Basic Research for the Hydrogen Fuel Initiative

Control of Hydrogen Release and Uptake in Condensed Phases

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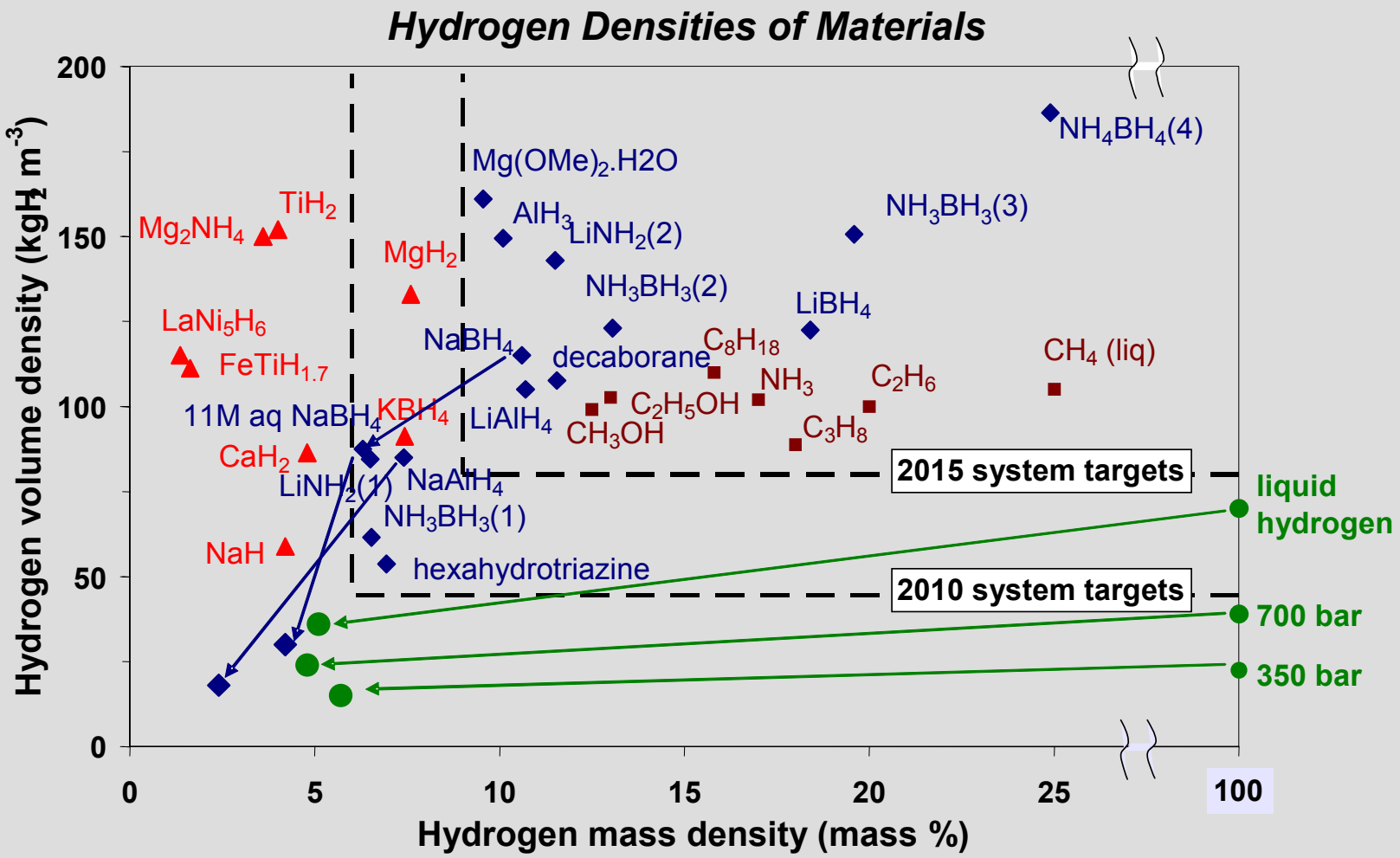
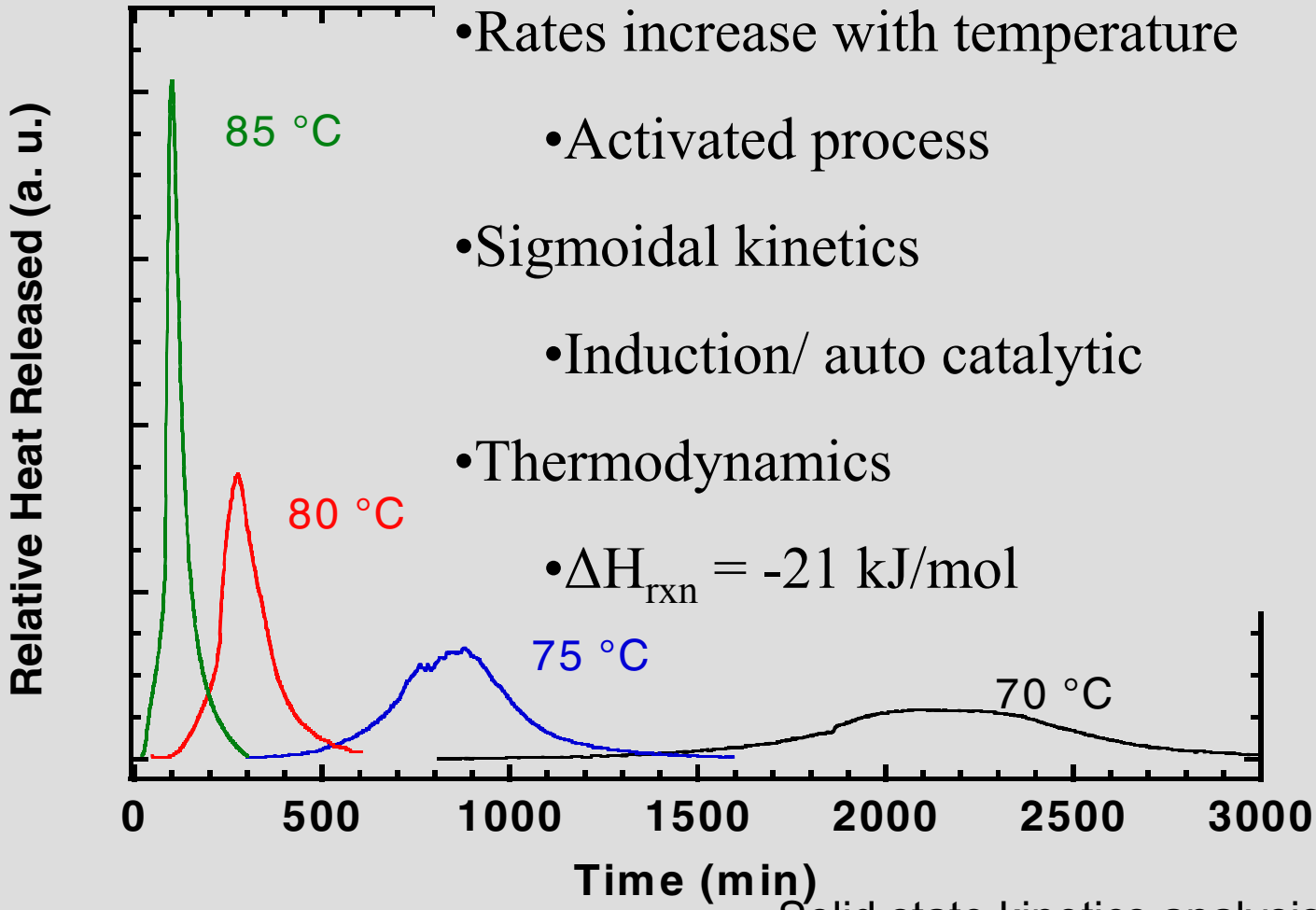
Hydrogen-rich ammonia borane (AB)



