Materials for Hydrogen Storage: From Nanostructures to Complex Hydrides

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Outline

- **Materials Requirement for Hydrogen Storage**
- **Nanostructured materials:**

  Boron Nitride Nano Cage

  Metal Coated Carbon Fullerenes

  Organo-Metallic Frameworks
- **Complex light metal hydrides - Sodium Alanates**

Acknowledgement

- **Carbon and Boron Nitride Nano Structures:**

  Q. Sun, Q. Wang, VCU

  Organo-metallic frameworks

  K. Boggavarapu, A. Kandalam

- **Sodium Alanates:**

  Sa Li, VCU,

  C. M. Araujo, and R. Ahuja, Univ. of Uppsala

Work Supported by the Department of Energy

Hydrogen Storage Requirements

Transportation Applications

- High gravimetric (9 wt %) and volumetric density (70 g/L)
- Fast kinetics
- Favorable thermodynamics
- Effective heat transfer
- Long cycle lifetime for hydrogen absorption/desorption
- Safety, durability, and cost effectiveness

75% of U.S. oil consumption is used to meet transportation energy needs

Hydrogen Storage Media

- **Gaseous storage – High Pressure**
  - Energy content = 4.4 MJ/L (at 10,000 psi)
  - compared to that of 31.6 MJ/L for fossil fuel.
  - Costs associated with compression, leakage and safety are issues of concern.
- **Liquid Storage - Cryogenic Temperatures**
  - Density of liquid of H_2 at 20 K= 70 g/L
  - Energy content = 8.4 MJ/L
- **Solid State Storage**

Materials Requirements

- For high gravimetric density (9 wt %) host materials must consist of light elements: Li, Be, B, C, N, Na, Mg, Al
- Difficulties: Bonding of hydrogen is strong (covalent or ionic) and thermodynamics and kinetics are not ideal
- Ideal Bonding: not too weak or not too strong
- Ways of altering the chemistry of hydrogen bonding: nanostructuring or catalysis

Atomic and Electronic Structure

Atomic Clusters

- Linear combination of atomic orbitals
- Gradient Corrected Density Functional Theory
- Gaussian Basis sets, and Gaussian 98 code
- Geometries optimized without symmetry constraint

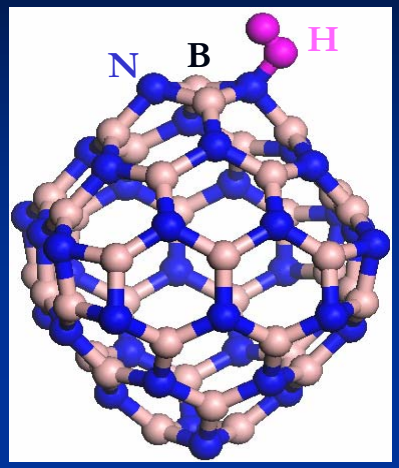
Crystals

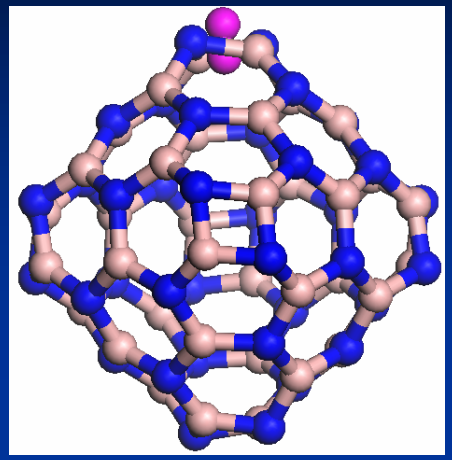
- Supercell Band Structure Methods within Gradient Corrected Density Functional Theory

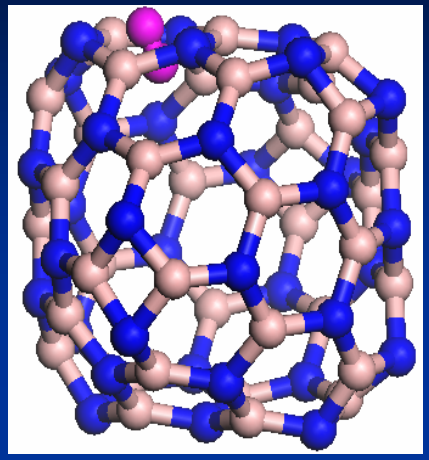
Boron Nitride Cage

Q. Sun, Q. Wang, and P. Jena, "Storage of molecular hydrogen in B-N cage: Energetics and thermal stability", Nano Letts. **5**, 1273 (2005)

Passage of H_2 into the $B_{36}N_{36}$ cage

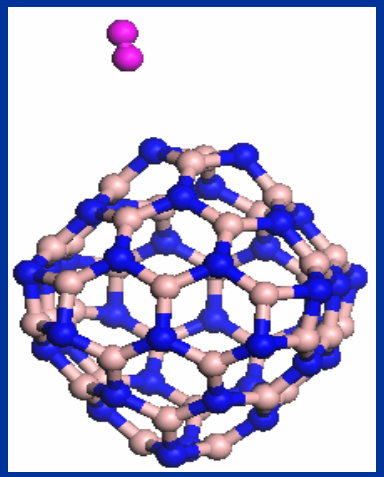


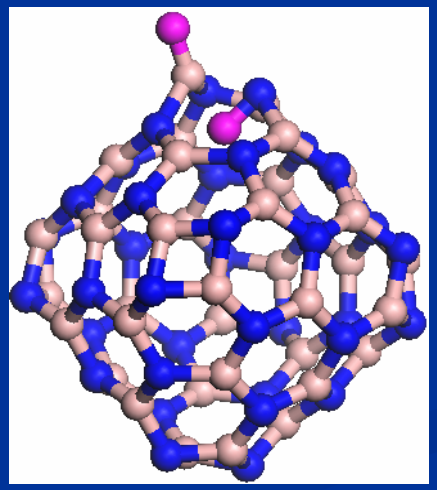


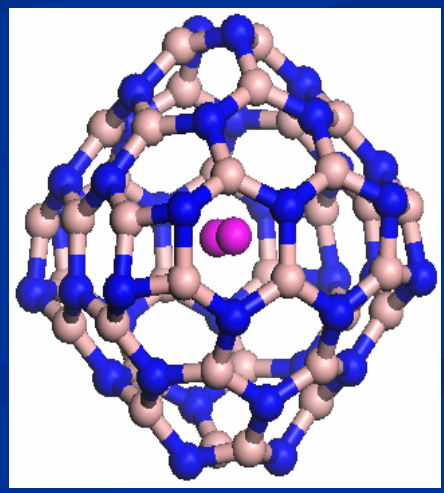


square

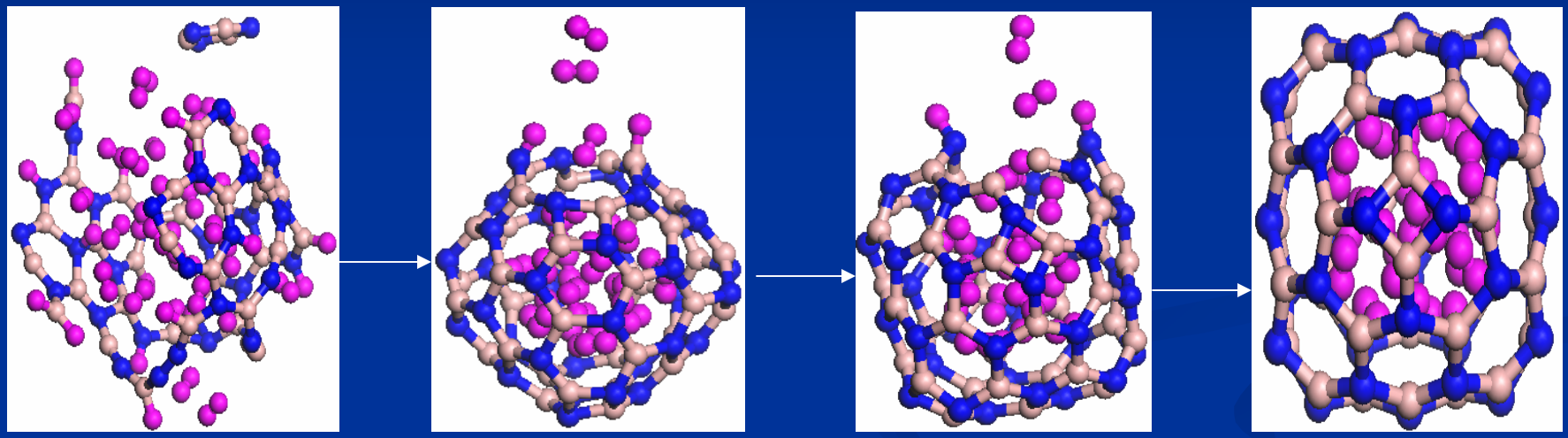
hexagon





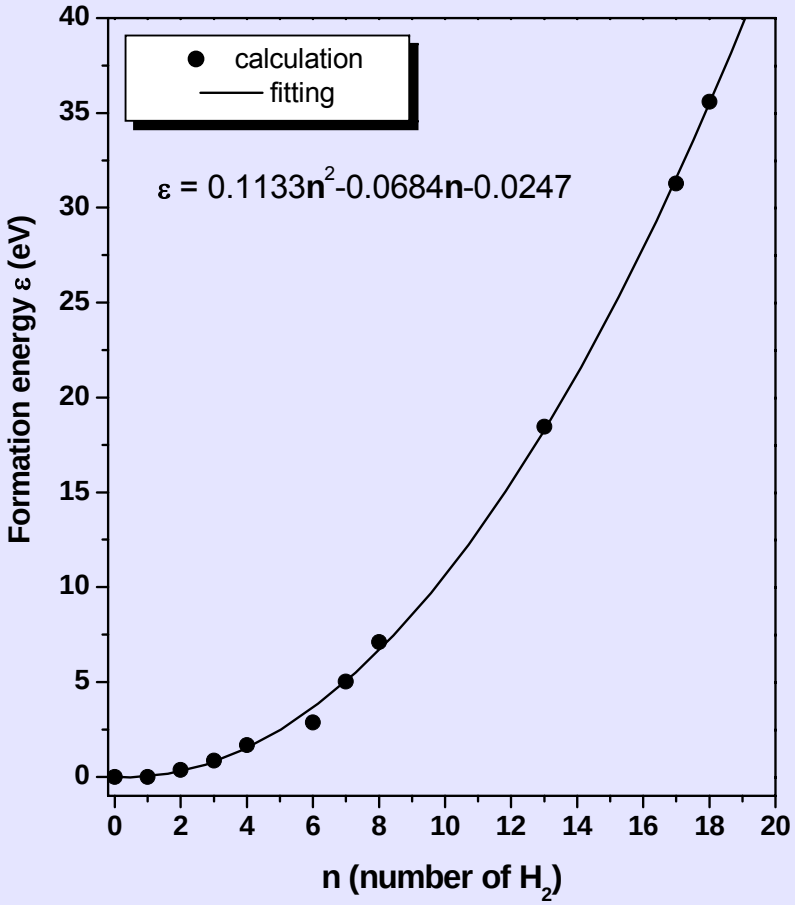


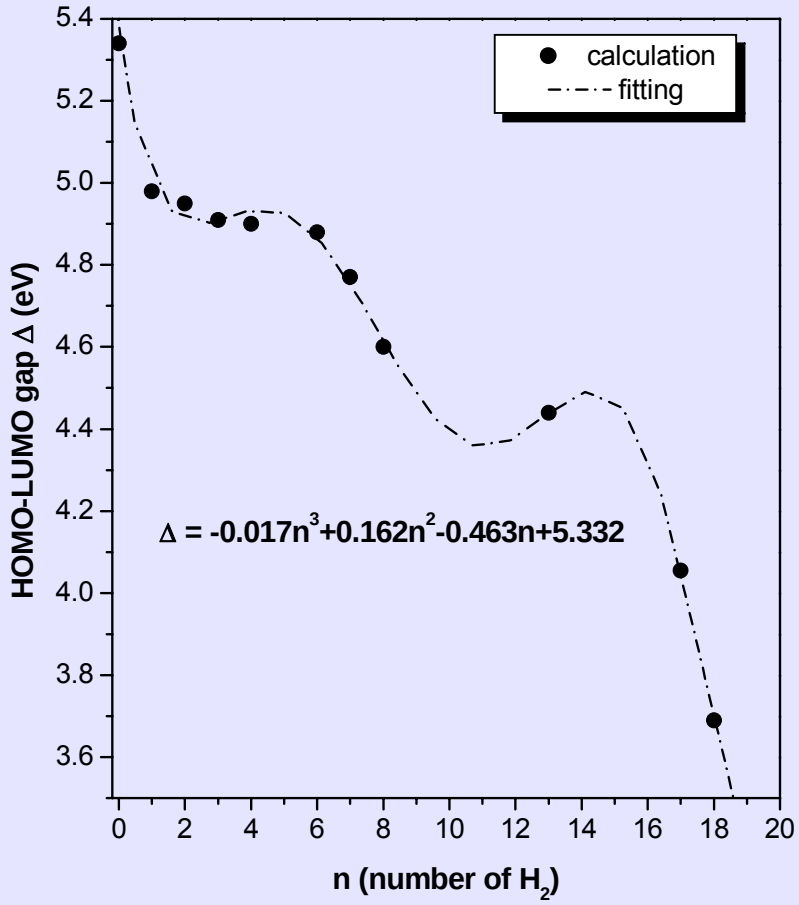
How many H_2 can be inserted inside the cage ?



