U.S. DEPARTMENT OF ENERGY | Office of Science

Post-Combustion CO_2 Capture: Beyond 2020, a BES Perspective

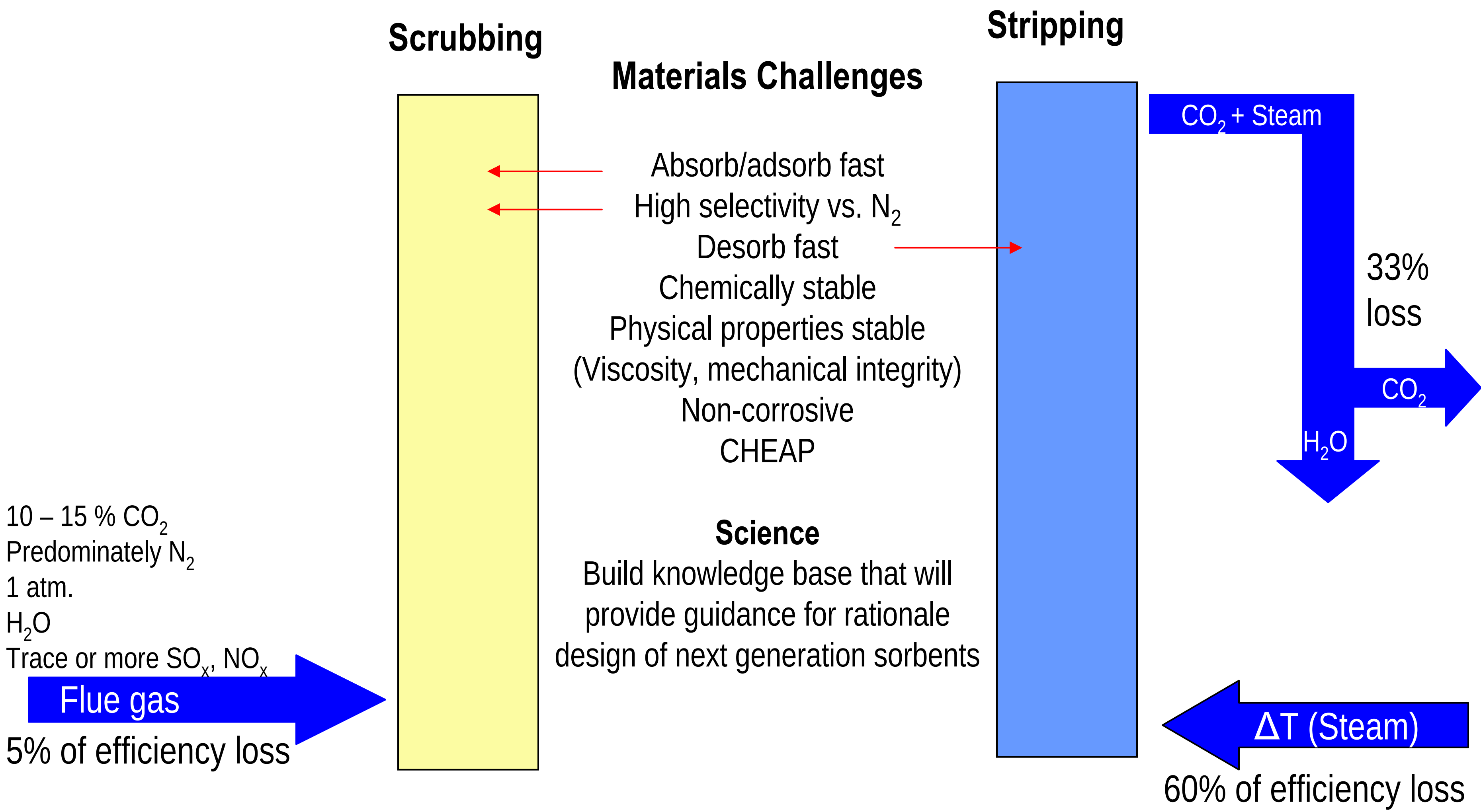
Presented to Office of Science and Fossil Energy

August 24, 2009

Outline

- Post-combustion Capture: Background and Challenges
- BES Current Portfolio relevant to CO_2 Capture
- Going Forward

Post-Combustion Capture



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Key Characteristics for CO_2 Capture (Post-Combustion)

- **Perform in presence of water (steam) and trace contaminants including SO_x and NO_x, etc.**
- **Temperature stability over a wide temperature range**
- **If Solid sorbent – mechanical stability, If liquid – no viscosity change**
- **Sustainable**
- **Cheap (scale)**

- **High selectivity for CO_2 over N_2**
- **Work in dilute streams (10% CO_2)**
- **Rapid kinetics for capture (scrubbing) and regeneration (stripping)**
- **Low energy regeneration (stripping)**
- **Non-corrosive**
- **High cycle life**

Challenge - Scale

- 30 Giga tons of Anthropogenic CO_2 in 2004
- Take 13.5 million Houston Astrodomes to hold that at atmospheric pressure*
- CO_2 from US electricity 2006 – only 1.05 million Houston Astrodomes

*From: George C. Marshall Institute Policy Outlook, June 2008.