George Thomas

What we know…

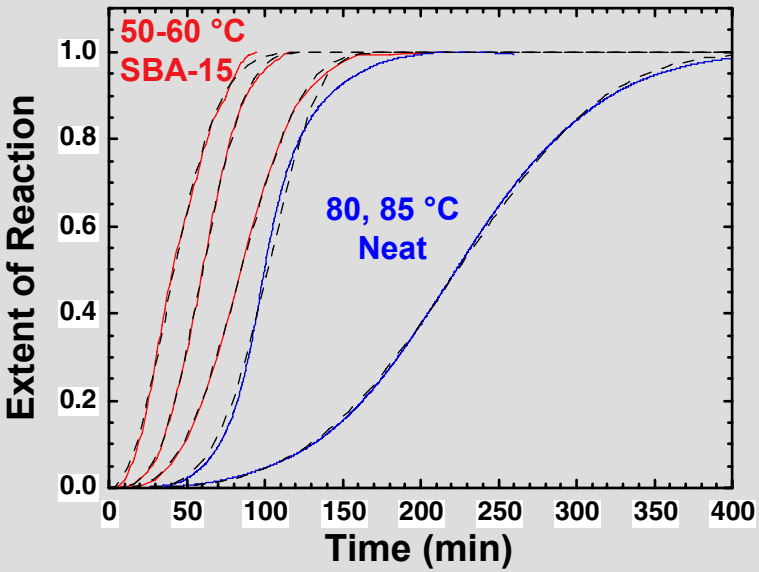
$$NH_3BH_3(s) \rightarrow (NH_2BH_2)(s) + H_2$$

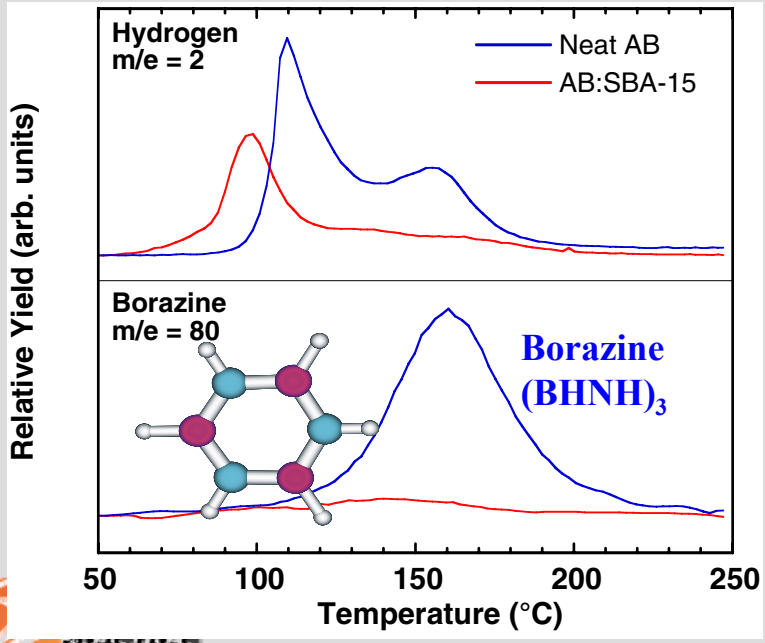


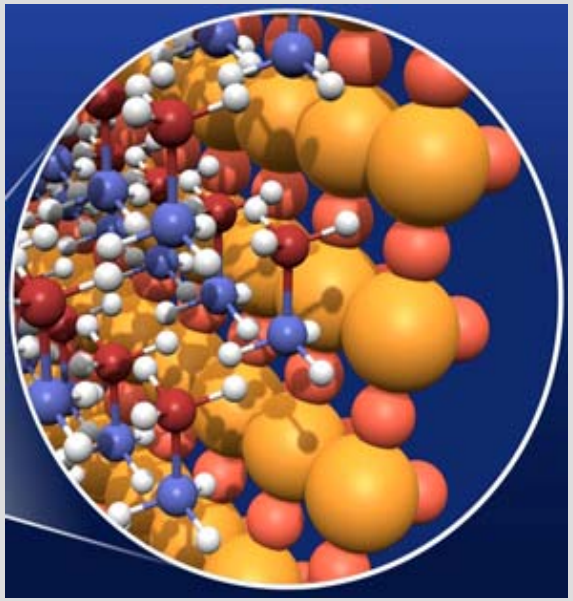
- Rates increase with temperature
  - Activated process
- Sigmoidal kinetics
  - Induction/ auto catalytic
- Thermodynamics
  - ΔH_{rxn} = -21 kJ/mol