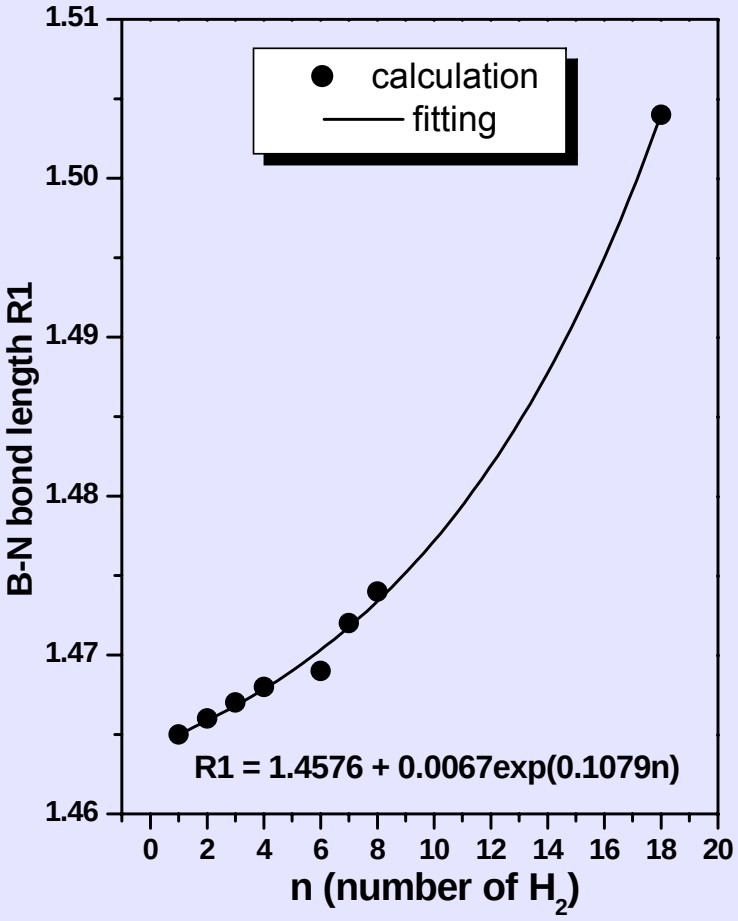
$36H_2$ $24H_2$ $20H_2$ $18H_2$

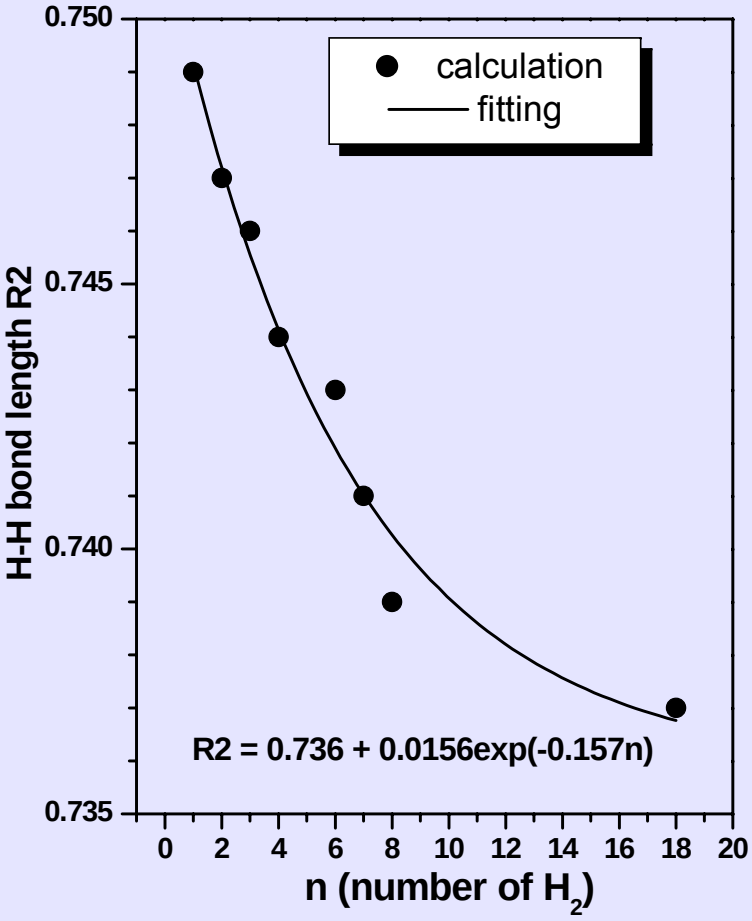
Energy and gap





Changes in bond length



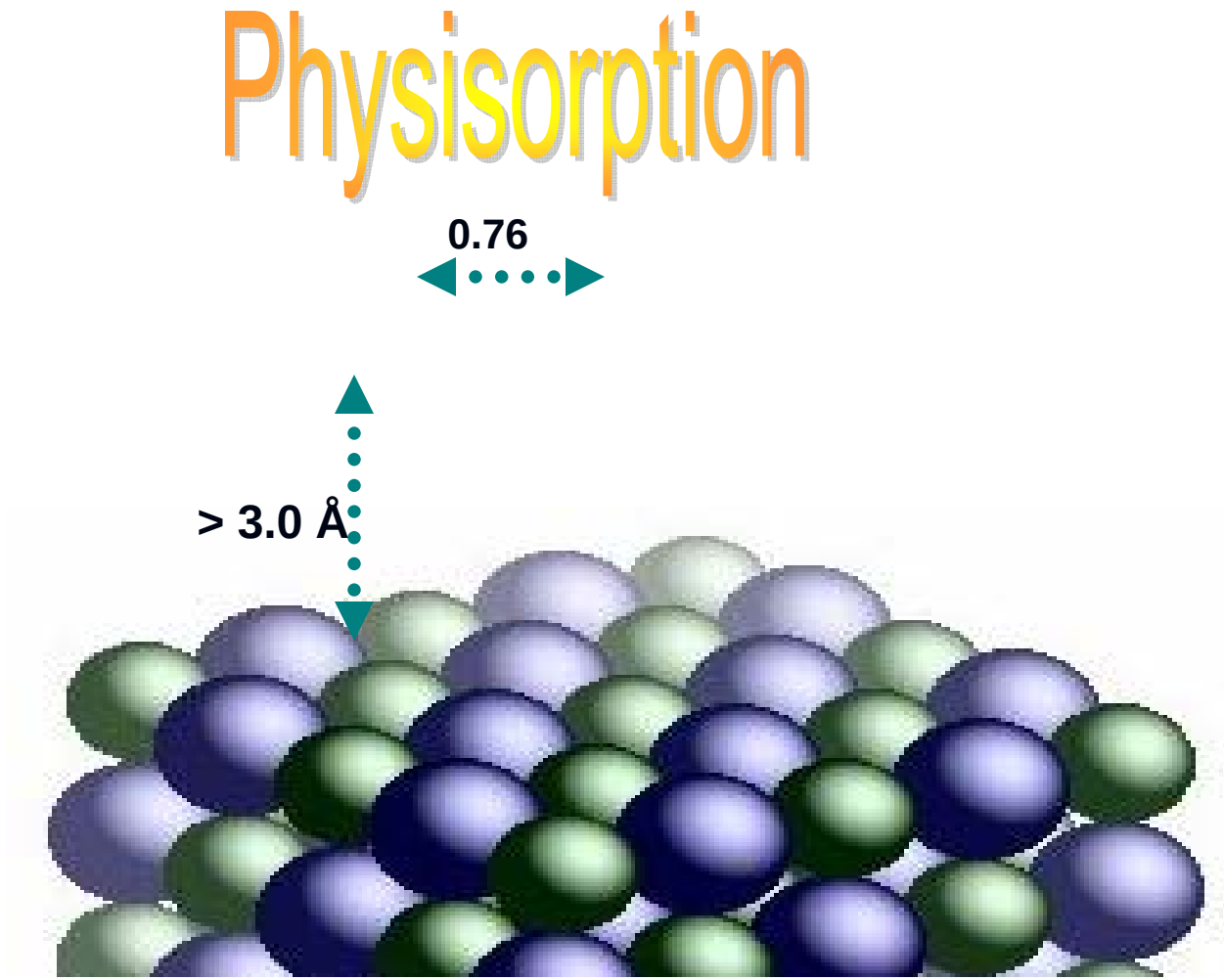


Summary

- Boron Nitride Cage can store hydrogen in molecular form, but the energy costs are high and thermodynamically unstable

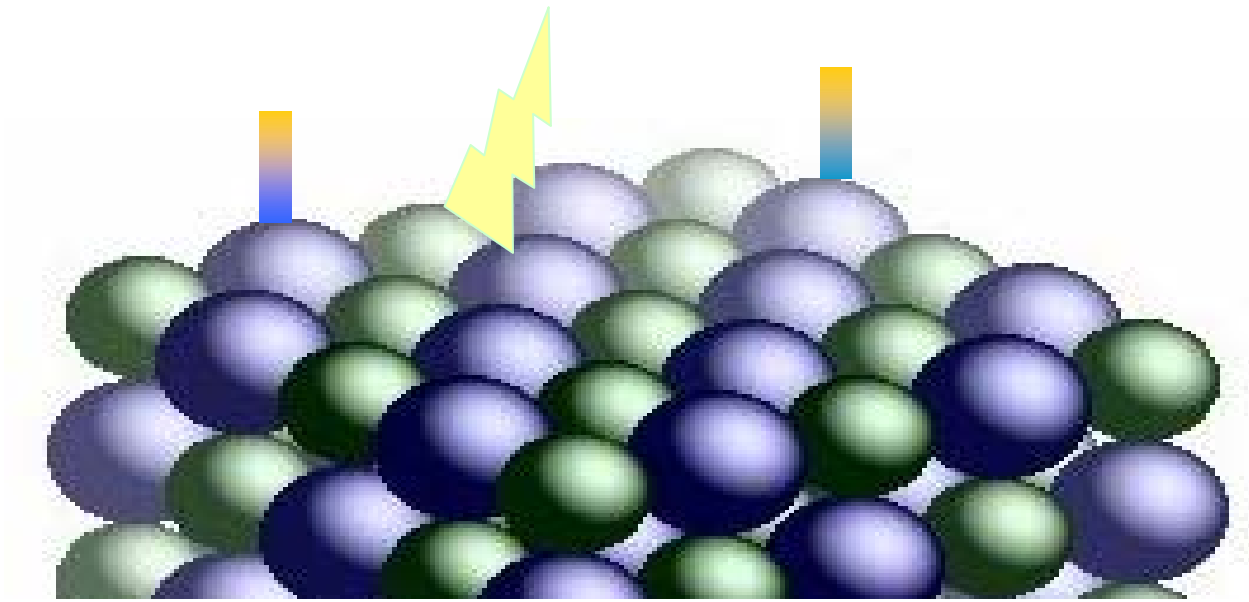
- Boron Nitride Cages are not suitable for hydrogen storage

Nature of Hydrogen Bond



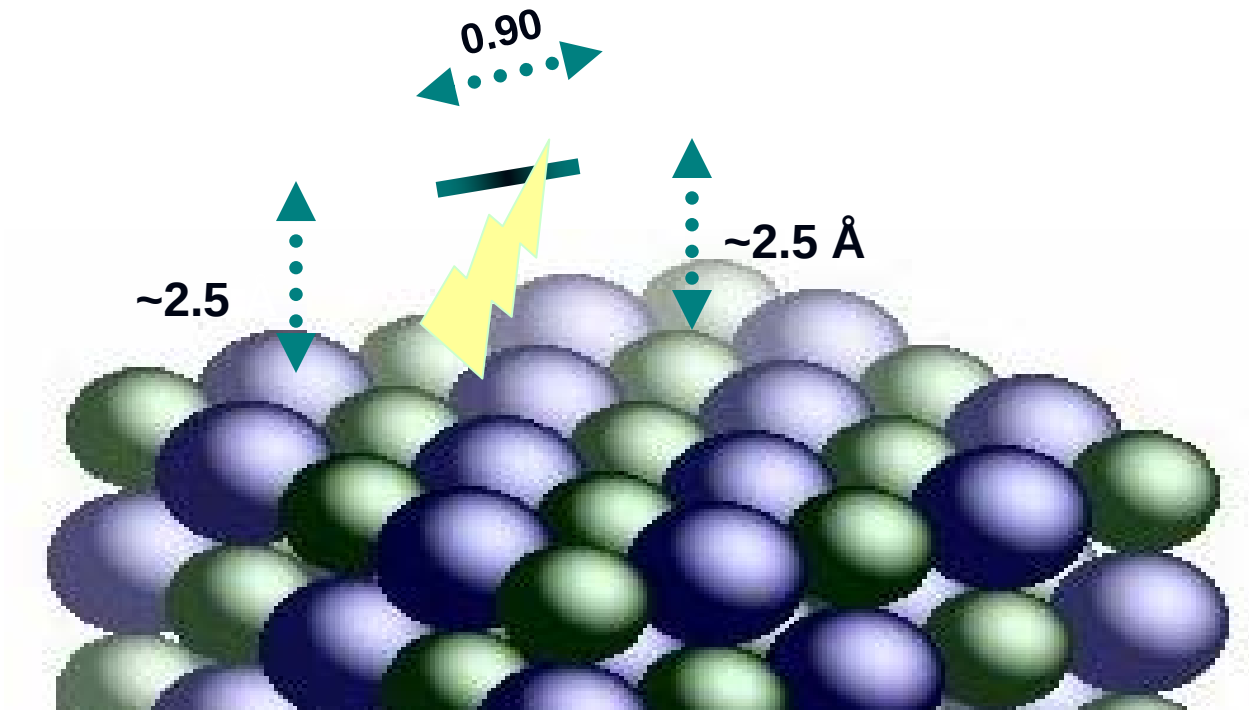
Nature of Hydrogen Bond

Atomic-Chemisorption



Nature of Hydrogen Bond

Molecular-Chemisorption



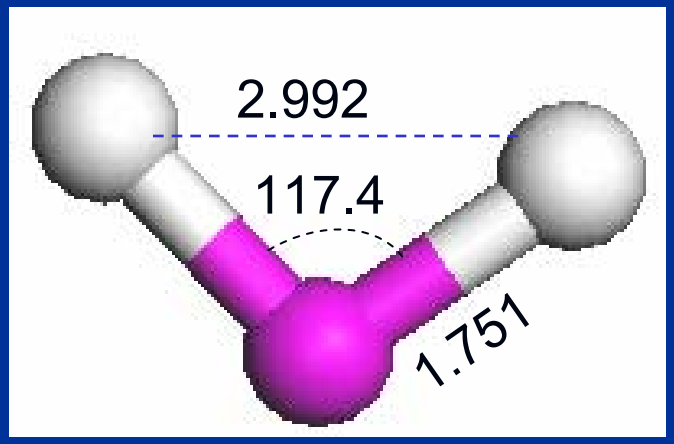
Lessons from early studies on clusters

- J. Niu, B. K. Rao, and P. Jena, "Binding of hydrogen molecules by a transition-metal ion", Phys. Rev. Letters **68**, 2277 (1992)
- B. K. Rao and P. Jena, "Hydrogen uptake by an alkali metal ion", Europhys. Lett. **20**, 307 (1992)
- J. Niu, B. K. Rao, P. Jena, and M. Manninen, "Interaction of H_2 and He with metal atoms, clusters, and ions", Phys. Rev. B **51**, 4475 (1995)
- G.J. Kubas, Acc. Chem. Res, 21, 120(1988)

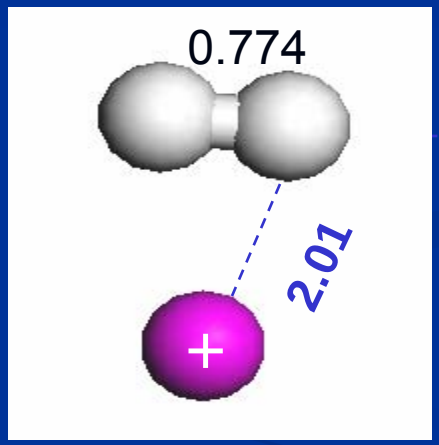
TiH_2 and Ti^+H_2 cluster

Ti_2: r =1.90 (exp. 1.91) E_B = 3.68eV moment =2.0

H_2: r =0.749 (exp. 0.741) E_B= 4.536 eV (exp. 4.533)



