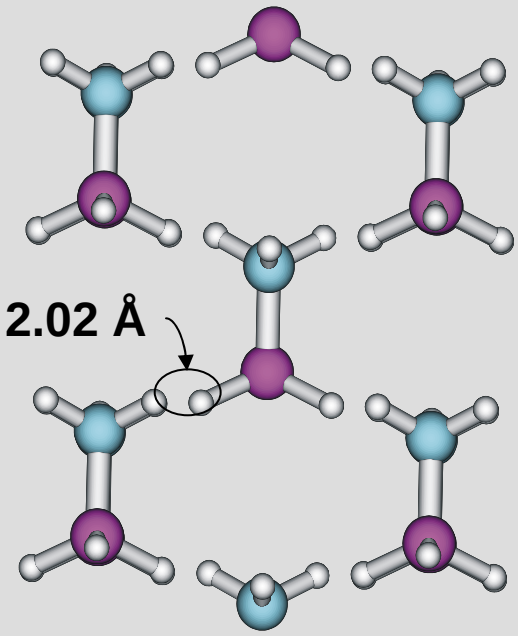
Raman microscopy



“top” of crystal (1) is crystalline AB, bottom (5) is amorphous AB + ??. Beginning of nucleation?

Growth?

Intermolecular vs. Intramolecular



Literature: Reaction Pathways to H_2

Intermolecular

$2\ NH_3BH_3 \rightarrow NH_3BH_2\text{-}NH_2BH_3 + H_2$

or

Intramolecular

$NH_3BH_3 \rightarrow NH_2{=}BH_2 + H_2$

$n\ NH_2{=}BH_2 \rightarrow (NH_2BH_2\text{-}NH_2BH_2)_n$

$\delta-$ $\delta+$

BH ----- HN Dihydrogen bond

Hydride atoms act as Proton acceptors

Nucleation?

Do we have dehydrocoupling of ionic or neutral intermediates?

Ionic pathway

$2\ NH_3BH_3 \leftrightarrows [NH_3BH_2NH_3]^+[BH_4]^-$ (isomerization, no H_2 loss)

AB DADB

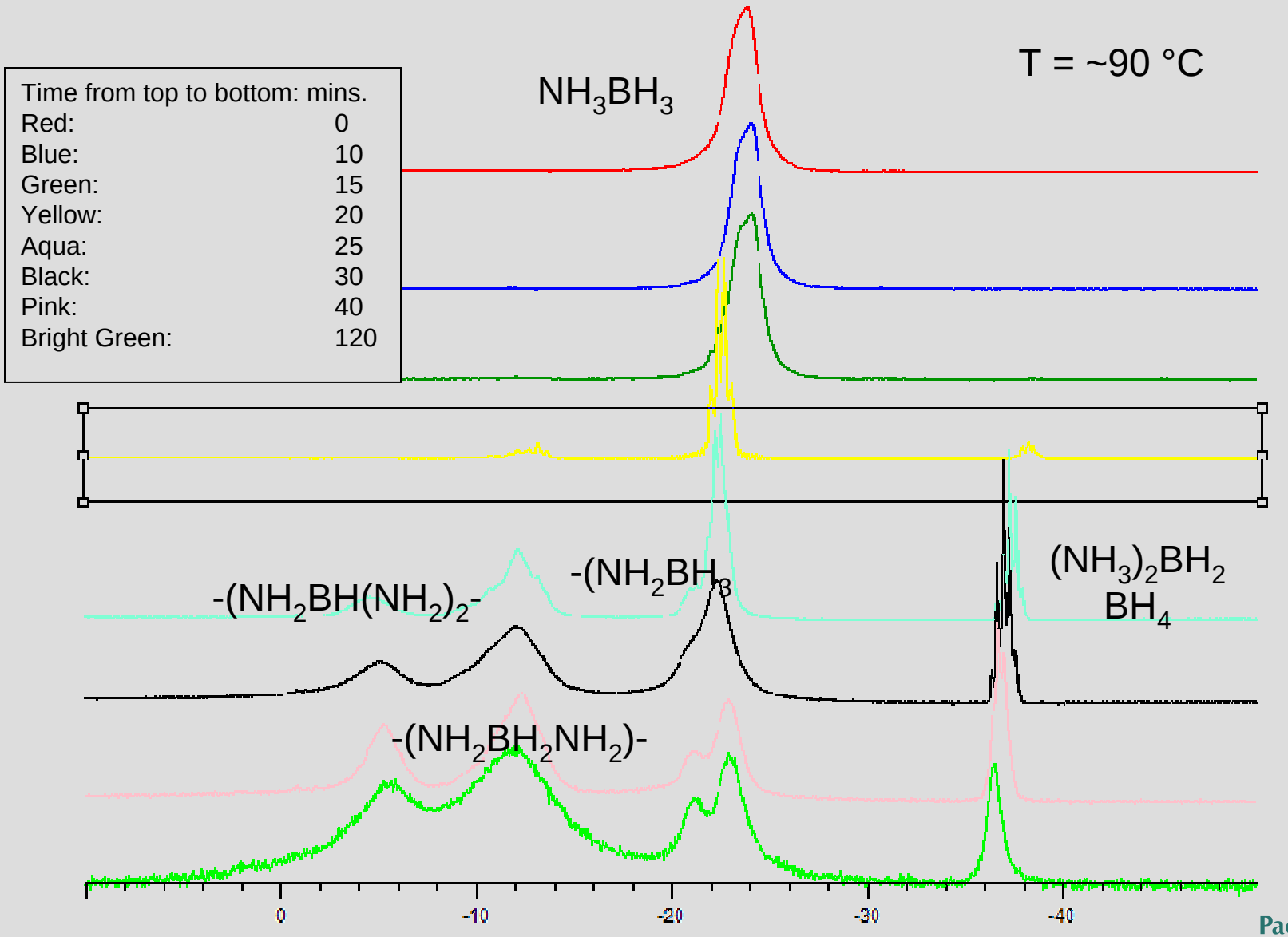
$NH_3BH_3 + [NH_3BH_2NH_3]^+[BH_4]^- \rightarrow [NH_3BH_2NH_2\text{-}BH_2NH_3][BH_4]^- + H_2$