Solid state kinetics analysis

… and on scaffolds







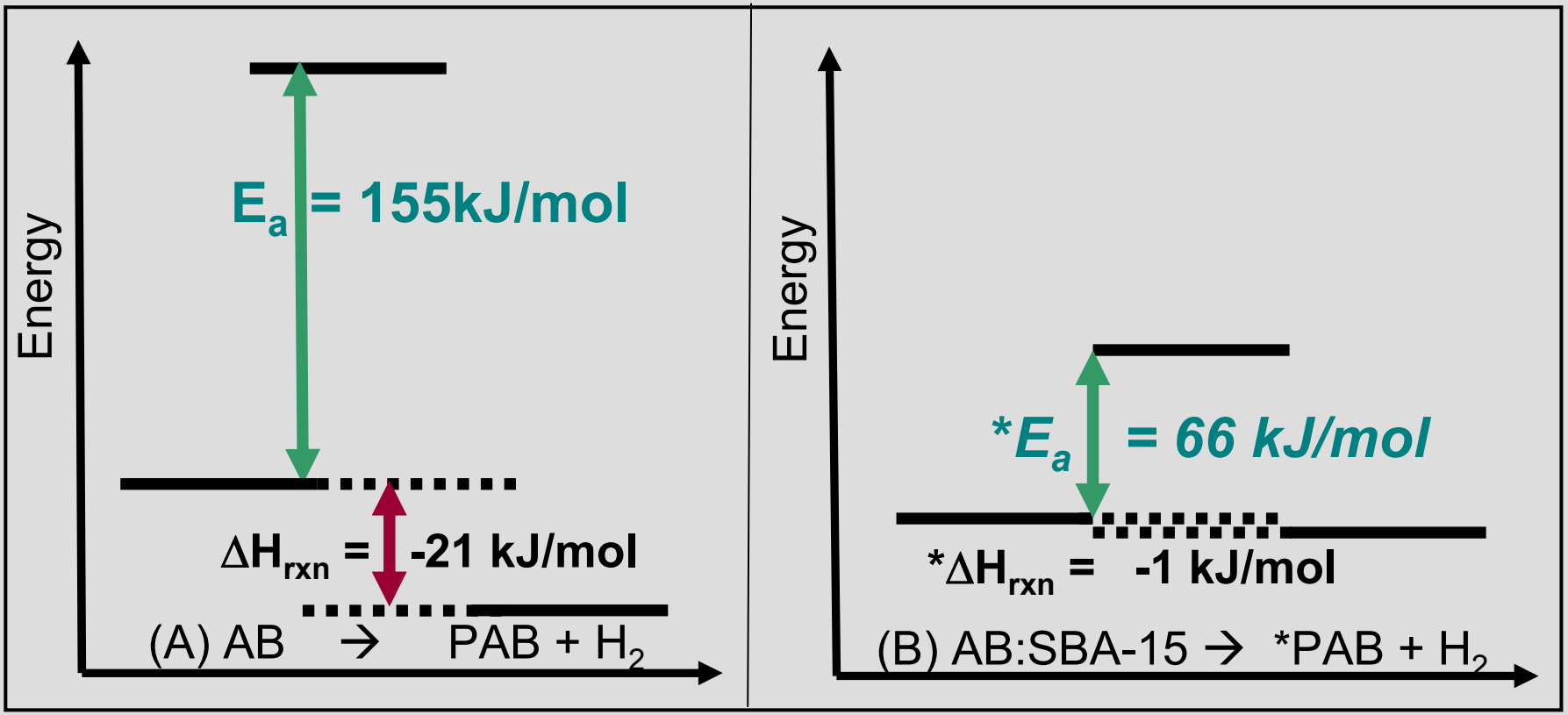
Ammonia borane in SBA-15

Scaffolds:

. enhance rates of H_2 release
. enhance purity of H_2
(little borazine)
. thermodynamics

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

Summary of AB chemistry



- Selectivity of H_2 release from AB
  - No borazine seen in volatile products or left behind in scaffold.
  - No cyclized products observed in NMR and DSC data show process is less exothermic
- Reactivity for H_2 release from AB
  - 1-2 orders of magnitude faster!

Fundamental Questions

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

How is the H_2 released?

Why is there an induction period?

What is the role of the dihydrogen bond?

Can we control the decomposition pathways?

What materials catalyze hydrogen release?

Does the reaction proceed by ionic or neutral pathways?

How does the scaffold interface change reactivity?

What is hydrogen doing <u>before</u> it is released?

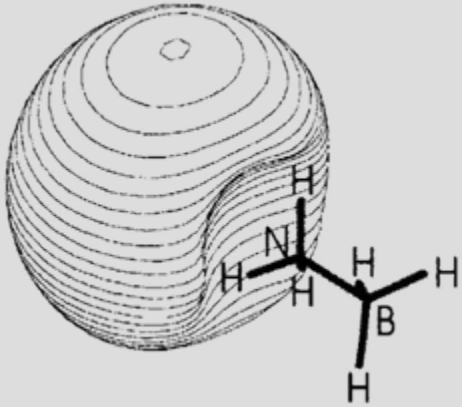
Approaches

- Multi-nuclear 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 (for structure and spectroscopic studies)
- EXAFS spectroscopy
  - Operando (in-situ) catalysis studies. Gives x-ray like data for structural studies of catalytic induced transformations.

