Carbon nanotubes for Energy and Environmental Applications

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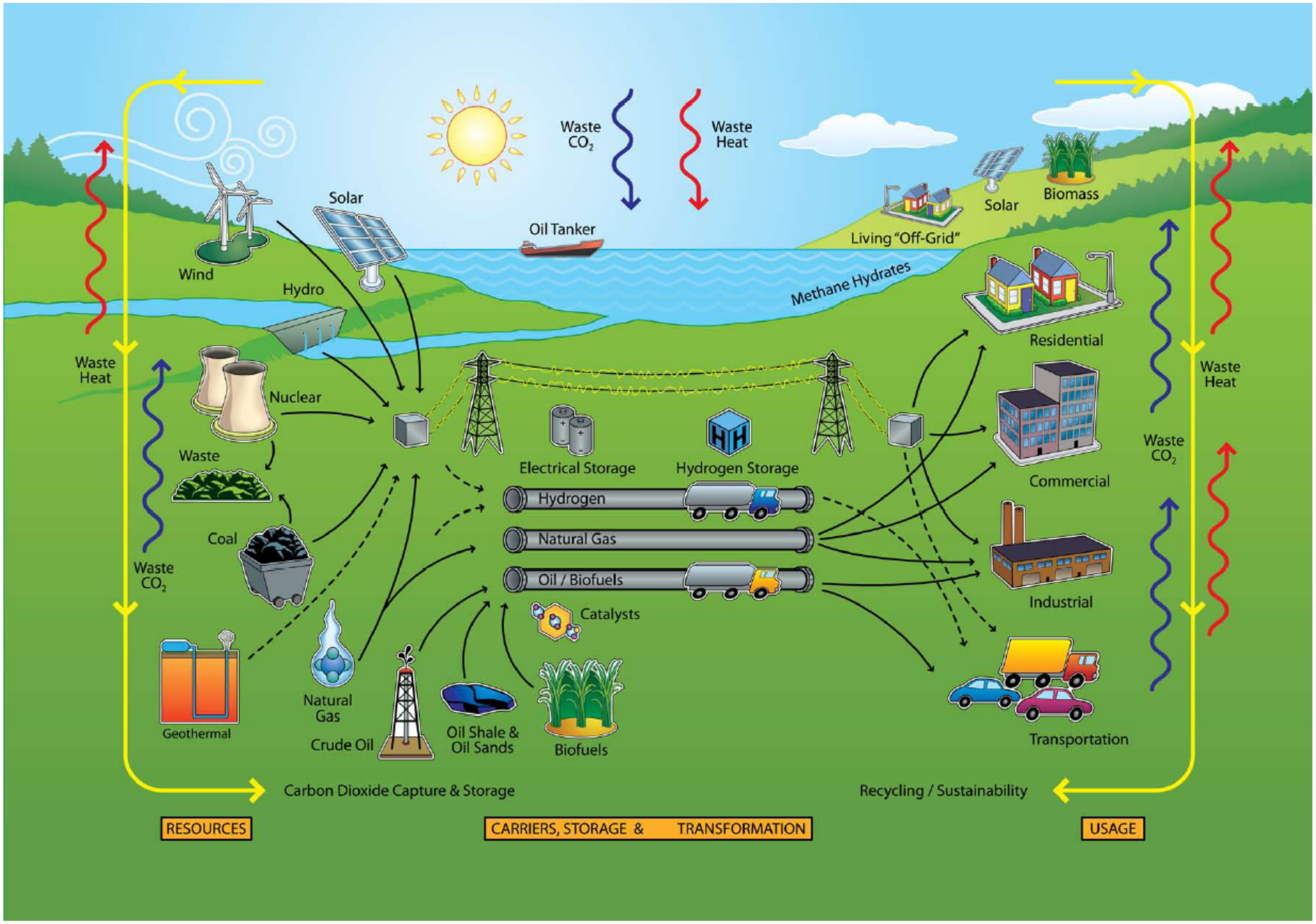
Energy and environment

"Energy can be neither created nor destroyed,
but can only be transformed from one form to another."

- Energy and materials - a continual and mutually enriching relationship
- Materials produce energy or enable energy to be transferred into useful forms.
- Energy makes possible the production of a broad range of materials for society
- Materials store and deliver energy—the batteries, wires and switches, hydrogen, and biofuels that convert energy from other forms.

Energy landscape



http://www.mrs.org: Harnessing Materials for Energy

Possible applications

- Harnessing Energy through H generation and storage
  - H_2O dissociation on defective carbon substrates
  - Thermal decomposition of methane (CH_4)
  - H_2 storage in/on Carbon nanostructures
- Addressing the carbon footprint through CO/CO_2 sequestration/activation
  - Sequestration and selective oxidation of CO on graphitic edges
  - CO_2 activation on metal oxide interfaces
- Solar energy utilization
  - First principles design of novel organic photovoltaic materials

Introduction: Chemical Reactions

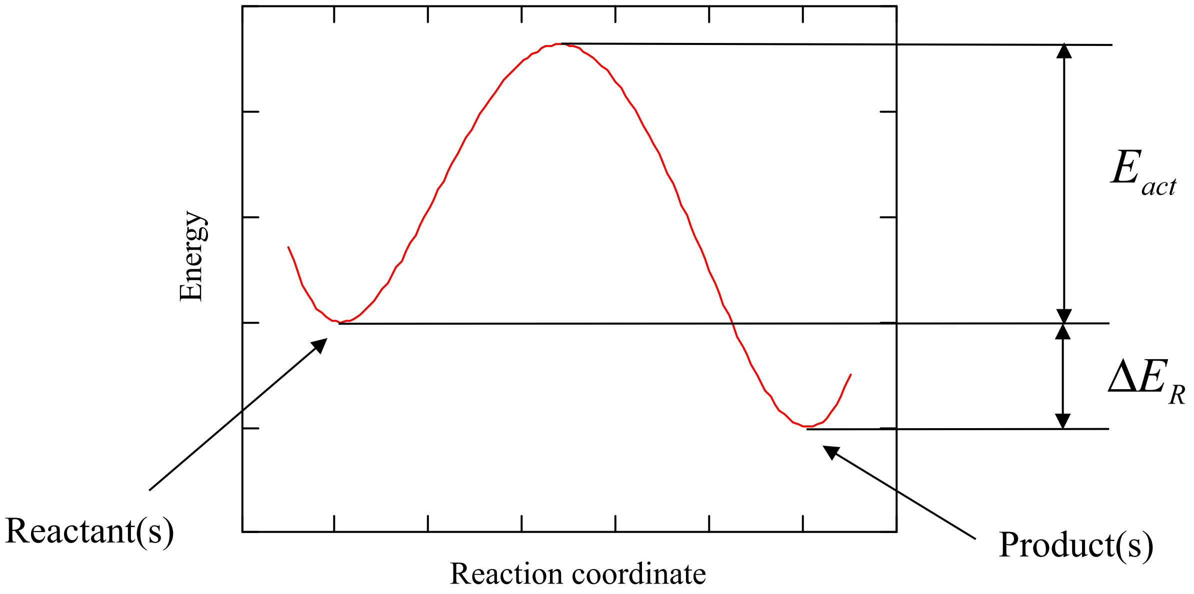
Chemical Reaction:

- A process that results in the interconversion of chemical species.
- A chemical species is defined as “An ensemble of chemically identical molecular entities that can explore the same set of molecular energy levels on the time scale of the experiment” (From IUPAC glossary of terms used in physical organic chemistry, available online at http://www.chem.qmul.ac.uk/iupac/gtpoc/)
- Key point: Species are defined in terms of a time scale.