Neutral pathway

$2\ NH_3BH_3 \rightarrow NH_3BH_2\text{-}NH_2BH_3 + H_2$

If $[NH_3BH_2NH_3]^+[BH_4]^-$ is an intermediate, should see it by in-situ solid state ^{11}B NMR

^{11}B NMR 800 MHz Ammonia Borane



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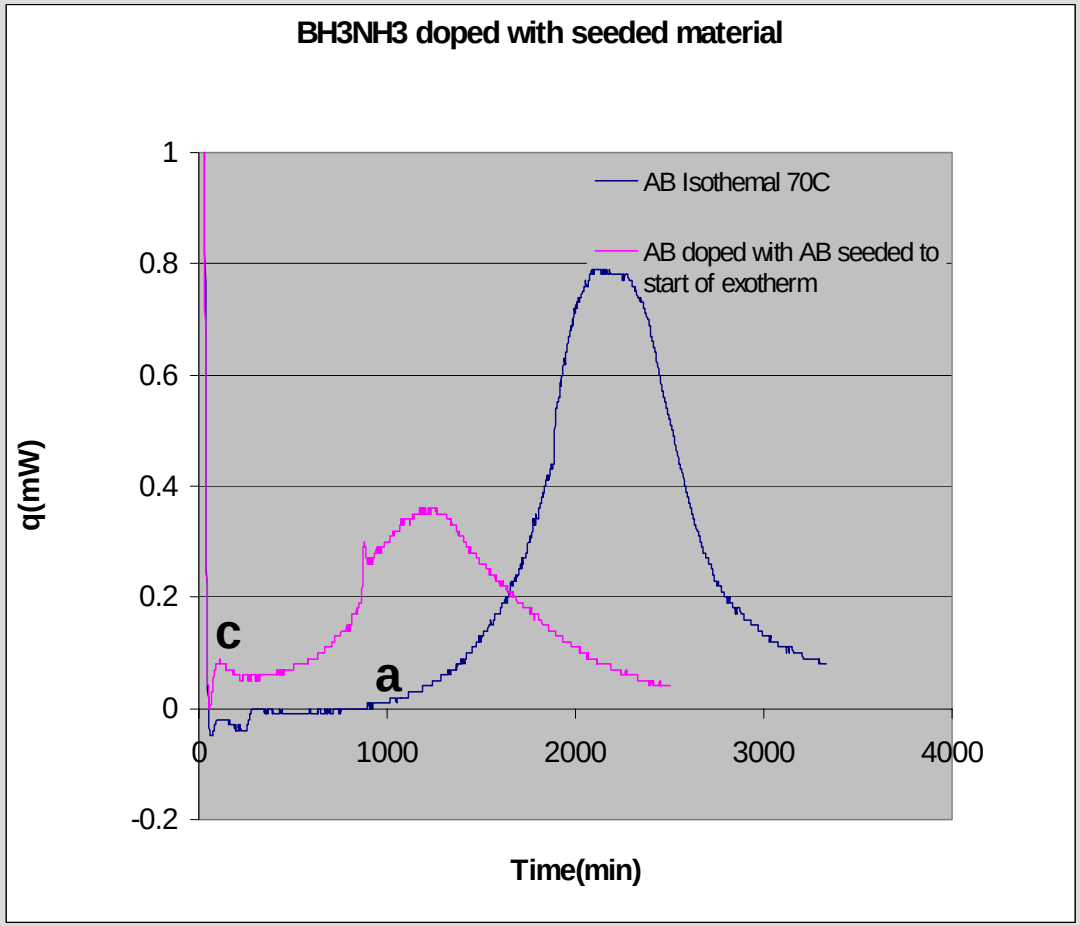
Nucleation seeding