Combination of experiment & theory to gain fundamental understanding of interactions between protic/hydric hydrogen

Molecular NH_3BH_3

- $H_3B \leftarrow NH_3$ Electron donor-acceptor (dative) bond. The lone electron pair of NH_3 delocalizes over an unoccupied 2p orbital of B.

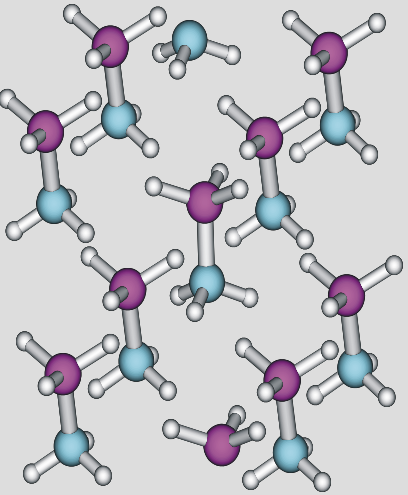


-Large dipole moment (5.3 D) illustrated by effective atomic charges: -0.46 (N), 0.27 (H(N)), 0.39 (B), -0.25 (H(B))

-the length of the dative BN bond 1.67 A. A barrier for rotation around the BN bond less than 9 kJ/mol

- The calculated dissociation energy for $NH_3BH_3 \rightarrow BH_3 + NH_3$ is 109 kJ/mol. The dative BN bond is stronger than a hydrogen bond but weaker than a valence bond

Crystalline NH_3BH_3



- Synthesis by Shore and Parry in 1955
- Density 0.74 g/cm^3, mp 124 °C, 19.5wt% H_2
- $NH_3BH_3 \rightarrow H_2$ + *polyaminoborane* at < 100 °C.

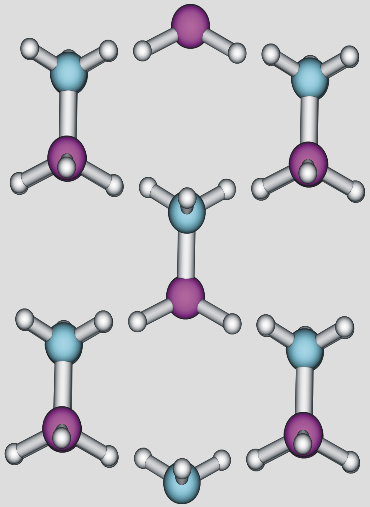
- AB in equilibrium with diammoniate of diborane

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

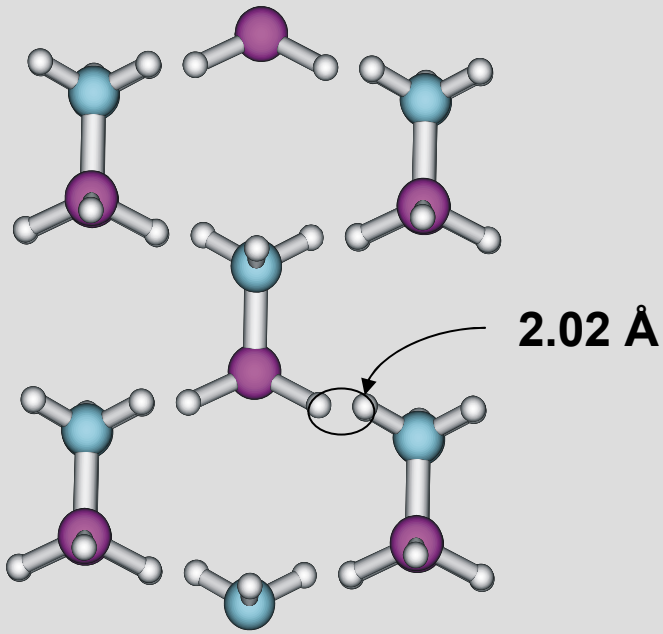
•First order-disorder phase transition at 225 K, the low T structure is orthorhombic, the high T tetragonal

•Electrostatic bonding between H^+ and H^- (dihydrogen bond)

