Multicomponent Gas Separations Using Porous and Nonporous Organic Crystalline Solids

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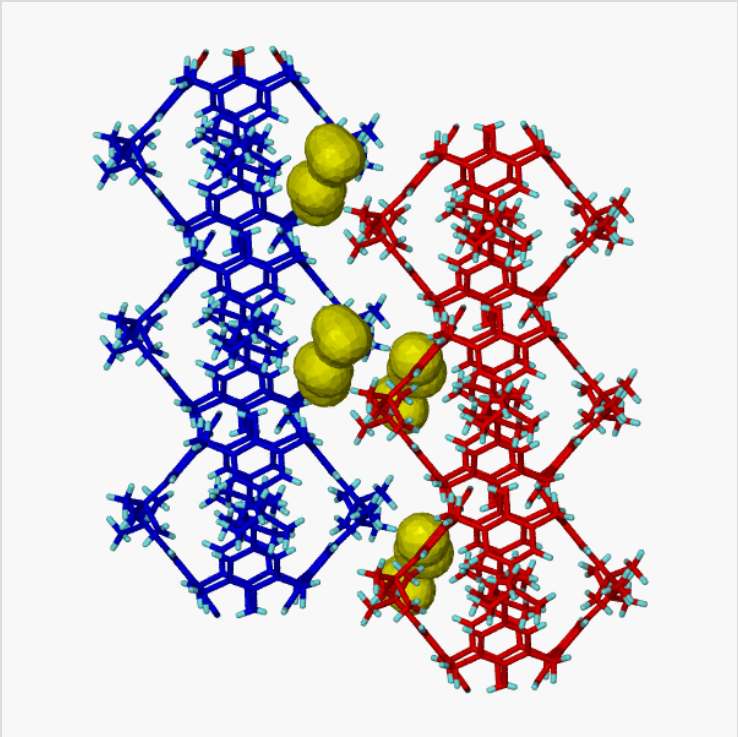
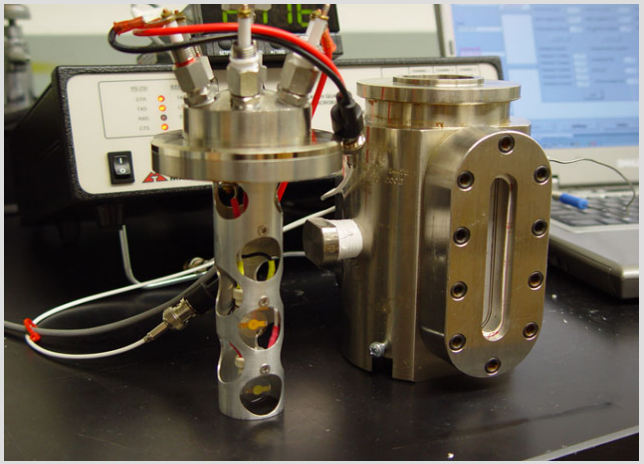
Why Organic Solid Sorbents?

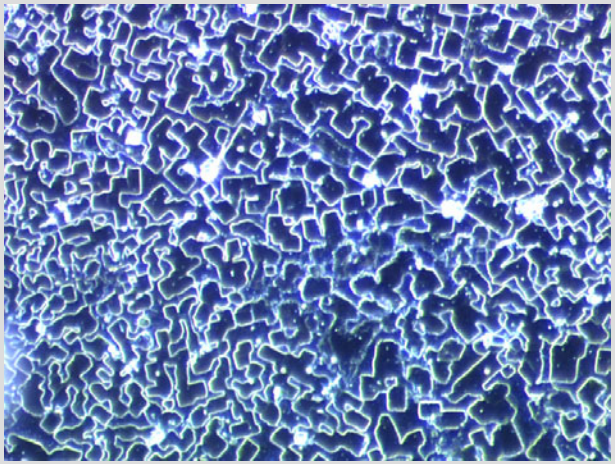
- Several classes of organic solids (including clathrates) are stable at high temperatures (250°C+)
- Cage/pore properties can be tailored to targeted guest
  - Completely different stability range as compared with gas hydrates
  - Molecular engineered selectivity for CO_2 (or other gases)
- Can be produced in engineered structures, i.e. thin films, membranes, microporous materials
- No covalent/ionic chemical bonds involved – gas separation and retrieval cycles performed without degradation of the host



