Computational Engineering and Science in Industry:

Case Study of Hydrogen Storage for Energy Applications

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Outline

- **The Industrial Landscape**
- **How Do Modeling and Simulation add Value?**
- **Air Products, Energy, and Hydrogen**
- **Materials for Hydrogen Storage**
- **Summary**

The Industrial Landscape

Goal: Make $ by Solving Problems

- **Increasingly Competitive and Technically Challenging World**
  - **Globalization**
  - **Easy problems already solved**
- **Need to Decrease**
  - **Cost**
  - **Risk (of failure and loss)**
- **Need to Increase**
  - **Optimality**
  - **Learning**
  - **Financial Benefit**

- **How Do Modeling and Computing Achieve these Goals?**

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What can Modeling do to add value?

- **Decrease Costs**
  - Replace Experiments with Modeling or Simulation
  - Make Better Use of Existing Experimental Information
  - Generate Insights Which Suggest New or Better Experiments
- **Increase Revenue**
  - Decrease Development Time
  - Increase Scope of Intellectual Property
  - Develop Better Solutions
- **Improve Decision Making**
  - a = probability project makes it to next stage of R&D
  - Increase a for "Good" Projects
  - Decrease a for "Bad" Projects
  - Provide information for systems that do not yet exist

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Why Computing?

- **The disciplines of science and engineering have naturally progressed to include descriptions of reality (*models*) that incorporate significant *complexity*: large numbers of interacting components producing emergent phenomena.**
  (E.g. quantum mechanics of a collection of molecules with all of their electrons, global warming, complex economies)
- **These models are difficult to solve, simulate, and optimize…**
- **… computing is an important tool for dealing with this complexity and harnessing the power of the models**

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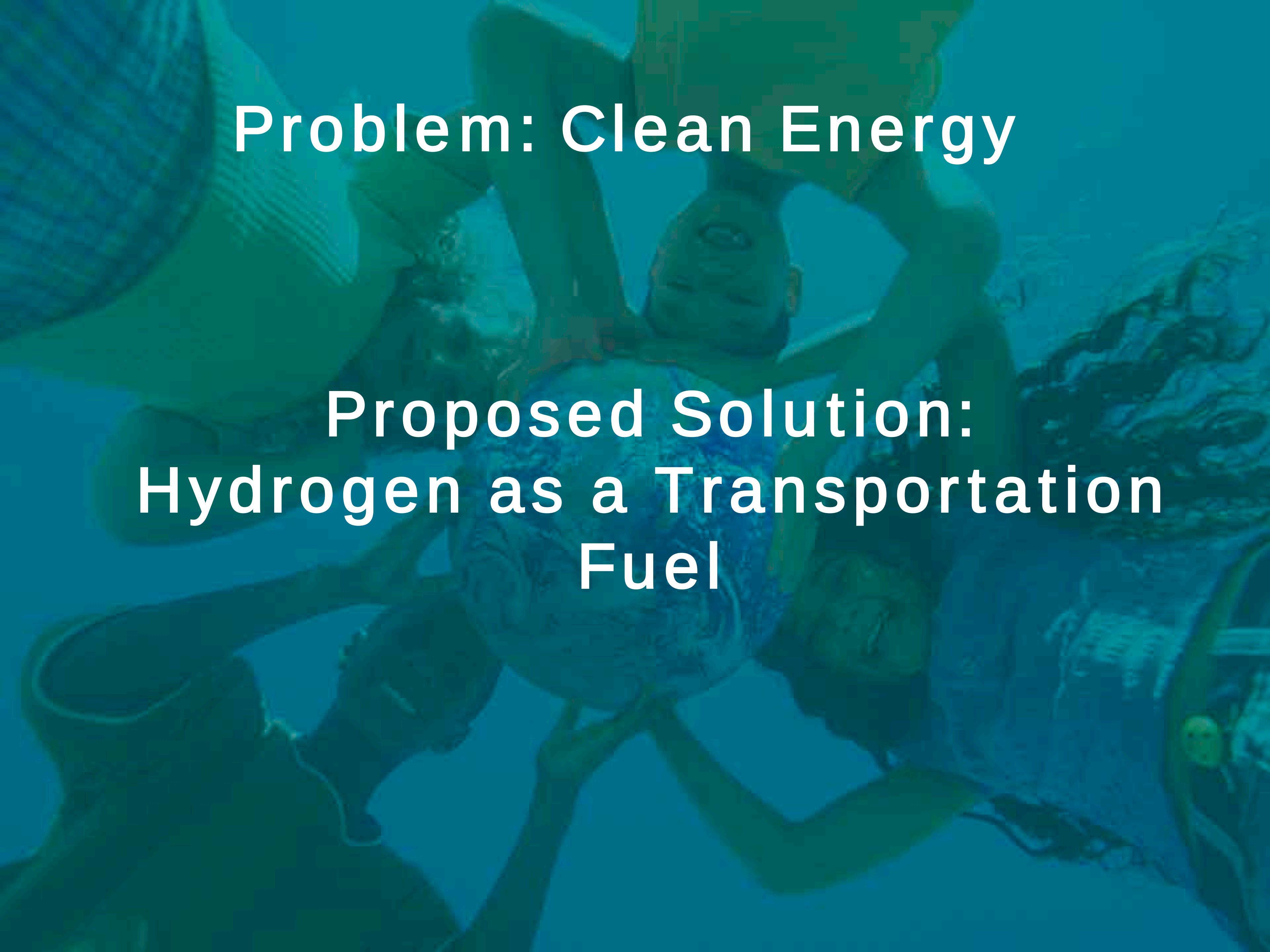
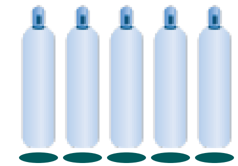


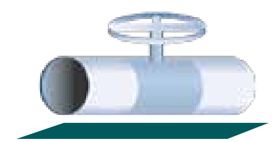
Problem: Clean Energy

Proposed Solution: Hydrogen as a Transportation Fuel

Air Products' Hydrogen Experience

- World leader in industrial hydrogen supply
  - Own, operate, and distribute hydrogen in Americas, Europe, Asia
  - Operate over 60 plants, 7 pipelines, produce >1.75 million tons/year
  - Multiple technologies, SMR is by-far largest in volume
- Demonstration leader in hydrogen fueling infrastructure
  - >90 fueling stations – 16 countries
  - Technology advances include mobile fueling, underground liquid storage, dispensing, onsite generation, storage
  - Global safety leader