Challenge - Science

Conundrum

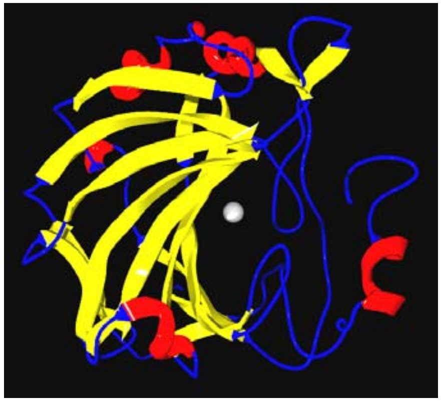
- To remove CO_2 from flue gas selectively and rapidly → strong bond
- To strip the CO_2 from scrubber with little energy need → weak bond

- Analogy – Superglue
- Challenge – Find the acetone – lower energy trigger

Photos from - http://www.supergluecorp.com/ - car originally from Australian TV show “Clever”

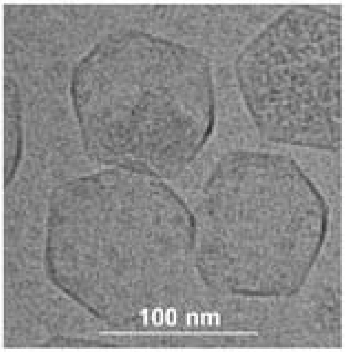
Biology and CO_2

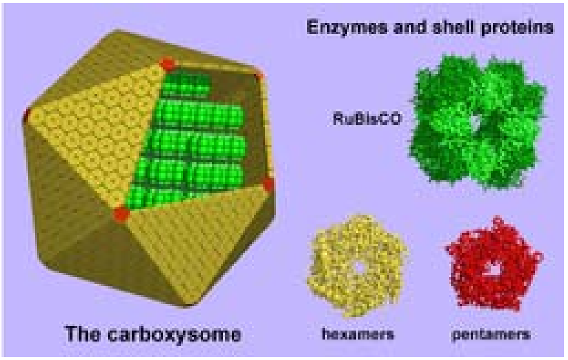
- Nature and CO_2
- Plants
  - Deal with dilute CO_2 (not efficiently)
  - Carbonic Anhydrase - in plants – increases CO_2 concentration
  - RuBisCO – plant enzyme converts CO_2 to sugar – 3 CO_2/sec



Ribbon diagram of human carbonic anhydrase with Zn atom in center

- Bacteria
  - Carboxysome - concentrates CO_2 levels to increase chemical transformation
  - Strategy: Concentrate, isolate and transform



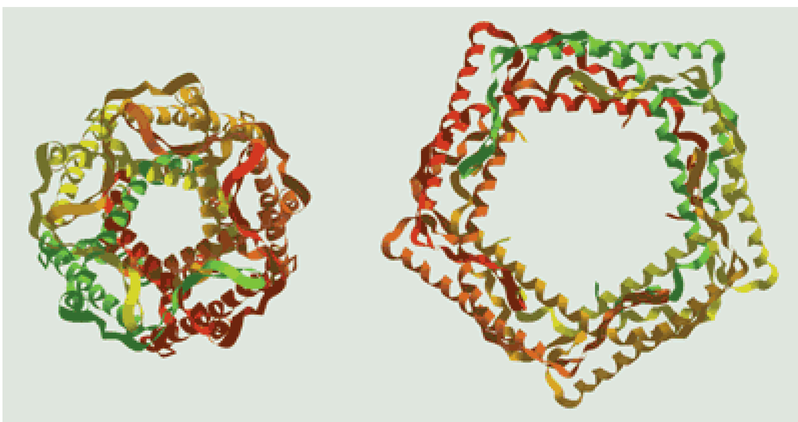


Carboxysomes – protein bacterial organelles
on left is electron microscope image,
on right is model of structure

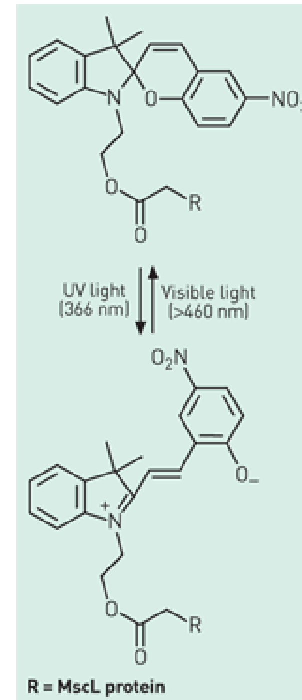
Source: http://en.wikipedia.org/wiki/File:Carbonic_anhydrase.png and http://en.wikipedia.org/wiki/Carboxysome

Nature's Triggers

- While nature does not deal with CO_2 ideally for post-combustion capture – can provide hints for non-thermal triggers
  - Ecoli have a channel protein that opens and shuts with pressure –
    - Has been modified to open and shut with light[1]



Channel proteins modified with spiropyran opens or closes channel with light.



Reversible spiropyran photo-switch.

