

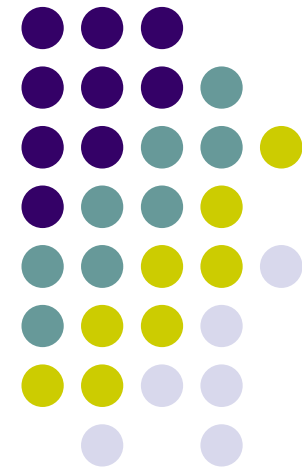
# A novel CO<sub>2</sub> capture system



MIDN William Eucker IV  
United States Naval Academy  
Annapolis, MD

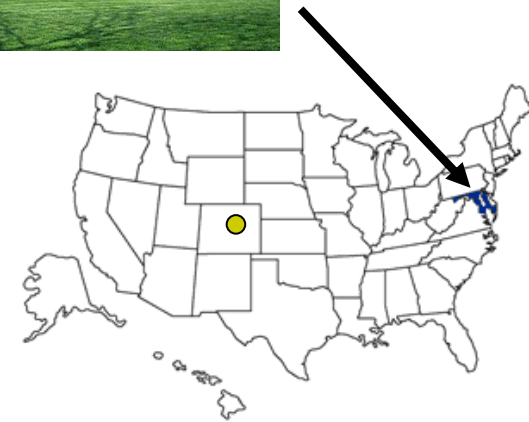


ICENES 2007  
Istanbul, Turkey



# USNA: Basics

- Federal Military Academy
- **Established:** 1845
- **Superintendent:**  
VADM Rodney Rempt, USN
- **Undergraduates:** 4,000
- **Location:** Annapolis, Maryland, USA
- **Campus:** Naval base, 338 acres
- **Motto:** *Ex Scientia Tridens*
- **Mascot:** Bill the Goat
- **Athletics:** Extensive varsity + intramural program (27v,100%)
- **Admission rate:** 11%
- **Website:** [www.usna.edu](http://www.usna.edu)