Introduction: Chemical Reactions

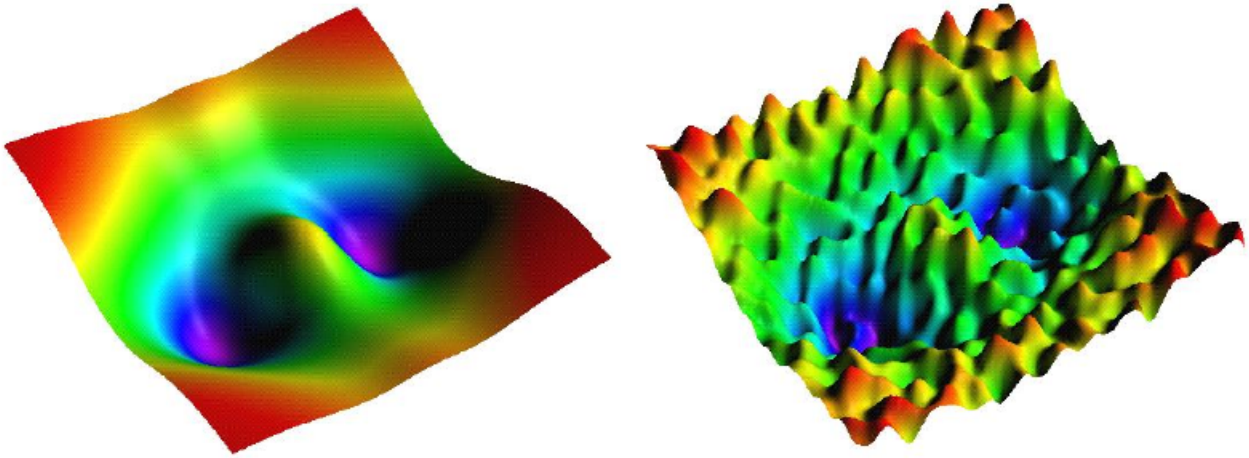
- Chemical reactions are activated processes: the system needs to overcome an energy barrier to get from one state to another.

- In this sense, chemical reactions are analogous to other physical processes such as nucleation, diffusion in solids, etc.



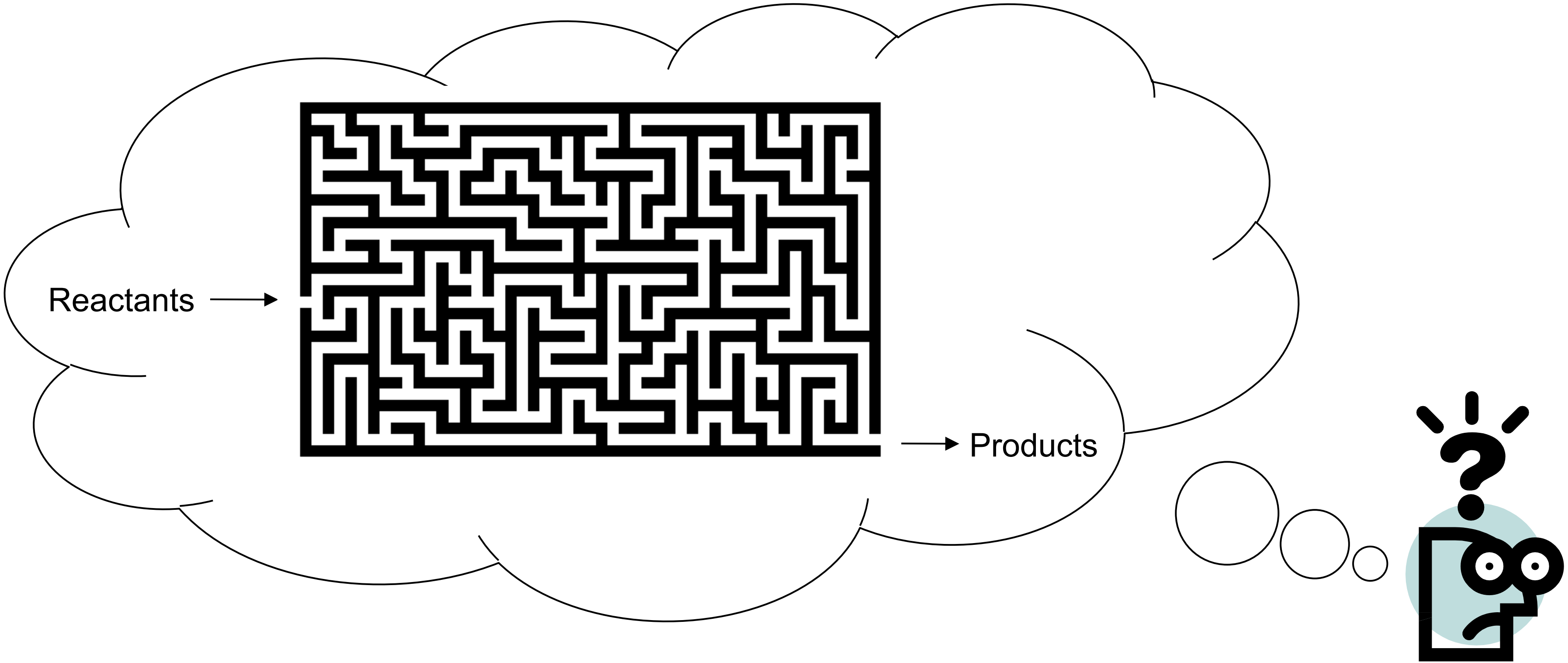
Introduction: Chemical Reactions

- Chemical reactions often involve the breaking/formation of chemical bonds, and hence the description of a chemical reaction is a quantum mechanical problem.
- If we use the Born-Oppenheimer approximation, the potential energy of the system will depend only on the positions of the atomic nuclei. A surface that depicts how the ground state energy of the system varies as a function of the atomic configuration is usually called a *potential energy surface* (PES).
- In many cases, we do not know *a priori* what the possible products will be because the energy landscape is too complicated.



Finding reaction mechanisms

- Not easy in general. Especially difficult for more than one reactant.



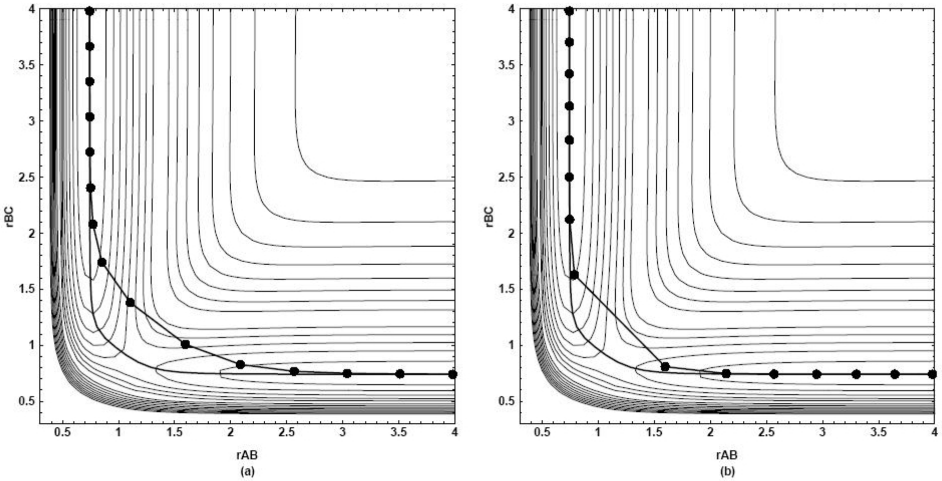
Reactants

Products

(Maze created using the maze generator at http://www.BillsGames.com/mazegenerator)

Finding reaction mechanisms

- Chain-of-states methods: Minimize the energy of an ensemble of images (or ‘states’) of the system, connected together by springs. The initial and final images correspond to the reactants and the products.