E_B = -1.115eV



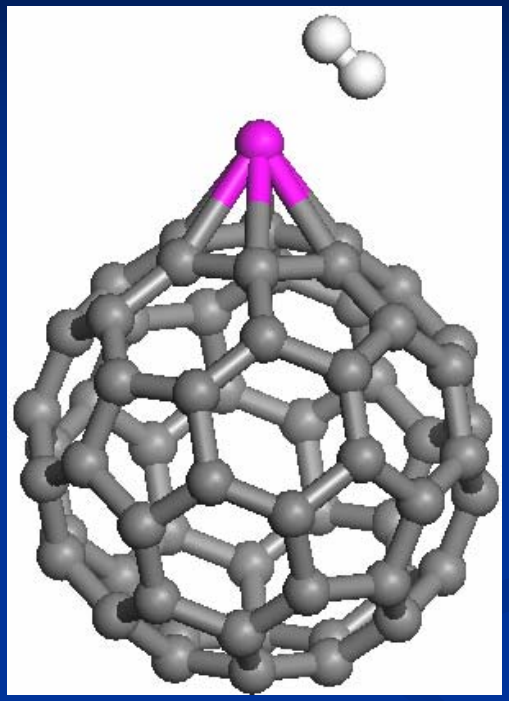
E_B = -1.073eV

TiH_2 Ti^+H_2

Ti coated C_{60}

Q. Sun, Q. Wang, P. Jena, and Y. Kawazoe,

J. Am. Chem. Soc. (Communication) 127, 14582 (2005).

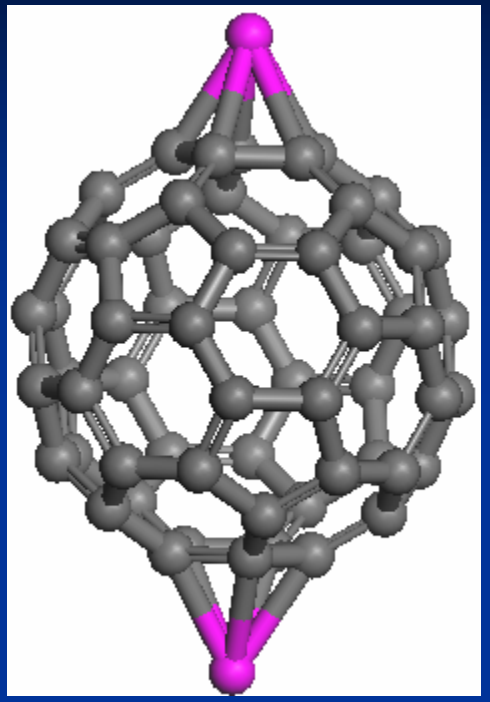


E_ab = 0.55eV/H2

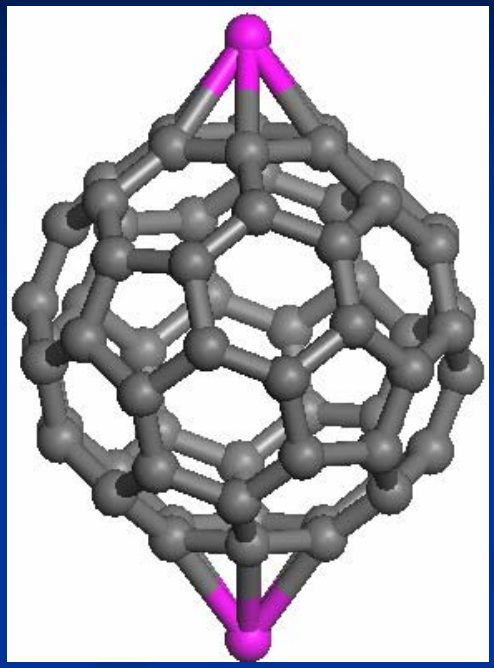
R(Ti-H) = 2.0

R(H-H) = 0.81

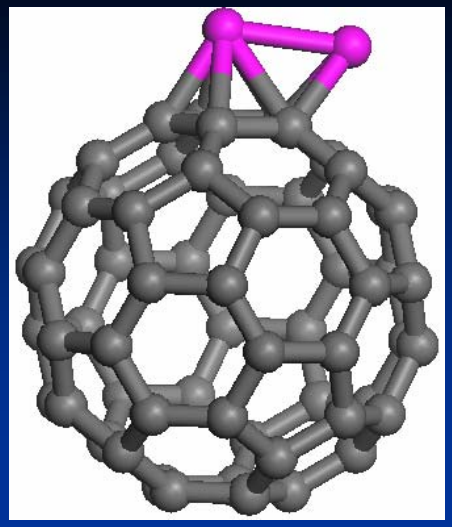
Moment = 2.0

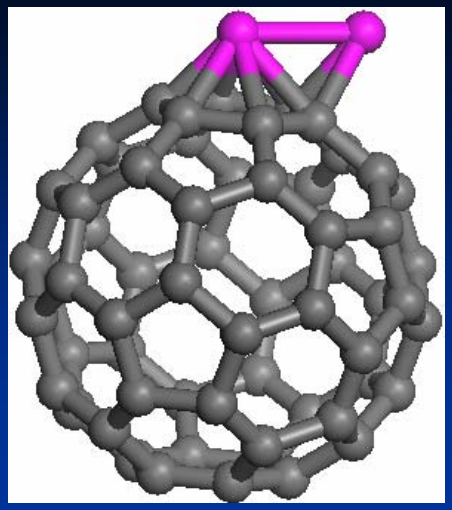


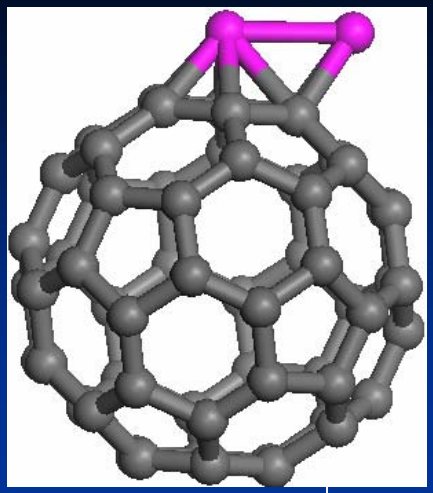
1.902eV/Ti M=6.0

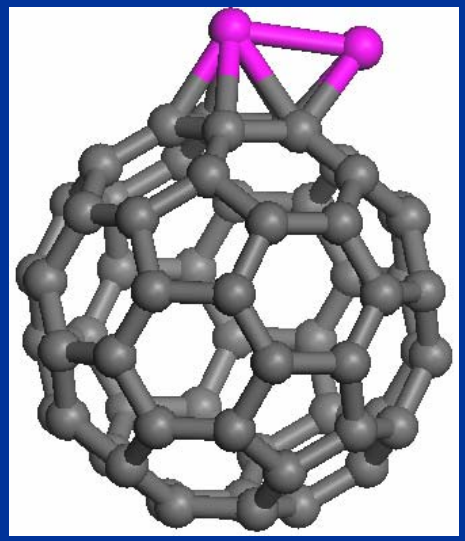


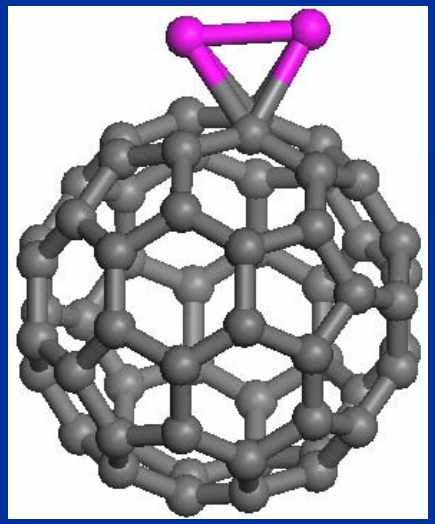
2.384eV/Ti M=4.0

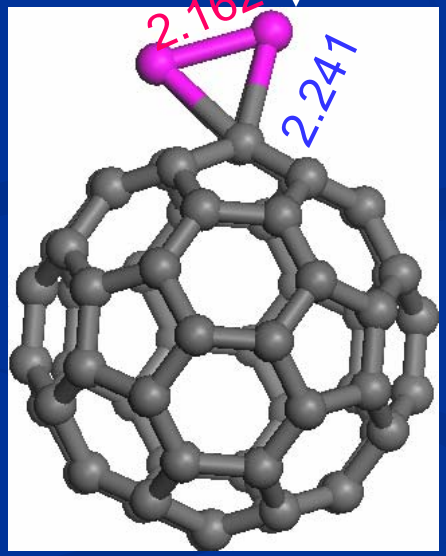








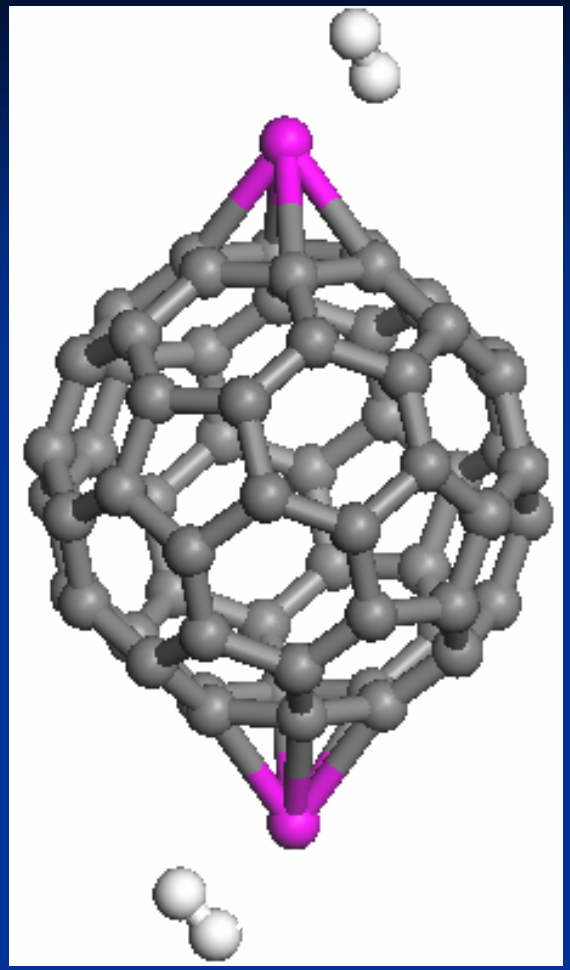




2.915eV/Ti M=1.90

2.958eV/Ti M=2.0

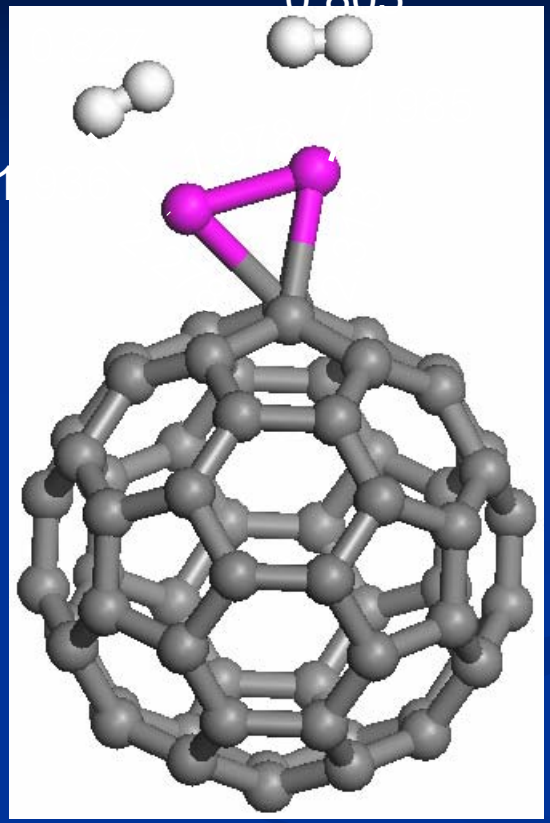
3.03eV/Ti M=1.80



EB = 0.55 eV /H2

Moment = 4.0

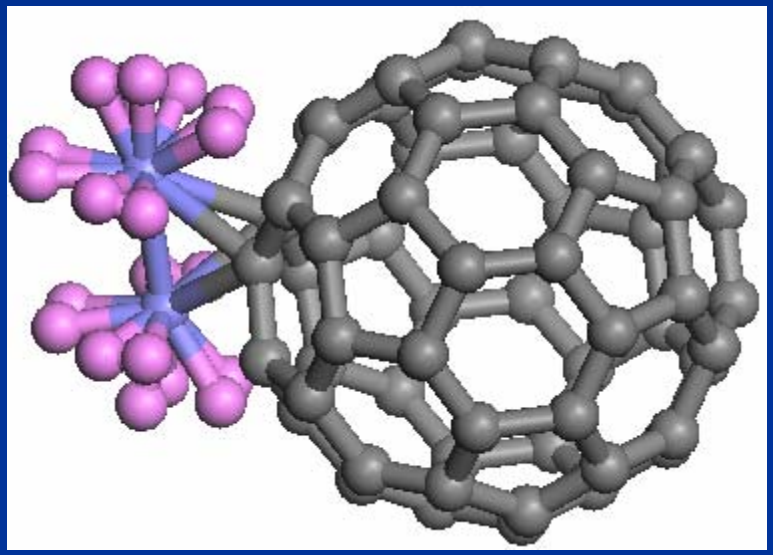
(+ 0.924eV)



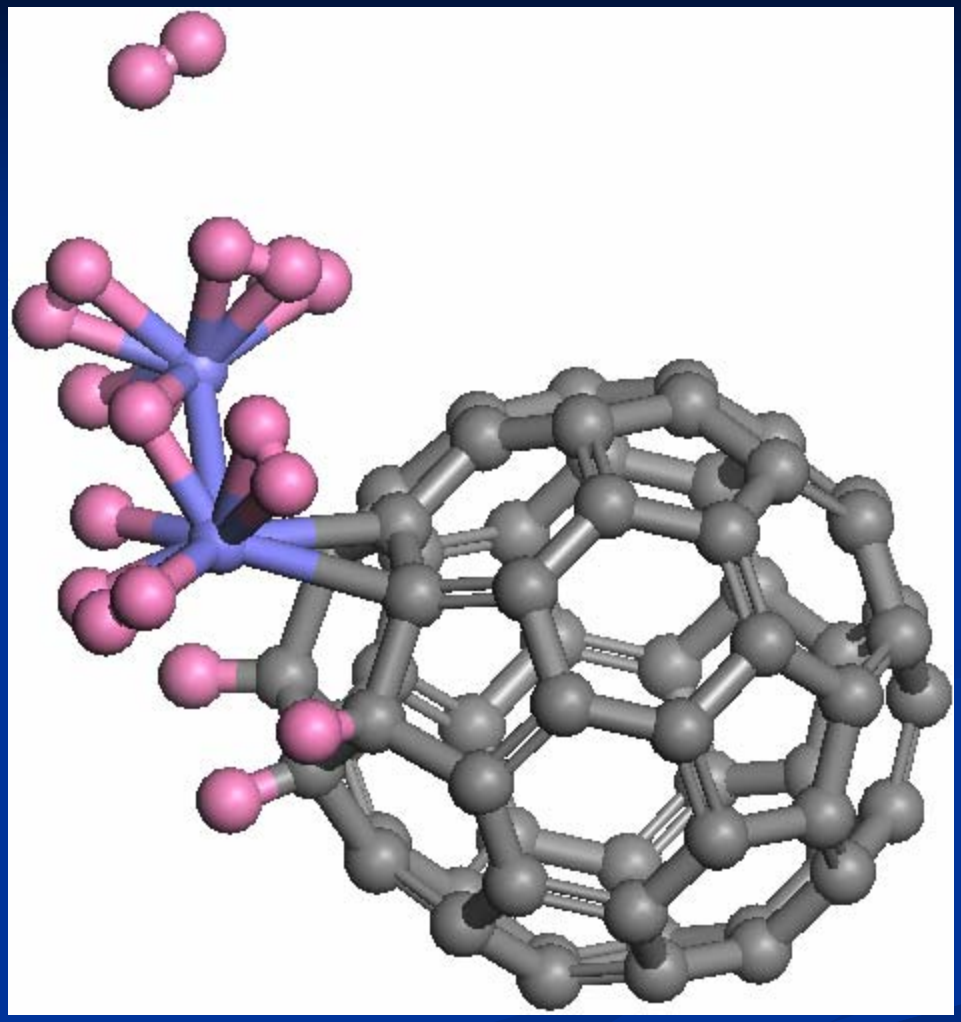
EB = 0.378 eV / H2

Moment = 2.24

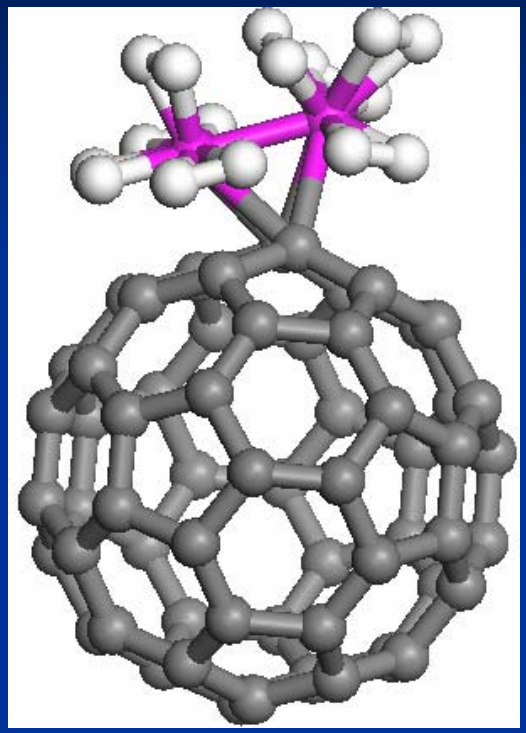
(0.0)

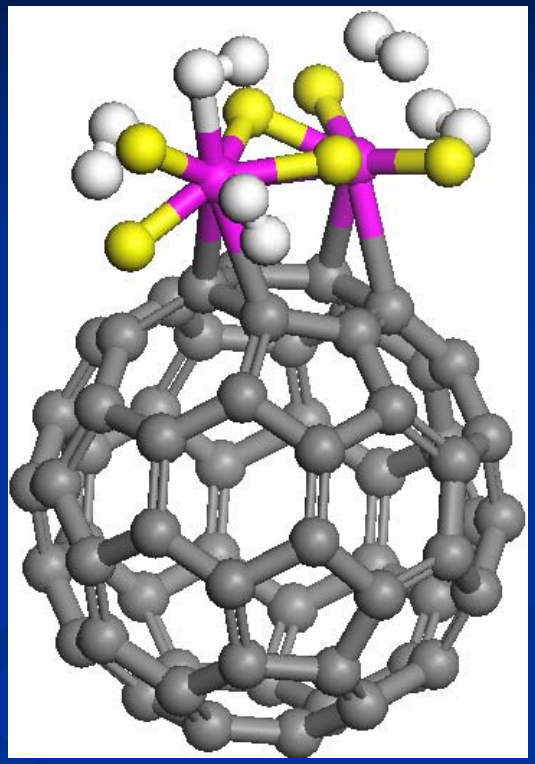


5 H_2 molecules on each Ti



H_2 seen to desorb





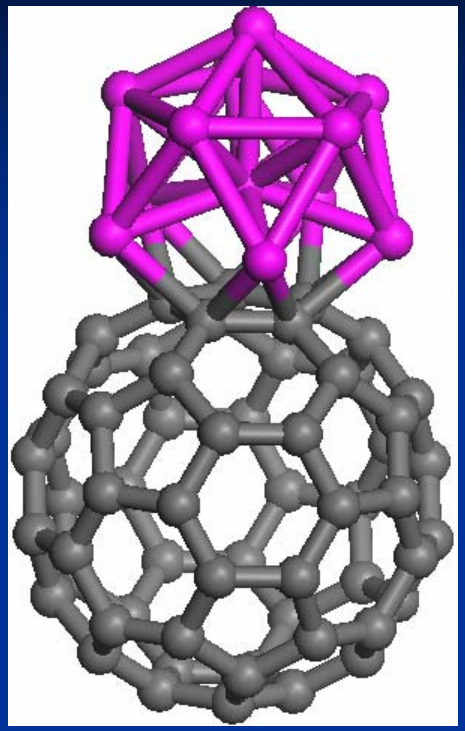
4 H_2 molecules on each Ti atom

E = 0.40 eV / H_2

R(Ti-Ti) = 2.855

R(Ti-C) =2.333—2.347

R(Ti-H2) =1.94

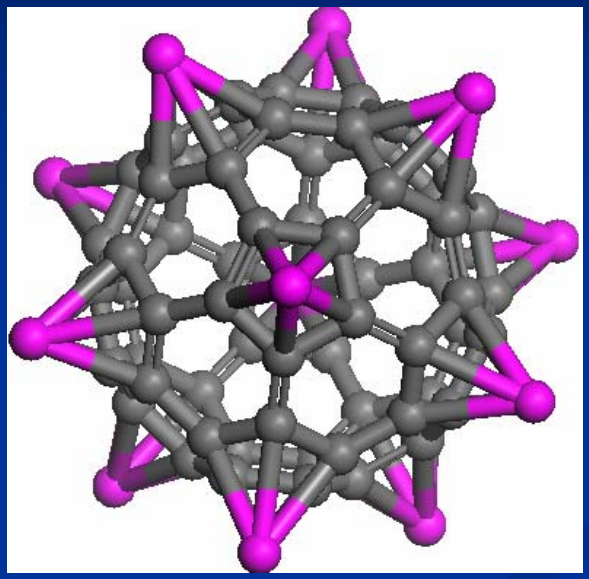


NM

E=0.0eV

M=0.0

C1

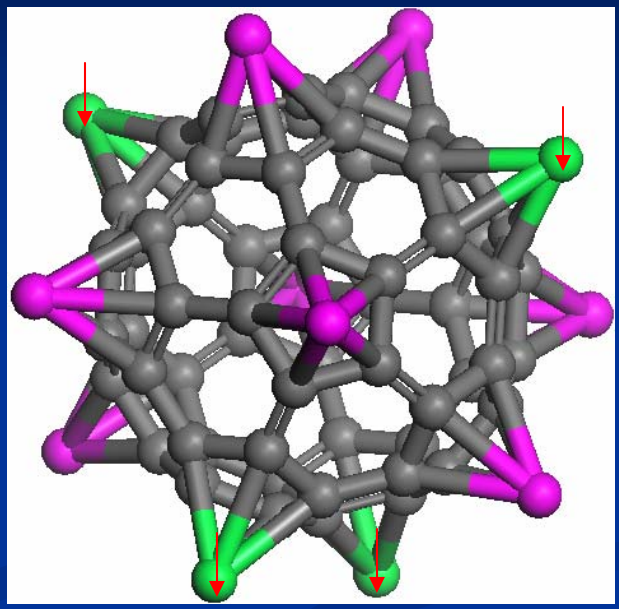


FM

E=+24.8eV

M=36.0

Ih



Ferri

E=+24.52eV

M=12.0

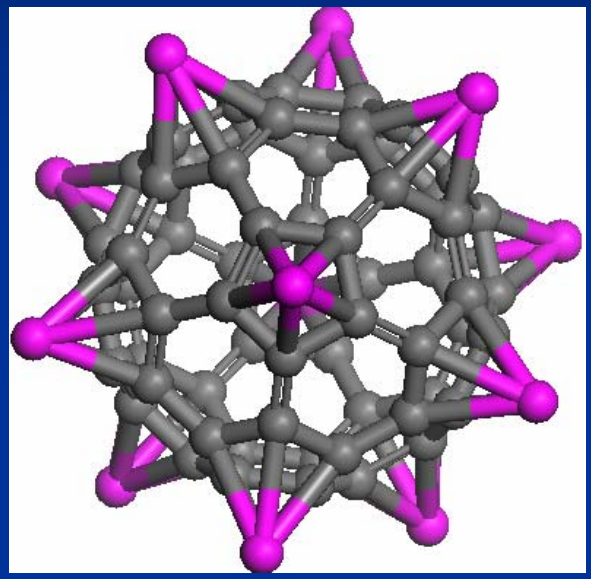
C2v

Summary

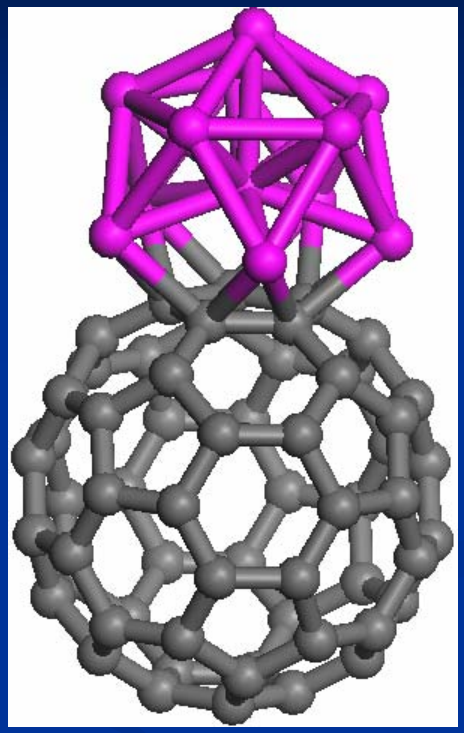
- Hexagonal site is the most stable site for Ti atom.
- Ti atoms tend to form clusters on C_{60} surface.
- For isolated Ti atom on hexagonal site, hydrogen is absorbed in molecular form.
- Clustering of Ti atoms make some hydrogen molecules dissociate, resulting in hydrogen bonded to Ti in atomic form more strongly. This would affect the hydrogen release and storage efficiency.