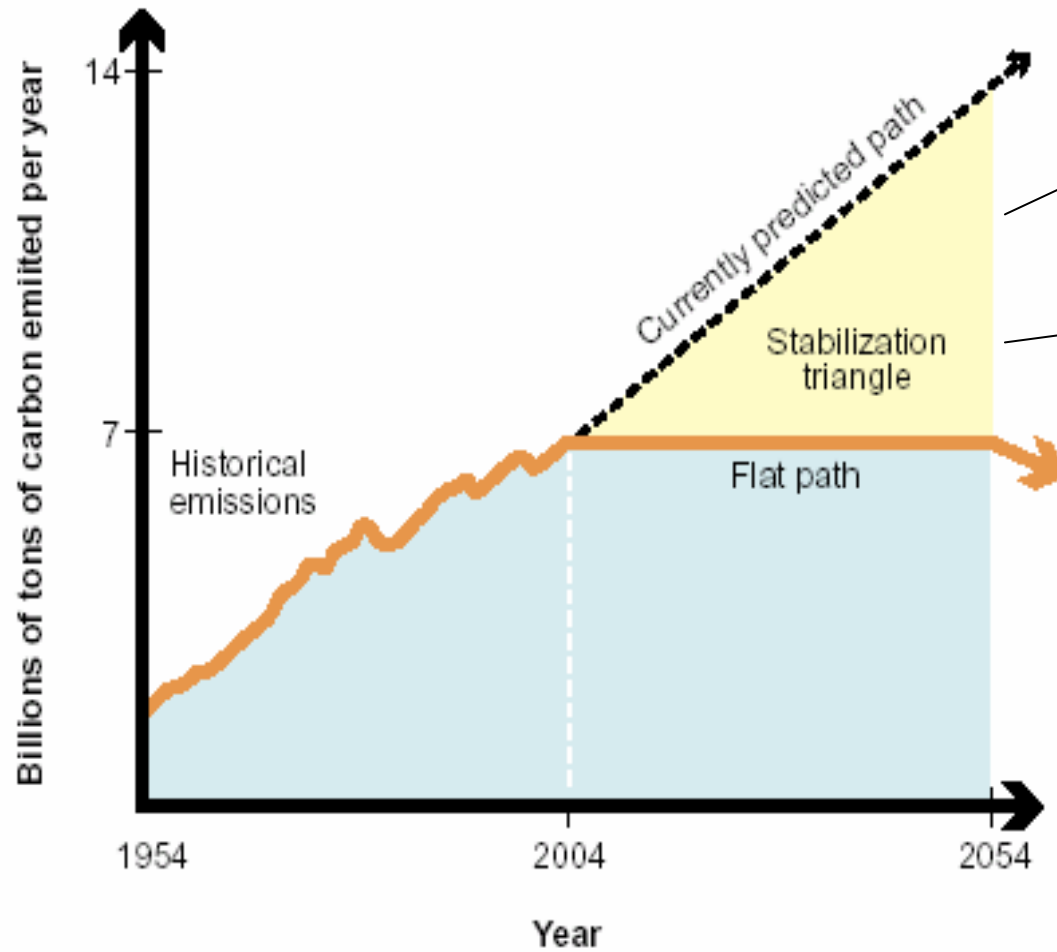
MIDN W. EUCKER



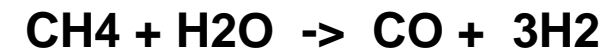
# Outline

- **Why do we want to capture CO<sub>2</sub>?**
- Background
  - Room Temperature Ionic Liquids
  - Solubility
- Investigative Method
- Results: PES Scans
- Analysis: Energetics vs. Solubility
- Continuing Project Plan
- Conclusions
- Acknowledgements

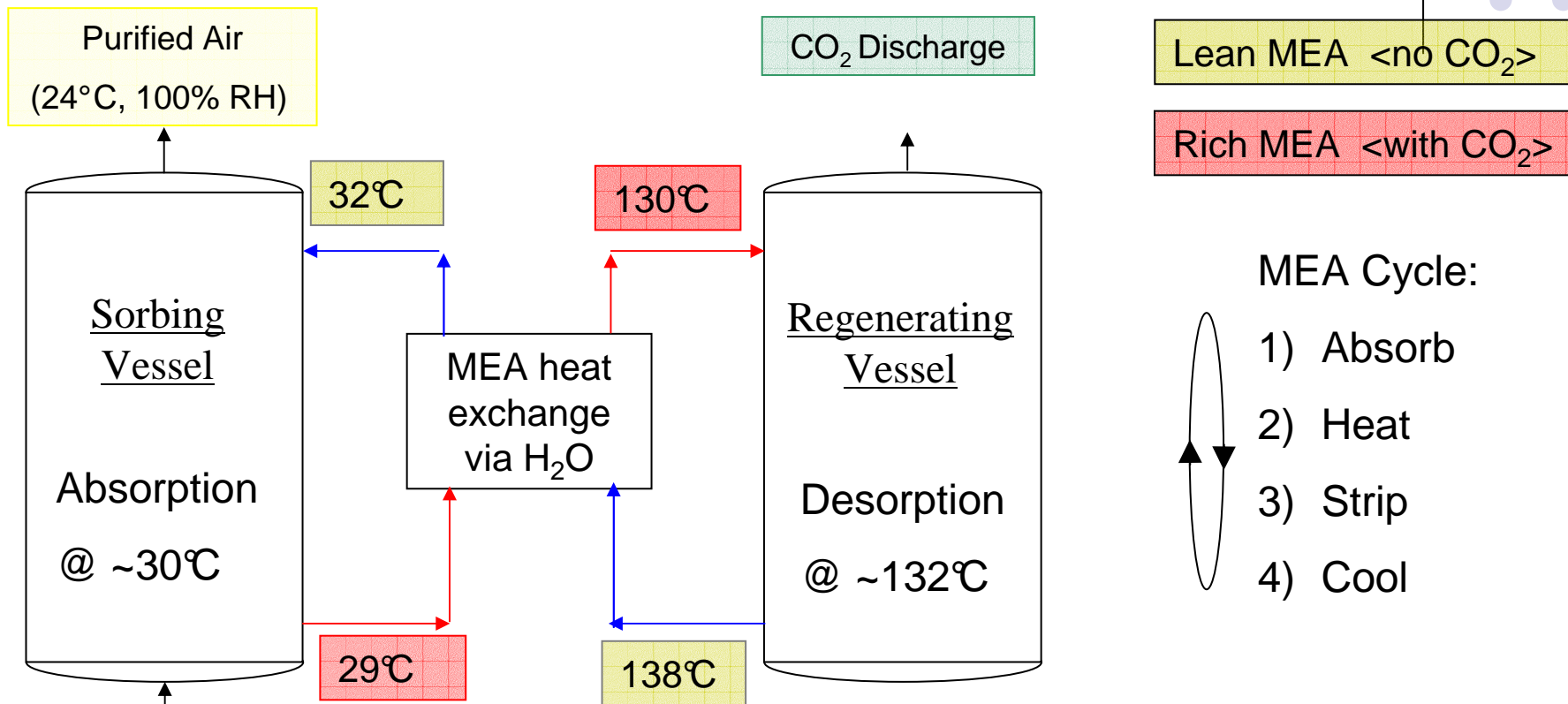
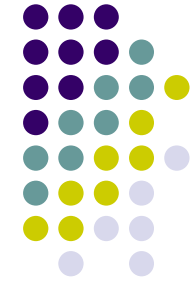
# Global Challenge