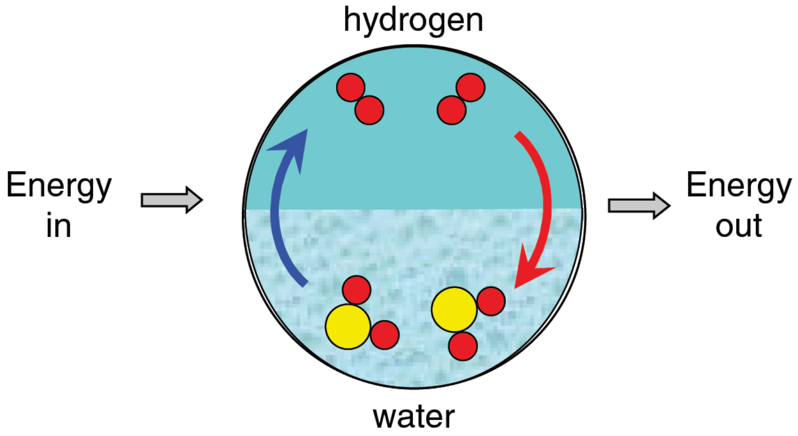
(a) (b)

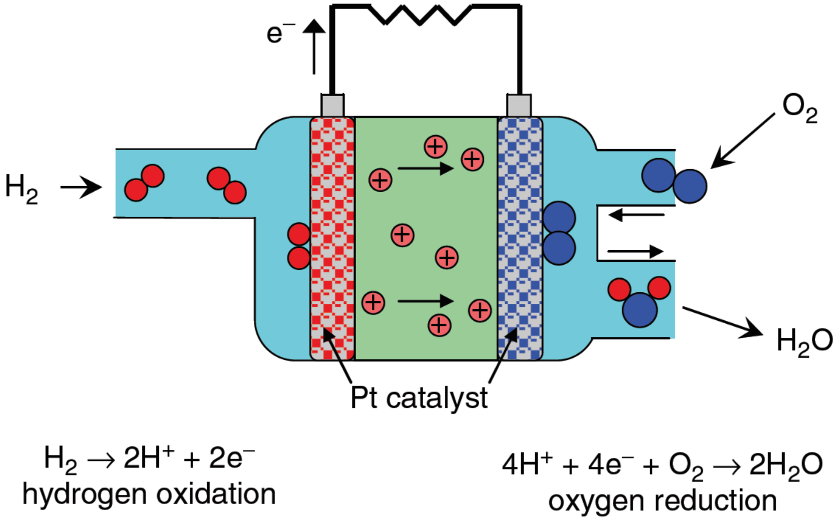
- An useful technique: Nudged Elastic Band (NEB) Method.

H_2O dissociation on defective carbon substrates

Harnessing Energy through H generation and storage

- Hydrogen–water cycle.
- Sustainability is maintained if renewable energy is used to split water and the energy released is used only for work and heat.





$H_2 \rightarrow 2H^+ + 2e^-$
hydrogen oxidation

$4H^+ + 4e^- + O_2 \rightarrow 2H_2O$
oxygen reduction

- Basic operation of a fuel cell.
- The net input of the fuel cell is hydrogen and oxygen
- Its net output is water, electricity, and heat.

Carbon nanostructures as catalytic media

- Catalysis is the essential technology for chemical transformation
- Carbon substrates regarded as media for energy conversion and storage – carbon catalysis
- Defects in carbon nanostructures:
  - Detrimental effect to hydrogen storage

    OR
  - Catalytic role in the dissociation of small molecules
- Why not use defective carbon substrates as nano-scale catalysts rather than fuel tanks?
- Graphitic nano-carbon: simple and easy to model
- Flexible - can explore different geometries (graphene walls, nanotubes, nanohorns, other fullerenes)
- Can modify reactivity in various ways:
  - vacancies, doping, addition of functional groups, etc.

Carbon nanostructures and the dissociation of water

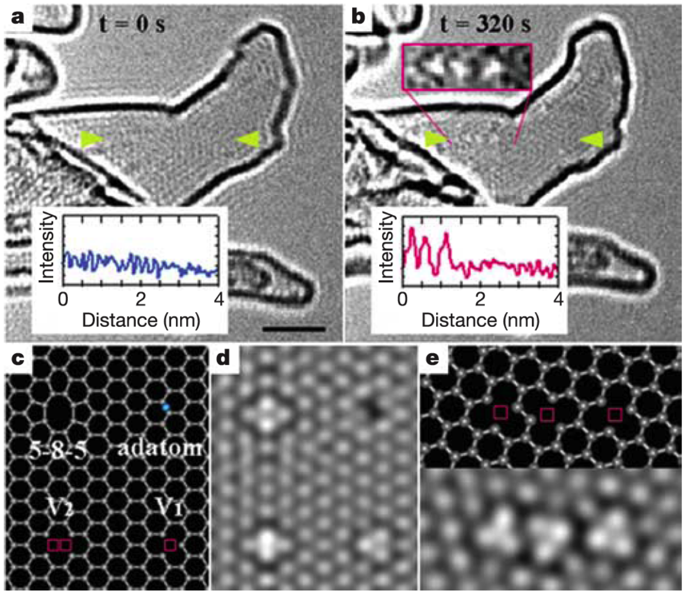
- Catalytic potential of a mono-vacancy site
- Formation energy of a graphene single vacancy (GSV) is $E_f = 170 \pm 10$ kcal/mol
- H_2O dissociation in free space:

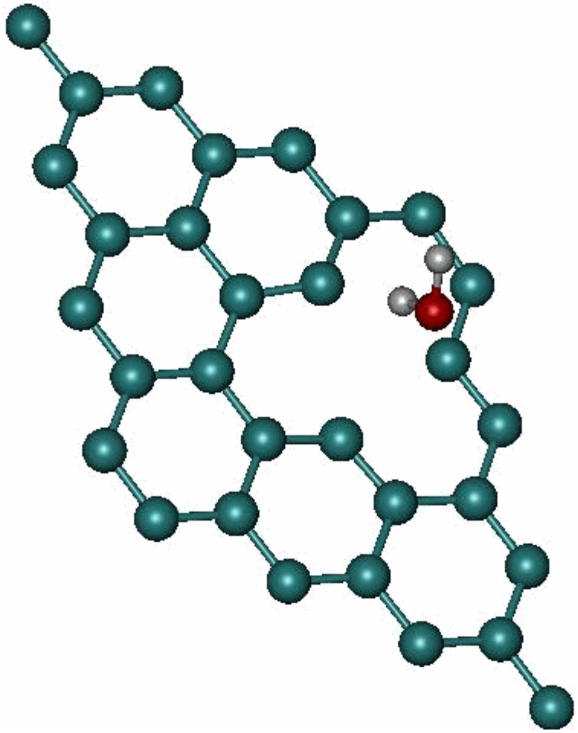
$$H_2O \rightarrow H_2 + 1/2O_2 , \quad \Delta H \text{ (0 K)} = 116 \text{ kcal/mol} , \ E_A = 131 \text{ kcal/mol}$$

- Not isogyric reaction: spin is not conserved, oxygen moves from the spin-singlet surface (H_2O) to a spin-triplet state (O atom).
- Fundamental limitation: breaking a water molecule requires an excess energy of 45 kcal/mol to excite the molecule to a higher spin state prior to the dissociation.
- The direct thermolysis of H_2O is effective at $T \geq 2500$ K
- Possible solutions to overcome these high activation barriers (E_A) are:
  - photo-excitation, enzymatic and biochemical reactions, electrolysis, etc.
  - Defects in graphitic materials, however, have the potential to dissociate water, since the formation energy is comparable to reaction enthalpy.