Li Coated C_{60} Fullerene

- Q. Sun, P. Jena, Q. Wang, and M. Marquez, "First Principles Study of Hydrogen Storage of $Li_{12}C_{60}$," J. Am. Chem. Soc, 128, 9741-9745, (2006)



E=0.0eV

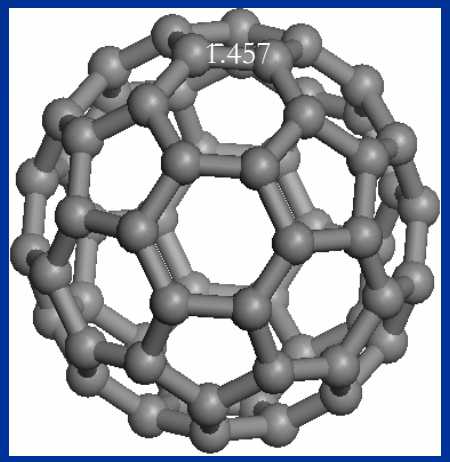


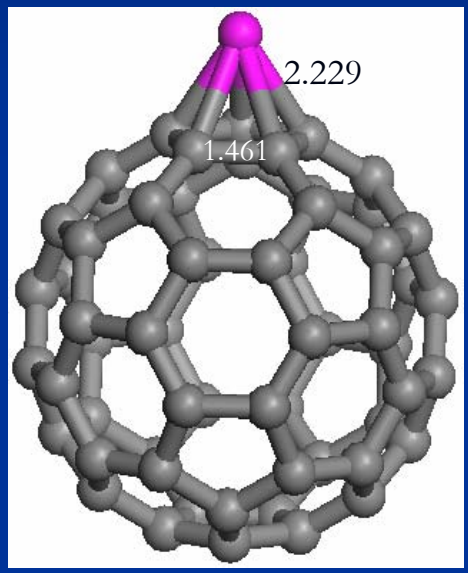
E= + 2.20eV

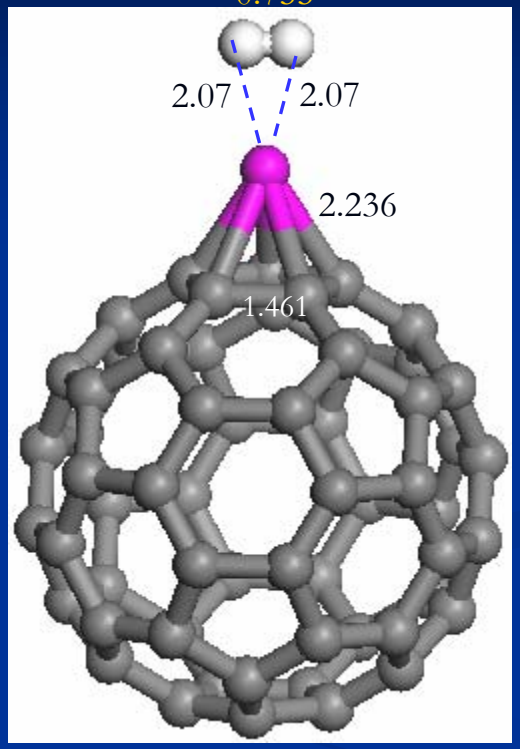
0.755

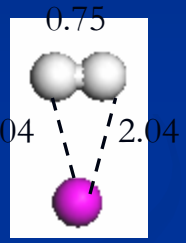
E=0.18 eV

E=0.25 eV







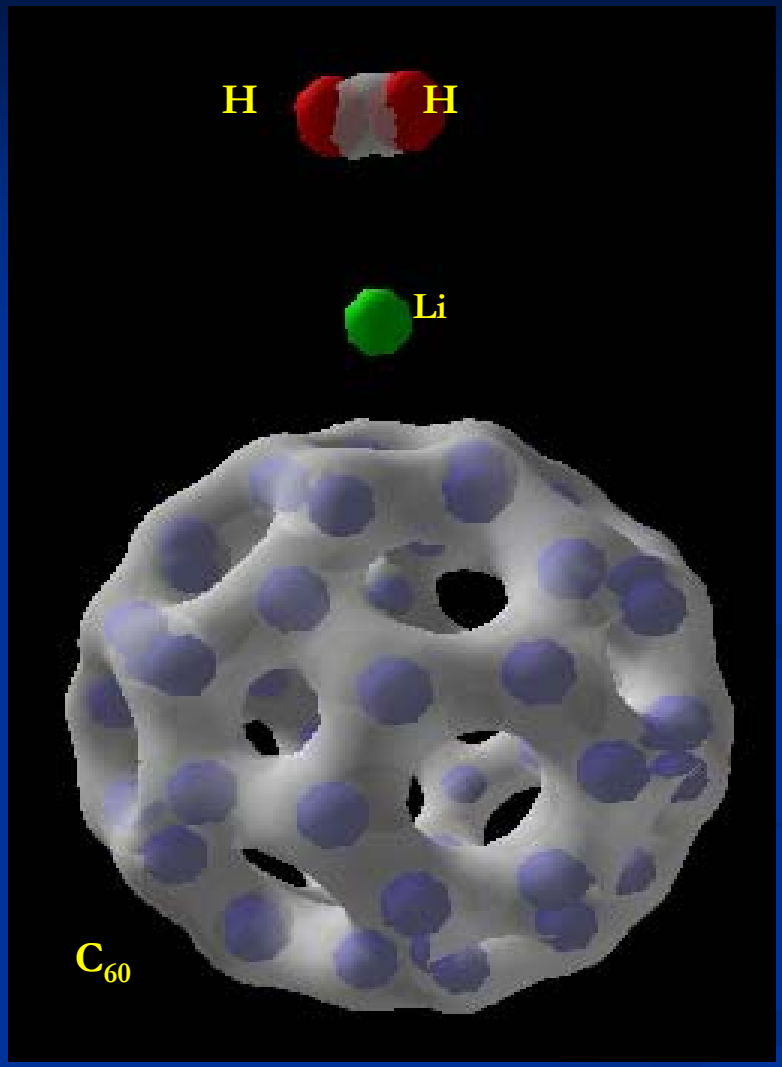


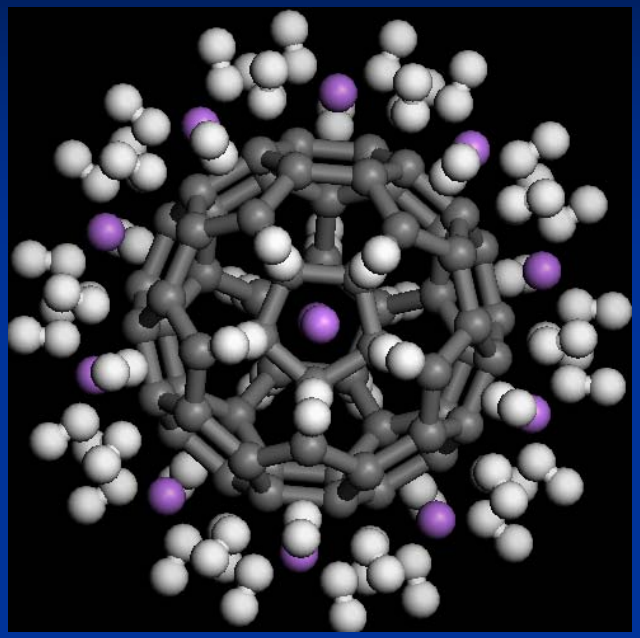
Li^+-H_2

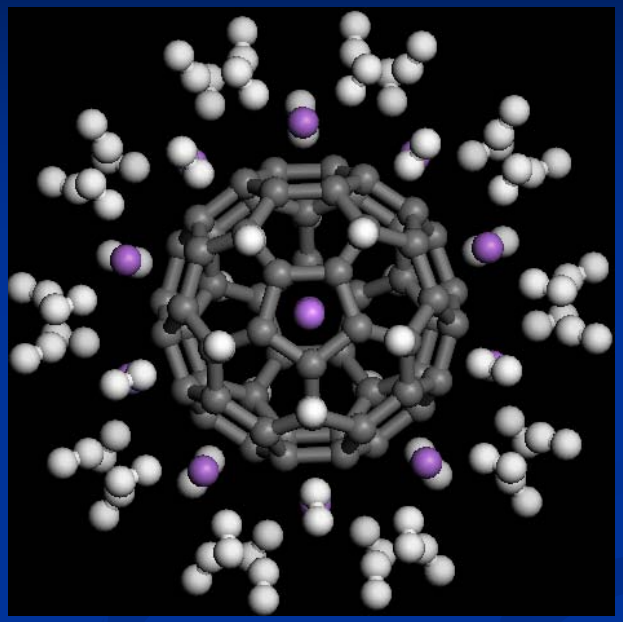
C_{60}

C_{60}-Li

C_{60}-Li-H_2


H
H
Li
C_{60}





Interaction energy: 4.50eV

Weight percent: 13%

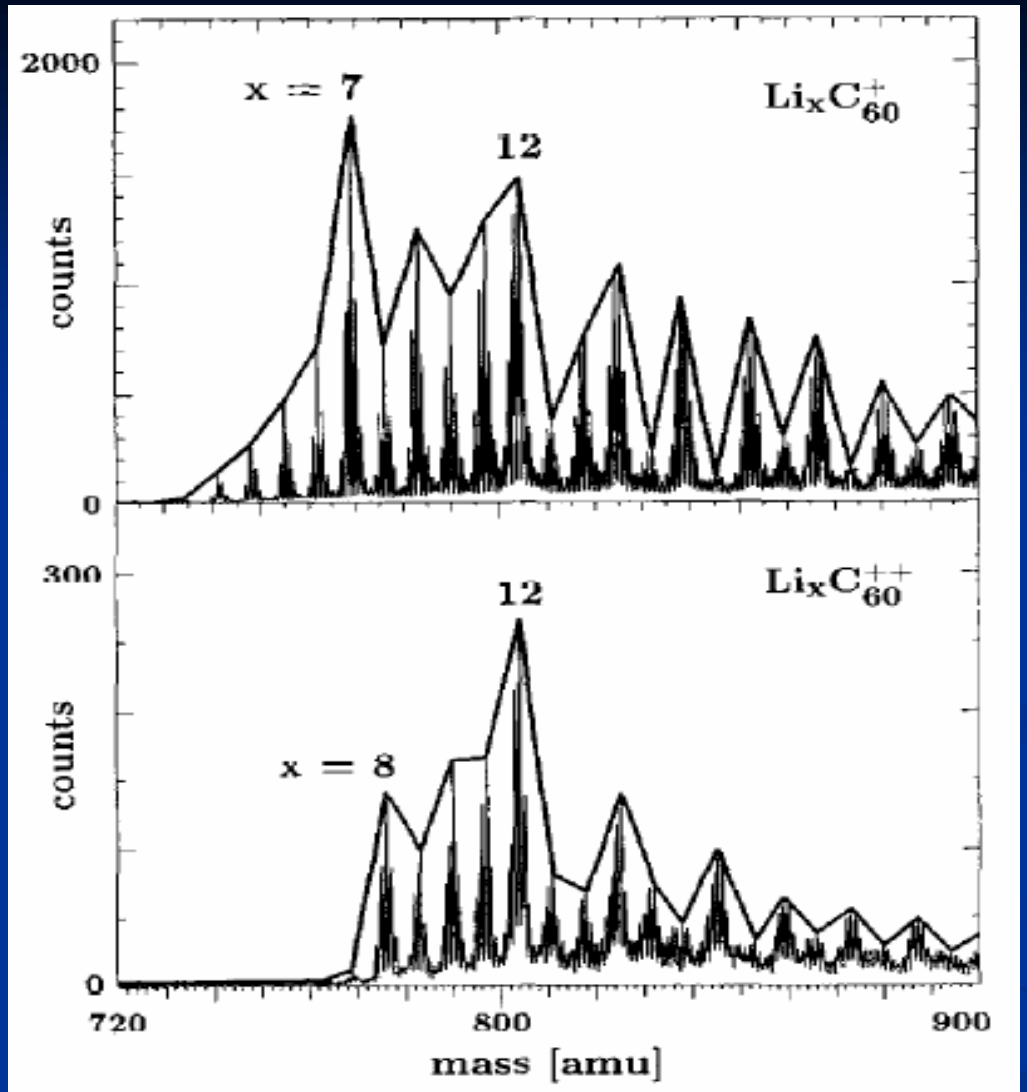
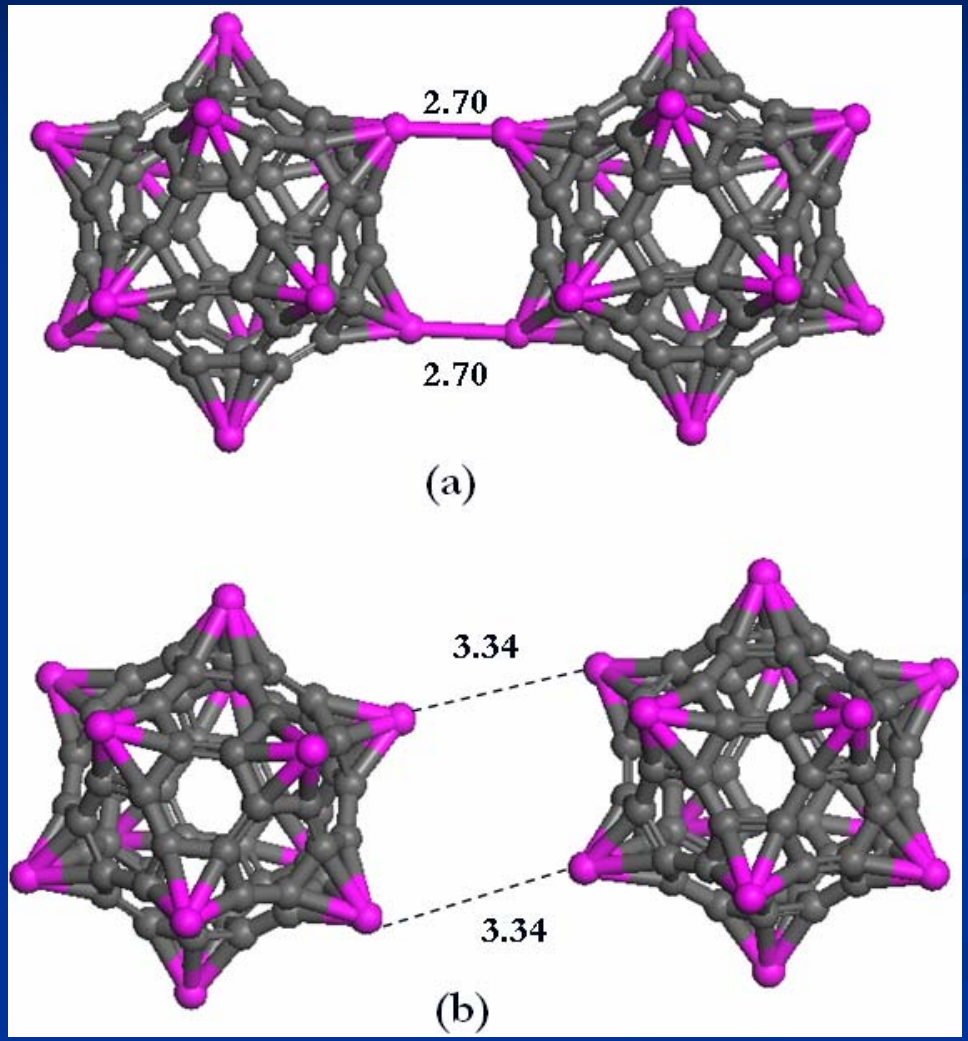


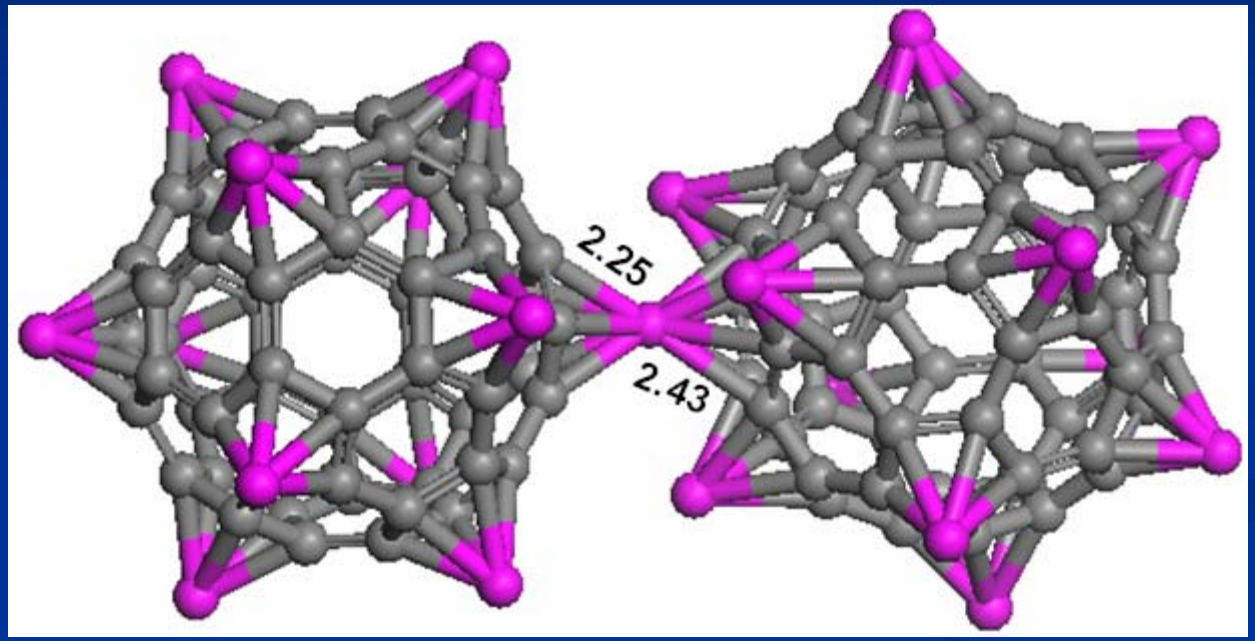
Fig. 9. Mass spectra of singly (top) and doubly (bottom) ionized $C_{60}Li_x$ clusters: note the prominent features at $x = 7$ for singly ionized and $x = 8$ for doubly ionized clusters and at $x = 12$ in both spectra.