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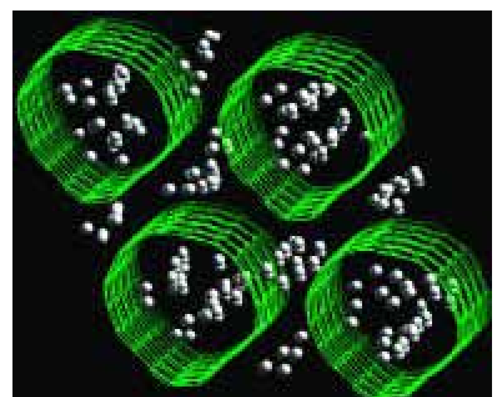
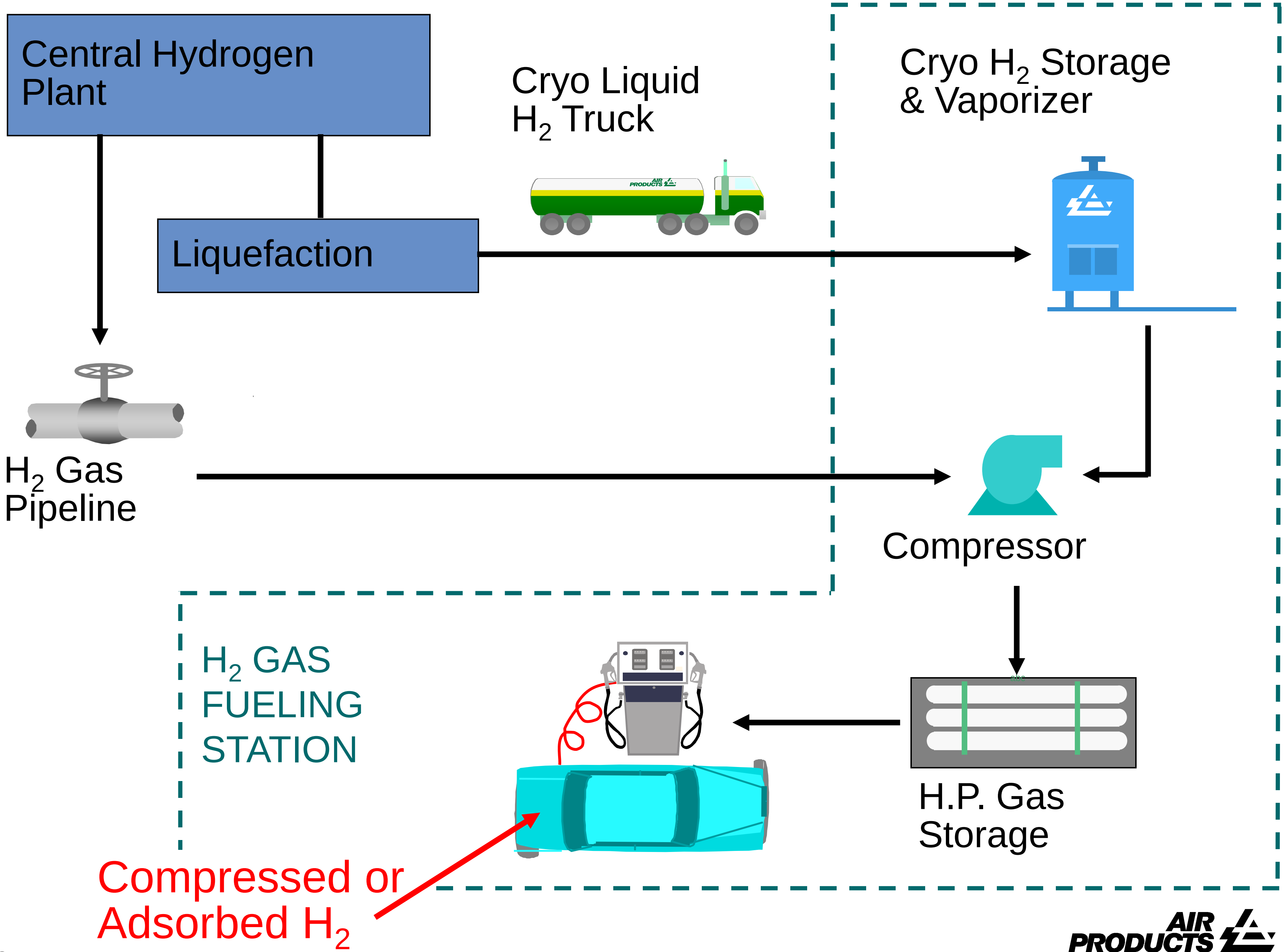
Benning Road H_2 Station Washington, D.C.

Key Hurdle: Transportation and Storage of Hydrogen as a Fuel

- Liquefaction
  - delivered as a cryogenic liquid: (-425°F), 100 psig
- Compression
  - Stored on-board at High Pressure
- Physical Adsorption – H-H bond intact
  - High surface area solids (activated carbons, carbon nanotubes, zeolites)
- Chemisorption – H-H bond broken
  - Metal hydrides (FeTi, $LaNi_5$)
  - Advanced hydrides ($NaAlH_4$)
  - Chemical hydrides ($NaBH_4$)
  - Carbon materials




Central Hydrogen Plant
Liquefaction
Cryo Liquid H_2 Truck
Cryo H_2 Storage & Vaporizer
H_2 Gas Pipeline
Compressor
H.P. Gas Storage
H_2 GAS FUELING STATION
Compressed or Adsorbed H_2
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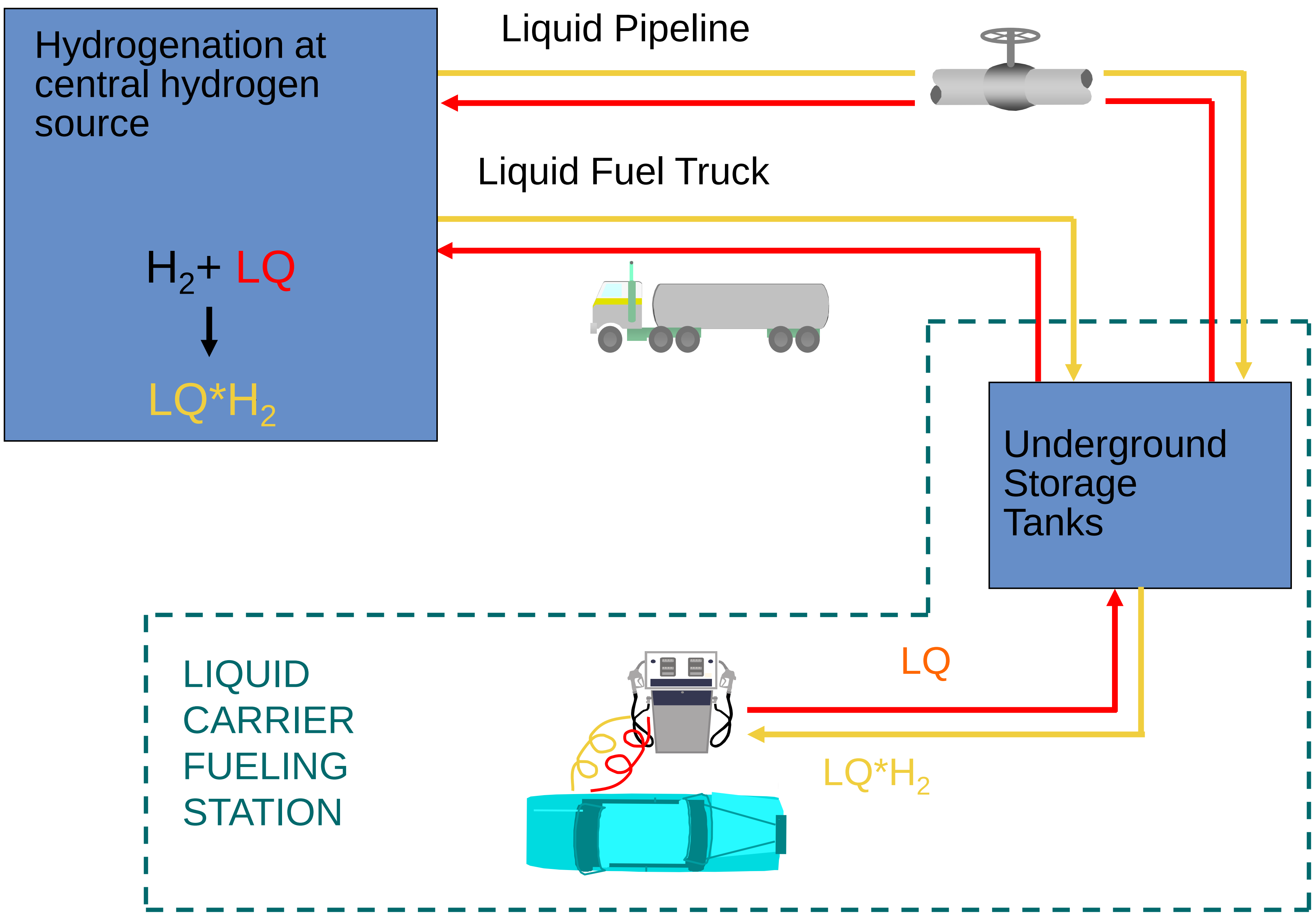