Gas Absorption/Desorption Measurement

- Quartz Crystal Microbalance (QCM) system
  - CVD step
    - Purifies compound after bulk synthesis step
    - Isolation from contact with atmosphere
  - Direct measurement of mass change
    - Avoids complications with pressure-based isotherm measurements
    - No buoyancy problems to address as with TGA
    - Highly sensitive technique (nanogram quantities)

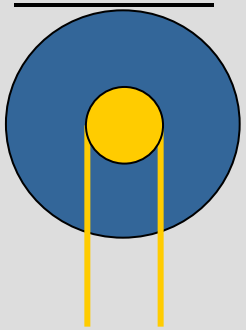




QCM Measurements

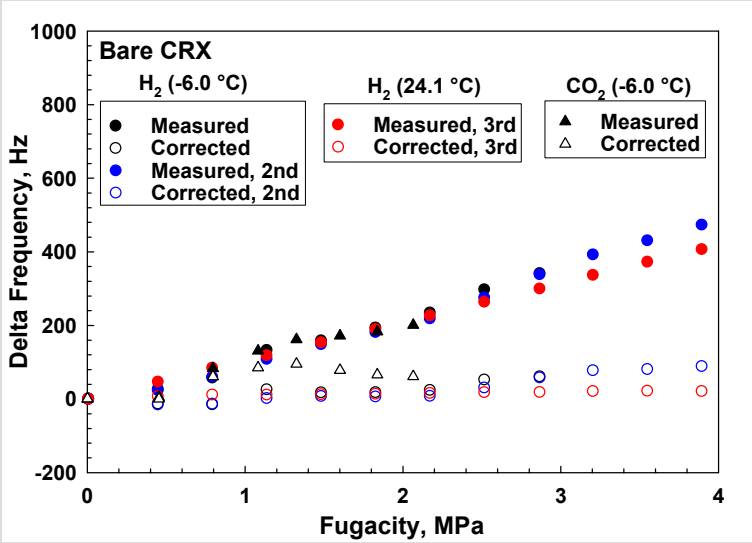
- Mass change is proportional to change in oscillator frequency but…
- Correction factors are required for:
  - Pressure (+)
  - Viscosity (-)
  - Surface Roughness (-)
  - Temperature (+)
    - Not significant between 0°C and 70°C but important outside these limits