•The calculated <u>cohesive energy</u> is 74 kJ/mol

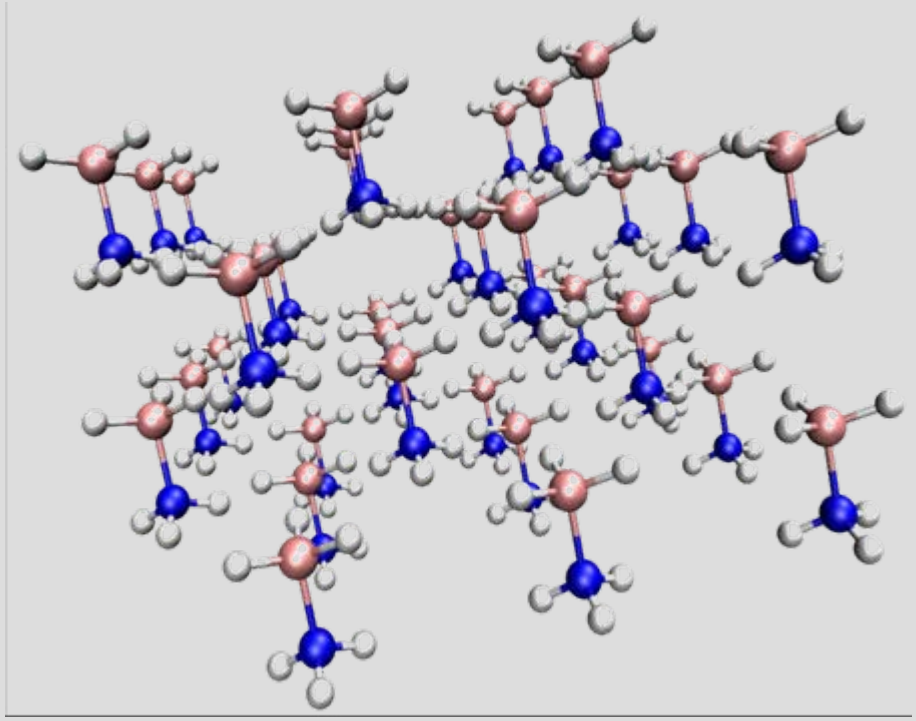


Dihydrogen Bonds



δ- δ+

BH ----- HN



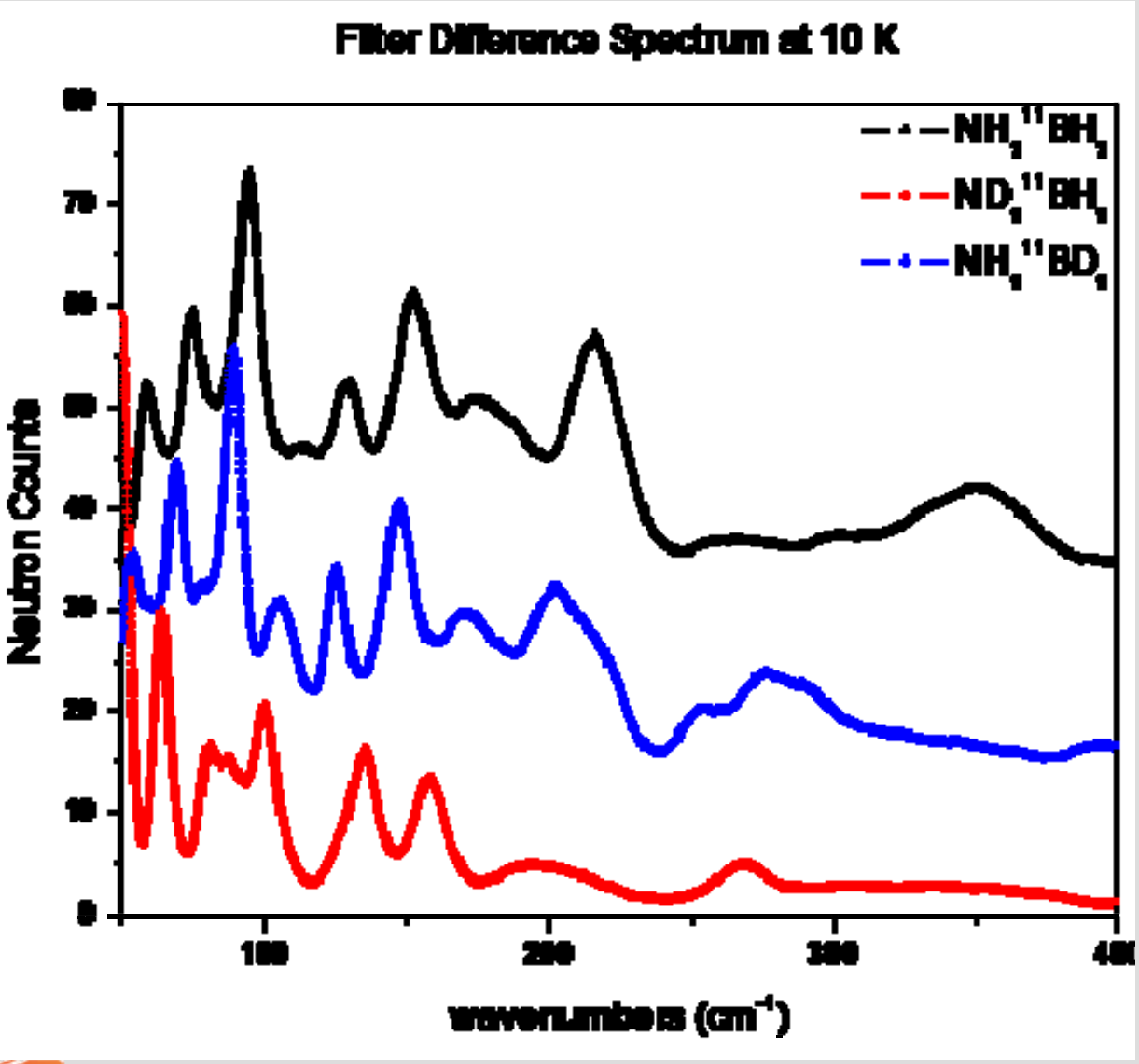
Dihydrogen bond

Hydride atoms act as Proton acceptor

Soft vibration modes, where are they?

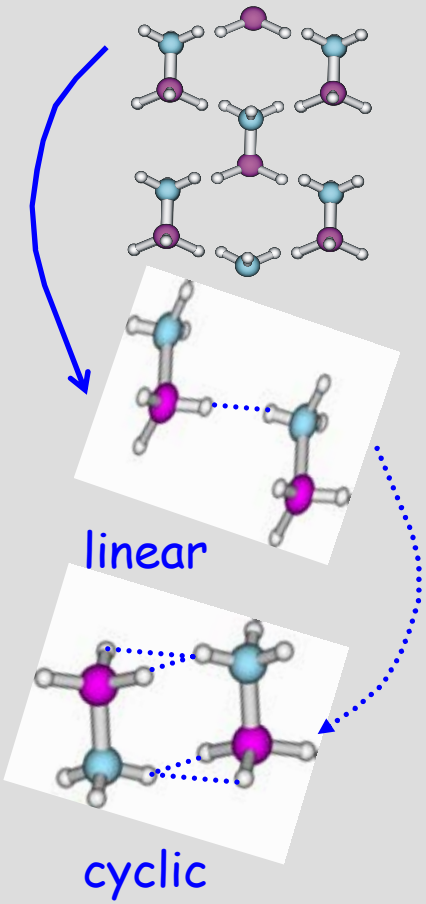
Klooster, et. al. *JACS*, **1999**, *121*, 6337.)