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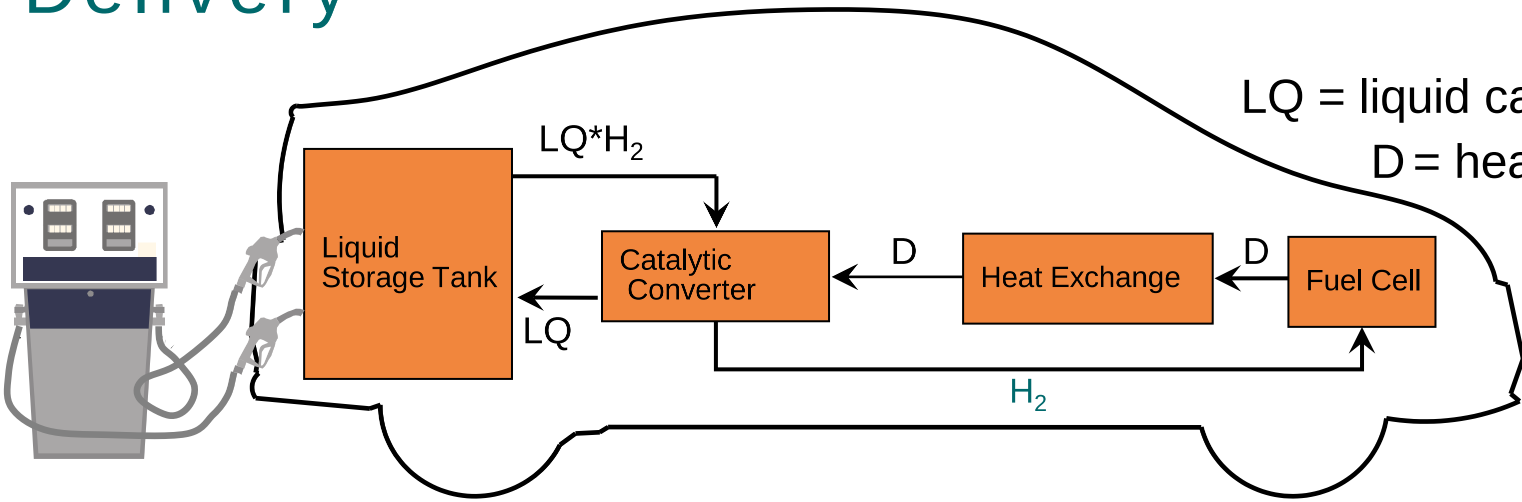
Liquid Storage & Delivery

An off-board regenerable liquid carrier for vehicles and stationary H_2 gas delivery



- Conformable shape liquid tank with design to separate liquids; 18.9 gallons for 5 kg hydrogen at 7 wt. % and unit density
- Heat exchange reduces the vehicles' radiator load by *ca.* 40% (for DH of 12 kcal/mol H_2 and 50% FC efficiency)

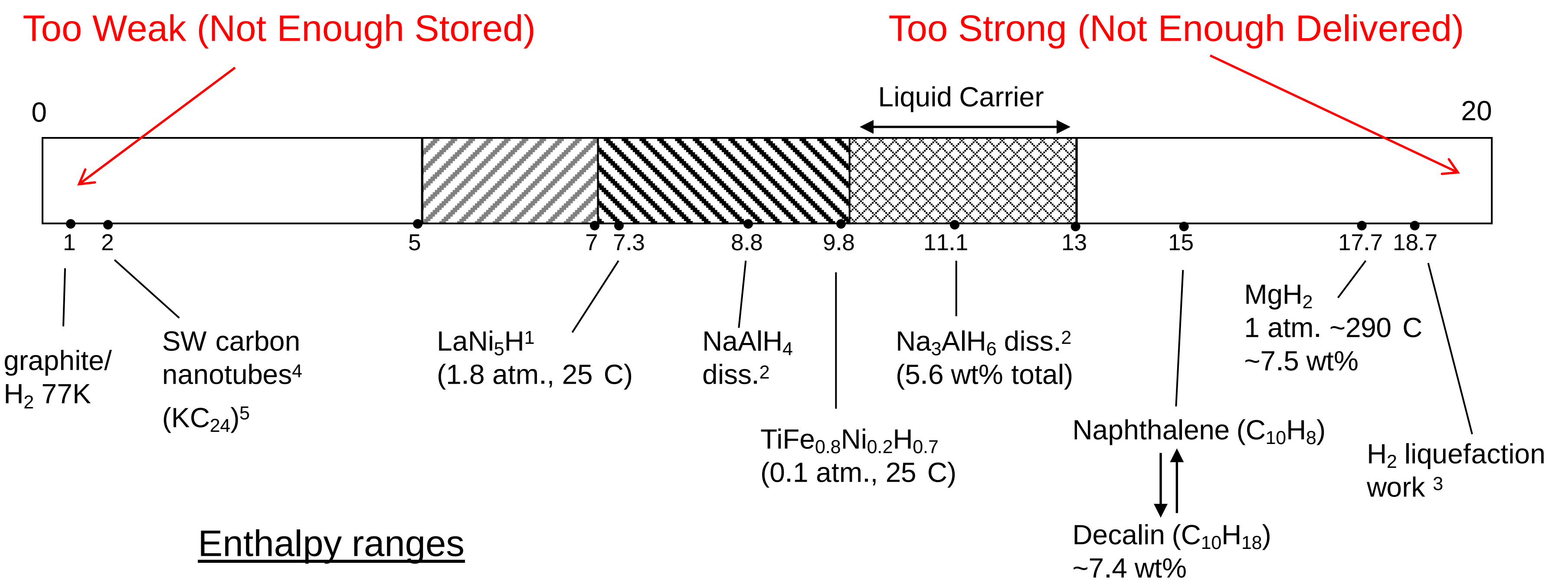
$$LQ^{*}H_2 + \text{heat (DH)} \underset{\text{P > 50 atm., Catalyst}}{\overset{\text{Catalyst, P < 10 atm.}}{\rightleftharpoons}} LQ + H_2$$

Maximum energy efficiency: by (a) recovering the exothermic (-DH) of hydrogenation and (b) utilizing the waste heat from the power source to supply the DH for the endothermic dehydrogenation.

Task: If possible, design optimal H_2 Storage Materials

- **High Storage capacity (e.g. 9 wt. % DOE target)**
- **High *Deliverabl*e Capacity**
- **Speed of Delivery**
- **Toxicity**
- **Cost of Material**
- **Cost/Complexity of Process & Infrastructure**
- **…**

Observed and Desirable H_2-Containment Enthalpies (-ΔH, kcal/mole H_2)



<u>Enthalpy ranges</u>

5-7 kcal/mole H_2 – Strong Physisorption
7-13 kcal/mole H_2 – Weak to Moderate Chemisorption
10-13 kcal/mole H_2 – Optimal for liquid carrier

1. G. Sandrock, J. of Alloys and Compounds 293-295, 877 (1999)
2. B. Bogdanovic, G. Sandrock, MRS Bulletin (2002), p. 712
3. W. Peschka, “Liquid Hydrogen: Fuel of the Future”, Springer-Verlag p. 65
4. M. Haas et al., J. Mater. Res. <u>20</u> (12) 3214 (2005)
5. K. Watanabe et al., Proc. R. Soc. London <u>A333</u>, 51 (1973)

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Preliminaries for Studies of H_2 Storage

- **Work performed principally by…**
  - **Hansong Cheng**
  - **Alan Cooper**
  - **Guido Pez**
  - **With U.S. DOE EERE Hydrogen, Fuel Cells & Infrastructure Technologies Program**
- **The tools used in the studies shown here consist of quantum chemical calculations.**
  - **(DFT, VASP, DMol, PW91, RPBE, Energy Minimization, *ab initio* MD…)**
- **Many of the calculations were infeasible 10 years ago. Improvements in algorithms, software, and HPC hardware have made them possible for a small group in a medium-sized chemical company... with some help from colleagues and supercomputer centers.**