Nucleation seeding of solid AB enhances rate of H_2 release.

a) Heat AB for 1000 minutes to synthesize 'seeds'

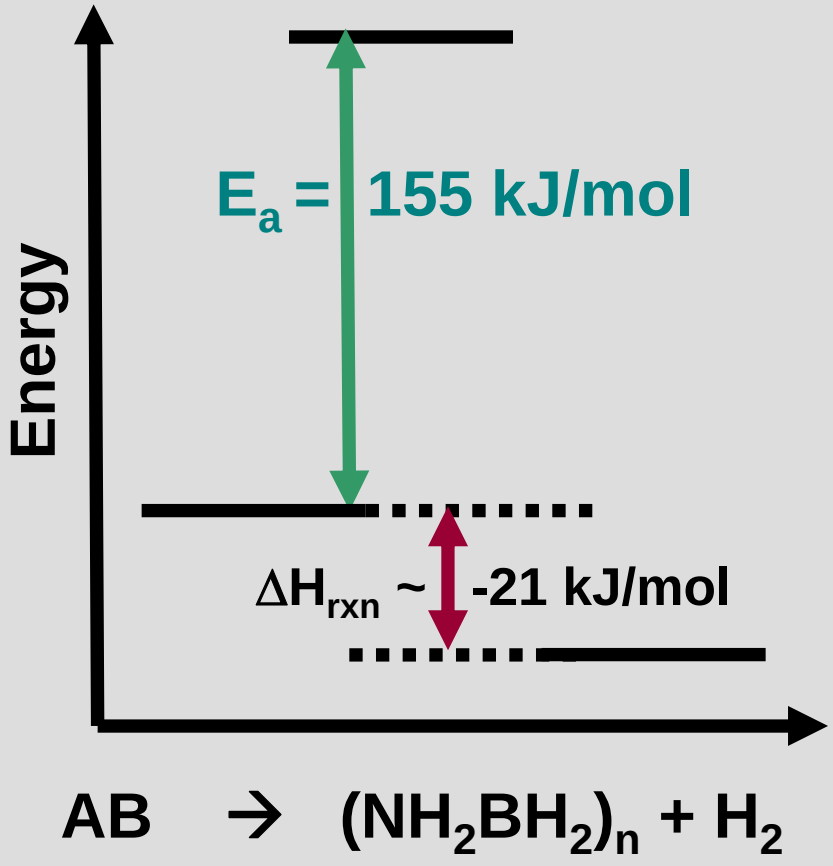
b) Mix seeds with fresh AB

c) Heat AB mixture decreased induction time

What is the nucleation step?