Interaction between $Li_{12}C_{60}$ clusters-I



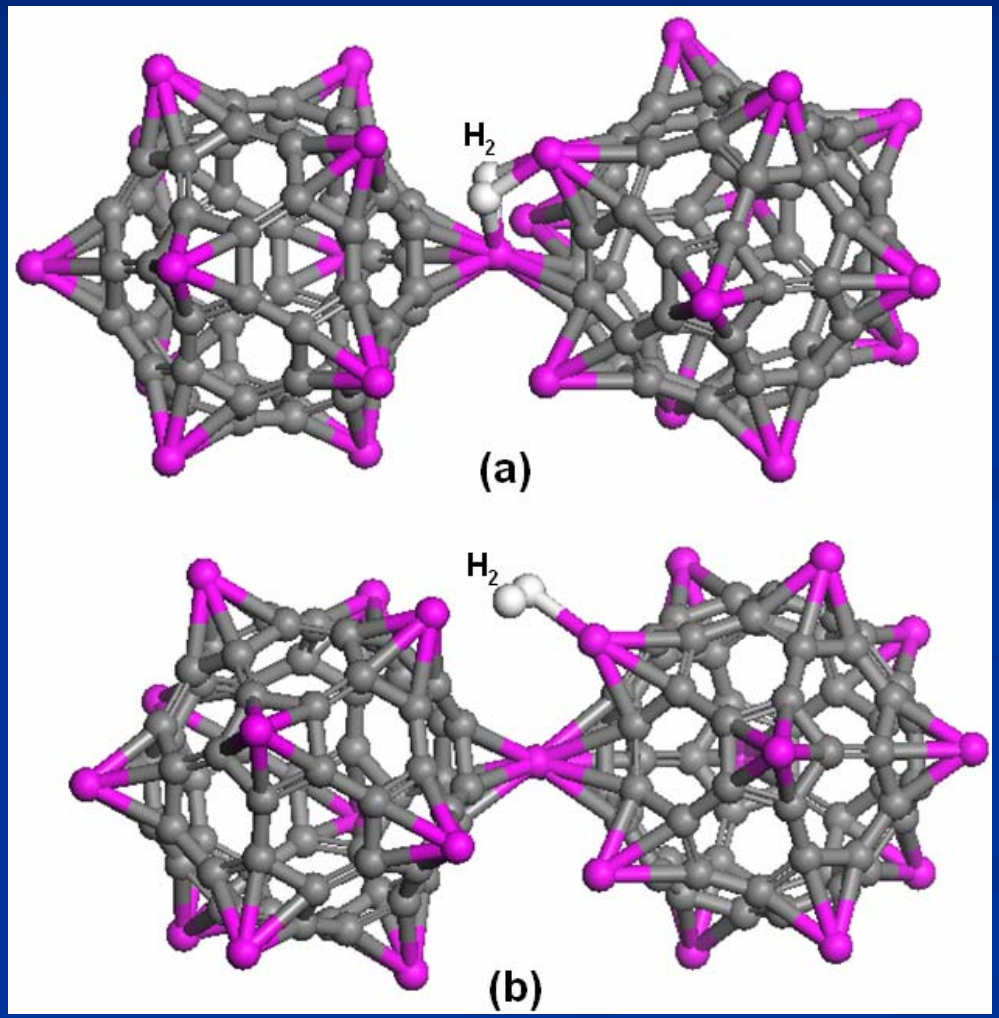
E=0.4 eV

Interaction between $Li_{12}C_{60}$ clusters-II



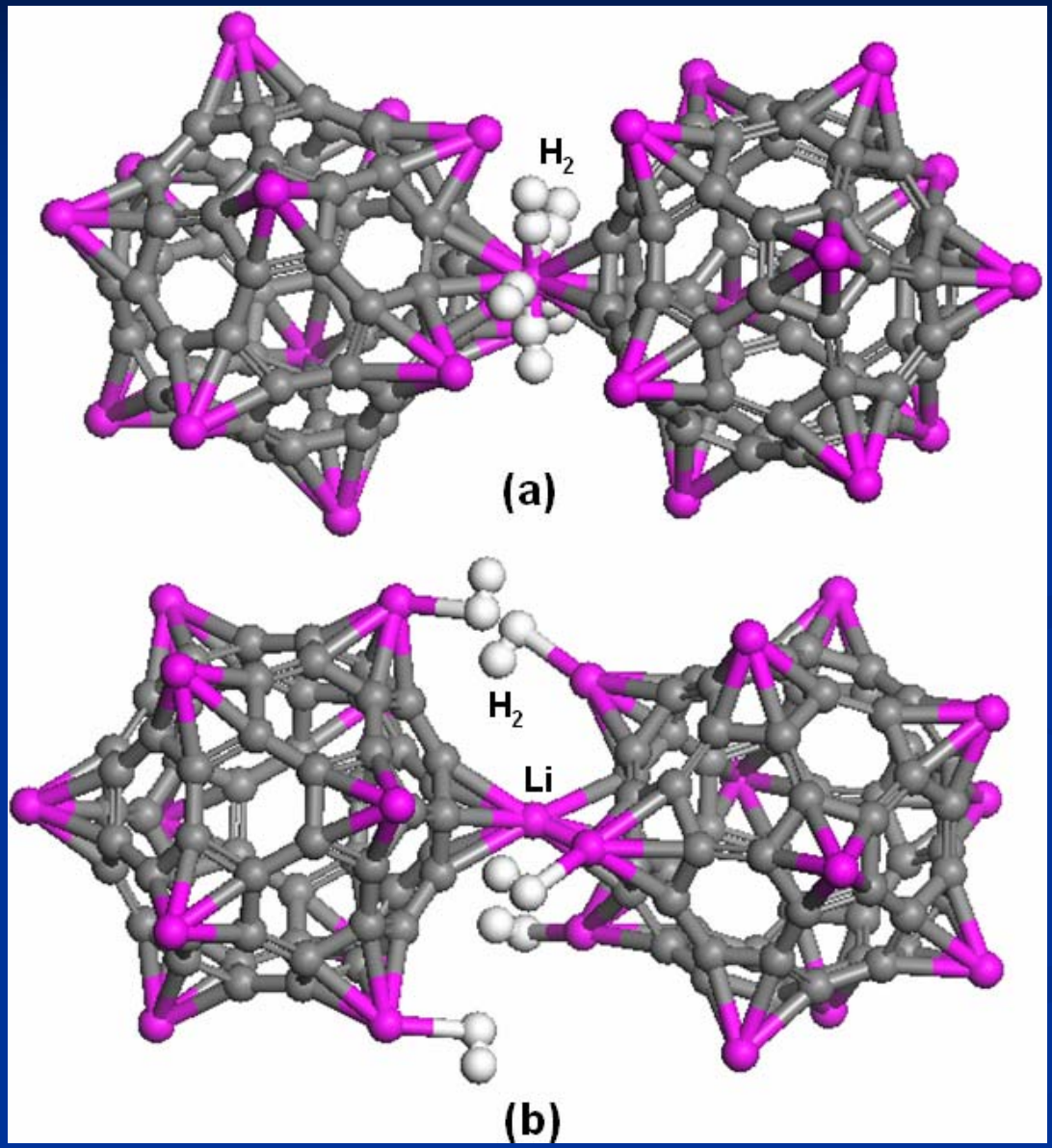
E=1.18 eV

Interaction of H_2 with $Li_{12}C_{60}$ dimer



E_{H2}= 0.18 eV

Interaction of H_2 with $Li_{12}C_{60}$ dimer



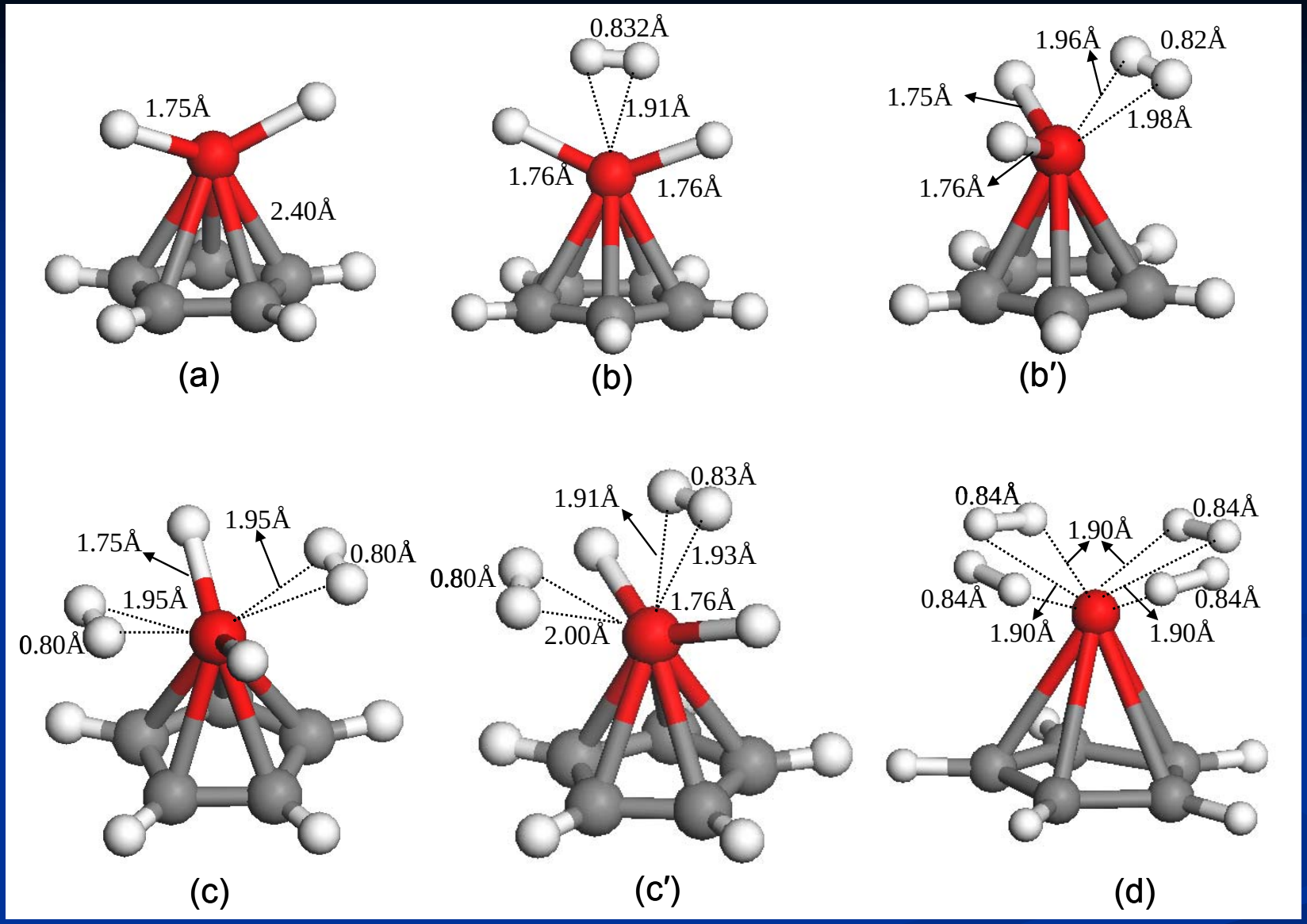
E= 0.18 eV/H_2

Summary

- Li atoms do not cluster on C_{60} fullerene surface
- Li atoms bind strongly to the fullerene
- Hydrogen atoms bind molecularly
- Binding energy of H_2 is small, but significant
- High gravimetric and volumetric density
- $Li_{12}C_{60}$ has already been synthesized in the lab.
- Interaction between $Li_{12}C_{60}$ dimers do not destroy the cluster geometry

Interaction of H_2 with Ti supported on organic molecules

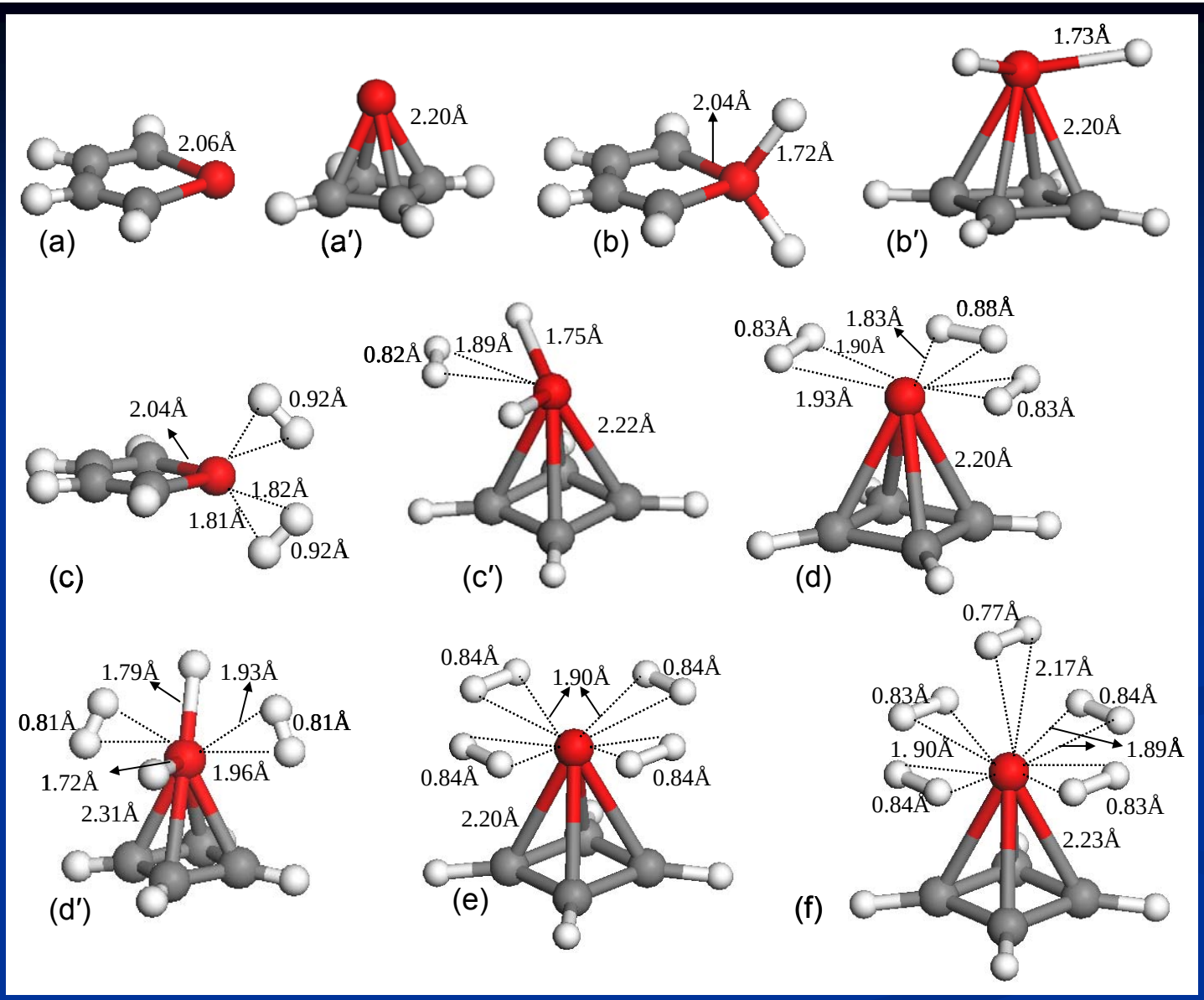
- C_5H_5
- C_4H_4
- C_8H_8



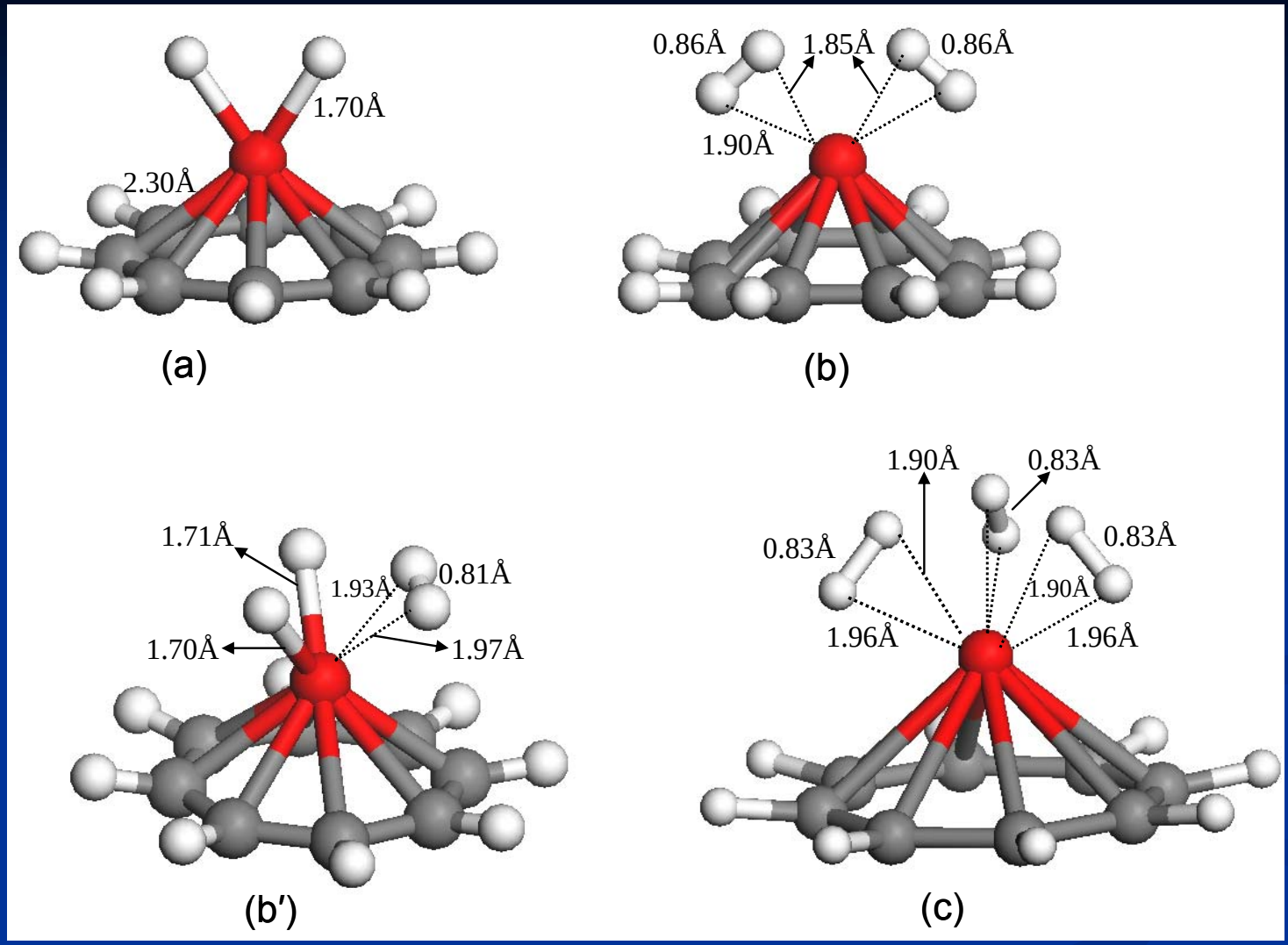
Optimized geometries of Ti C_5H_5 $(H_2)_n$, (n=1-4) along with important bond lengths (Å). The energy difference (ΔE) between (b) and (b') is 0.12 eV; (c) and (c') is 0.02 eV with (b) and (c) being lower in energy than (b') and (c'), respectively.