Catalytic role of defective carbon substrates in the dissociation of water

$H_2O \rightarrow H_2+O$





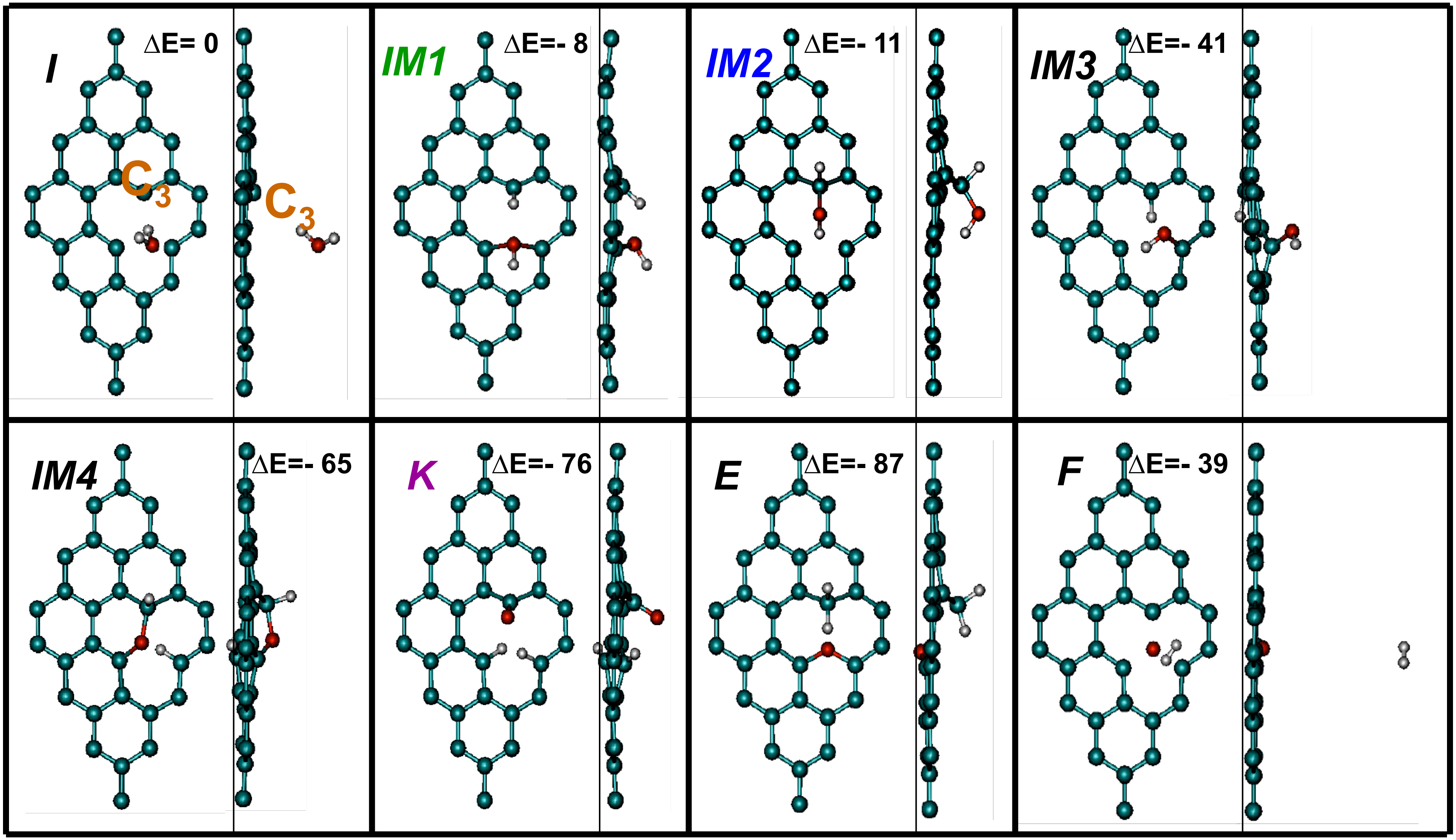
Defects in graphitic materials have the the potential to dissociate water (formation energy comparable to reaction enthalpy) and they have been observed in native carbon nanotubes - they exists! ***(Iijima et al. Nature, 2004)***

Complex reaction mechanism with many intermediate states - spin singlet

NEB + Metadynamics + Rational Function Optimization

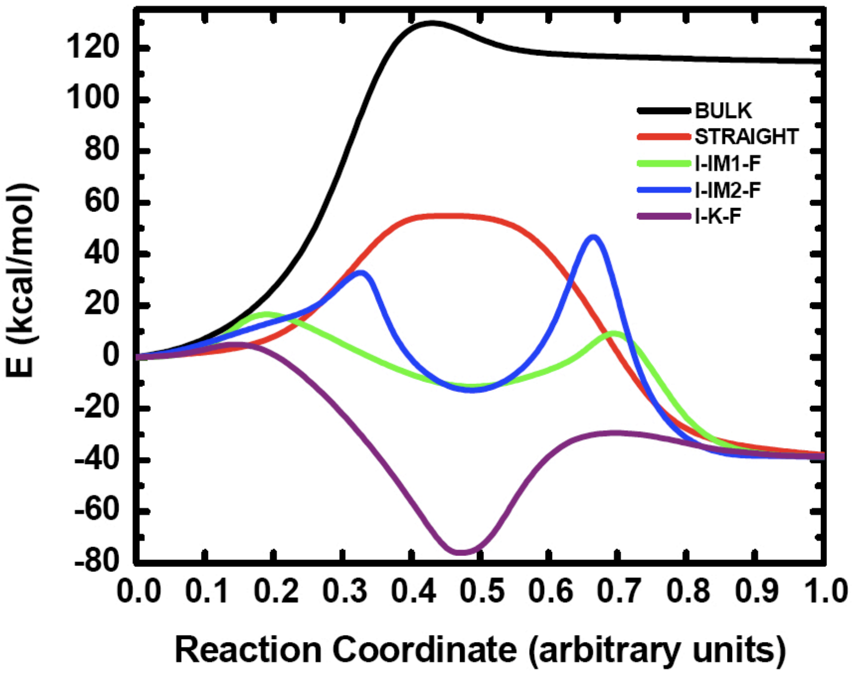
Intermediate Stable States in H_2O splitting over GSV

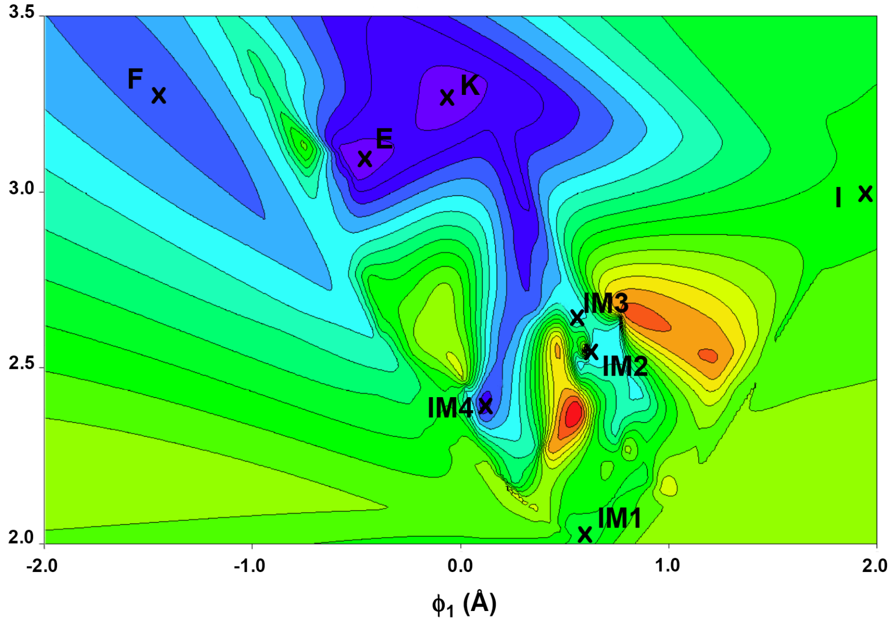
Energies in kcal/mol



Catalytic role of defective carbon substrates in the dissociation of water

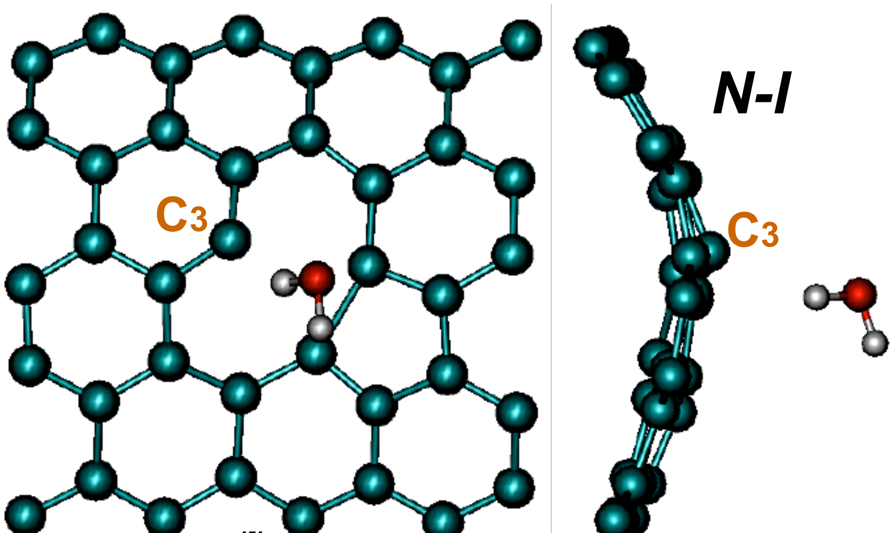
$H_2O \rightarrow H_2 + O$





Potential energy surface for water dissociation on a vacancy in graphene - low energy barriers wrt the direct thermal splitting due to the ability of the carbon substrate to keep the reaction on the spin singlet surface