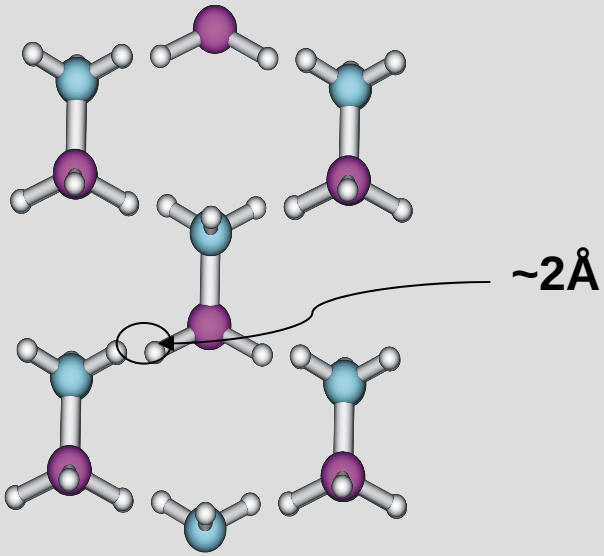
We must know this to better control rates of H_2 evolution!

Solid state AB energetics



- Intermolecular reaction of AB leads to H_2 in the solid state
- Diammoniate is important intermediate
- Rates of H_2 release can be *controlled* in the solid state
  - Enhance kinetics with nucleation seeding or scaffold

Role of dihydrogen bonds in H_2 release:



$\delta-$ $\delta+$

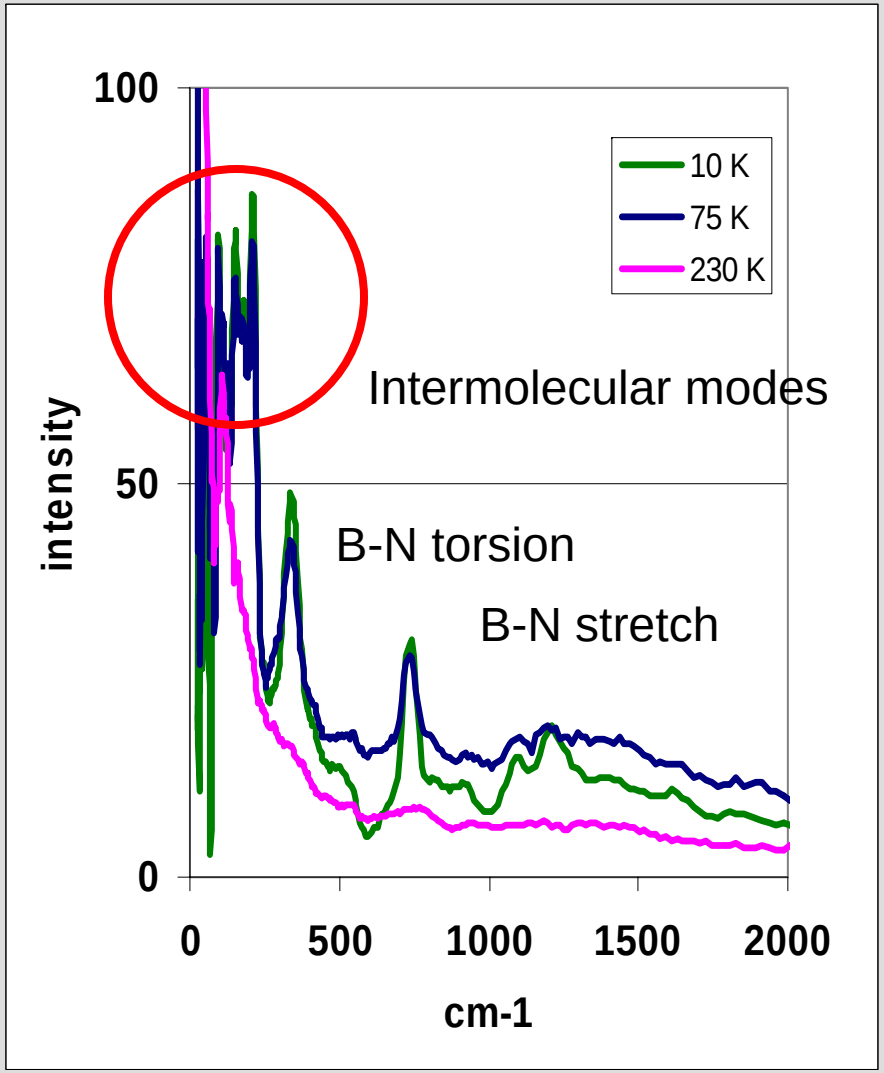
BH ----- HN Dihydrogen bond

Hydride atoms act as Proton acceptor*

Use neutron scattering (INS and QENS) methods to study properties of H-rich materials.