Quartz Crystal Oscillator

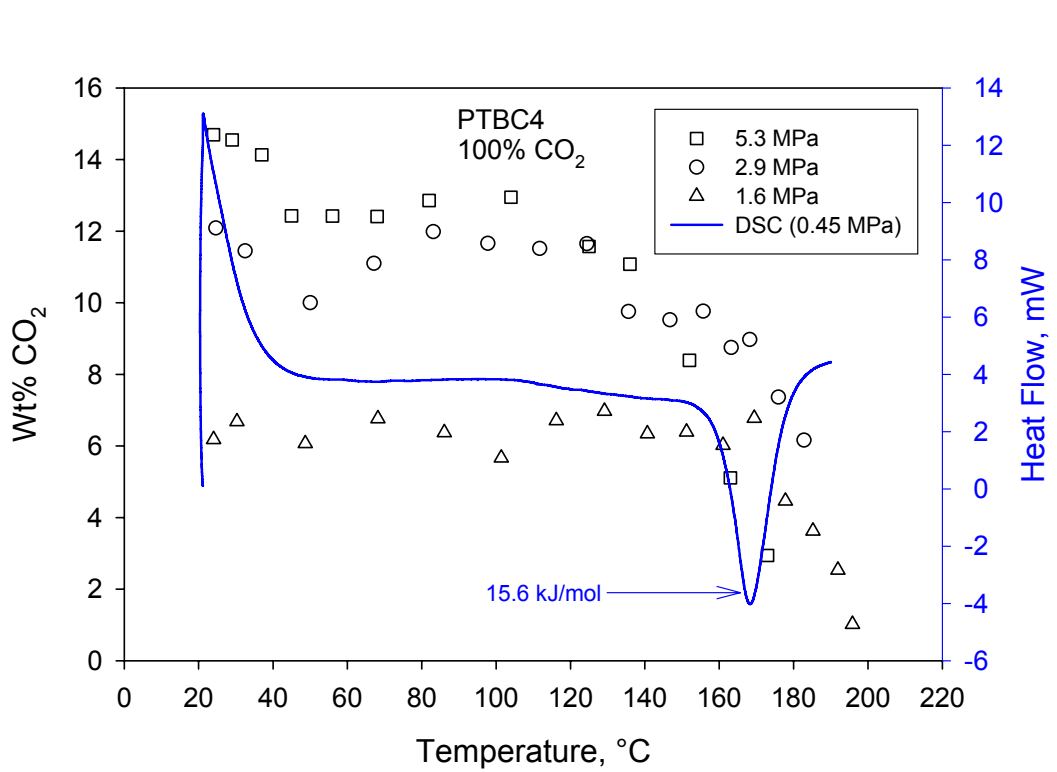


Sauerbrey Equation

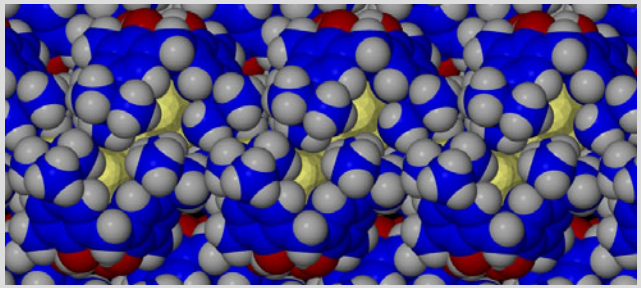
$$\Delta f = \frac{-2\Delta m}{A\sqrt{\mu_q \rho_q}} f_o^2$$