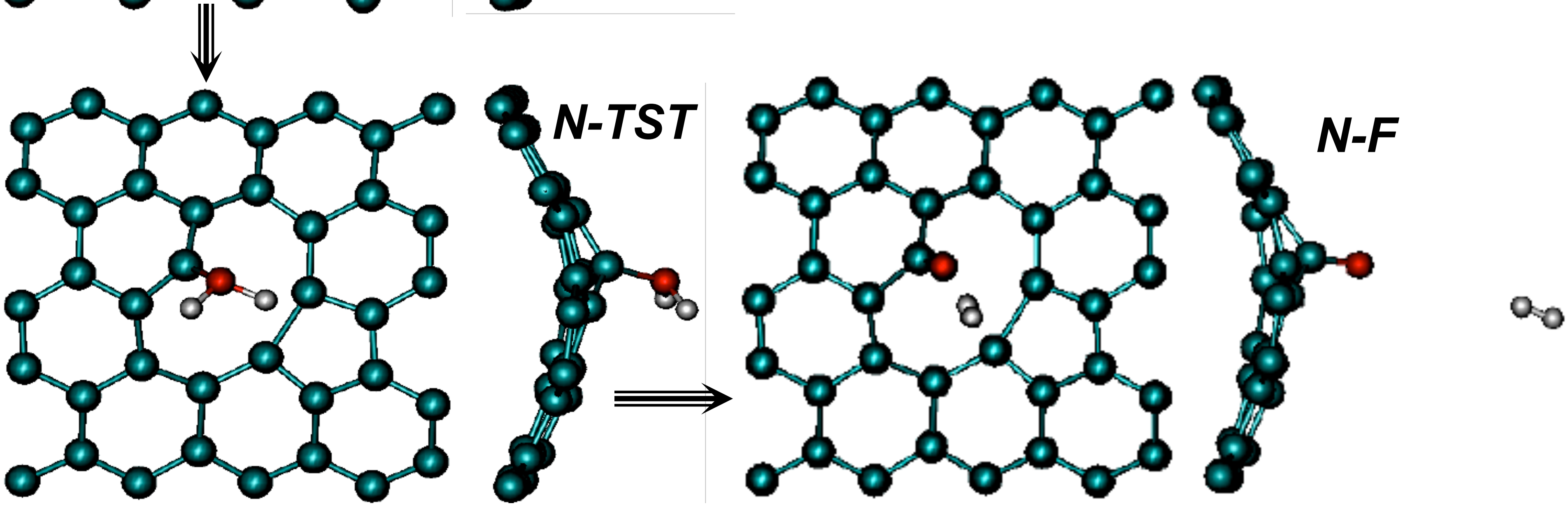
Dissociation of H_2O over a (10,10) nanotube vacancy



Reconstructed CC bond ~ 1.65 Å

System less reactive –
one “dangling bond” atom C_3

Direct dissociation process with a
very low energy barrier: E_A = 23 kcal/mol



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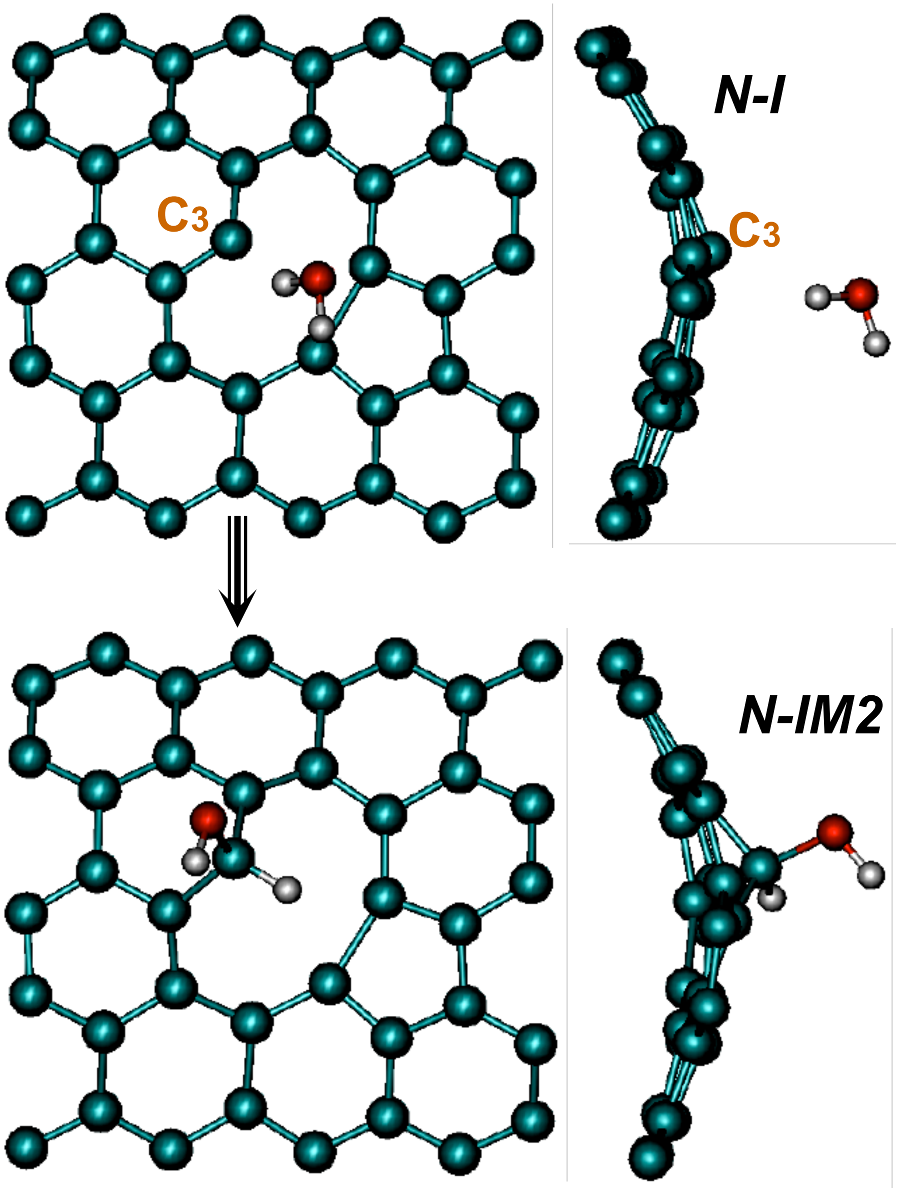