  - Synapses electrical field triggers release of neurotransmitter

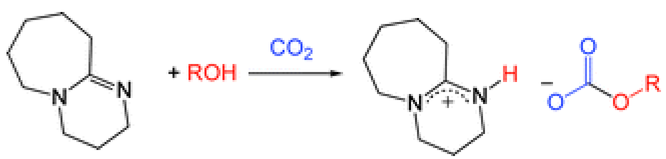
[1]Source – *Science,* **2005**, *309*,755, Copied from C&E News report http://pubs.acs.org/cen/news/83/i31/8331notw1.html

Novel Approaches: Base + Alcohol

Alternate science approach may offer a better pathway in the future   Heldebrant, PNNL

- Eliminate water and H bonding – reduces energy of stripping
  - Lower specific heat of organic liquids
    - Same strip temperature, considerable energy savings

- Organic amidine or biological guanidine base plus alcohol
  - Binds CO_2 – reversed with heat
  - Higher binding capacity for CO_2 than commercial MEA (monoethanolamine)
    - Design base to minimize hydrogen bonding – more energy savings



- Demonstrated uptake in 50% CO_2/ 50% N_2 , strip 90 to 130 C
- Issue - water form bicarbonate salt of base – strips MEA temperature

Source: Heldebrant et al. *Energy Procedia,* 1 (2009) 1187-1195

Science – Beyond 2020

- CO_2 sorbent that can be stripped with minimal energy
  - Look to Nature for ideas on triggers but unlikely to be a biological solution
  - Electrical, electrochemical, pressure, light, pH, phase change (liquid crystal)*
  - Nanoscale approaches

- Build the knowledge base to facilitate a rationale design of sorbents from first principles
  - Advanced computational modeling and theory - First-principles methods for capture and release of nonpolar molecules
  - Advanced characterization tools, including those supported by BES, to
    - Identify structure of binding sites
    - Understand kinetics and thermodynamics of sorption/desorption in realistic conditions
  - New chemistries for advanced sorbents
    - New sorbents
    - Synthesis

*Source: *Advanced Post-Combustion CO_2 Capture*, prepared for Clean Air Task Force, Howard Herzog, Jerry Meldon and Alan Hatton

Current BES Related Research

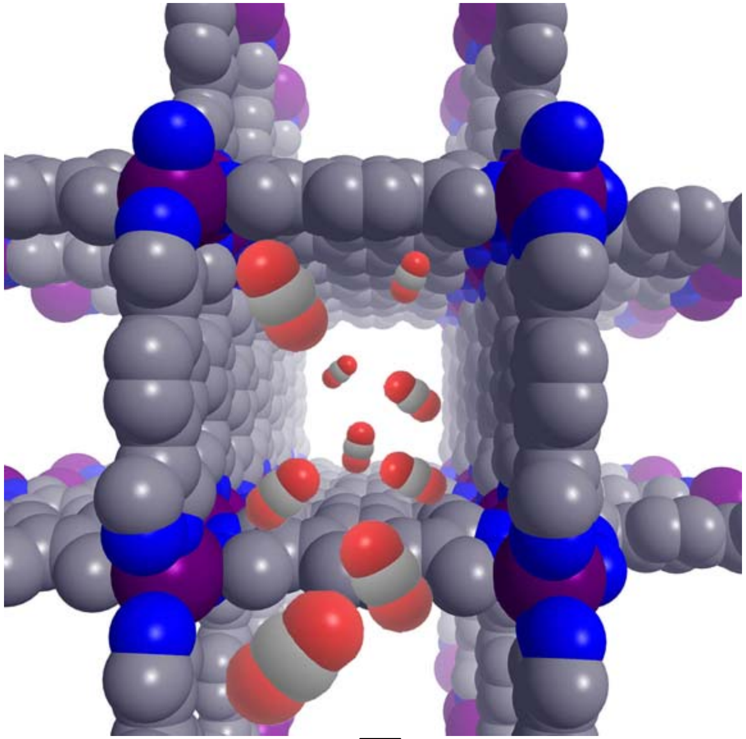
- **Directly related (EFRC funding) – CO_2 from N_2**
  - Zeolitic imidazolate framework (ZIFs) , metal organic frameworks (MOFs), membranes for separation
  - Synthesis, characterization, computation/modeling
- **CO_2 Binding/Separation**
  - Often from CH_4
  - MOFs, ZIFs
  - Polymer membranes
  - Computation, theory, modeling
- **Hydrogen – Binding and Separation**
  - H_2 sorbents
  - Inorganic clathrates, MOFs
  - Membranes
- **Separation Sciences, Materials, Theory & Computation**
  - Membrane synthesis
  - Transport
  - Theory and Computation

EFRC: Gas Separations for Clean Energy Technologies: (Smit, Berkeley)

Synthesis: Generate high surface area MOFs & self-assembled synthetic biomimetic polymer films