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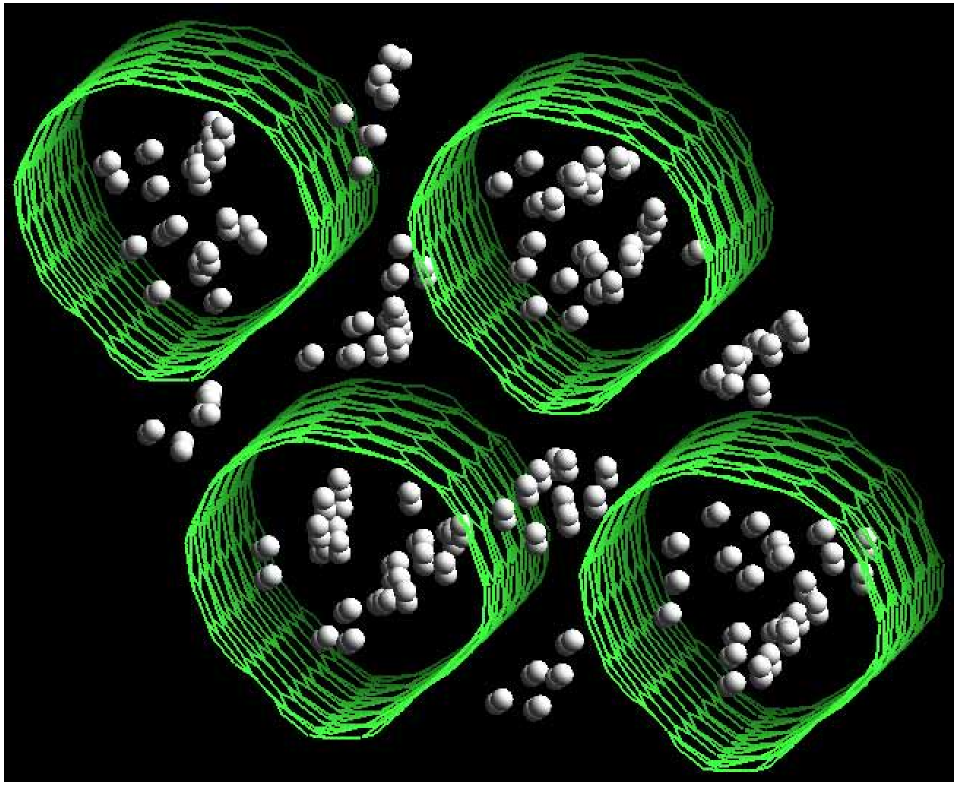
Hydrogen Storage: Early Work

ab initio MD of H_2 in Single Walled Carbon Nano Tubes



- Some experimental claims of very high levels of H_2 adsorption. Real?
- Calculated heats of adsorption in good agreement with careful experiments.

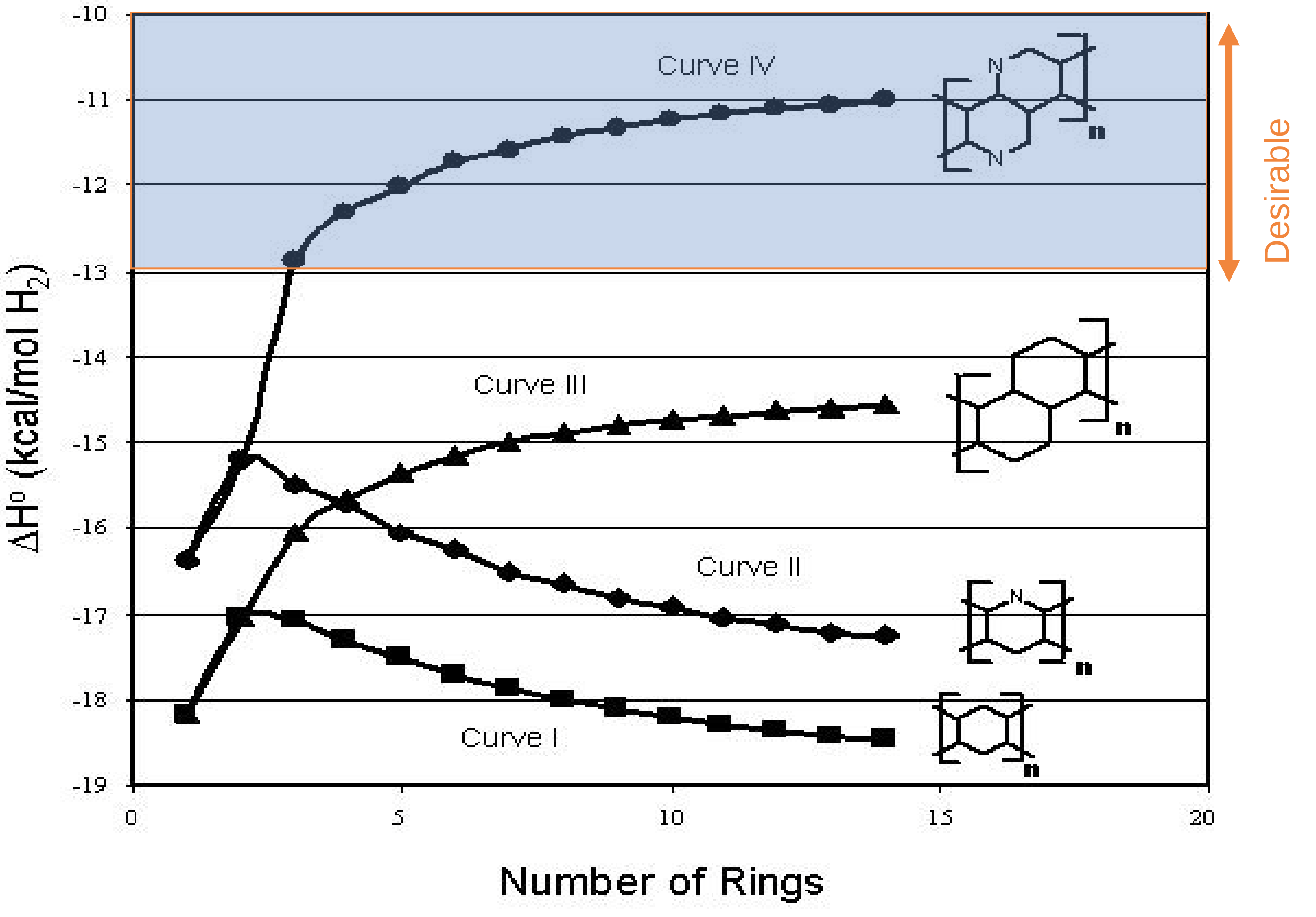
DH_{Expt} (kcal/mol) (95% swnt, 7-14Å)	DH_{Sim} (kcal/mol) (7.8Å, 11.8Å)
4 – 4.8	4.8, 3.3

- Large C-C-C bond angle deformations are observed and are important for interactions with H, H_2.
- Adsorption energies much higher than previously published calculations using classical simulation methods: enhanced potential from curved surface.