Hydrogen Storage and the 18 electron rule

- Ti $3d^2\ 4s^2$ Total number of electrons = 4
- C_5H_5 Total number of electrons = 5
- $TiC_5H_5(H_2)_4$ Total number of electrons = 17
- TiC_5H_5 cannot accommodate more than 4 H_2 molecules
- TiC_4H_4 can accommodate 5 H_2 molecules
- TiC_8H_8 can accommodate 3 H_2 molecules



Optimized geometries of Ti C_4H_4 $(H_2)_n$ (n=1-5) along with important bond lengths (Å). The energy difference (ΔE) between (a) and (a') is 0.35 eV, (b) and (b') is 0.29 eV, (c) and (c') is 0.07 eV, and (d) and (d') is 0.05 eV with (a), (b), (c), and (d) being lower in energy than (a'), (b'), (c'), and (d'), respectively.



Optimized geometries of Ti C_8H_8 $(H_2)_n$ (n=1-3) along with important bond lengths (Å). The energy difference (ΔE) between (b) and (b') is 0.02 eV with (b) being lower in energy than (b').

Table I. Energy gain ΔE_n (in eV) due to the successive addition of H_2 molecules to $Ti(C_mH_m)$ complexes

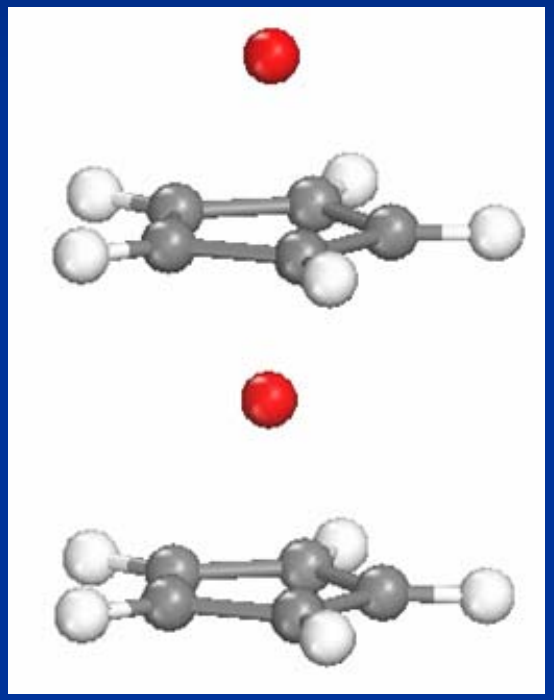
System	*n*	ΔE_n (eV)	
		DMol[a]	Gaussian[b]
$TiC_5H_5(H_2)_n$	1	1.36	1.26
	2	0.51	0.47
	3	0.45	0.54
	4	0.56	0.56
$TiC_4H_4(H_2)_n$	1	1.03	1.10
	2	0.26	0.43
	3	0.47	0.30
	4	0.75	0.77
	5	0.22	0.35
$TiC_8H_8(H_2)_n$	1	1.07	1.12
	2	0.28	0.30
	3	0.36	0.20

a: PW91/DNP *b:* PW91PW91/(SDD: Ti; 6-31G**: C, H)

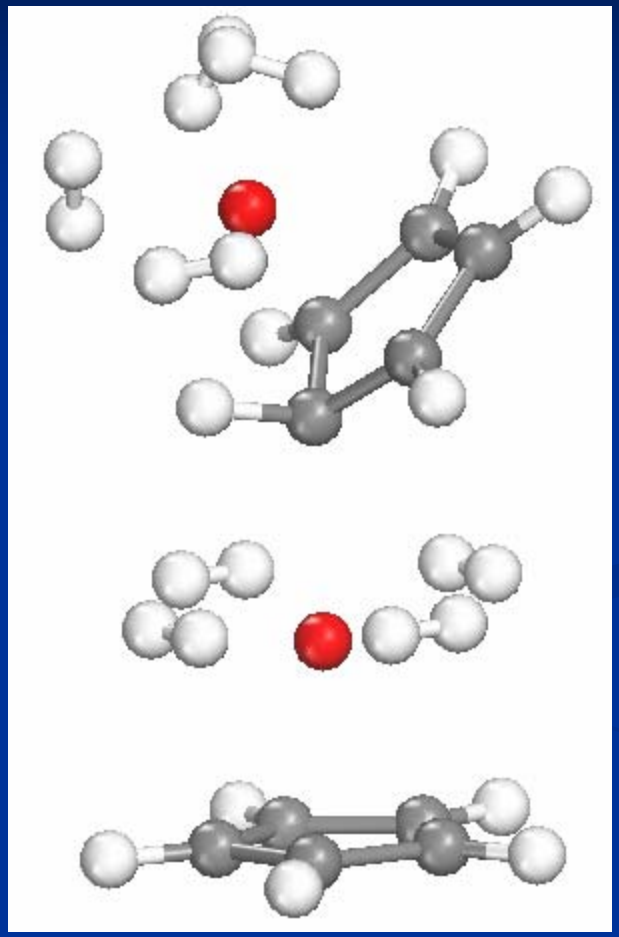
Hydrogen Storage in multi-decker complexes

- $(C_5H_5Ti)_n$, $(C_5H_5)_{n+1}Ti_n$
- $(C_6H_6Ti)_n$, $(C_6H_6)_{n+1}Ti_n$

Choosing substrates to prevent clustering

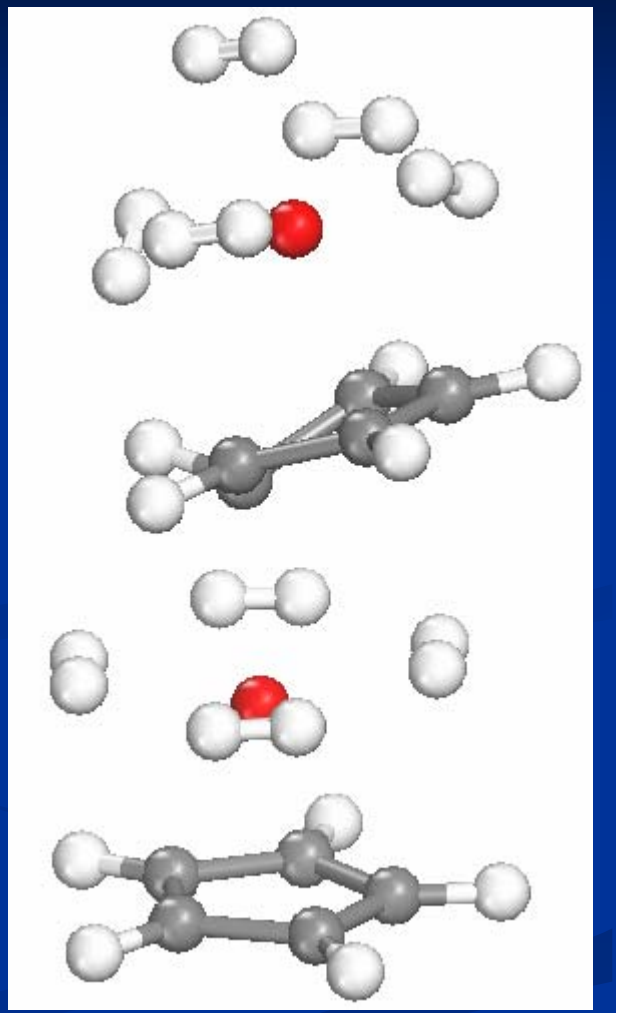


$(C_5H_5Ti)_2$



$[(C_5H_5Ti)_2]\ (H_2)_8$

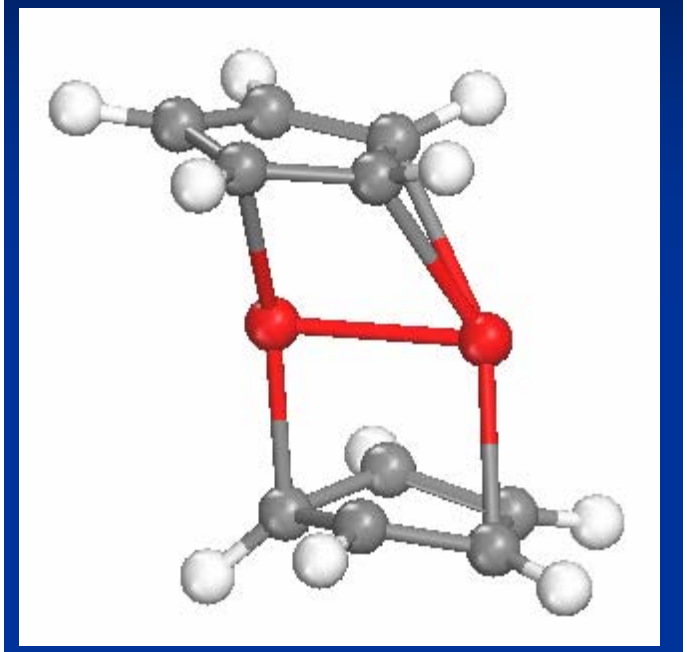
$BE/H_2 = 0.35$ eV



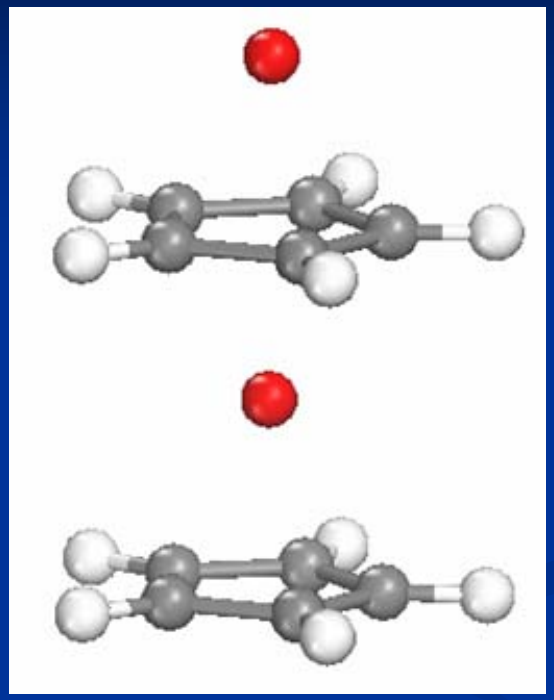
$[(C_5H_5Ti)_2]\ (H_2)_9$

$BE/H_2 = 0.30$ eV

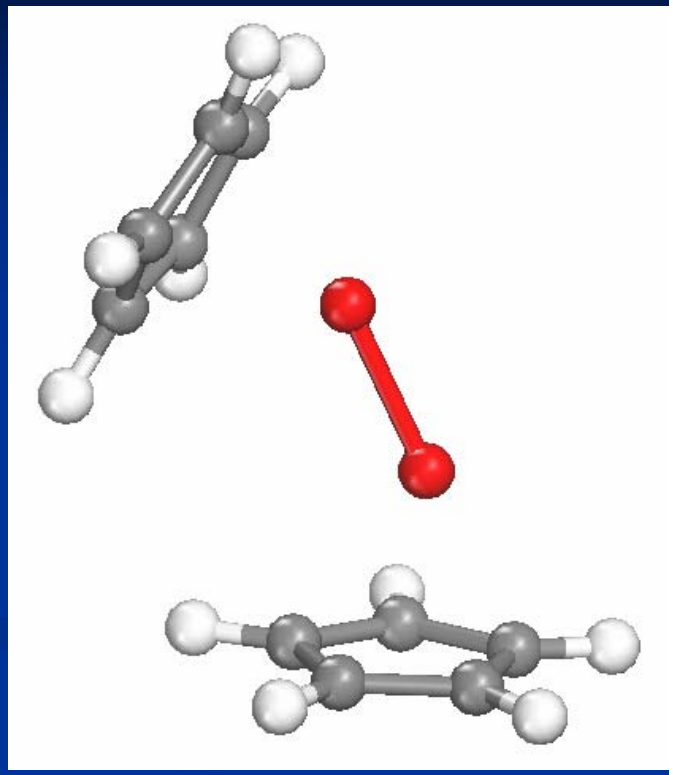
$(C_5H_5Ti)_2$



ΔE = 0.00 eV

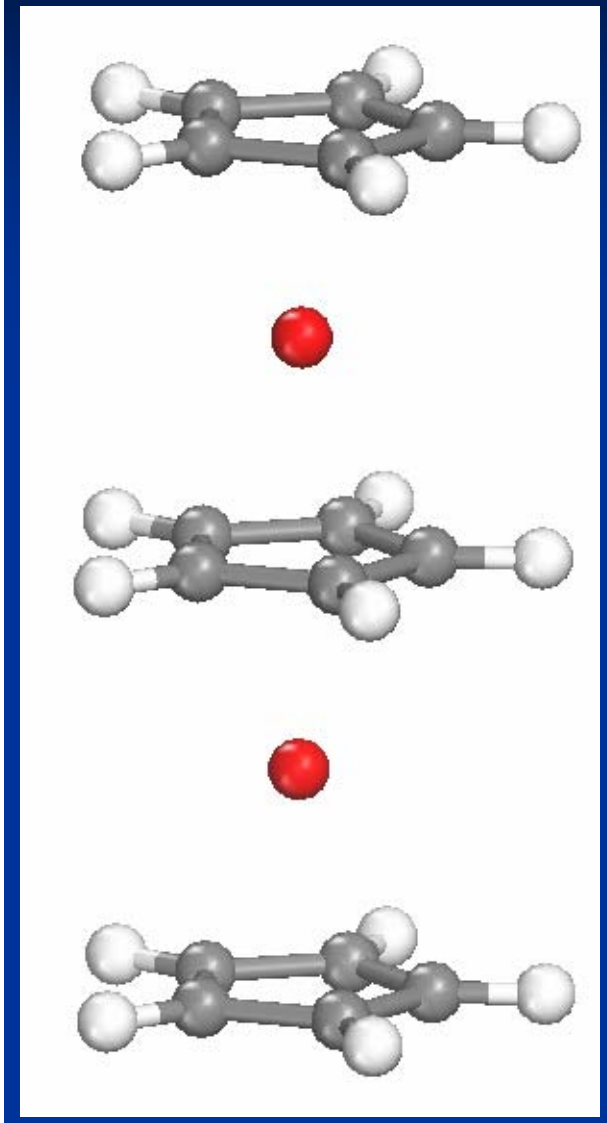


ΔE = 0.50 eV

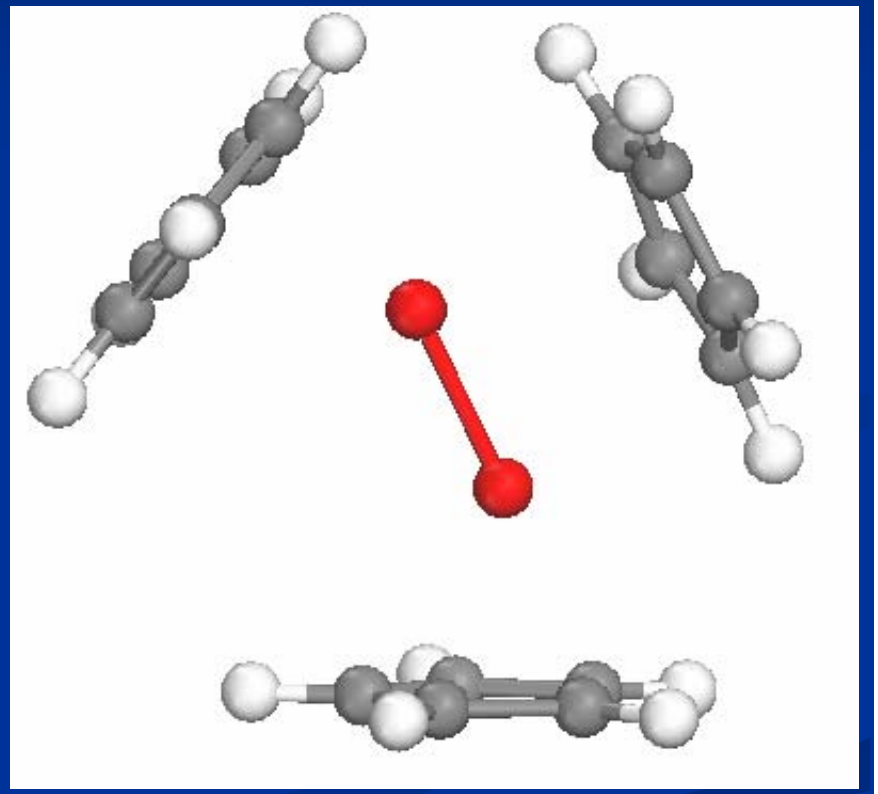


ΔE = 1.02 eV

$(C_5H_5)_3Ti_2$



? ?