**EFFICIENCY!**



# Current CO<sub>2</sub> Removal System



MEA Cycle:



- 1) Absorb
- 2) Heat
- 3) Strip
- 4) Cool



Monoethanolamine (MEA) reaction

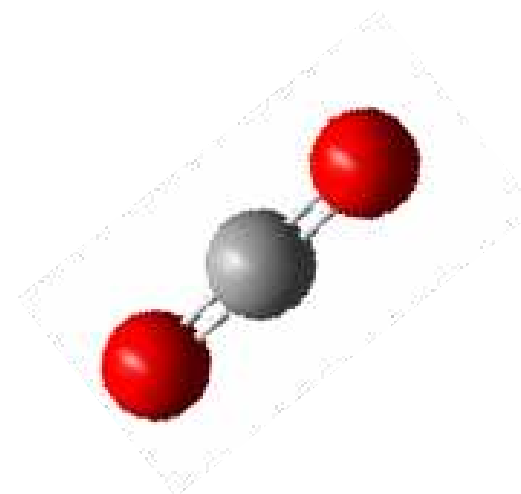


# Fleet Operational Challenge

- Submarine atmosphere purification system: CO<sub>2</sub> Scrubber
  - Health & safety of 100+ sailors
  - Function of ship
- Gas produced via metabolic respiration
  - 24 L per hour per person → 5.2 kg CO<sub>2</sub>/hour !
  - Chemically inert asphyxiant
- Problems with current CO<sub>2</sub>-sorbent: monoethanolamine (MEA)



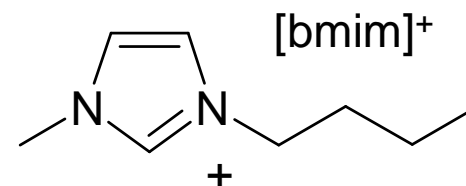
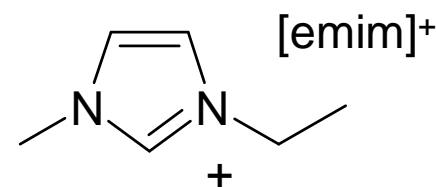
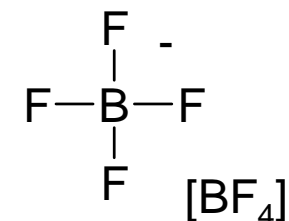
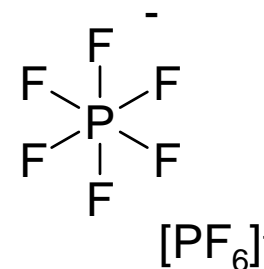
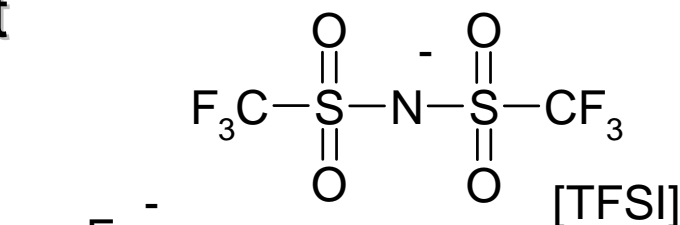
- Short lifecycle
- Bulky and heavy
- Corrosive
- Physiologically toxic
- Foul smelling
- High vapor pressure



# Background I: RTILs



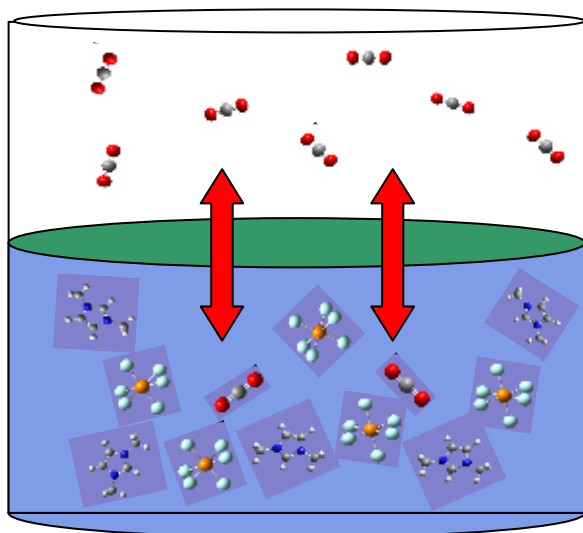
- What? Salts which are liquids at ambient temperatures
  - e.g. NaCl is a molten salt @  $T > 800^\circ\text{C}$
- Why? Properties + Advantages
  - “Tunable” molecules
  - **Nonvolatile**