H. Cheng, G. P. Pez, A. C. Cooper, *J. Am. Chem. Soc.* 123, 5845 (2001).

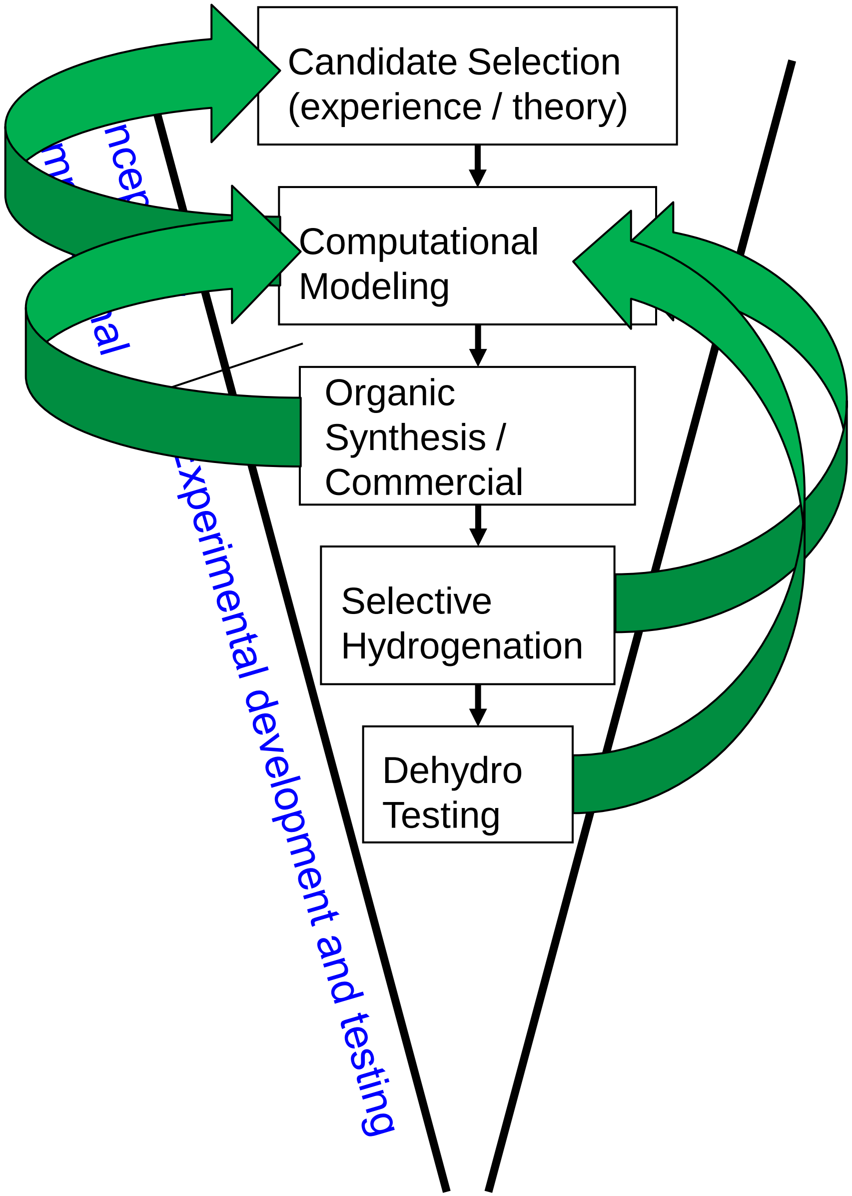
M. K. Kostov, H. Cheng, A. C. Cooper, G. P. Pez *Phys. Rev. Lett.* 89, 6105 (2002)

Enthalpies of Hydrogenation



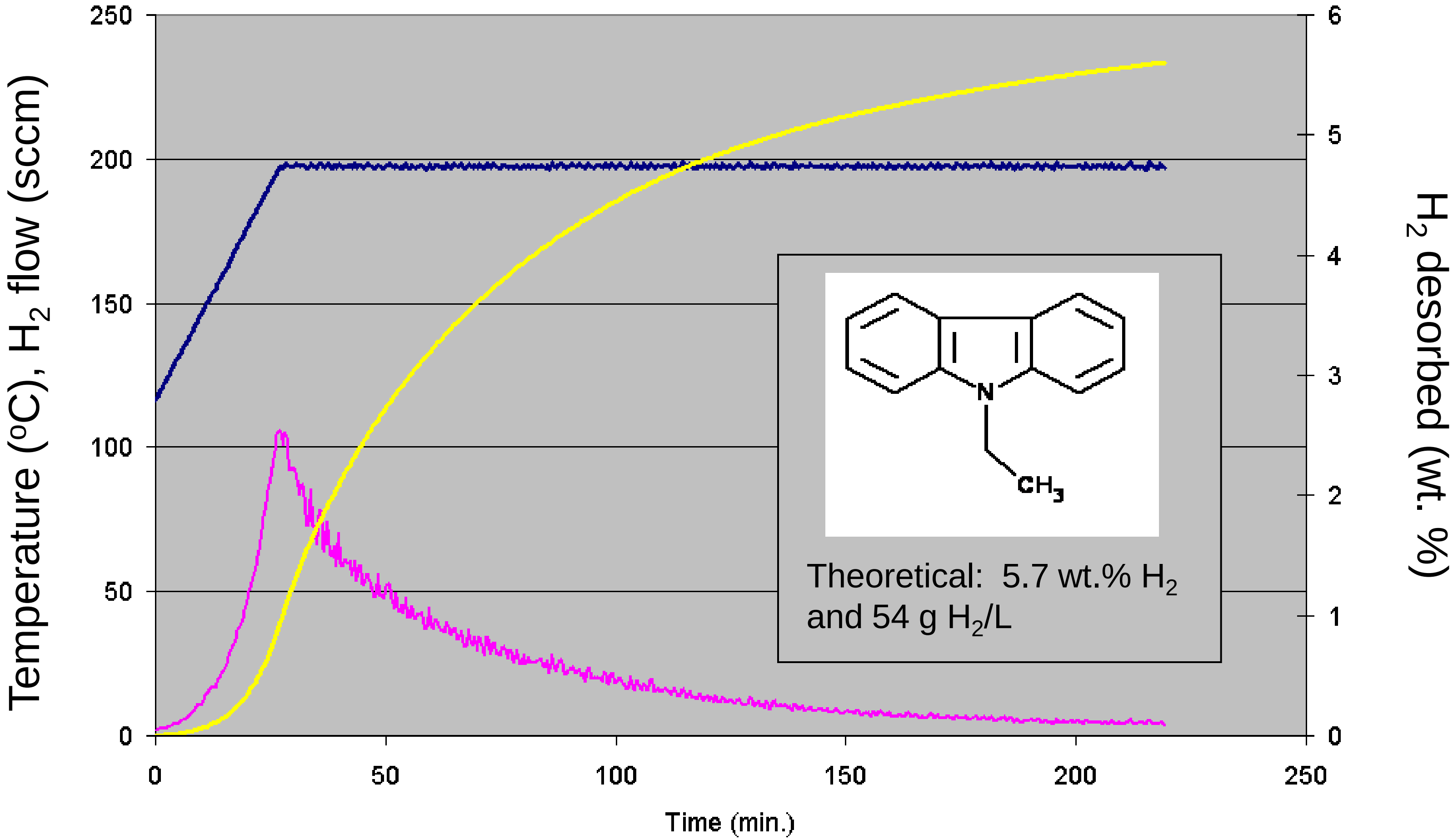
U.S. Patent 7,101,530

Discovery Approach



- **Carrier Selection**
  - **Selection based upon structure/property relationships**
- **Computational Modeling**
  - **Must use proper models**
- **Organic Synthesis**
  - **High purity compounds**
- **Selective Hydrogenation**
  - **99+% selective!**
  - **Many different types of molecules**
- **Dehydrogenation Testing**
  - **Large variation in rates between catalysts**
  - **Must also be 99+% selective**