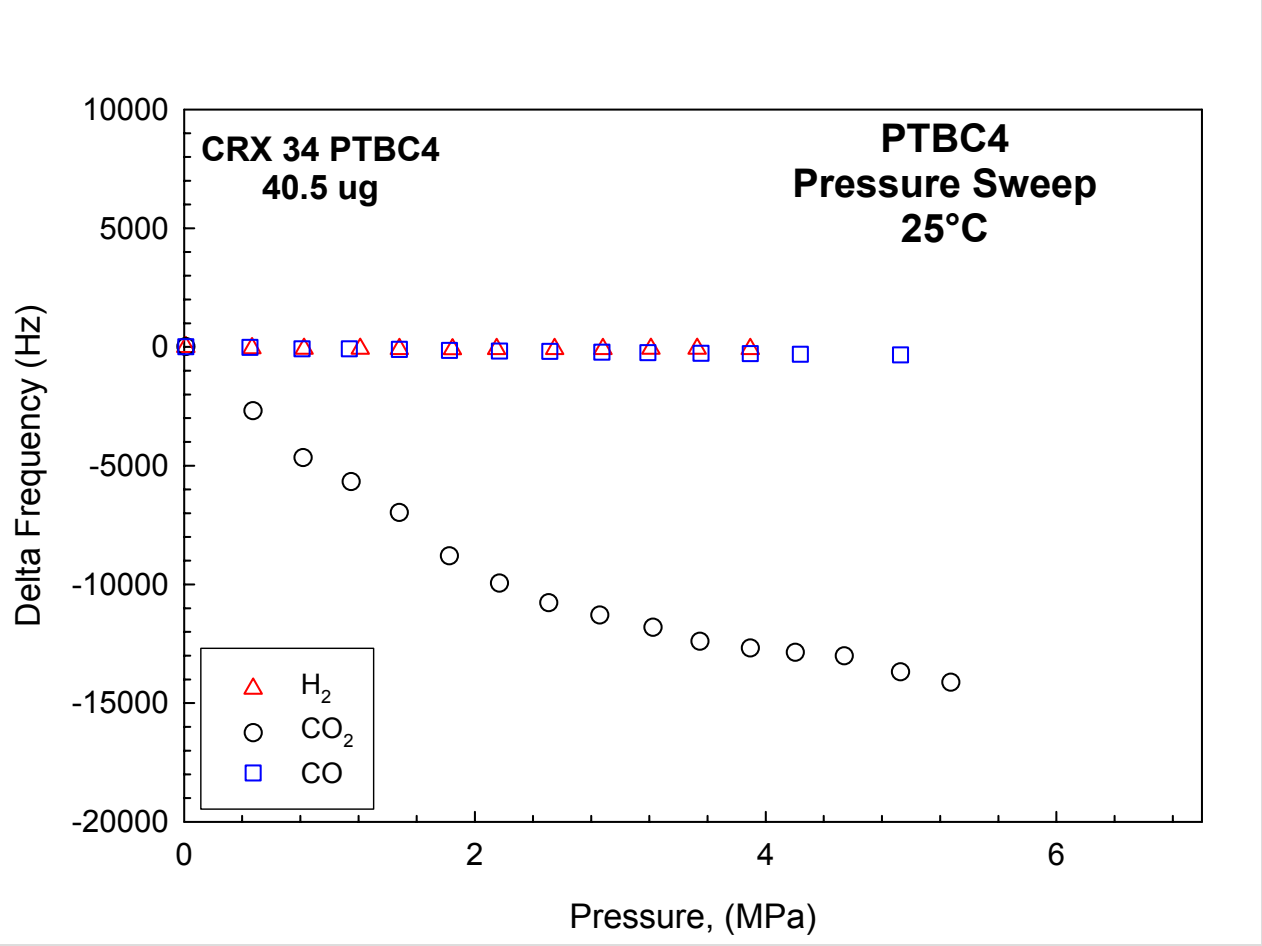
Mass Loading on PTBC4



- Material has remarkable ability to retain CO_2 at high temperatures
- Mass loading in MEA/ DEA/Selexol is on the order of 5 to 7 wt% CO2