*Klooster, et. al. *JACS*, **1999**, *121*, 6337

Inelastic neutron scattering



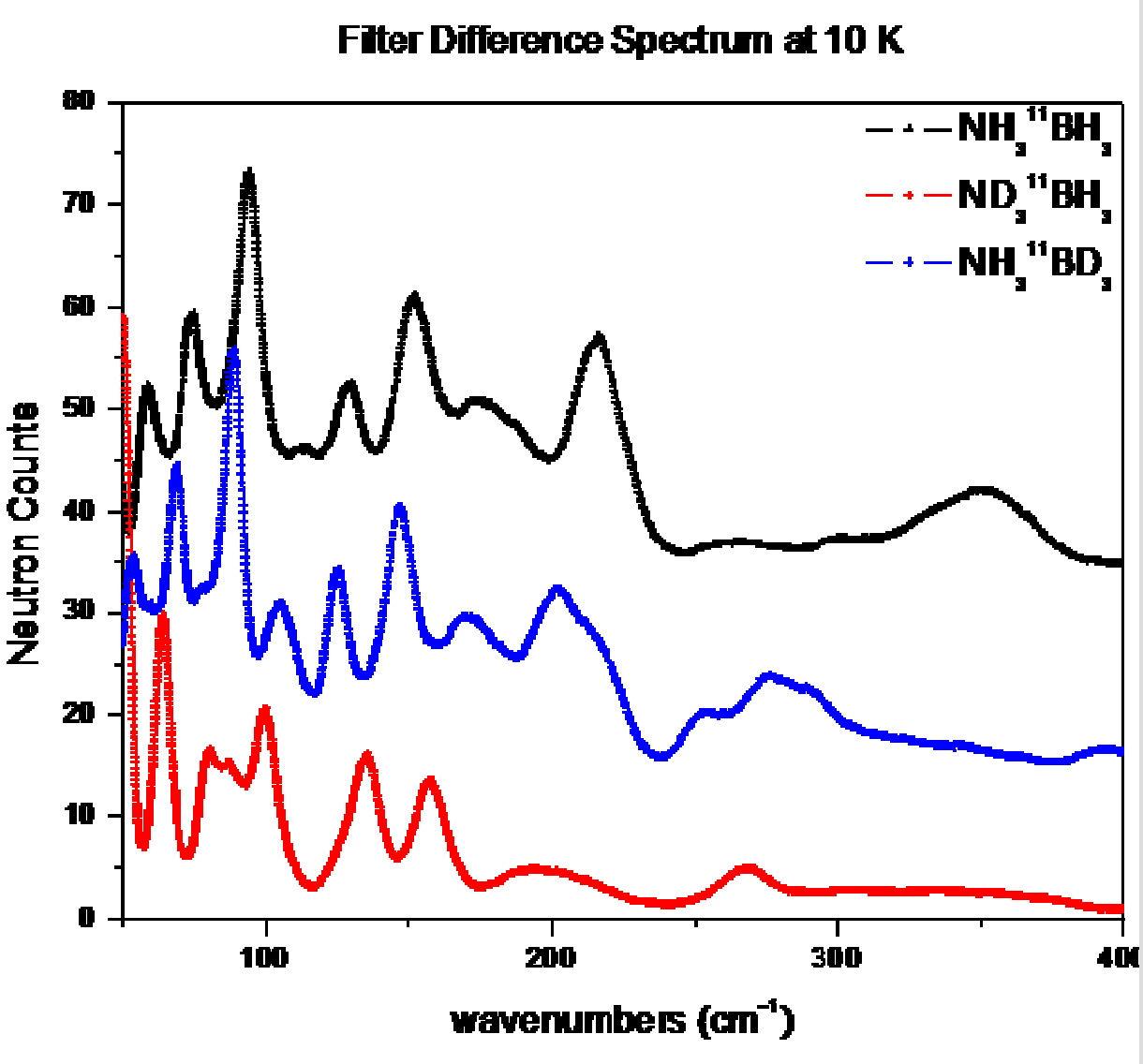
$^{11}BH_3NH_3$ Vibrational spectra

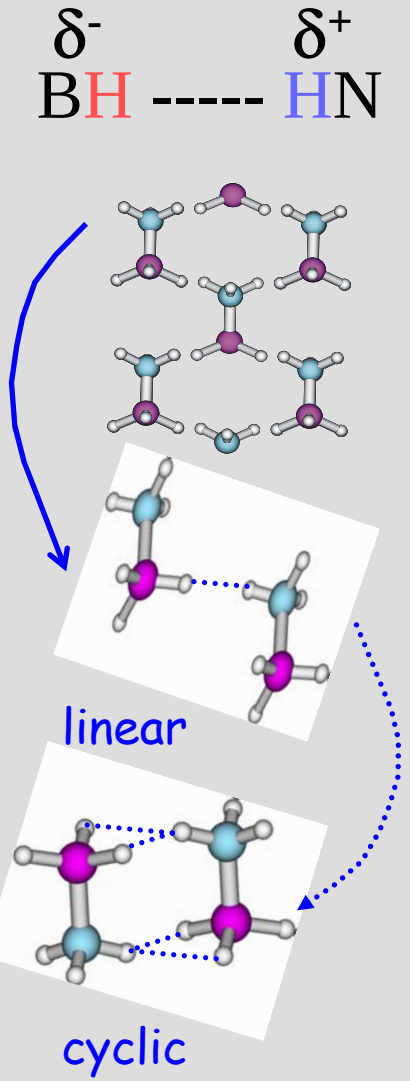
FDS provides approach to measure low frequency vibrational modes due to intermolecular interactions

Experimental data to bench mark theory

To facilitate identification of modes use selective D/H labeling to 'hide' transition.

Vibrational studies of dihydrogen bonding

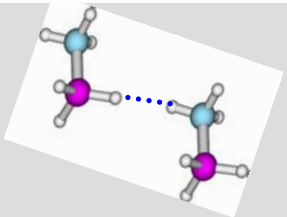




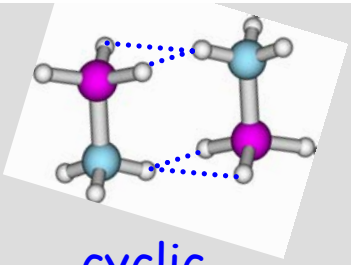
LANSCE

Computational analysis of dihydrogen bonding

		Calculations on AB dimer (MP2)				FDS spectra at 10K *(tentative assignments)*		
		linear	cyclic					
motion	mode	NH3BH3	NH3BH3	ND3BH3	NH3BD3	NH3BH3	ND3BH3	NH3BD3
molecular rock		52				59	64	53
rock		74				75	81	69
bend	A_u		93	86 [-7]*	84 [-9.5]	94 (+1)	87 [-8]	89 [-5]
						110		105
torsion	B_g		132	101 [-23]	117 [-11]	129 (-3)	99 [-23]	125 [-3]
rock	A_g		150	139 [-8]	141 [-7]	152 (+2)	135 [-11]	147 [-3]
torsion	A_u		193	142 [-26]	168 [-13]	180 (-13)	158 [-13]	170 [-6]
stretch	A_g	122	204	201 [-2]	191 [-6]	211 (+7)	198 [-6]	202 [-4]