All analogs of the planar stable states are present

N-IM2 is the precursor of all the other possible intermediate states

N-E is still the global minimum of the PES

N-I ➔ *N-IM2*: *E_A= 21 kcal/mol*

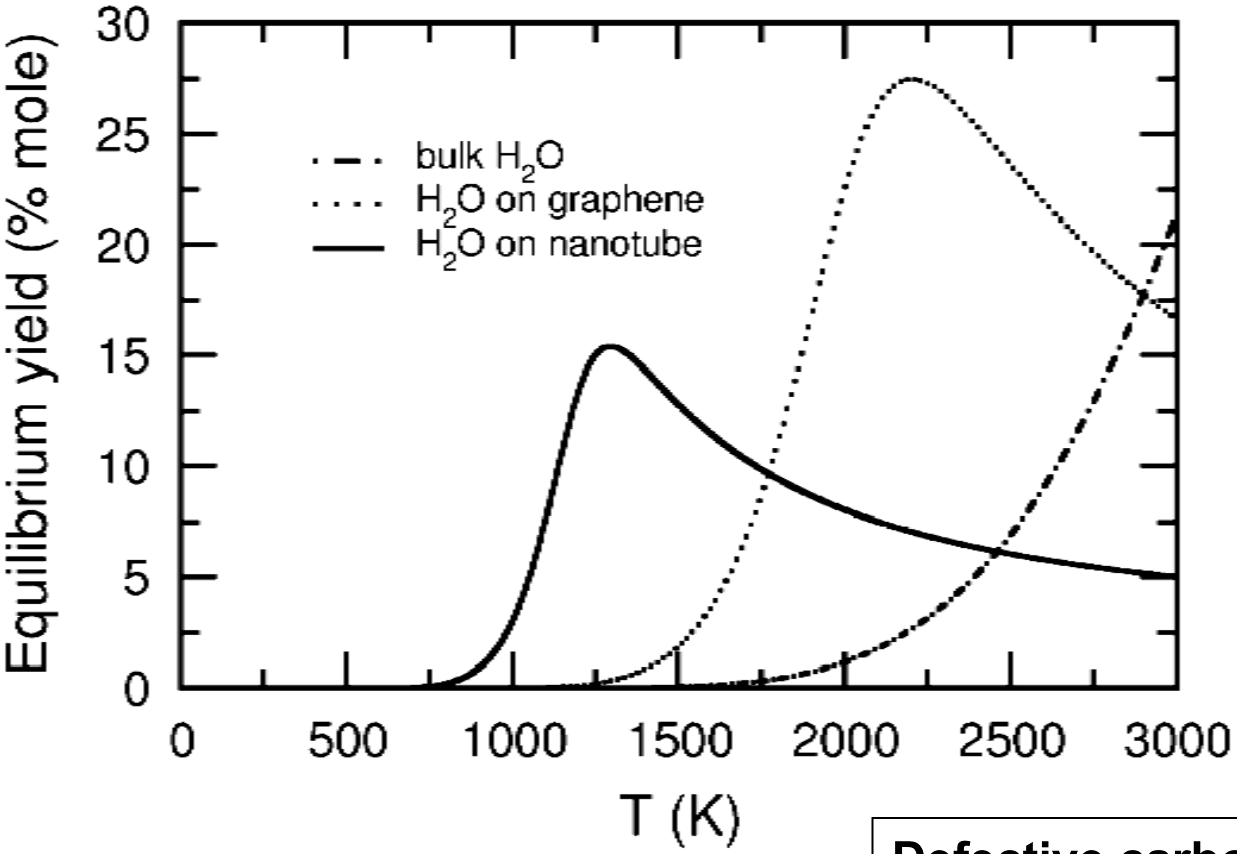
N-IM2 ➔ *N-K*: *E_A= 24 kcal/mol*

N-K ➔ *N-F**: *E_A= 38 kcal/mol*

N-E ➔ *N-F** : *E_A= 48 kcal/mol*

Curvature improves energetics for the H_2O dissociation reaction

Equilibrium Yield



Ideal-gas equilibrium yields (fraction of the water that is converted to hydrogen at equilibrium in % mole) for the dissociation of water on a single vacancy in a nanotube and a graphene sheet as compared with the direct thermolysis of the water .

Defective carbon substrate can produce hydrogen from water at temperatures at least a factor of 2 lower for hydrogen yields comparable to the free space reaction

(Santiso, Kostov, George, Gubbins and MBN, PRL 2005)

Regeneration of the vacancy

Methods to remove O atom

- Chemical and thermal purification methods – come with the side effect of damaging the carbon network and preferential desorption of CO and CO_2 .

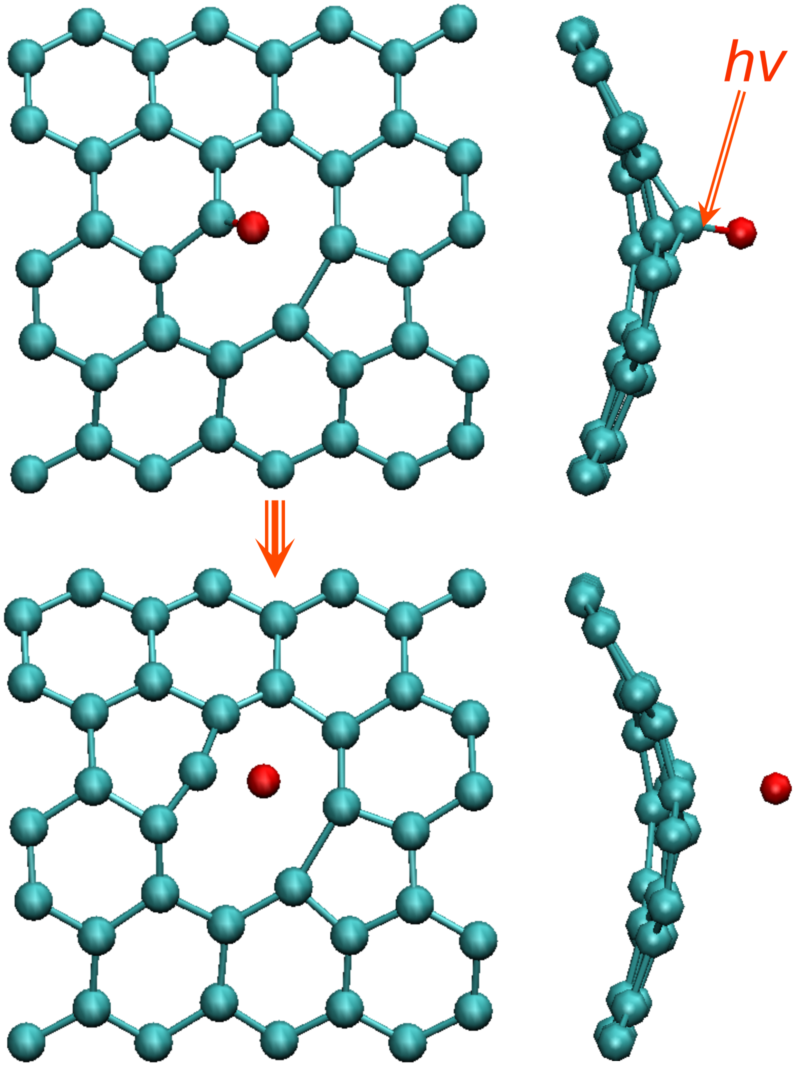
- Photodesorption of O atom by a resonant Auger process with excitation energy E (O 1s → O 2p) ≈ 530 eV. Oxygen desorbs spontaneously with no damage to the carbon network.

(Tomanek et al, PRB, 2004)

Alternative

Multiphoton vibrational excitation:

Infrared laser pulses can be adapted to selectively excite and break the C-O bond. The corresponding C-O stretch is in the 6.0-6.1 μm region, which is well accessible to high-intensity CO and CO_2 lasers.



Addressing the carbon footprint through CO/CO_2 sequestration

Addressing the carbon footprint through CO/CO_2 sequestration

- Major challenges lie ahead in the discovery of efficient biomass conversion catalysts, as well as in the discovery of catalysts for conversion of CO_2 and possibly water into liquid fuels.

- CO_2 is a product both of carbon-containing fuel combustion and a number of the processes for making the fuels. It would be advantageous to dispose of the CO_2 in environmentally safe ways or, perhaps even better, to convert it into fuels or chemicals.

- Economical processes and catalysts for such conversions are lacking; the discovery of such catalysts and the creation of technology for CO_2 conversion is a massive challenge.