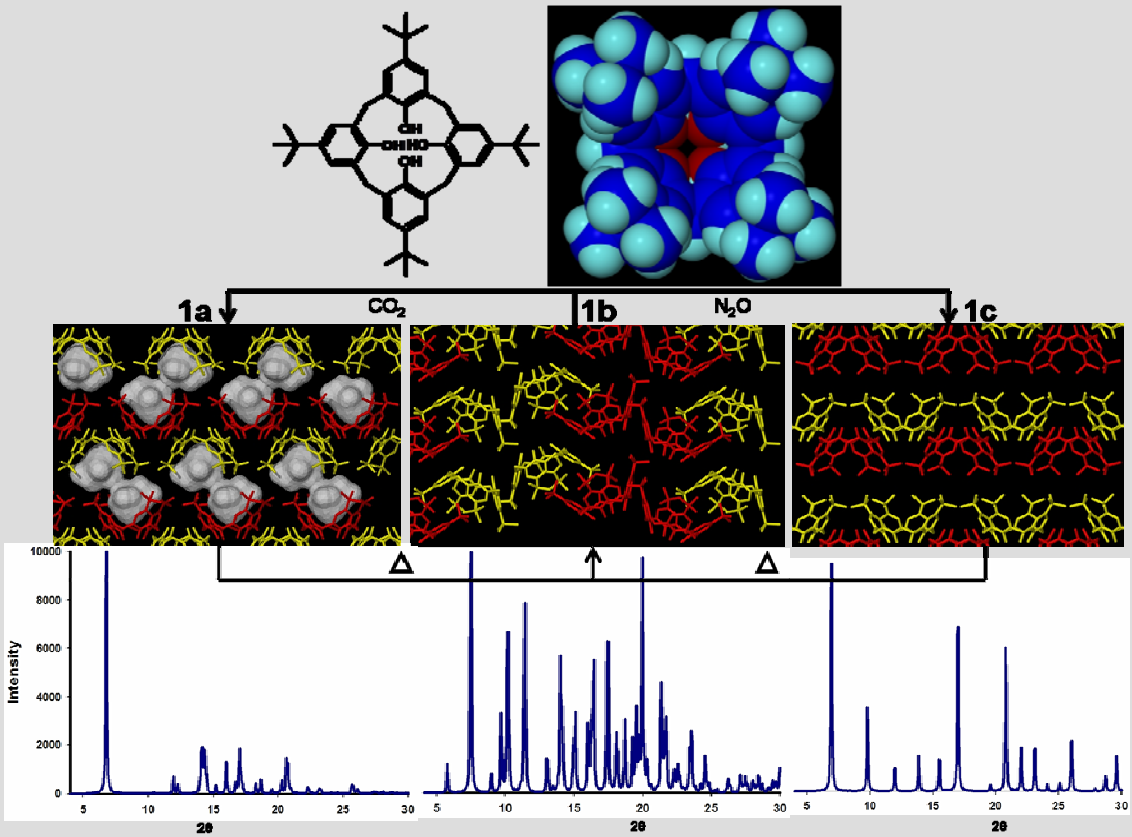
Uptake of CO and H_2

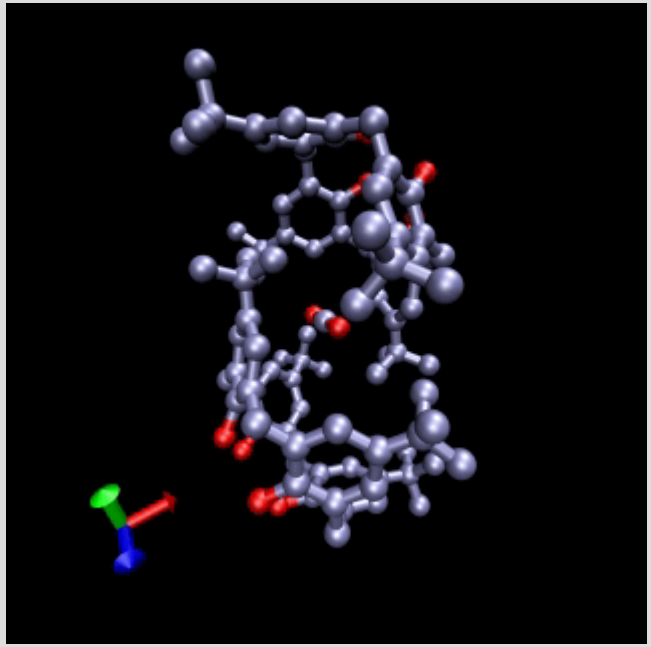


D8 Discover with GADDS

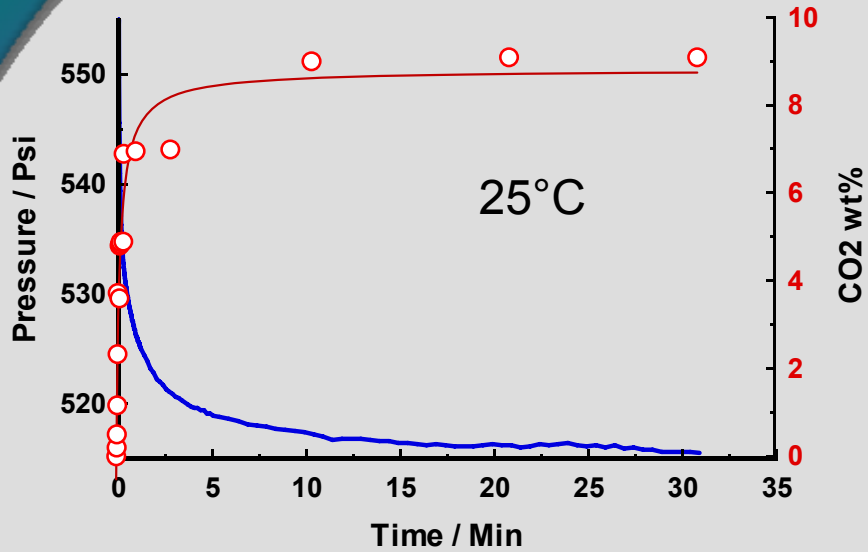
- X-Ray Photon Source
  - Rotating Anode
    - 18 kW
    - Transmission
    - Variable spot focus size
- High precision goniometer