rock	B_u		242	224 [-7]	218 [-10]	261 (+19)	-----	218 [-17]
torsion	A_u	256	295	283 [-4]	241 [-18]	298 (+3)	269 [-10]	253 [-15]
						327		
torsion	B_g	284	327	304 [-7]	265 [-19]	350 (+23)	317 [-10]	275 [-22]
υ(B-N)						764 (782)	725 (737)	756 (747)



linear



cyclic

δ^- δ^+

BH ----- HN

NH_3BH_3 **Summary**

- 12 wt% hydrogen at relatively low temperatures (<400 K)
- exothermic ~ 20 kJ/mol – need to regenerate by chemical pathway

- Mechanism of H_2 formation – Nucleation and Growth
- Induction period can be enhanced with scaffold or seeding

- INS provides low frequency vibrational modes to yield insight into di-hydrogen bonds – benchmark theory
- Computational approaches to understand dynamics

Future Directions

Understanding dihydrogen bonding interactions. How universal are these interactions in H storage materials?

$\delta-$ $\delta+$

MH ----- HY Dihydrogen bond

M is electropositive (Li, Mg, Ca, Na, Al, B)
Y is electronegative (N, O, P, etc.)

AB will react with itself or with other hydridic and/or protic hydrogen. E.g., MgH_2 ---H_3NBH_3 ---H_2NLi

Are thermodynamics of alternative reactions more favorable?

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