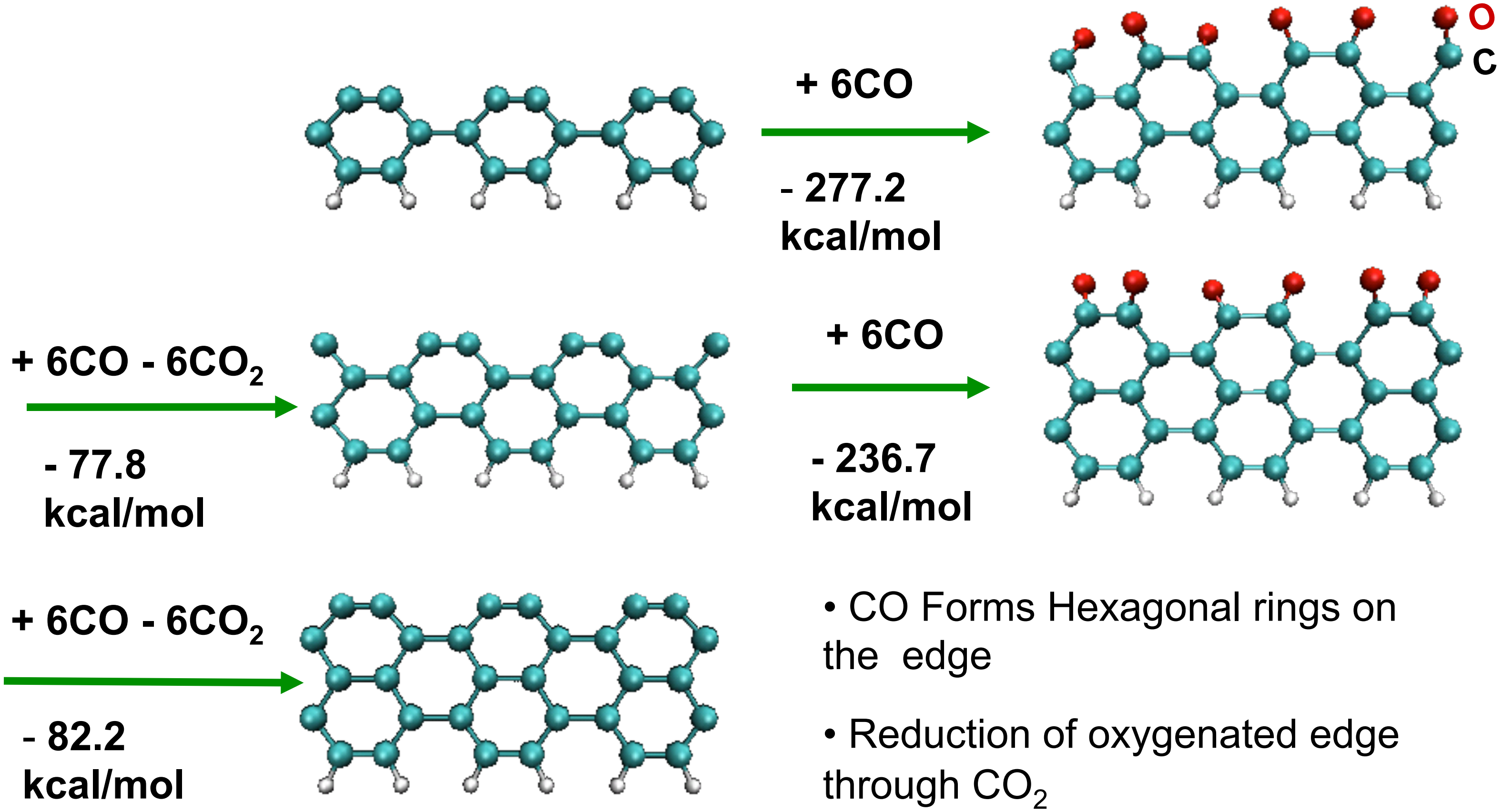
Carbon systems for CO/CO_2 management

- Reduce CO_2 emission by efficient CO management
- Adsorption of CO on carbonaceous material is relevant in the coal gasification process

- CO sequestration and selective oxidation on graphitic edges
- CO disproportionation (Boudouard reaction: $2CO \longrightarrow C_{solid} + CO_2$
    - accretion of the graphitic edge – important implications for the controlled growth of graphene sheets for electronics applications
- selective oxidation of CO: application to purification of syngas

$CO+H_2$, H_2 is preserved: $2CO+H_2 \longrightarrow C_{solid} + CO_2 + H_2$

Growth of Armchair Graphene edge



+ 6CO

- 277.2 kcal/mol

+ 6CO - $6CO_2$

- 77.8 kcal/mol

+ 6CO

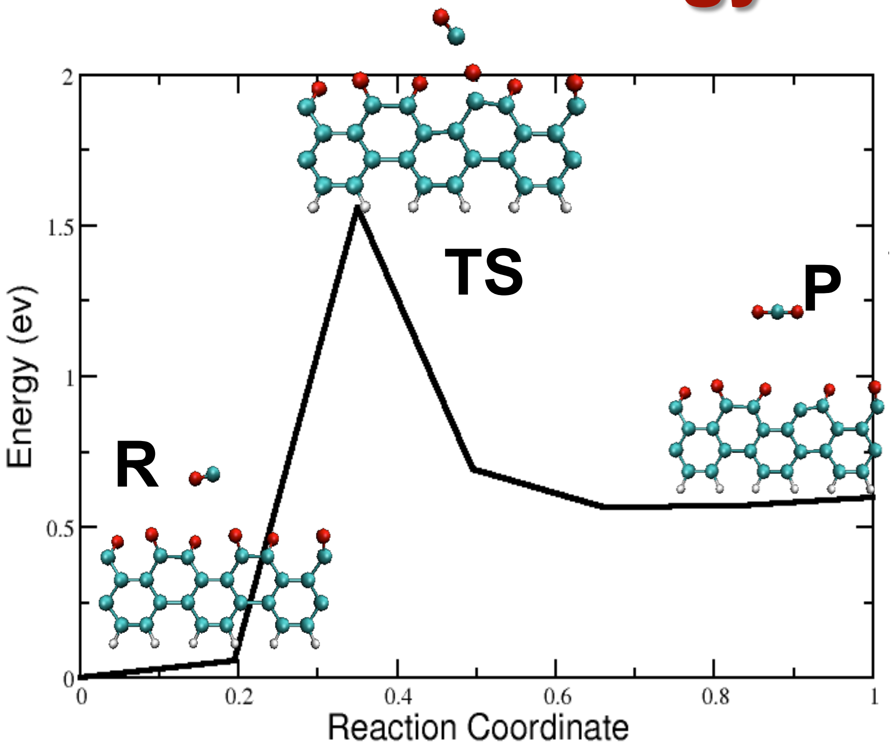
- 236.7 kcal/mol

+ 6CO - $6CO_2$

- 82.2 kcal/mol

- CO Forms Hexagonal rings on the edge
- Reduction of oxygenated edge through CO_2