  - Vertical and lateral movement of sample chamber
- Sample Stage
  - -100 to +227°C
- GADDS 2-D Detector
  - Real time data collection
  - 100 micron spatial resolution
  - 70° of data collected in seconds

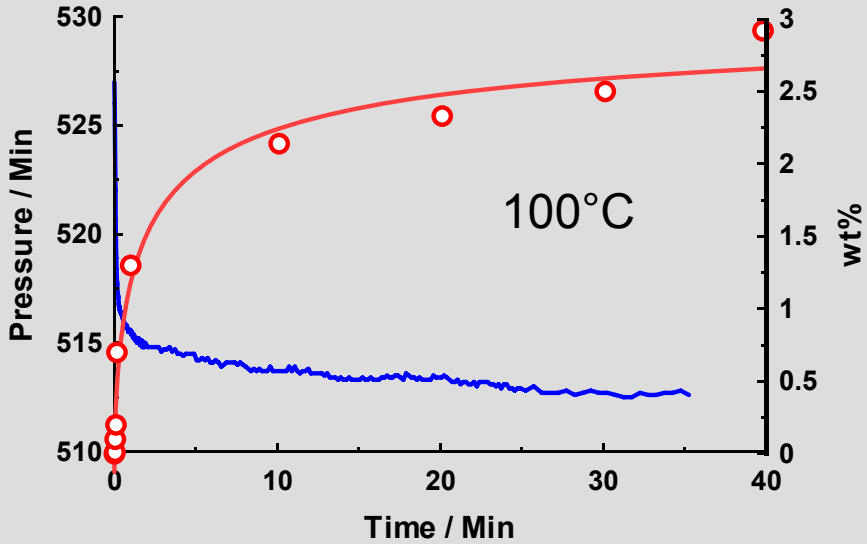
Molecular Dynamics Simulation of CO_2 Inclusion Phenomena in PTBC4