Hydrogen Generation from N-ethylcarbazole



GC/MS analysis after run termination showed evolution of 5.7 wt. % H_2

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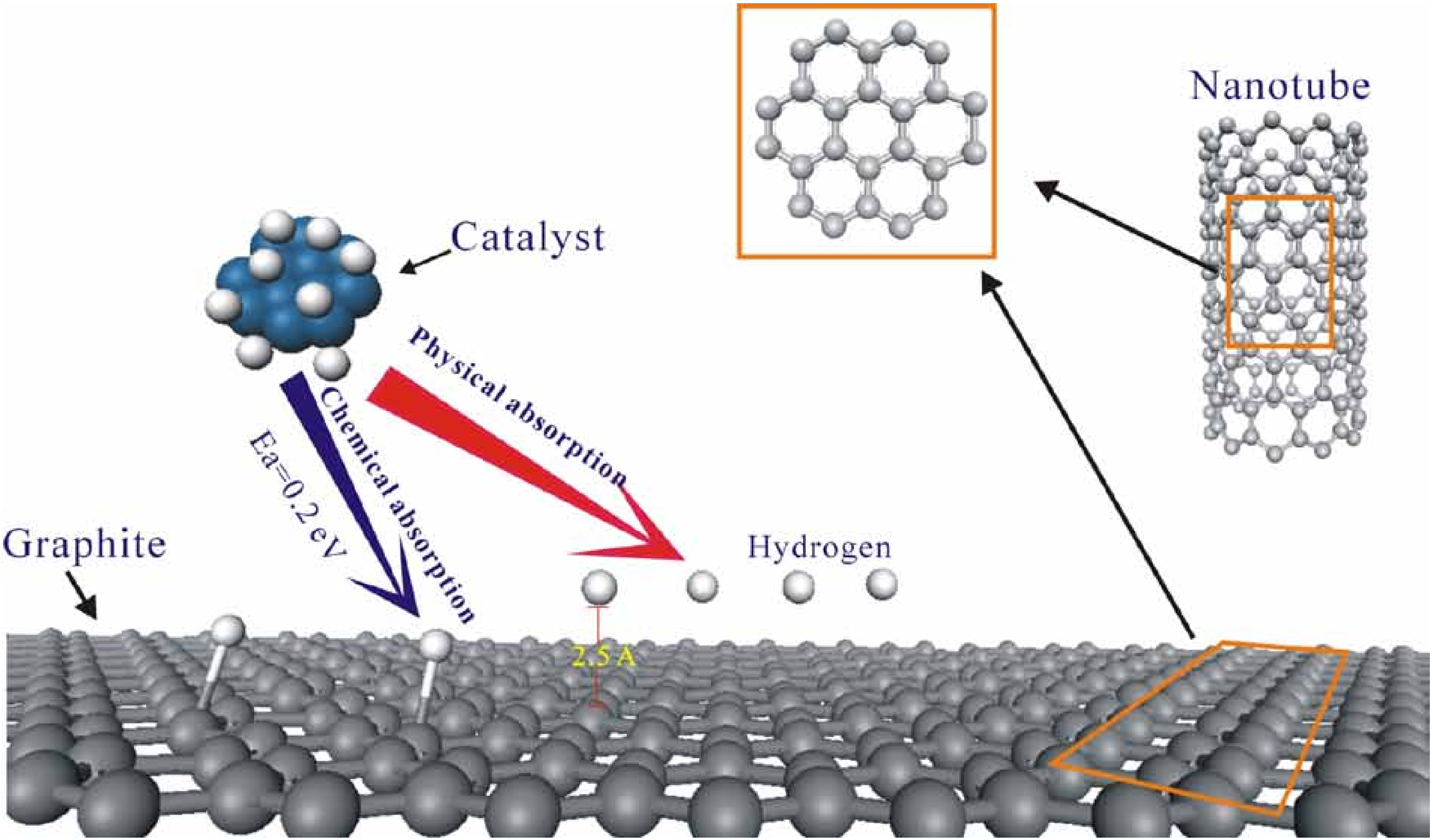
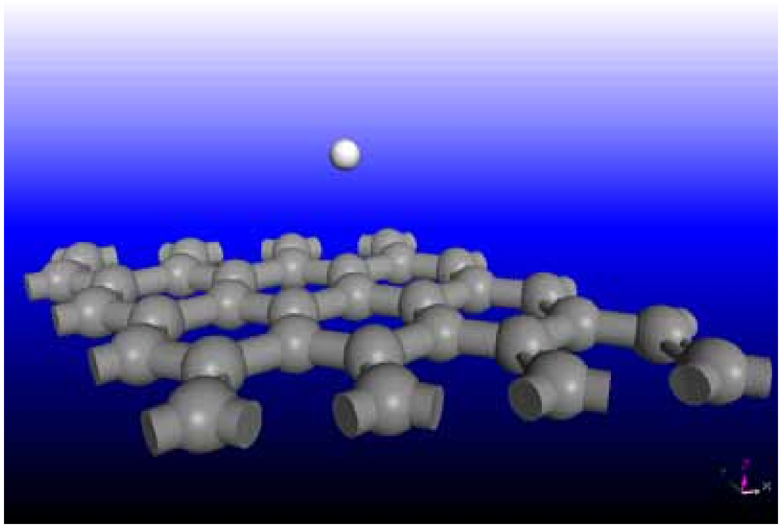
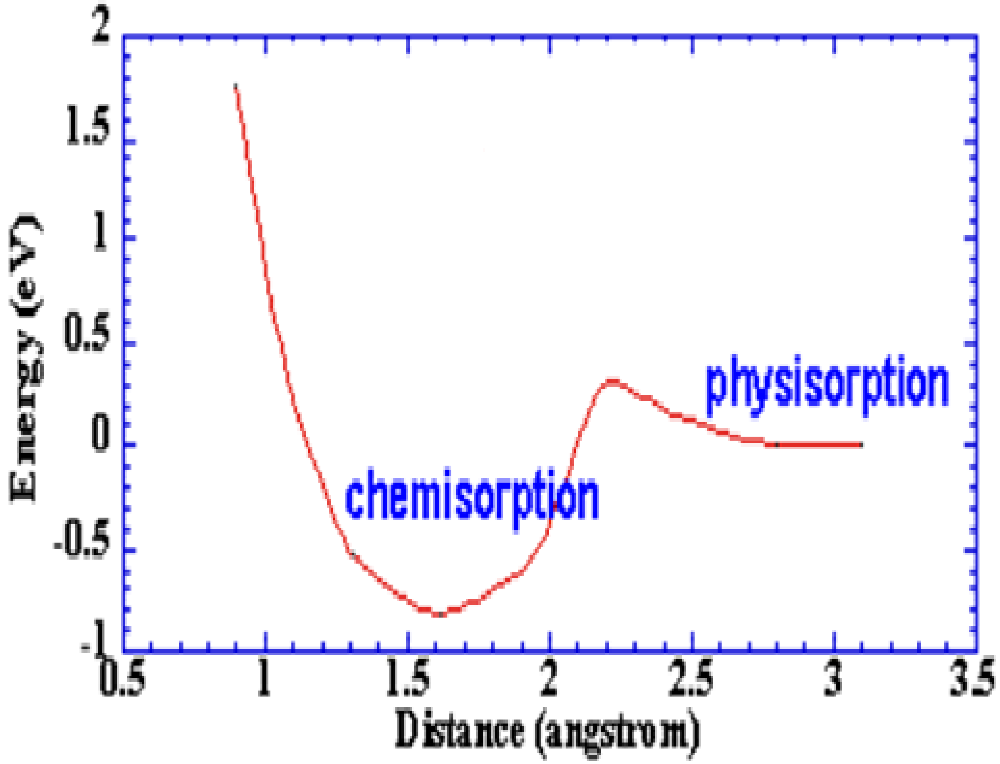
H_2 Storage via Catalytic Hydrogenation



Solids: H Adsorption on Graphene



Sha X., Jackson B., Surf. Sci. 496, 318 (2002)



There is an energy barrier of ~0.2 eV to prevent “cold” H atom from forming a C-H bond