Complex Light Metal Hydrides
and
Role of catalysts

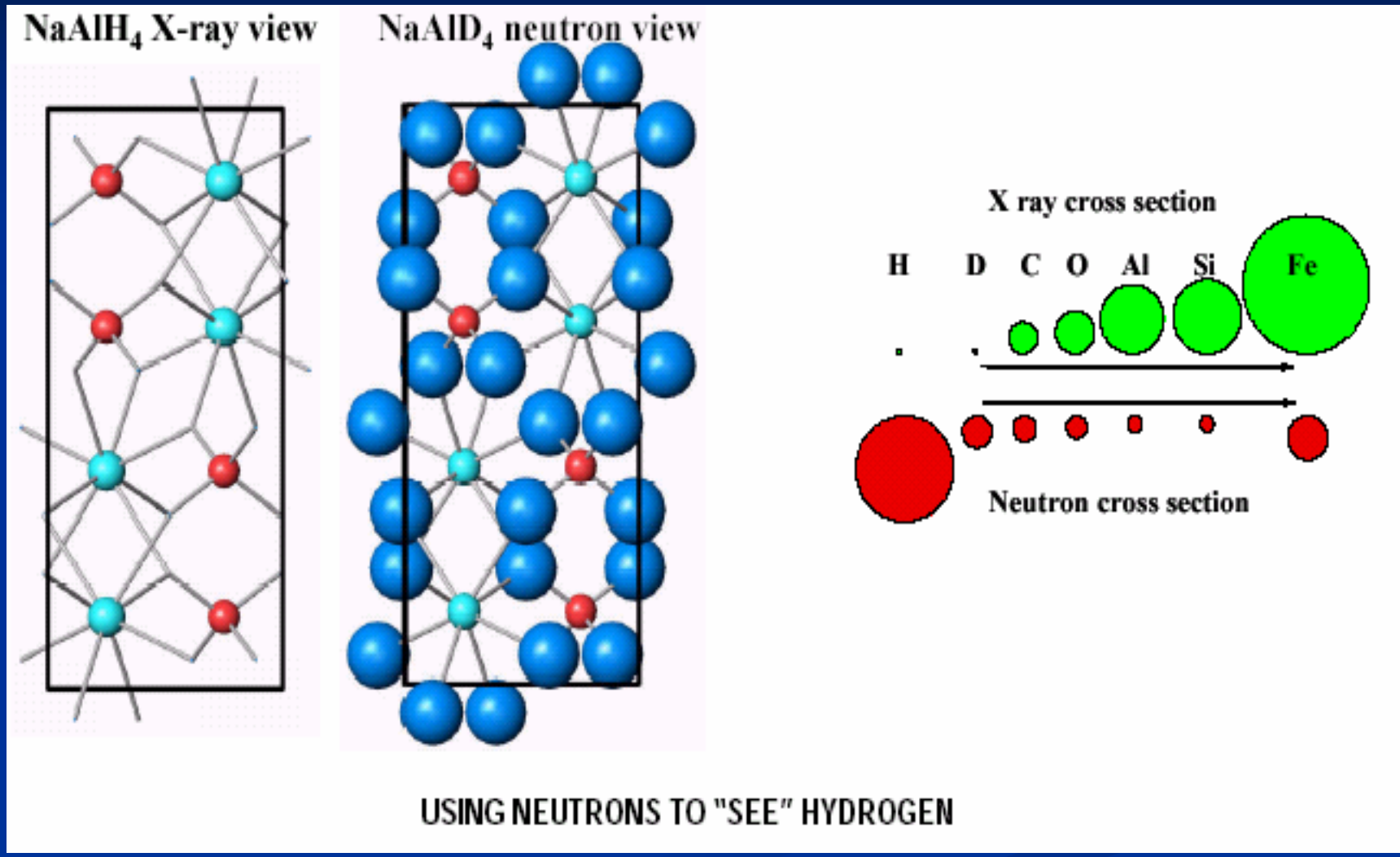
C.M. Araujo, R. Ahuja, J.M.O. Guillen, and P. Jena, Appl. Phys. Letts. **86**, 251913 (2005); C. M. Araujo, S. Li, R. Ahuja, and P. Jena, Phys. Rev. B (in press)

Table 3 Hydrogen Storage Capacities of Hydrides

Hydride	Hydrogen (wt%)[a]
$NaAlH_4$	7.5
$LiAlH_4$	10.6
$Mg(AlH_4)_2$	9.3
$NaBH_4$	10.7
$LiBH_4$	18.5
$Mg(BH_4)_2$	14.9

Sodium Alanates

Structure of Alanates



For more information, see website http://www.sc.doe.gov/bes/hydrogen.pdf

Sodium Alanate – $NaAlH_4$

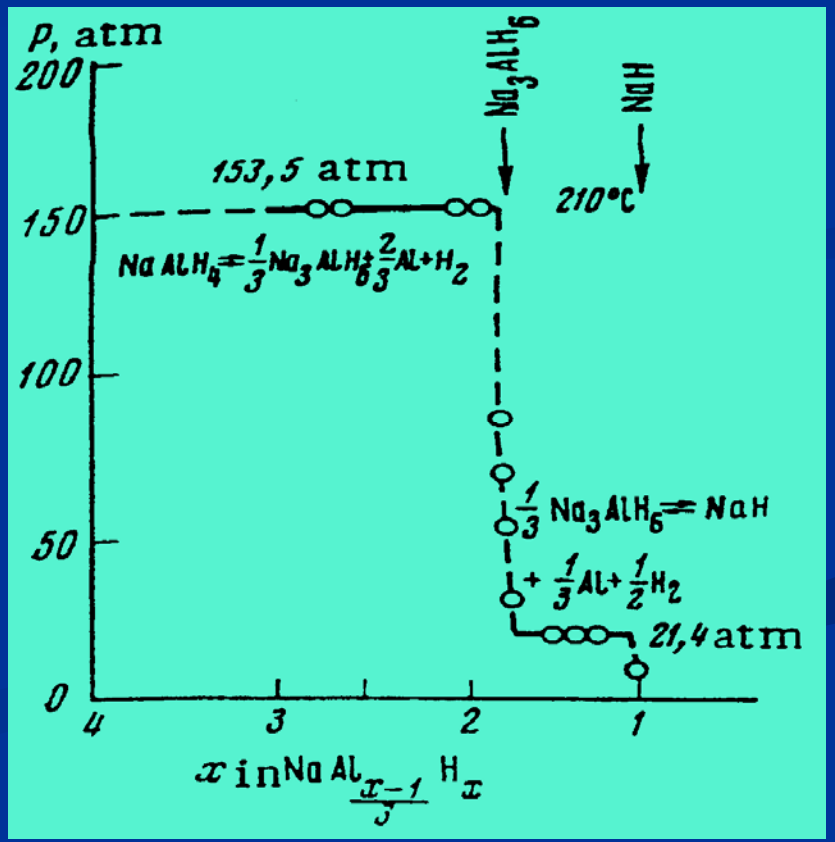
- Discovered: (Finholt & Schlesinger 1955)
- Direct Synthesis: THF, 140°C, 150 bar H_2 (Ashby 1958, Clasen 1961)
- Principal Use: Chemical Reducing Agent
- Sensitive to air and water exposure reacting strongly with O_2 and OH

- $NaAlH_4$ melts at 182°C
- PCT Desorption Measurements
- 2-step Decomposition

$$NaAlH_4 \leftrightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2$$

$$Na_3AlH_6 \leftrightarrow 3NaH + Al + \frac{3}{2}H_2$$

Dymova, T. N., Eliseeva, N. G., Bakum, S. I., And Dergachev, Y. M., Doklady Akademii Nauk. SSSR, 215 (6) (1974) 1369



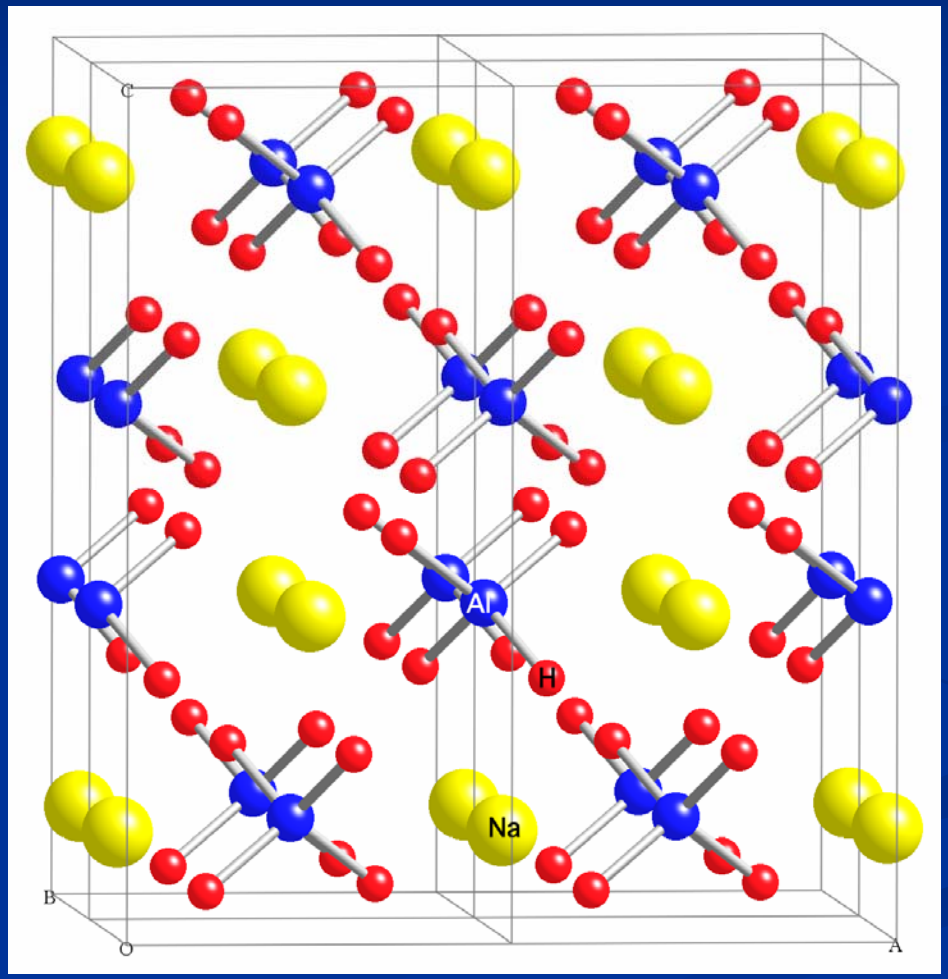
Fundamental Questions

- What is the nature of hydrogen bonding and how is it altered by the presence of $TiCl_3$?
- What happens to $TiCl_3$?
- Where does Ti go? (surface, substitutional, interstitial)
- What does it do and how does it do it?

Hypotheses

- $TiCl_3 + 3Na \rightarrow 3NaCl + Ti$
- Ti can occupy the Na or Al site on the surface, interstitial, or bulk site.
- Ti can combine with Al to form $TiAl_x$.
- Vacancies can be created at the Na and/or Al site.