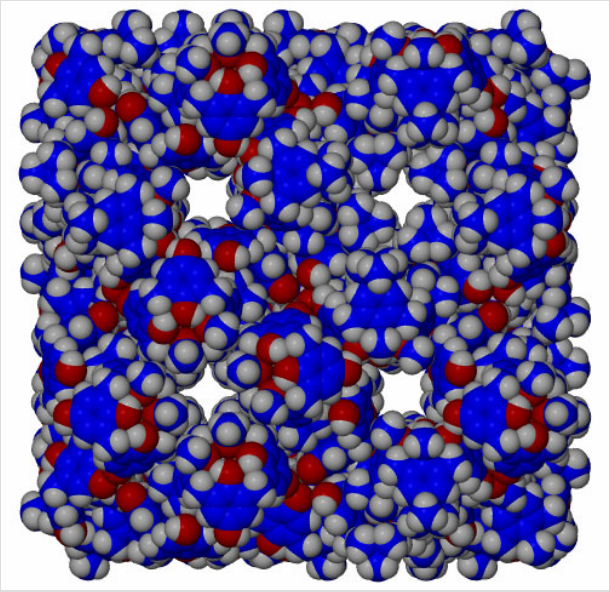


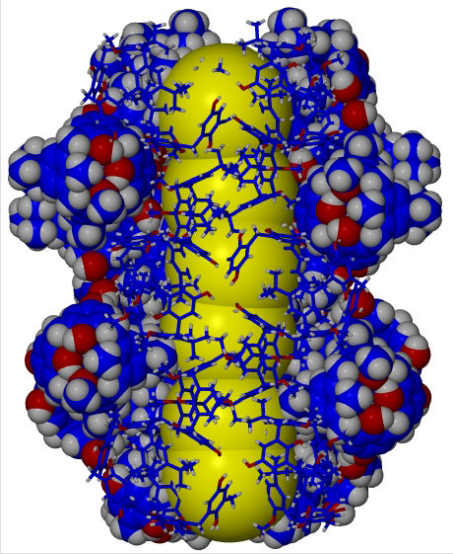


CO_2 uptake in Calixdihydroquinone

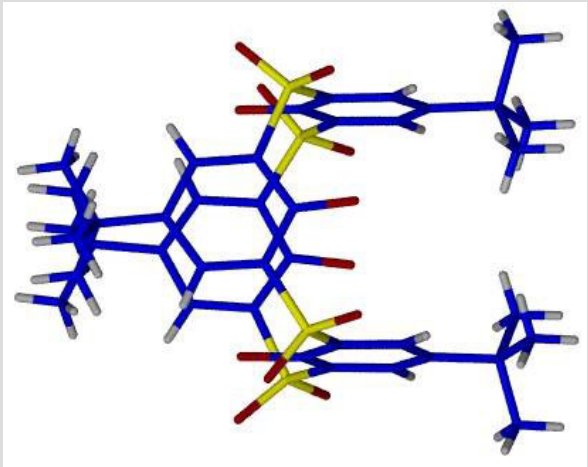






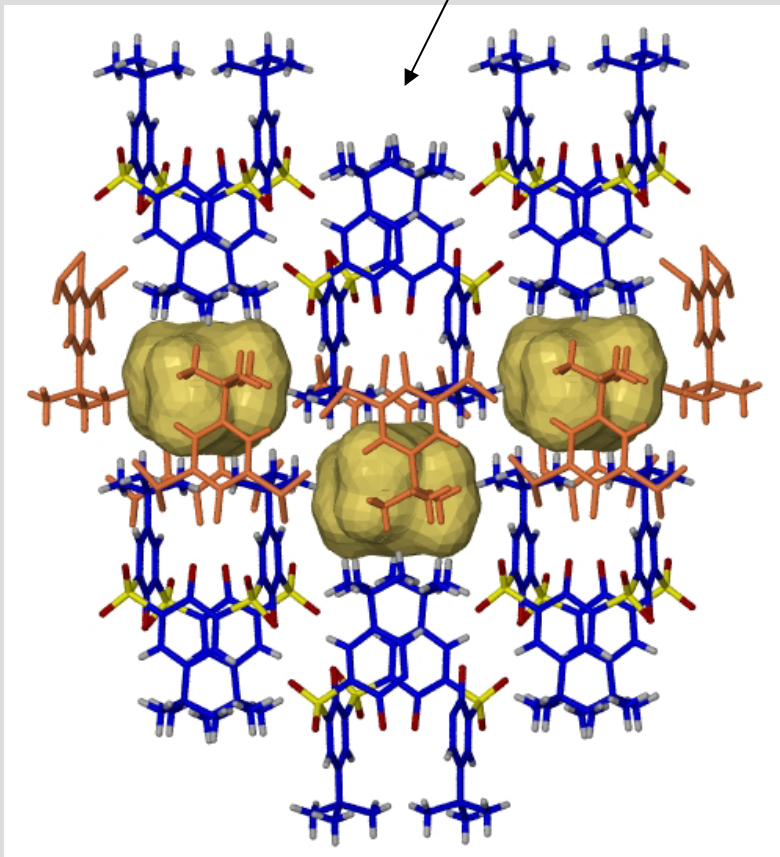


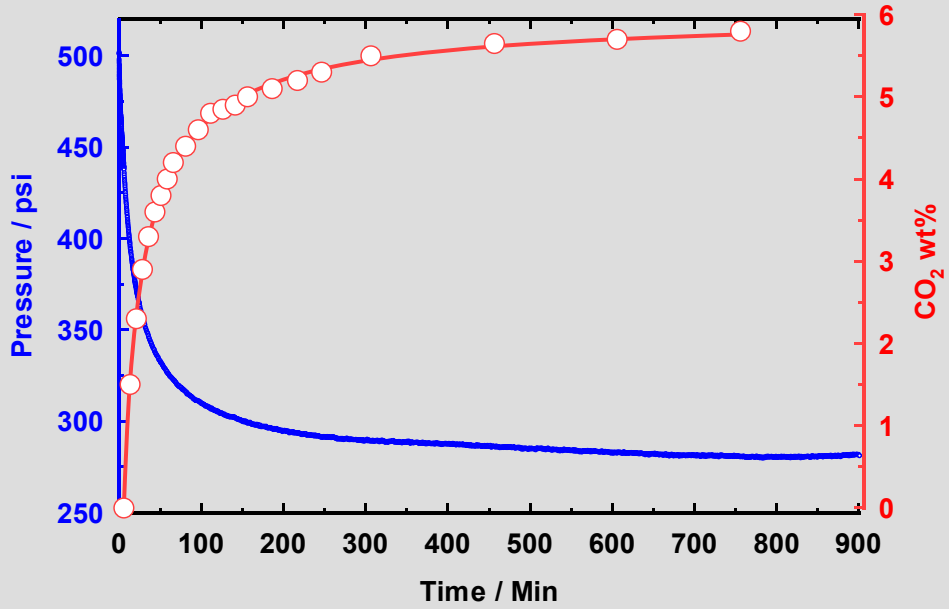
Uptake of CO_2 in Thiacalixarene Derivative