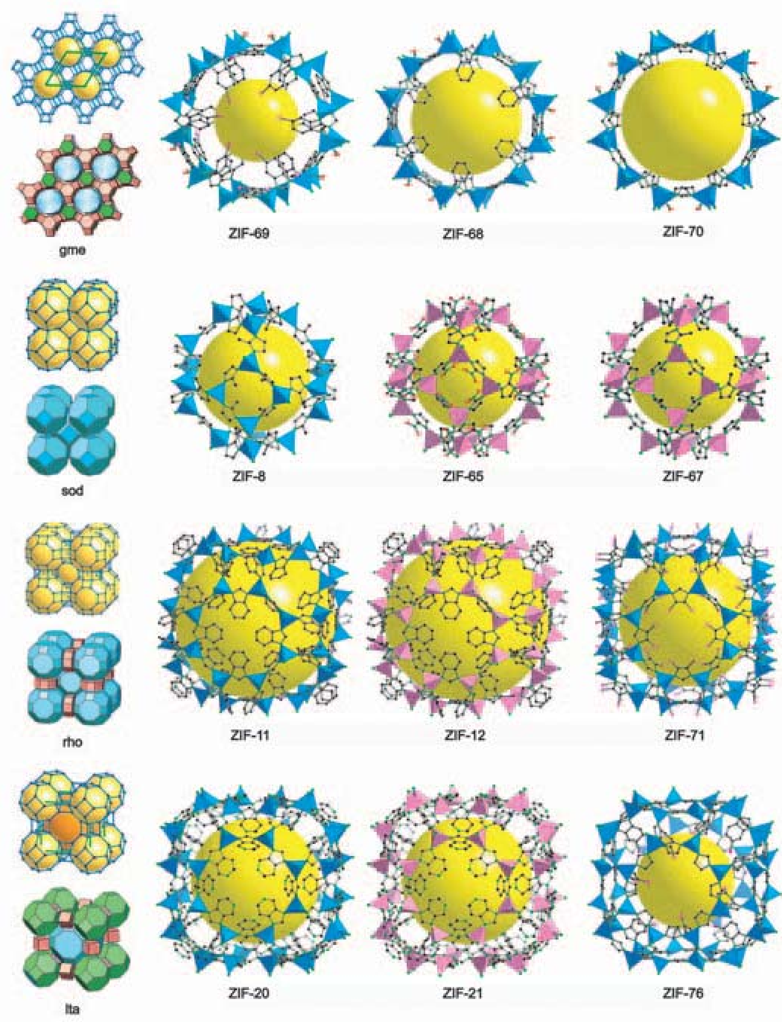
Characterization: Atomic-level structural characterization - before and after exposure to gas, accurate means of assessing the selectivity, kinetics, and thermodynamics of gas adsorbate binding – use to test computational models

Computational Separations: Strong computational component - understand chemical interactions at a molecular level, guide synthetic efforts



Goal: New strategies and materials for *energy efficient* selective *capture* or *separation* of CO_2 from gas mixtures based on molecule-specific chemical interactions

EFRC: Molecularly Engineered Energy Materials (Ozolins, UCLA)

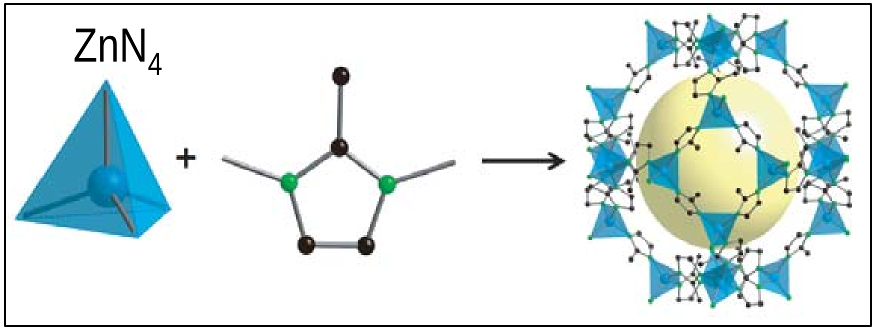


Capture is 1/3 of this EFRC: Novel ZIFs for gas separation including CO_2 capture

Yaghi – Synthesis, characterization

Asta – Electronic structure calculations

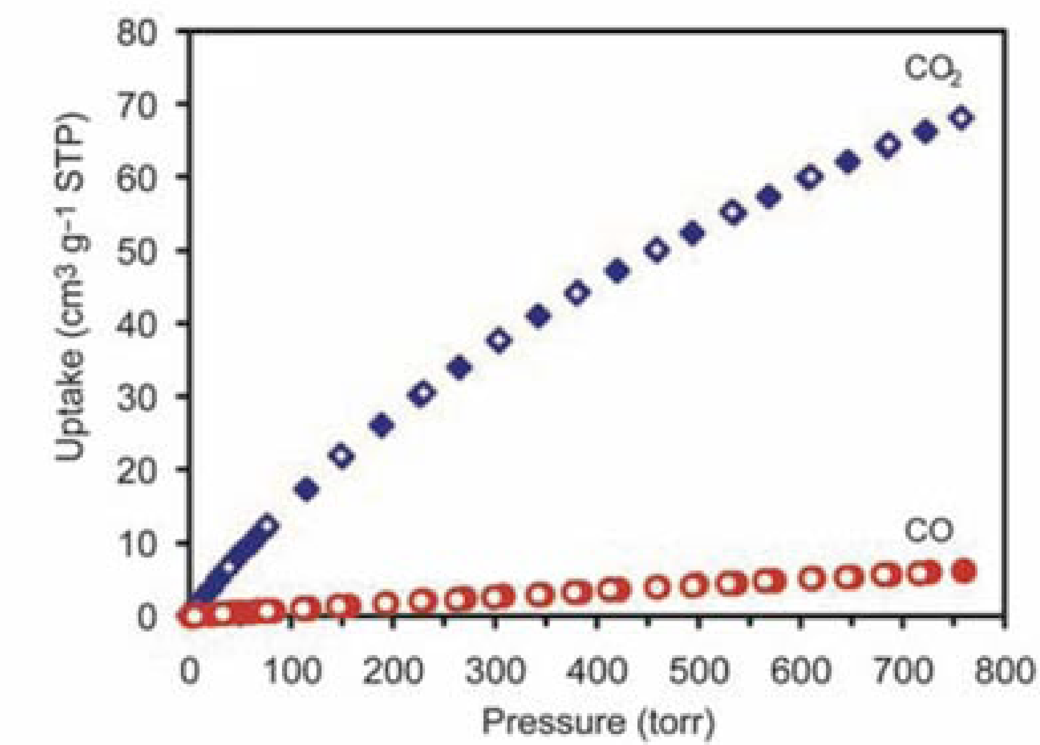
Laird & Houndonougbo – Monte Carlo Simulations