Vibrational studies of dihydrogen bonding



δ^- δ^+

BH ----- HN

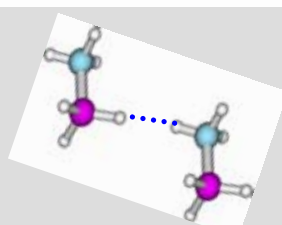


Computational analysis of dihydrogen bonding

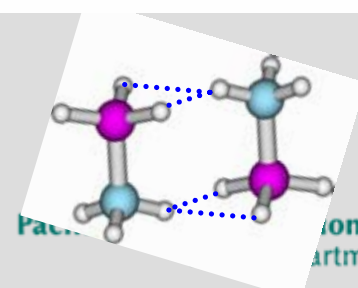
		Calculations on AB dimer (MP2)				FDS spectra at 10K *(tentative assignments)*		
		linear	cyclic					
motion	mode	NH3BH3	NH3BH3	ND3BH3	NH3BD3	NH3BH3	ND3BH3	NH3BD3
molecular rock		52				59	64	53
rock		74				75	81	69
bend	A_u		93	86 [-7]*	84 [-9.5]	94 (+1)	87 [-8]	89 [-5]
						110		105
torsion	B_g		132	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)

δ^- δ^+

BH ----- HN



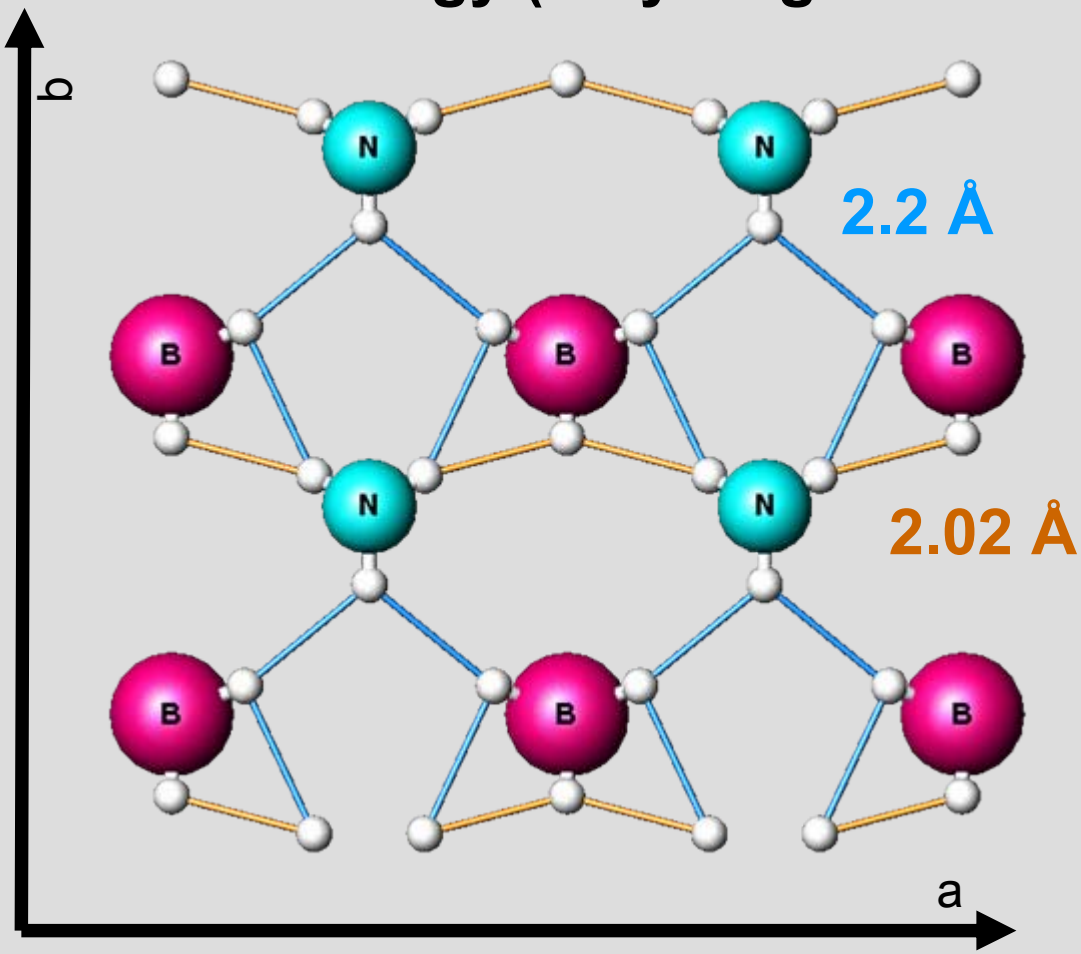
linear

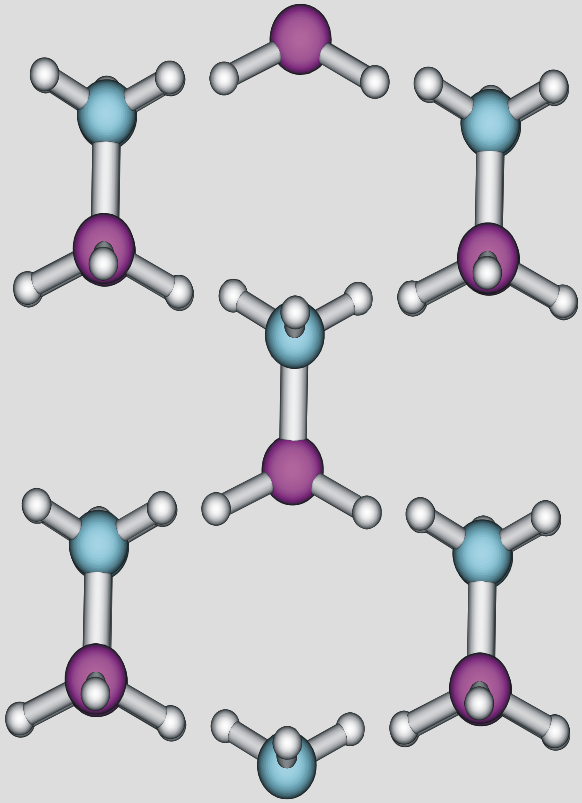


cyclic

Dynamics of $–BH_3$ and $–NH_3$ motion in AB

Cohesive energy (dihydrogen bonding) 74 kJ/mol…

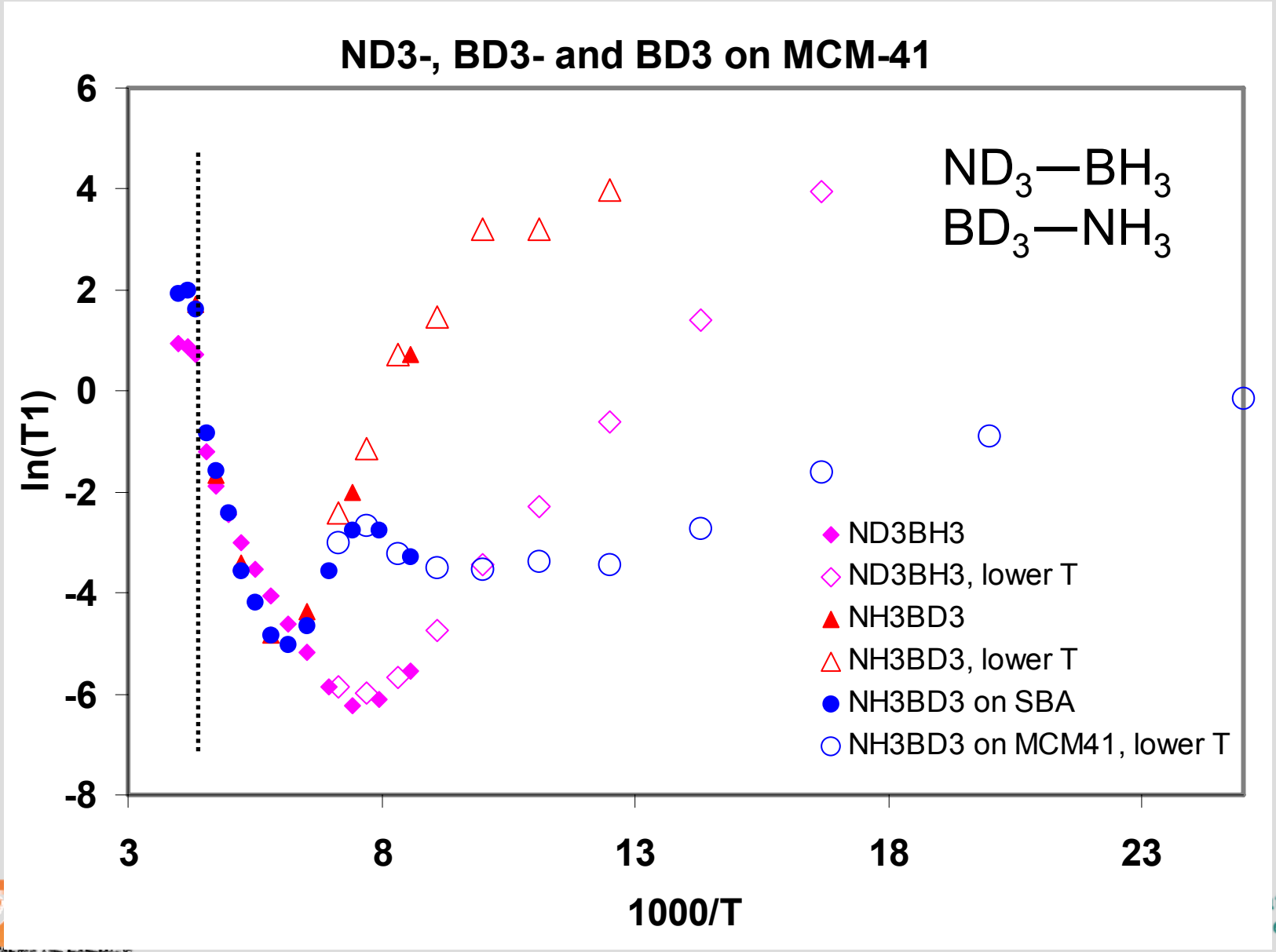




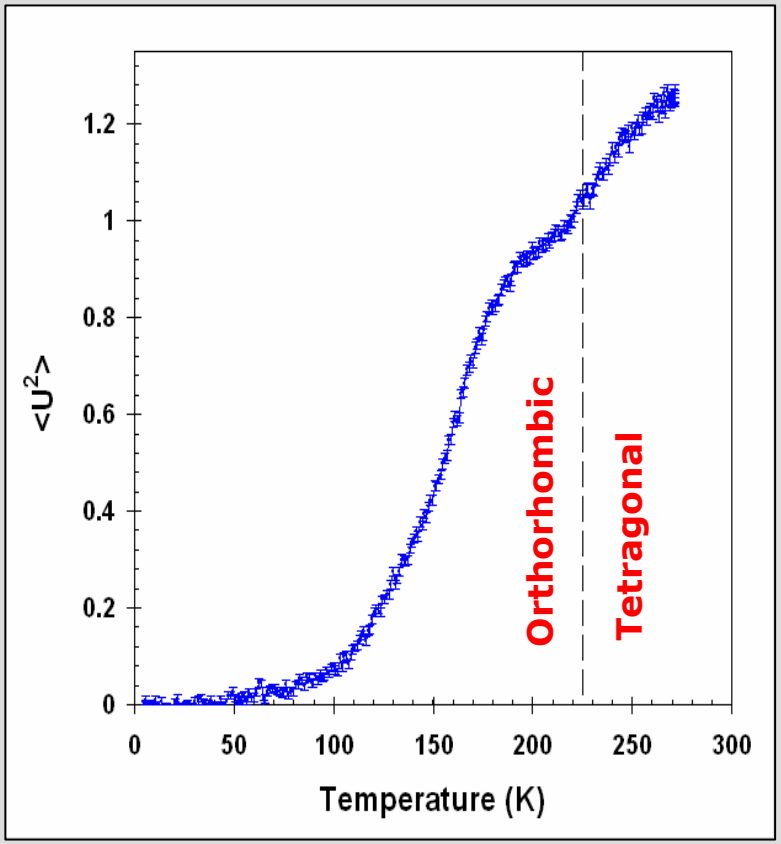
Are hydrogens locked into place?