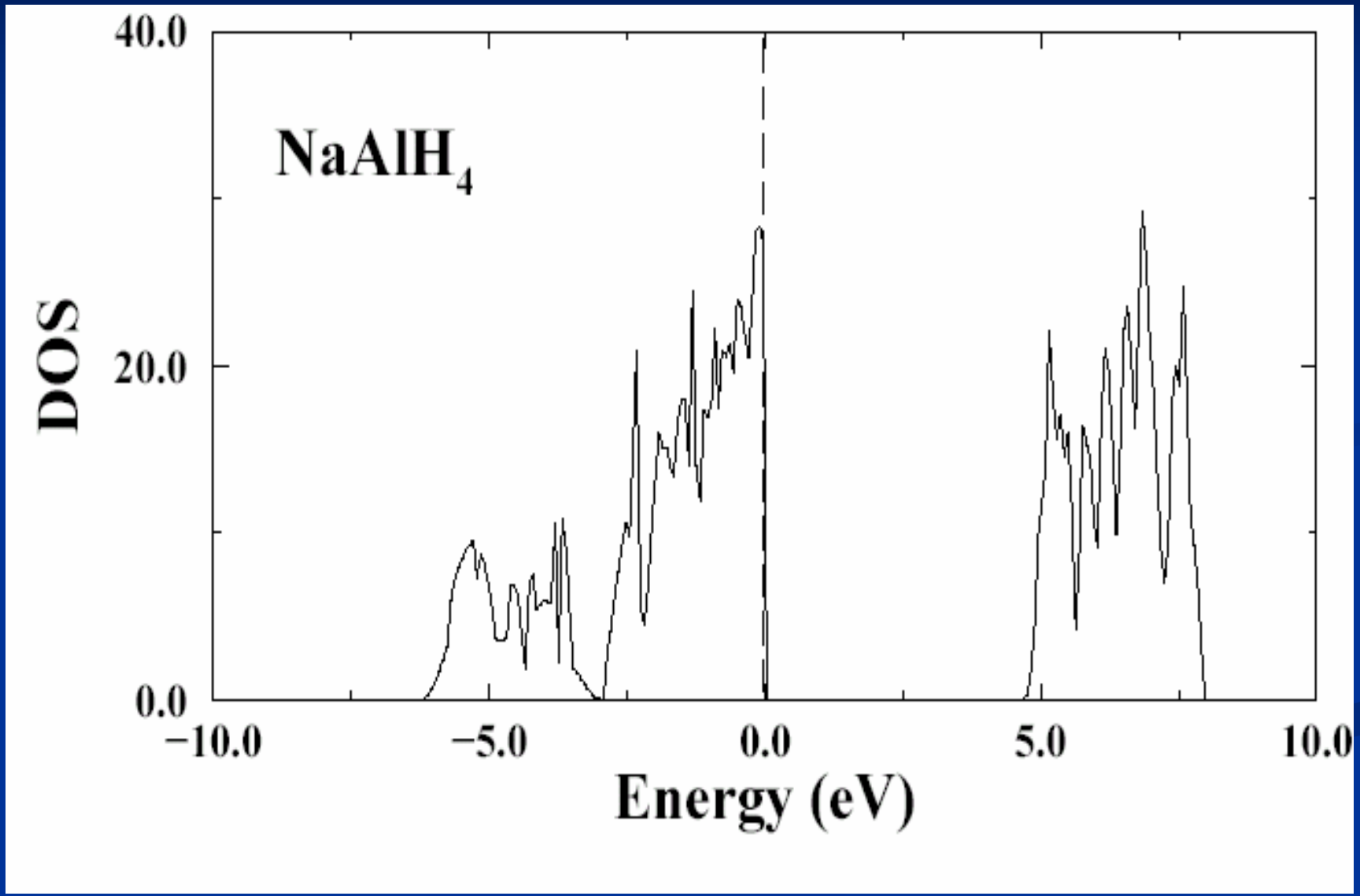
$NaAlH_4$ super cell



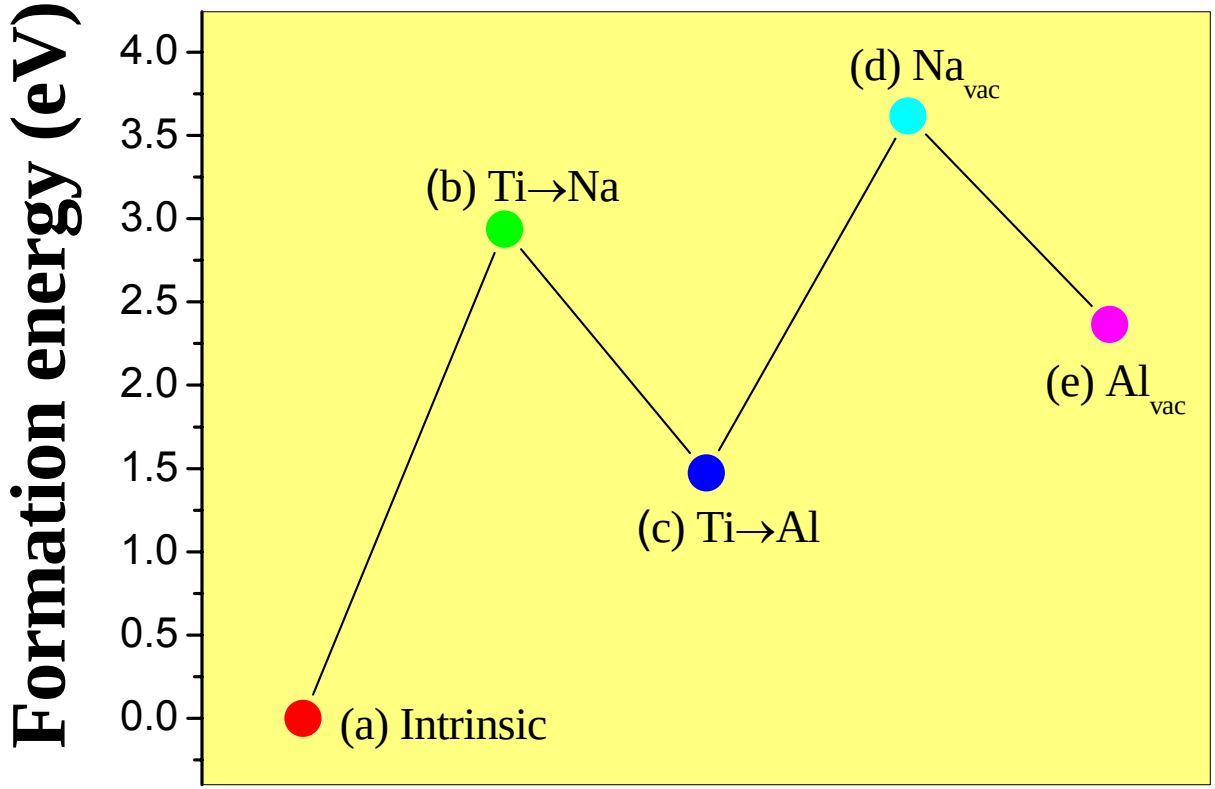
2x2x1

96 atom

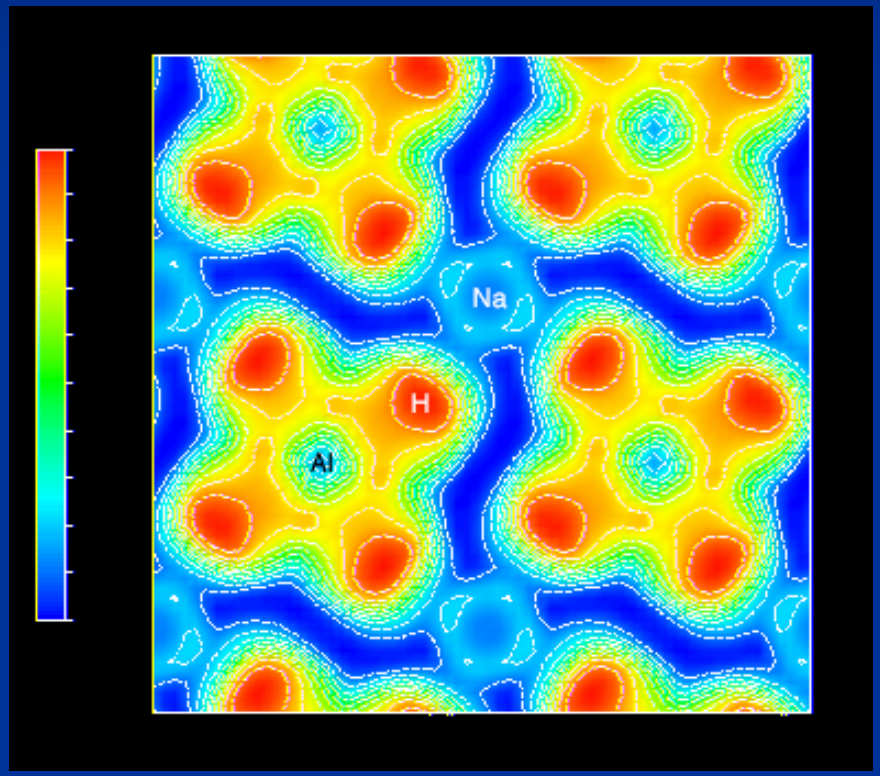
Total electron density of states of $NaAlH_4$ crystal



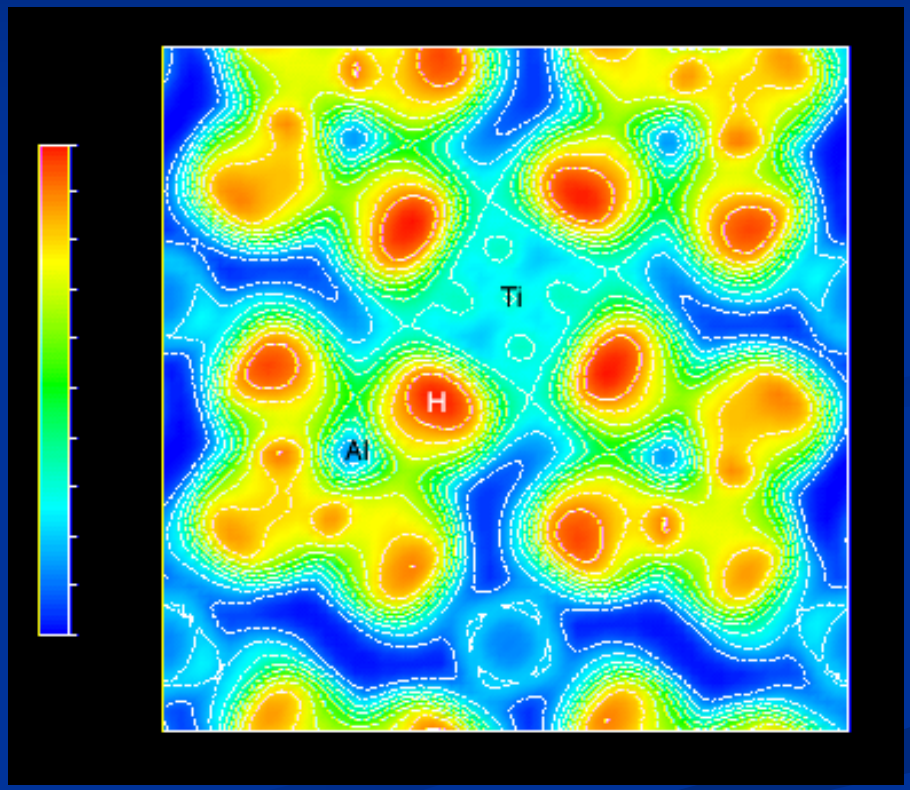
Formation Energy



Ti Substitution



Intrinsic



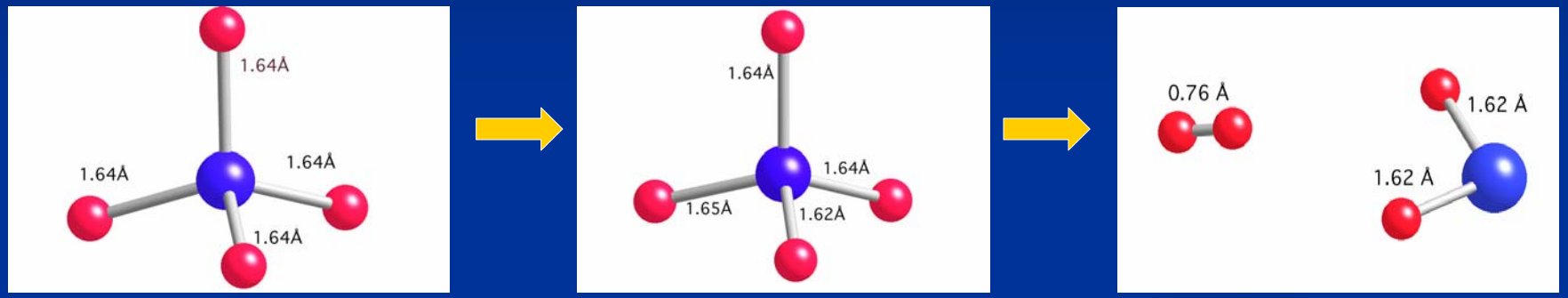
Ti→Na

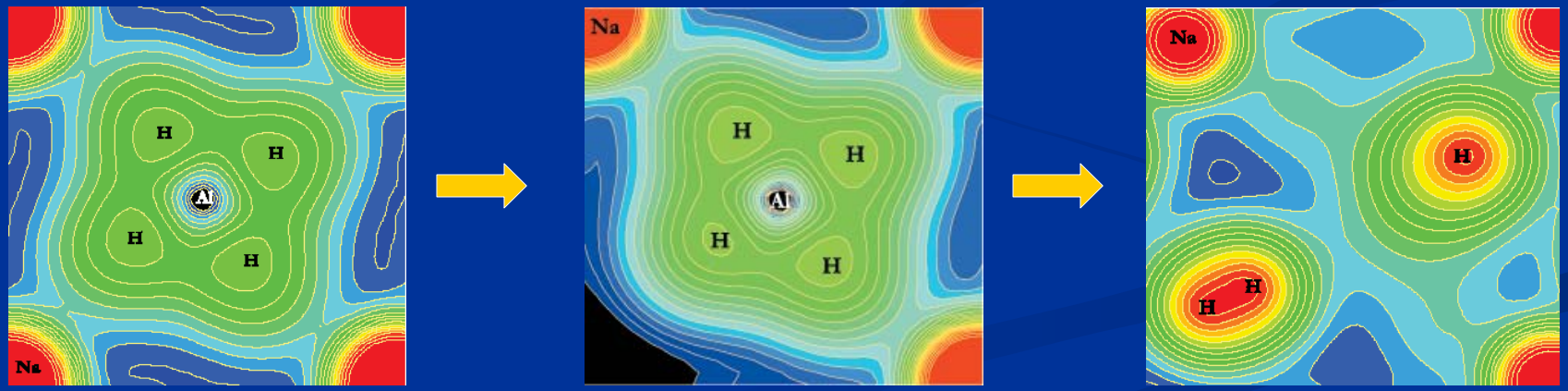
Na vacancy

$(AlH_4)^-$ perfect

Na vacancy – local minimum

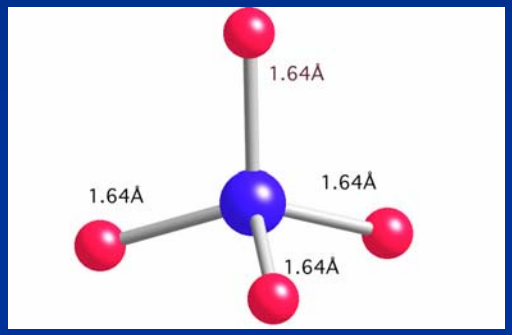
Na vacancy – global minimum



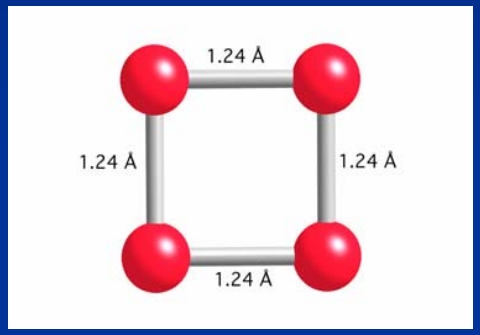


Al vacancy

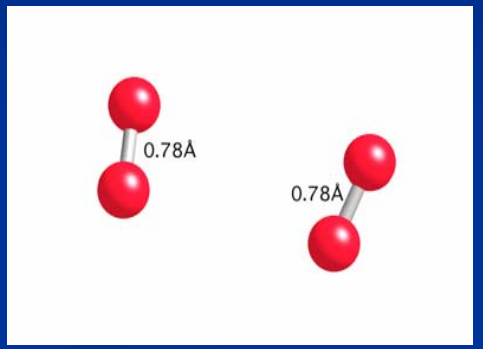
$(AlH_4)^-$ perfect

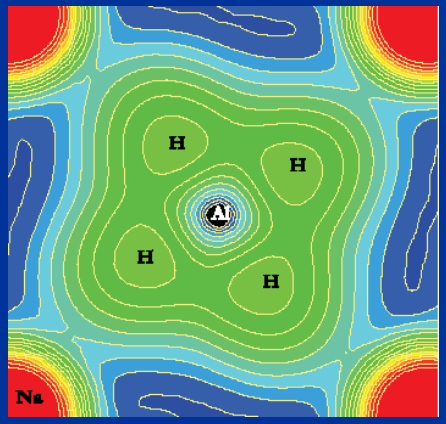


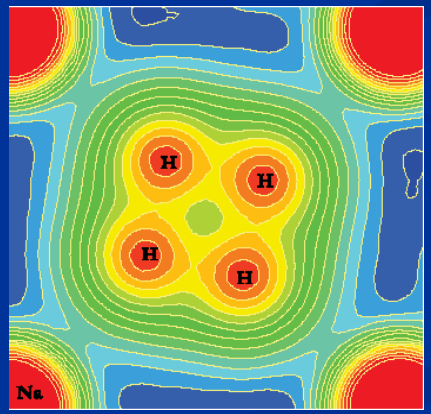
Al vacancy – local minimum

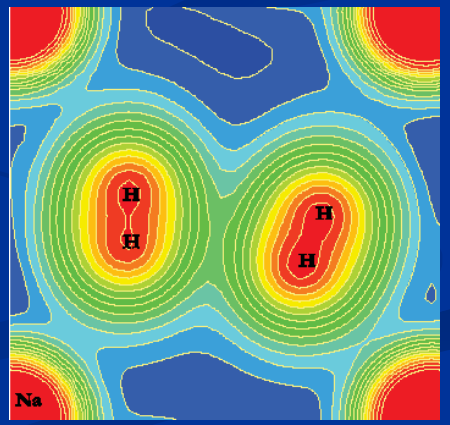


Al vacancy – global minimum

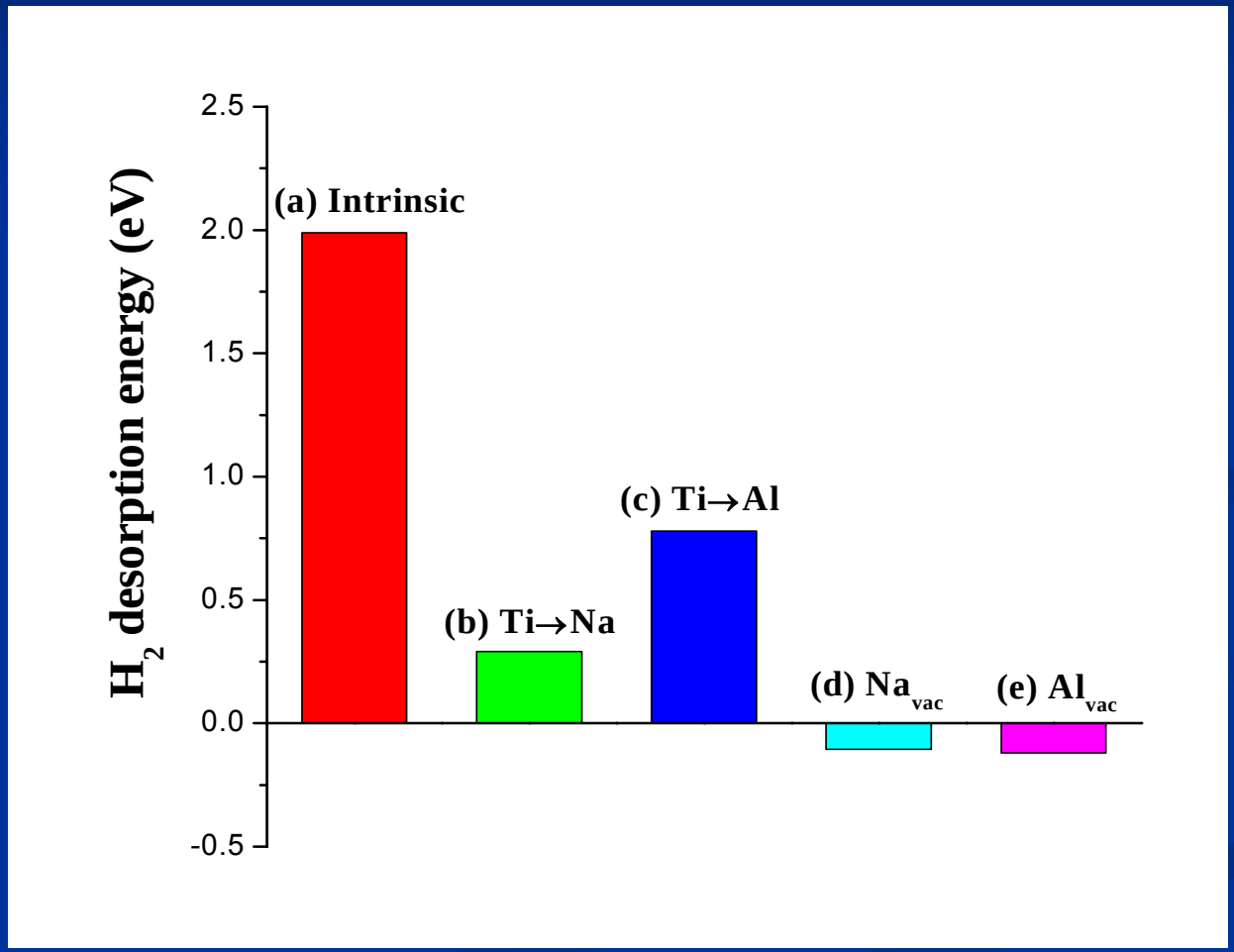








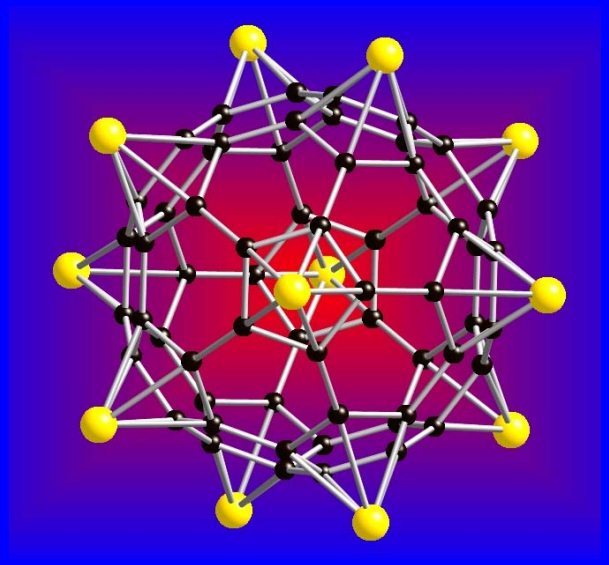
Hydrogen desorption energy



Conclusions

- Boron nitride and carbon nano-cages are not suitable
- Coating these cages with metal atoms may increase the hydrogen uptake
- The presence of Na and Al vacancies are more important than Ti substitution at metal sites: Hydrogen desorption is molecular and exothermic
- The dominant role of Ti in reducing hydrogen desorption temperature may be an indirect one - it leads to vacancy formation which in turn reduces hydrogen desorption energy.


Thank you!



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