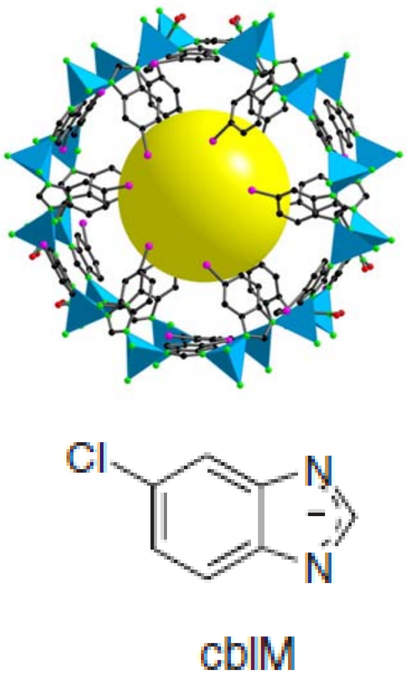


CO_2 Uptake in ZIF-69

Separate CO_2 from CO

- Surface areas to 1970 m^2/g
- Stable to 390 °C, 1 liter ZIF-69 holds ~83 liters of CO_2 at 273 K

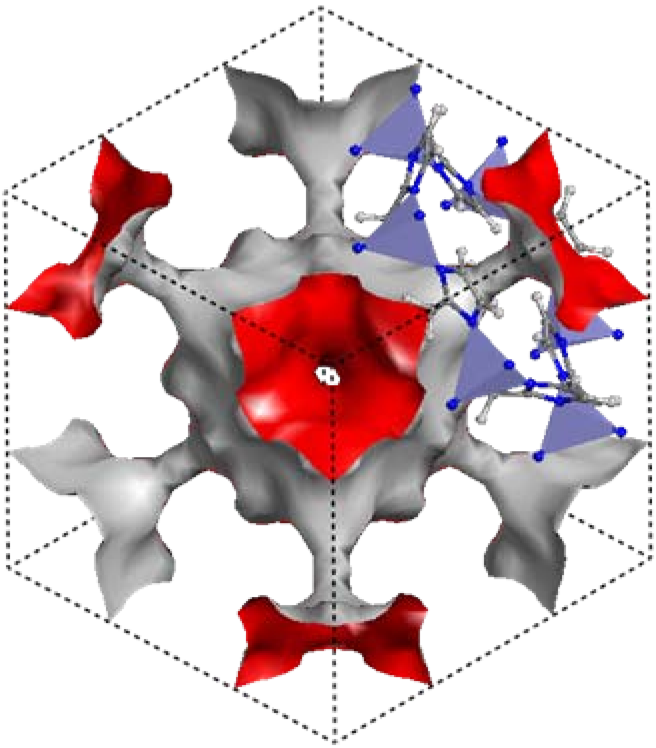


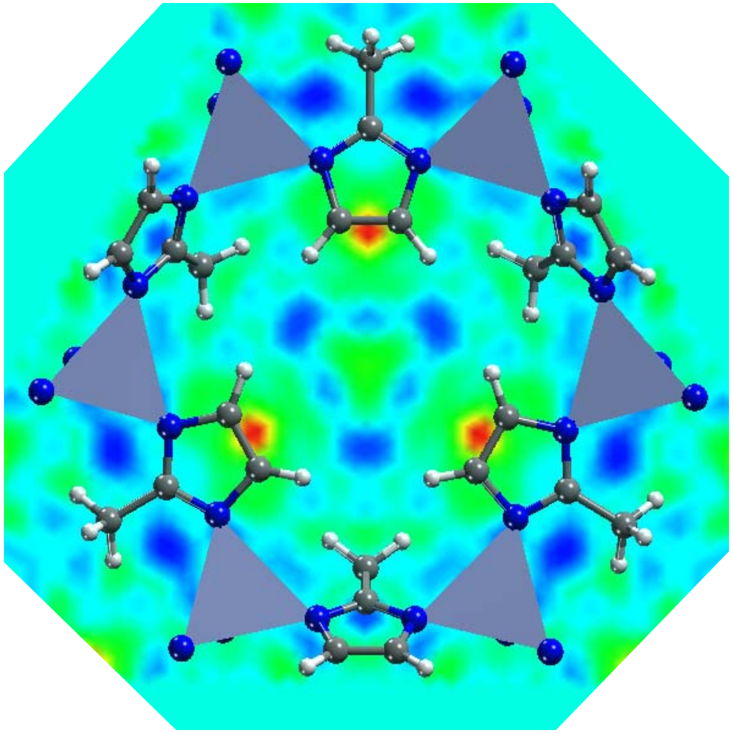


Gas adsorption isotherms of CO (red) and CO_2 (blue) into ZIF-69 at 273 K. Uptake and release are represented by solid and open symbols, respectively. ZIF-69 has been shown to have substantially greater uptake capacity for CO_2 over CO.