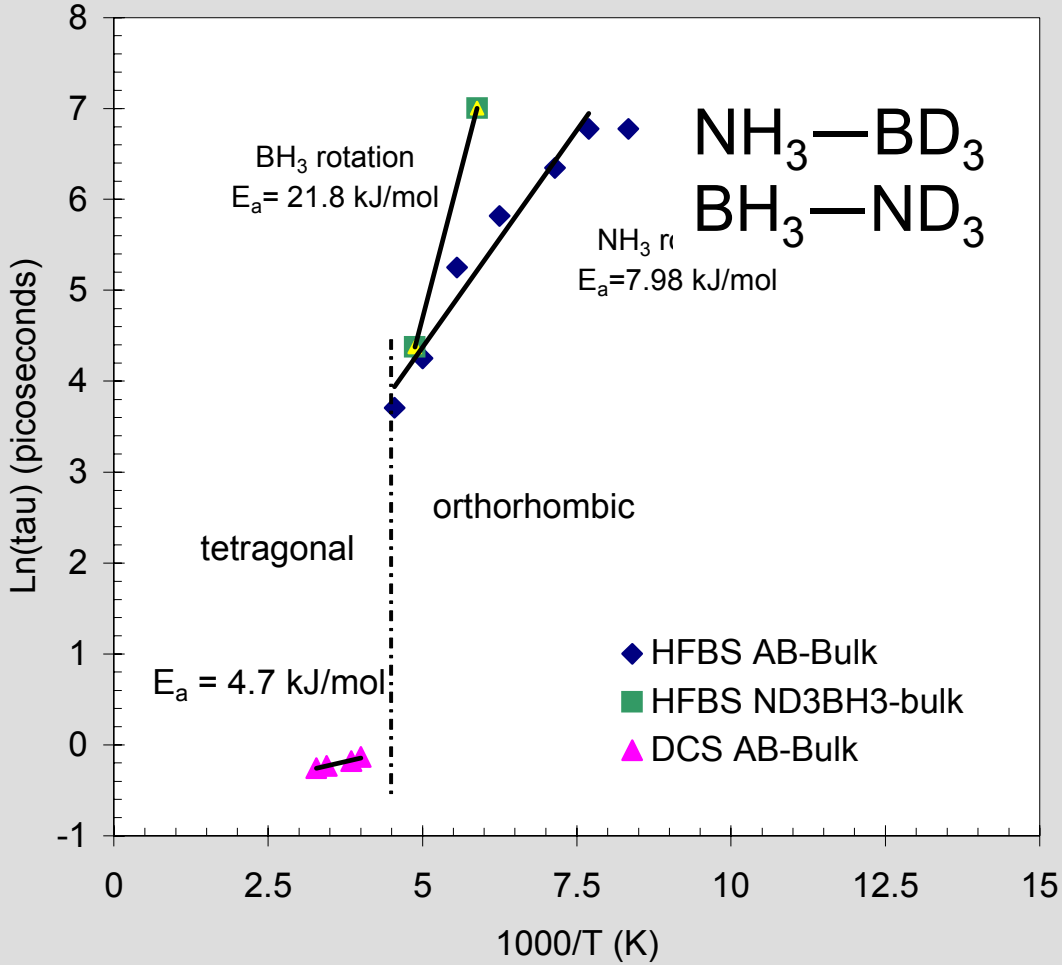
H-H 2.4 Å

^{2}H nuclear magnetic resonance (D-NMR)

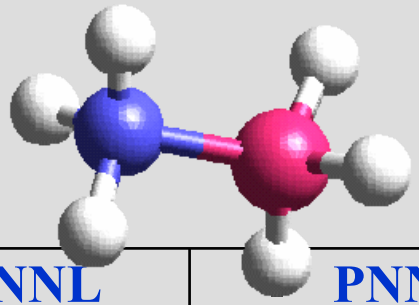


quasi-elastic neutron scattering (QENS)





Rotational energy barriers



	Reynhardt and Hoon	Penner et al	PNNL NMR	PNNL QENS
Solution				
E_a (kJ/mol)		11.7		
Orthorhombic				**HFBS**
NH_3/ND_3				NH_3BH_3
E_a (kJ/mol)	9.6	13.7 (ND_3)	14.6 (ND_3)	8 (NH_3)
BH_3/BD_3				ND_3BH_3
E_a (kJ/mol)	25	25.4 (BD_3)	22.7±2 (BD_3)	21 (BH_3)
Tetragonal				**DCS**
NH_3/ND_3				
E_a (kJ/mol)		7.3 (ND_3)	5.8 (ND_3)	
BH_3/BD_3				
E_a (kJ/mol)	5.9	5.9 (BD_3)		4.7 (BH_3)
Gas phase	9			

Summary

NH_3BH_3: Strong electrostatic interactions between hydridic and protic hydrogens, however hydrogen is very mobile.

Goal: 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.)

NH_xBH_x materials have both hydridic and protic hydrogen. These materials will react with itself or with other hydridic and/or protic hydrogen. E.g., MgH_2 ---H_3NBH_3 ---H_2NLi

What are thermodynamics of alternative reactions?

Contributors

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