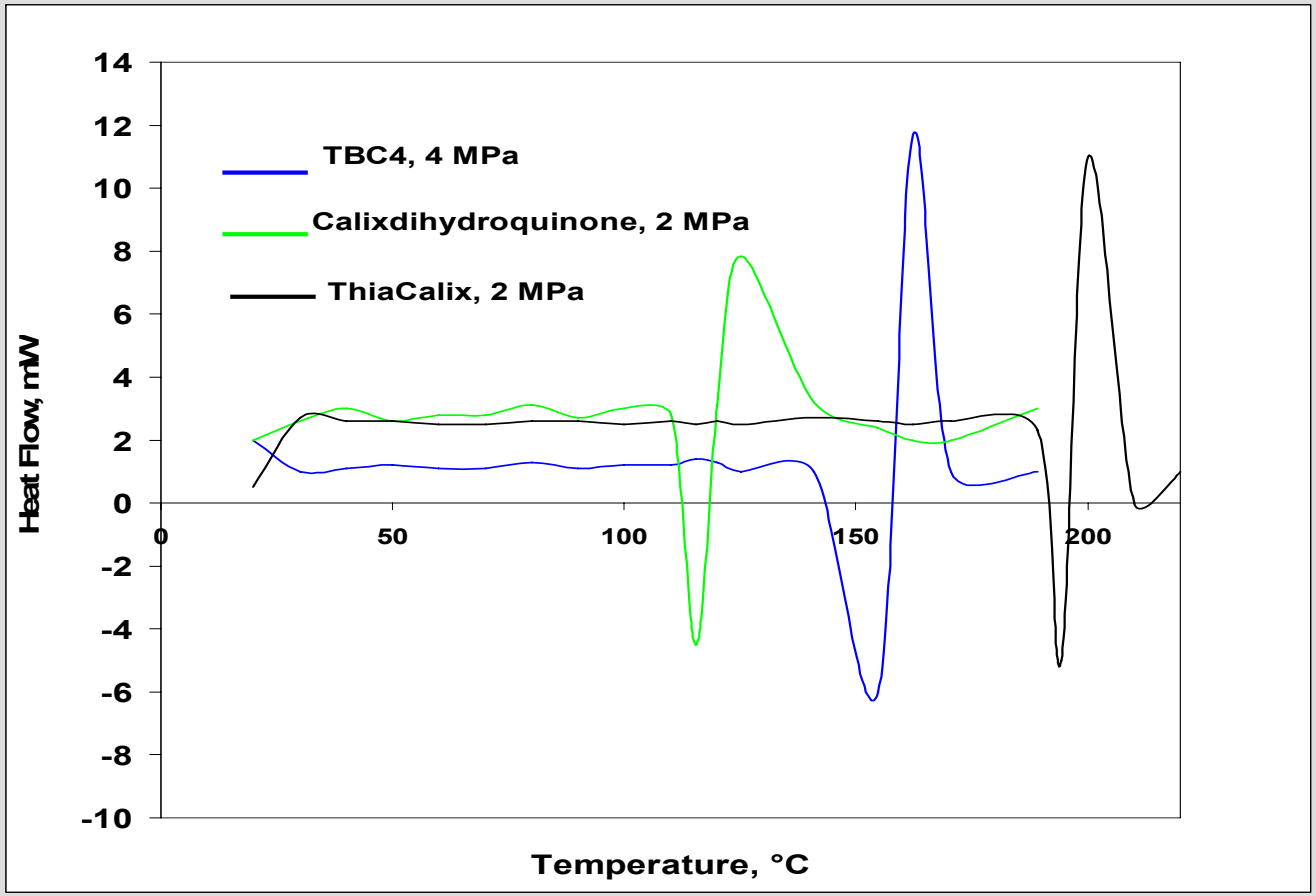
1,3-alternate conformer

Void space





CO_2 uptake at High Temperature using DSC in Porous and "Nonporous" Materials



Economic Analysis Basis

- Reference application and technology
  - IGCC power plant with CO_2 capture at near ambient temperature
  - Two-stage Selexol
- Alternative technology
  - Organic solid sorbent PTBC4 for CO_2 capture
  - Absorption data
    - Obtained from experiments with various particle sizes
    - Pellet data when available

Absorption Bed Modeling Inputs

(key inputs in red)

- Inlet Stream
  - Sorbate MW
  - Face velocity
  - Temperature
  - Total pressure and sorbate pressure
- Bed
  - Depth and cross sectional area
  - Void Fraction
- Adsorbent
  - Density
  - Starting loading and maximum loading
  - Absorption rate data

First Cut Economic Analysis

Power Output Analysis

	Reference Case	PTBC4 Case
Gross Power Output, MW	741.1	741.1
Selexol Process Power, MW	7.8	3.8
TBC4 Process Power, MW	0.0	3.2
Average CO2 Compressor Power, MW	28.9	28.9
Other Parasitic Power, MW	141.0	141.0
Plant Net Power Output, MW	563.4	564.1
Plant Annual Capacity Factor	0.85	0.85
Plant Annual Energy Output, MWh	4,194,779	4,200,646

Electricity Cost Analysis

	Reference Case	PTBC4 Case
Selexol, $/MWh	3.63	2.45
TBC4 CO2 Capture, $/MWh	0.00	0.63
CO2 Compression, $/MWh	1.36	2.44
Subtotal, $/MWh	**4.99**	**5.51**
All Other Components, $/MWh	35.16	35.12
Total Capital, $/MWh	40.15	40.63
Annual Fuel, $/MWh	14.00	13.98
Annual O&M, $/MWh	13.48	13.47
Grand Total, $/MWh	67.64	68.08

Conclusion

- Fundamental breakthroughs have occurred in
  - Precision measurement techniques for gas absorption/desorption with organic crystalline sorbents
  - High-pressure x-ray diffraction analyses
- Reasonably good mass loadings have been measured for CO_2 with multiple compounds (more are being synthesized and studied)
- No significant absorption of CO or H_2 detected
- Groundbreaking work completed on MD simulation with more to come
- All data so far suggests that continued research will unlock the potential of these materials for combined high-pressure, high-temperature CO_2 separations

Desorption Option Pros and Cons

- Thermal swing, pressure swing, or combination theoretically possible
- Thermal swing uses less valuable energy, but slower
- Pressure swing uses more valuable energy, but is quicker
- Quicker absorption/desorption allows smaller, less expensive beds
- Analysis will capture impacts of different thermal energy use and recompression requirements on power plant cost and performance