Yaghi's group, *SCIENCE* VOL 319 15 FEBRUARY 2008

Where Does Hydrogen Go in ZIFs? Apply Technique to CO_2





Calculated isosurface in ZIF-8

- **Available nanopore volumes are connected by narrow channels**

Difference Fourier analysis, showing the main-H_2 absorption sites in ZIF-8 are near the top of C-C bond of the linker and NOT the metal center

From: Taner Yildirim

Examples of BES-Supported Projects in Theoretical and Computational Modeling

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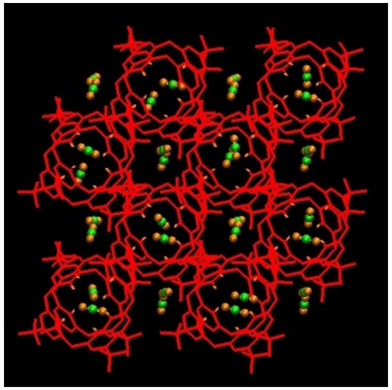


PNNL: Dang et al

One interpretation: Computer simulations show that at ambient temperatures, CO_2 molecules require ~ 4 times more energy than average to desorb. *Novel Strategies for selective heating may be necessary*.

Computational studies of load dependent guest dynamics and free energies of inclusion for CO_2 in low density p-*tert*-butylcalix[4]arene at loadings up to 2:1.

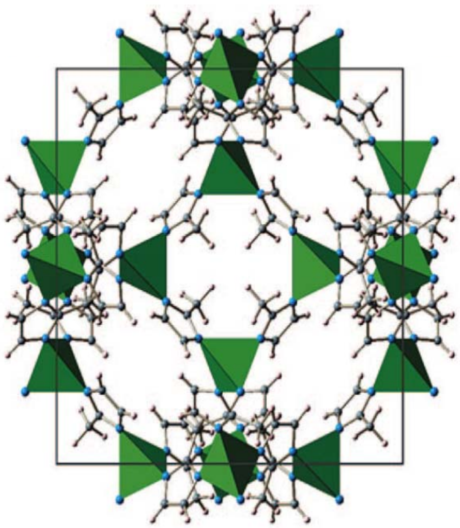
John L. Daschbach, Xiuquan Sun, Tsun-Mei Chang, Praveen. K. Thallapally, B. Peter McGrail, and Liem X. Dang. *J. Phys. Chem. A, Vol. 113, No. 14, 2009*

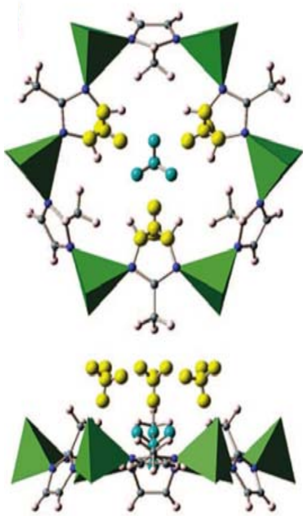
Theoretical and Computational Chemistry (Start FY09)**:** Modeling CO_2 capture and separation in zeolitic imidazolate frameworks (Wisconsin, Schmidt)

- Molecular Level Mechanism of CO_2 adsorption?
- Specificity of CO_2 over N_2 ?
- Mechanism for CO_2/N_2 Selectivity in ZIFs ?
- Thermal and Solvent Stability?

Neutron Diffraction

- Studied CD_4 absorption in a ZIF with a deuterated methyl imidazolate linker.