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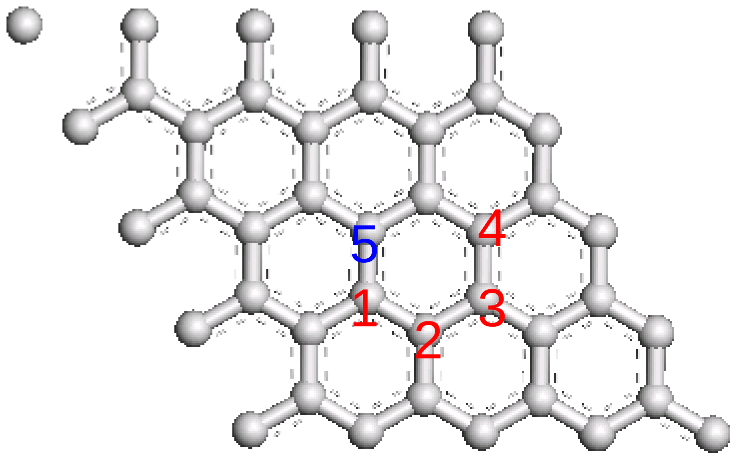
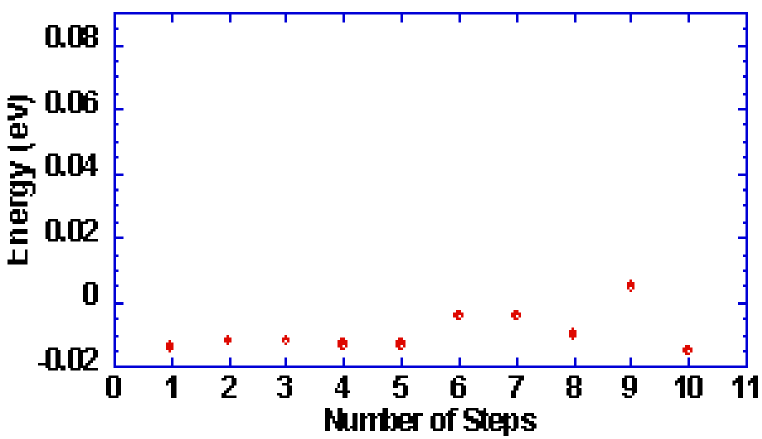
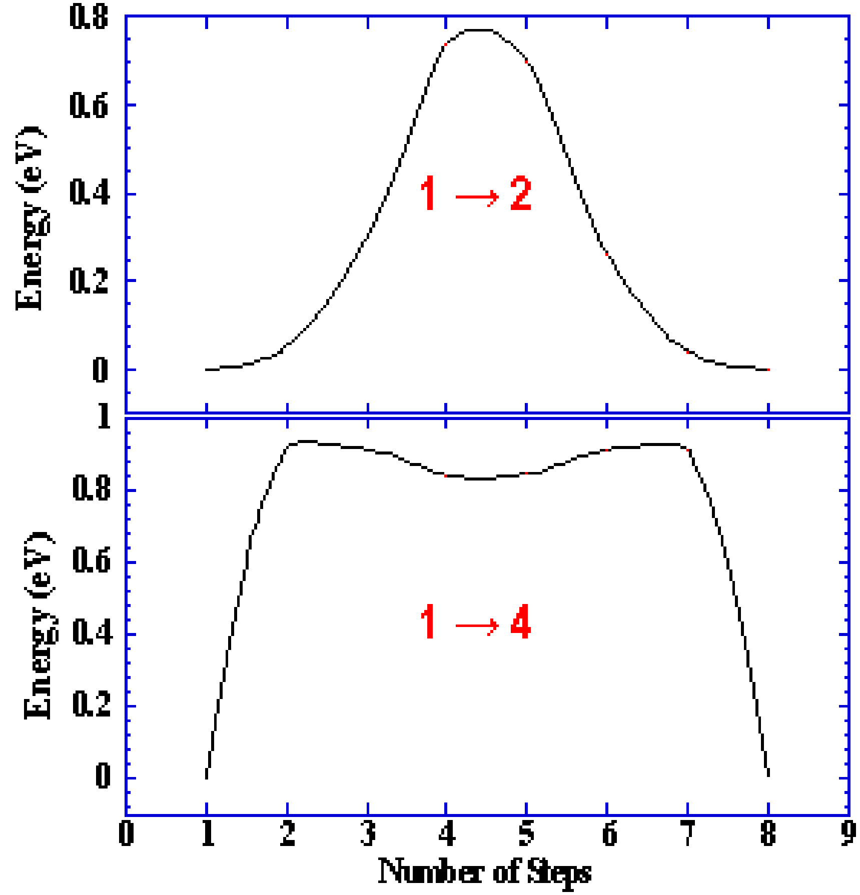
H Diffusion on Graphene







No energy barrier for physisorption

Energy barrier for chemisorption: 0.78-0.92 eV   If bonded, then STUCK

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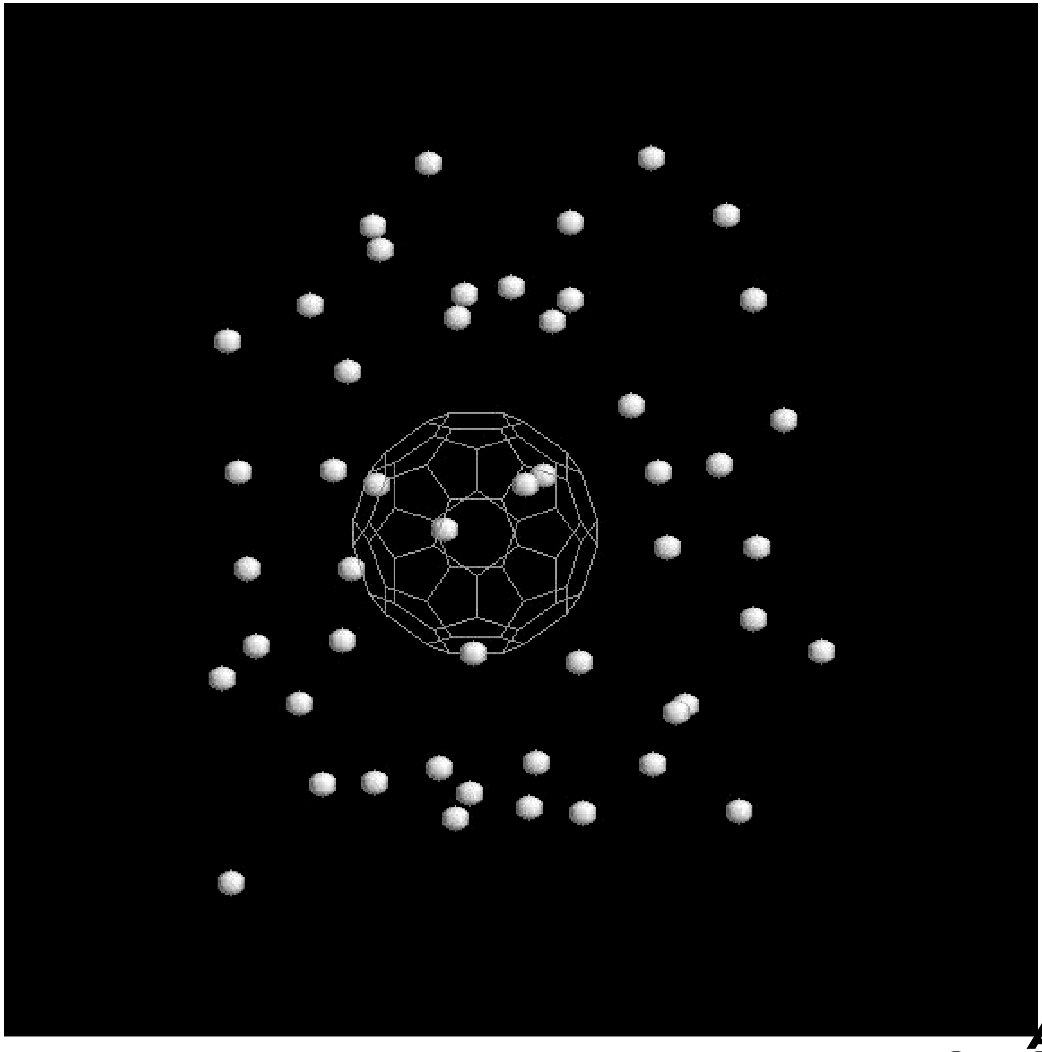
H Collision with C_{60}

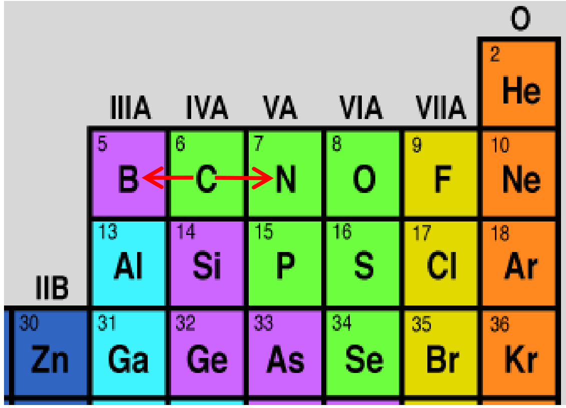
What does a "physisorbed" H atom do?