Activation energy barrier for Armchair edge

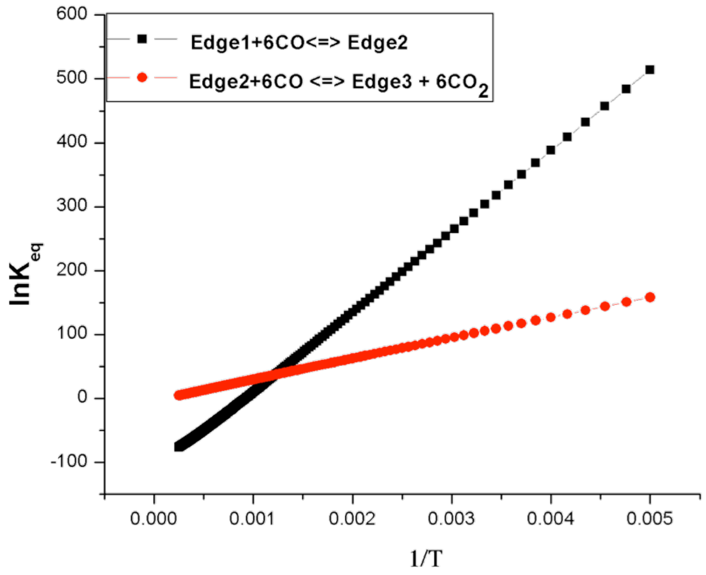


- Presence of dangling bonds makes the energy barrier (~ 1.5 ev) high

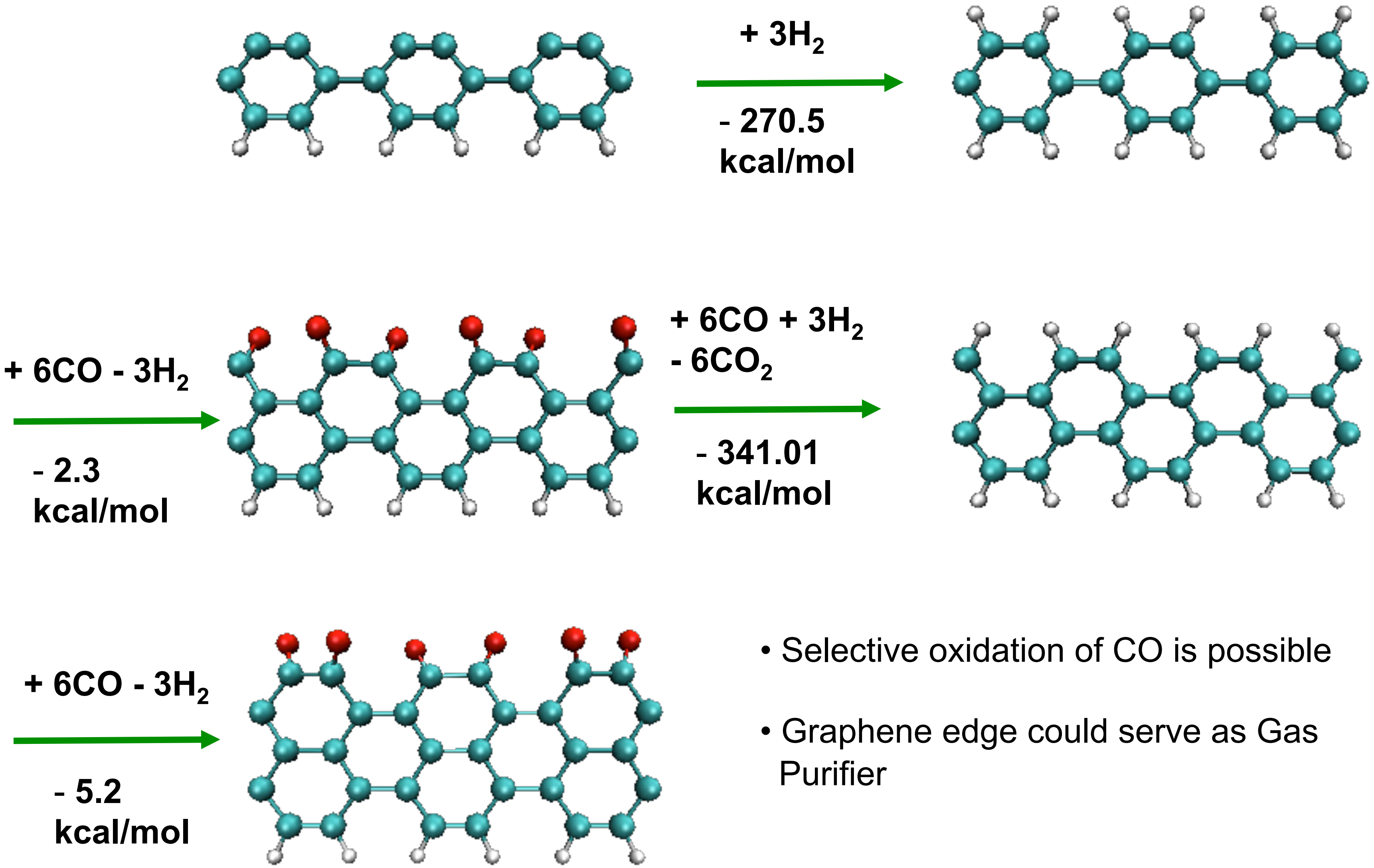
- Concerted process: unsaturated bonds exposed to CO molecules

- CO adsorbs to the edge exothermically

- Chemisorption of CO to the open edge is more favorable than CO readsorption to form CO_2 at low temperature



Energetics of graphene edge in CO+H_2



+ $3H_2$

- 270.5 kcal/mol

+ $6CO - 3H_2$

- 2.3 kcal/mol

+ $6CO + 3H_2 - 6CO_2$

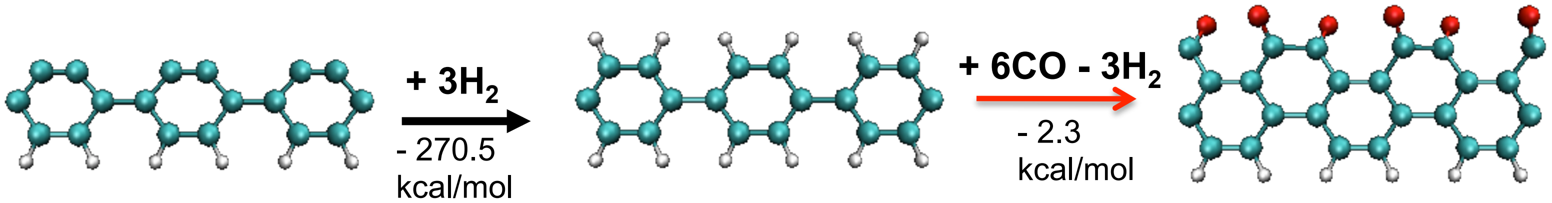
- 341.01 kcal/mol

+ $6CO - 3H_2$

- 5.2 kcal/mol

- Selective oxidation of CO is possible
- Graphene edge could serve as Gas Purifier

Temperature effect on reactions:Graphene+CO+H_2



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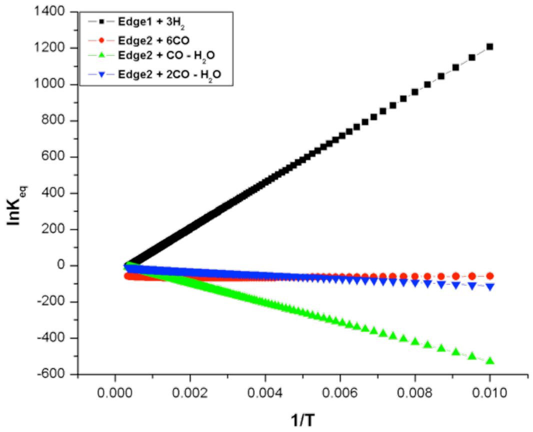
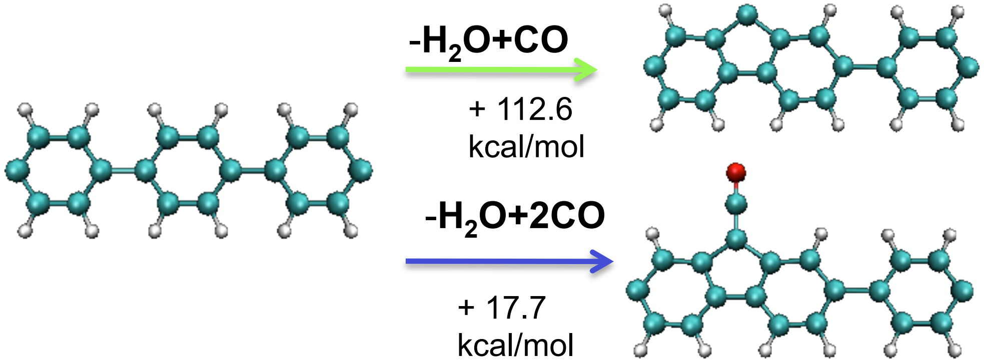




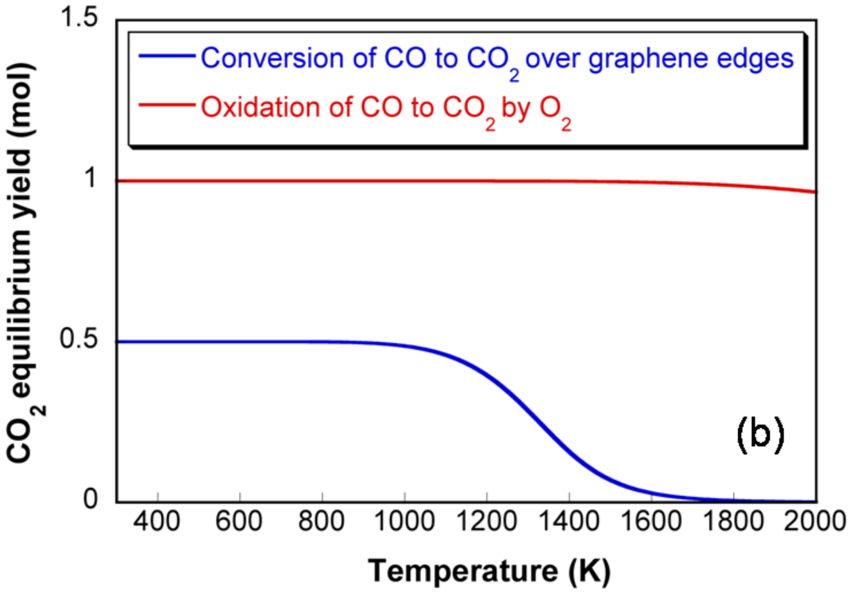
$-H_2O+CO$

+ 112.6 kcal/mol

$-H_2O+2CO$

+ 17.7 kcal/mol

- Selective oxidation of CO is possible at the edge
- At low temperature H_2 is preserved and yield of H_2O is low



http://ermes.physics.ncsu.edu