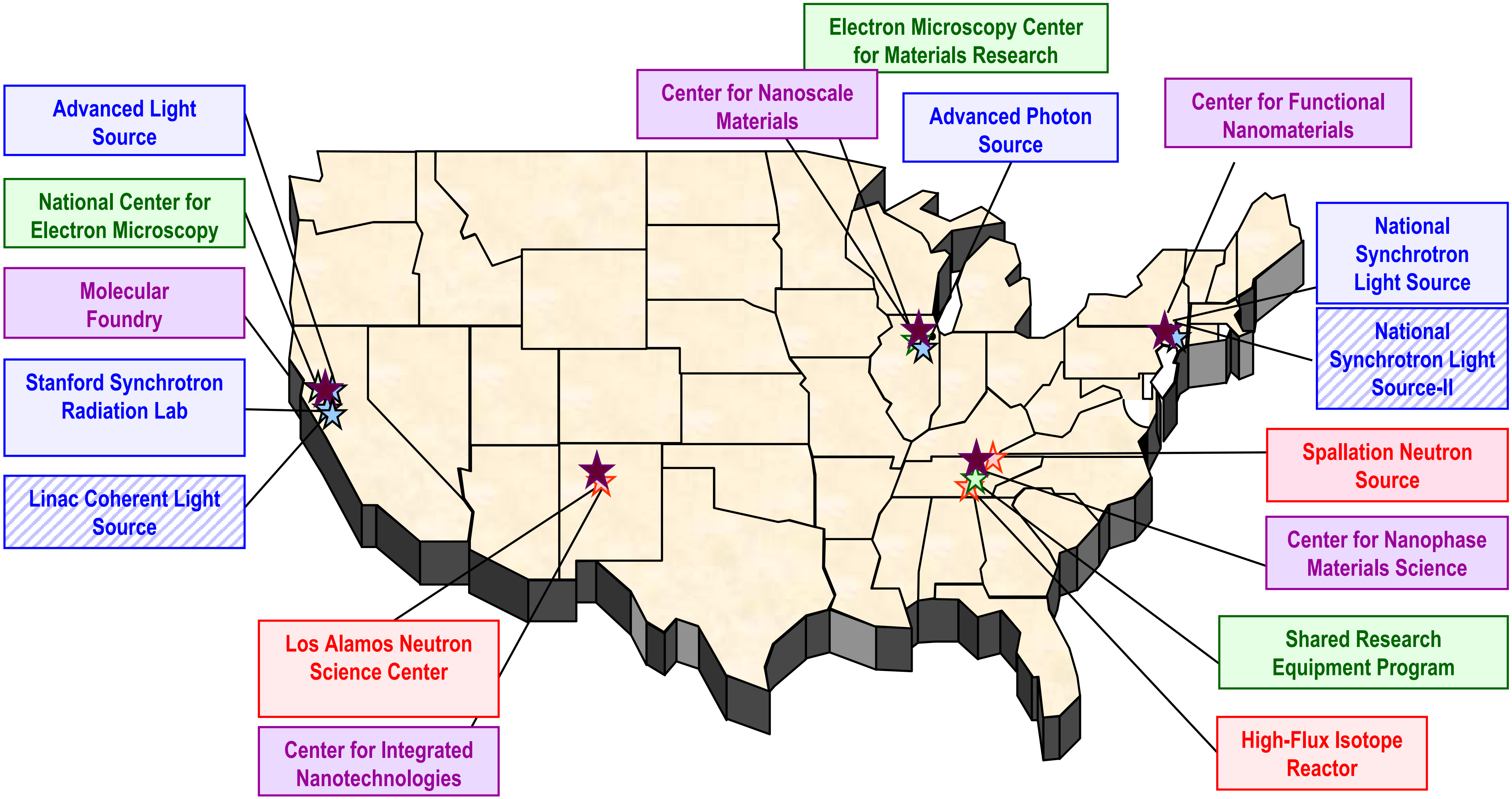




- Structure of ZIF
  - Changes with sorption
  - Changes with temperature
- Identify binding sites
  - Primary and stronger binding site - imidazolate
  - Secondary and weaker site - center

Note: This can be used with CO_2 since the organic linkers in the ZIF can be deuterated

BES Scientific User Facilities



- 4 Synchrotron Radiation Light Sources
- Linac Coherent Light Source (Under construction)
- 3 Neutron Sources
- 3 Electron Beam Microcharacterization Centers
- 5 Nanoscale Science Research Centers

"Basic Research Needs" Style Workshop – Carbon Capture Beyond 2020

- Timing – after Carbon Capture 2020 Workshop
- Build on output of Carbon Capture 2020 Workshop
  - Start - define the current state for both research and industrial needs (factual document)
  - Goal - Identify priority research directions for the challenges beyond 2020
- Educate basic researchers on the technical and scientific challenges of CO_2 capture
- Approach (Basic Research Needs style and format)
  - Integration with DOE BES, DOE FE, Academia, National Labs, and Industry
- Draft Charge:

  "Identify basic research needs and opportunities underlying post-combustion carbon capture technology, with a focus on new or emerging science challenges with potential for significant, long-term impact on the effective separation and capture of CO_2 in post-combustion gas streams."

Carbon Capture - Beyond 2020 Workshop

- Workshop format:
  - Plenary talks on technical and scientific challenges
  - Breakout panels focused on development of priority research directions
  - Crosscutting panel focused on identification of grand challenge science themes
  - Dedicated report writers to ensure rapid progress on written report
- Finite focus means moderate size: 50-75 participants, including agency reps
- Venue in the DC area to facilitate attendance by DOE staff
- 6 months timeline from initial planning to producing a final workshop report
  - Planning could begin in parallel with Carbon Capture 2020
  - Carbon Capture - Beyond 2020 workshop would be held after the report from Carbon Capture 2020 is available

- Thank you
- Questions?

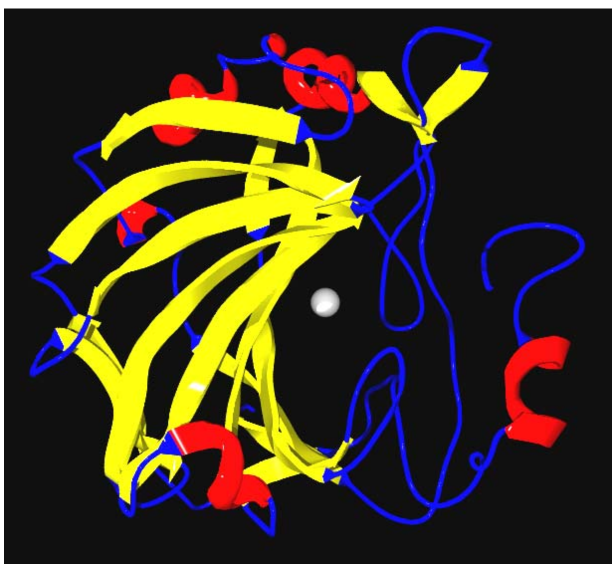
Biology and CO_2

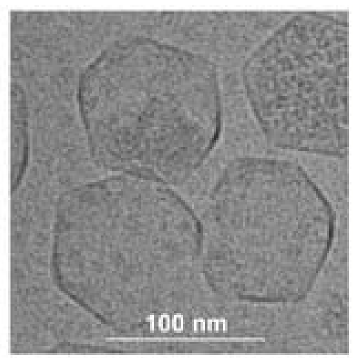
- Nature and CO_2
  - Also deals with dilute CO_2 (not efficiently)
  - Carbonic Anhydrase, in animals – interconvert CO_2 and bicarbonate, in plants – increases CO_2