- forming a C-H bond
- recombining with another H atom to form H_2



Improving on Graphite

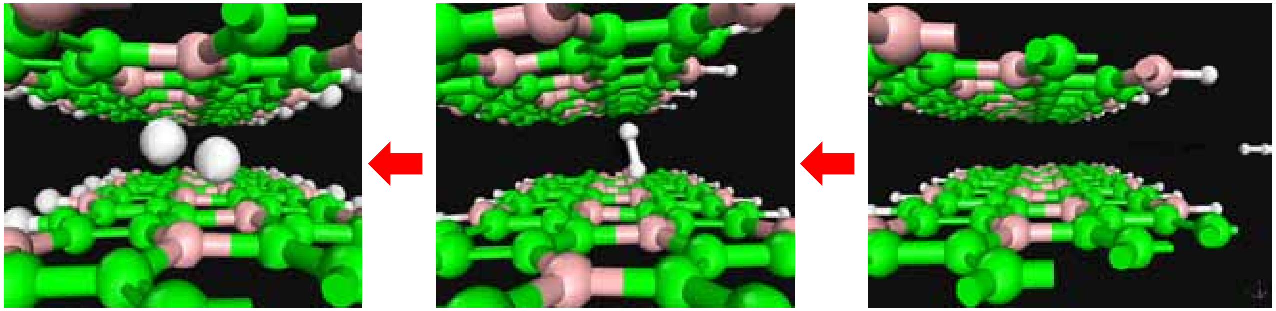
- **For the small molecules, we needed to decrease the interaction energy and added Nitrogen.**
- **For Graphene-based materials, we need to increase the average interaction energy.**

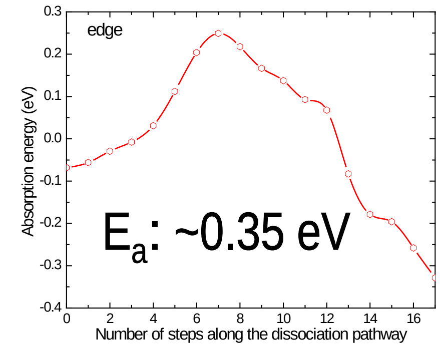


- **Add Boron**
- **BC_3 is known in the literature, and had been studied computationally, though with lower-quality methods (LDA) which over-predict the interaction energy.**

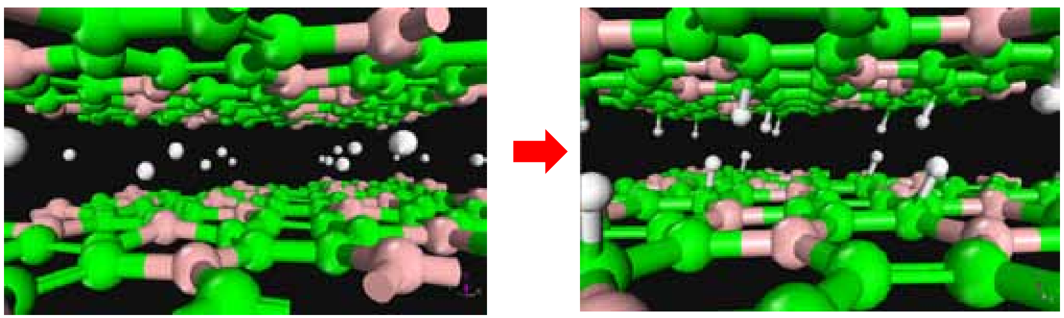
H_2 Dissociative Chemisorption in Bulk BC_3

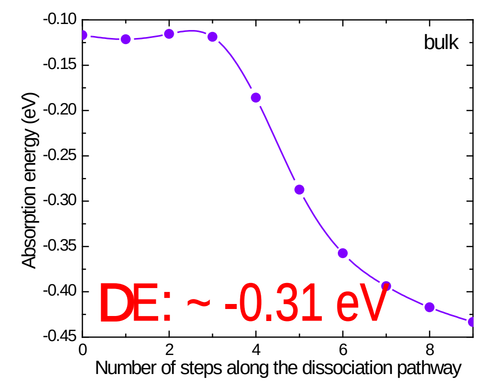
H_2 diffusion into BC_3 pore: facile



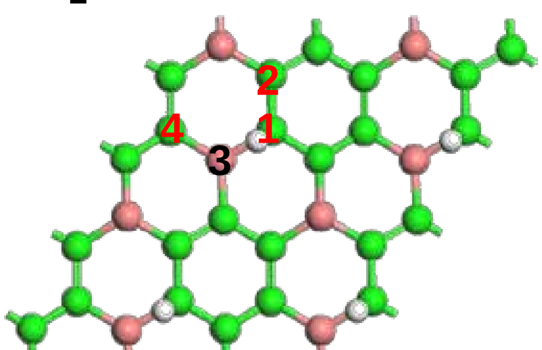


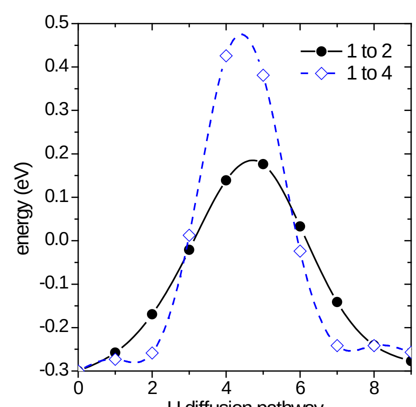
H_2 dissociation inside BC_3: facile





H_2 diffusion inside BC_3





barrier for 1 → 2: ~ 0.47 eV
barrier for 1 → 4: ~ 0.78 eV
barrier for 1 → 3: ~ 1.30 eV

H_2 dissociative chemisorption in bulk BC_3 is energetically possible

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Summary- Hydrogen Storage

- Liquid and Solid materials are being considered as Hydrogen carriers, (but none of the materials considered so far meet all of the criteria)
- Doping unsaturated Carbon-based Materials can be used to tune interaction energies. N↓ B↑
- It is not all about the heat or amount of adsorption: diffusion and catalysis are critical.
- Chemisorbed Hydrogen is quite immobile on graphene, but mobile in BC_3 at moderate temperatures.
- All of these phenomena can be fruitfully studied with computational quantum mechanics.

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Summary

- **Direct Benefits of Modeling & Computation**
  - **Confirm surprising experimental results**
  - **Uncover molecular mechanisms**
  - **Validate/Invalidate simple models / intuition**
  - **Visualize molecular phenomena**
    - **New insight**
    - **Communication**
  - **Computational Screening**
    - **Find lead compounds**
    - **Screen more systems than possible experimentally**
    - **Produce estimates of properties before synthesis & purification attempted or achieved**
- **All of which are used to develop more optimal solutions and to make better decisions**
- **A complementary partnership with experiment, experience, and theory**

Thank you

Richard Hamming, 1962

The Purpose of Computing
is Insight,
and for Numbers