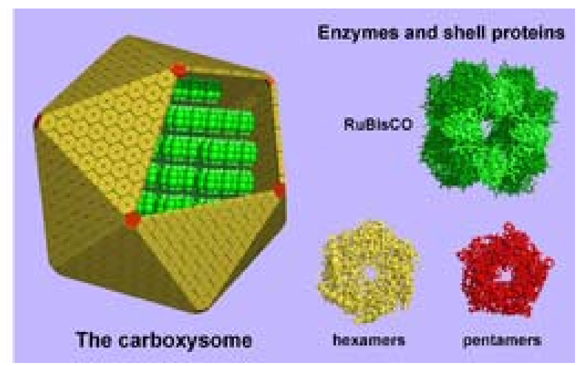
$CO_2 + H_2O \xrightarrow{\text{Carbonic Anhydrase}} HCO_3^- + H^+$ catalytic rates 10^4 to 10^6 per sec

$HCO_3^- + H^+ \longrightarrow H_2CO_3 \rightarrow CO_2 + H_2O$ (works in lungs) Low concentrations = 15 sec

  - RuBisCO – plant enzyme converts CO_2 to sugar– 3 CO_2/sec







Nature - concentrators in bacteria to increase CO_2 levels, strategy concentrate, isolate and transform

Source: http://en.wikipedia.org/wiki/File:Carbonic_anhydrase.png and http://en.wikipedia.org/wiki/Carboxysome

Basic and Applied R&D Coordination

How Nature Works ··· to ··· Design and Control ··· to ··· Technologies for the 21st Century

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Grand Challenges

How nature works

- Controlling materials processes at the level of quantum behavior of electrons
- Atom- and energy-efficient syntheses of new forms of matter with tailored properties
- Emergent properties from complex correlations of atomic and electronic constituents
- Man-made nanoscale objects with capabilities rivaling those of living things
- Controlling matter very far away from equilibrium

Discovery and Use-Inspired Basic Research

Materials properties and chemical functionalities by design

- Basic research for fundamental new understanding on materials or systems that may revolutionize or transform today's energy technologies
- Development of new tools, techniques, and facilities, including those for the scattering sciences and for advanced modeling and computation
- Basic research, often with the goal of addressing showstoppers on real-world applications in the energy technologies

Applied Research

- Research with the goal of meeting *technical milestones*, with emphasis on the development, performance, cost reduction, and durability of materials and components or on efficient processes
- Proof of technology concepts

Technology Maturation & Deployment

- Scale-up research
- At-scale demonstration
- Cost reduction
- Prototyping
- Manufacturing R&D
- Deployment support

BESAC & BES Basic Research Needs Workshops

BESAC Grand Challenges Panel

DOE Technology Office/Industry Roadmaps

Approaches Under Development

- Newer Materials
  - ZIFs – zeolite imidazole frameworks
    - Imidazoles increase selectivity
    - Non silicates – resistant to degradation from steam
  - Membranes – functionalized with amines or other groups to enhance selectivity (>200), increase cycle life
    - Chemical functionalization of polymer can increase selectivity beyond what is achieved with size separation
    - Fibrous membranes coated with amines (glass or carbon fiber mesh)
  - Poly (ionic liquids)
    - Some have higher sorption than ionic liquids
    - Avoid viscosity increases seen with some ionic liquids
  - Ion Engineering – amines in ionic liquids (65% cost savings over water)

Source: *Advanced Post-Combustion CO_2 Capture*, prepared for Clean Air Task Force, Howard Herzog, Jerry Meldon and Alan Hatton

Status of Current Technology

- Amines
  - Monoethanolamine (MEA) or amine blends - MEA with methyldiethanolamine (MEDA) or sterically hindered amines
  - NH_3
  - Can be aqueous solution in post-combustion
- Chilled ammonia (35 F)
  - ammonium carbonate to ammonium bicarbonate

- Advantages - amines
  - Selective, reversible, nonvolatile and somewhat inexpensive

- Disadvantages - amines
  - Corrosive, degrade esp. with O_2 or SO_2 present, require large thermal energy for stripping
  - NH_3 – less energy to strip but toxic vapor to deal with

Energy Management (Post- combustion)

- Total estimated cost to consumer
  - Capture and compression (typically 100 atm or more) adds 35 – 40% to price of generating electrical power (Monoethanolamine (MEA) Based)
  - Computer calculations – with piperazine + MEA only 20% increase

- Parasitic energy load
  - Capture + compression drops plants thermal efficiency from 38% to 29%
  - 60% - Steam taken from turbines for stripper reboiler - fundamental research focus
  - 33% - Electric to drive CO_2 Compressor
  - 5% - Electricity to drive flue gas through scrubber

Source: *Advanced Post-Combustion CO_2 Capture*, prepared for Clean Air Task Force, Howard Herzog, Jerry Meldon and Alan Hatton

Today's Carbon Capture Approaches – A Brief Review

- Pre-Combustion Capture
  - Applicable to plants where coal gasification is first processing step
    - Few existing plants – will apply mostly to new plants
    - CO_2 capture should be easier

- Oxy-Combustion
  - Generally involves cryogenic oxygen separation plant
  - Novel concepts involving oxygen transport membranes and chemical looping – lab/pilot scale development

- Post-Combustion Capture
  - Existing coal fired power plants
  - Commercial amine-based processes available from Fluor, Mitsubishi Heavy Industries,& others
    - Parasitic power requirements and cost -major challenges
  - Pilot and demonstration projects - "advanced amines," chilled ammonia, ionic liquid solvents
  - New approaches, "Breakthrough Concepts," - metal organic frameworks (MOFs), zeolite imidazole frameworks (ZIFs), membranes, and other sorbents - smaller scales