# Background II: Solubility

$$P_{CO_2} = k_{CO_2} X_{CO_2} \quad \longrightarrow \quad k_{CO_2} = \frac{[CO_2]_{gas}}{[CO_2]_{liquid}}$$



Solvent	$k_{CO_2}$
MEA	$14.4 \pm 1.6 \text{ atm}^{(1)}$
<i>bmim</i> <sup>+</sup> / <i>TFSI</i> <sup>-</sup>	$18.5 \pm 0.1 \text{ atm}^{(2)}$
<i>bmim</i> <sup>+</sup> / <i>PF</i> <sub>6</sub> <sup>-</sup>	$53.4 \pm 0.4 \text{ atm}^{(3)}$
<i>bmim</i> <sup>+</sup> / <i>BF</i> <sub>4</sub> <sup>-</sup>	$56.5 \pm 0.4 \text{ atm}^{(3)}$
H <sub>2</sub> O	$1639.0 \pm 1.1 \text{ atm}^{(4)}$

(1) Anthony, Brennecke, et al., *Int. J. Environmental Technology and Management*, Vol. 4, 2004, 105-115.

(2) Lee, Outcalt, *J. Chem. Eng. Data*, 2006, 51, 892-897.

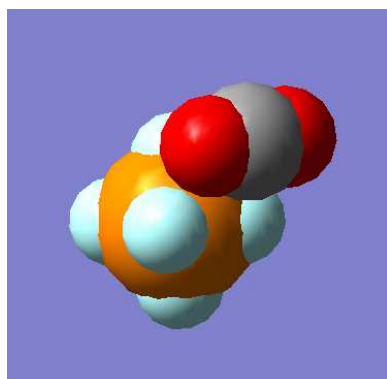
(3) Brennecke, Maginn, et al., *J. Am. Chem. Soc.* 2004, 126, 5300-5308.

(4) Hildebrand & Scott, *The Solubility of Nonelectrolytes*, Dover: London, 1964.

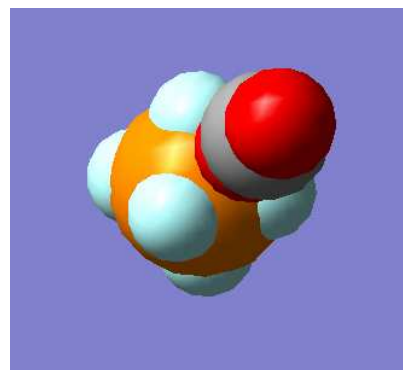
# Investigative Method: Molecular Physisorption



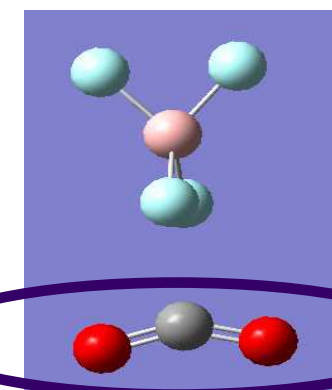
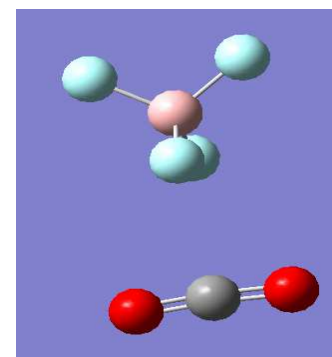
- How does CO<sub>2</sub> bind with RTIL anions?
  - Inter-molecular effects:



vs.



- Intra-molecular effects:



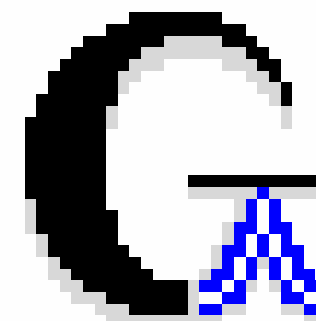
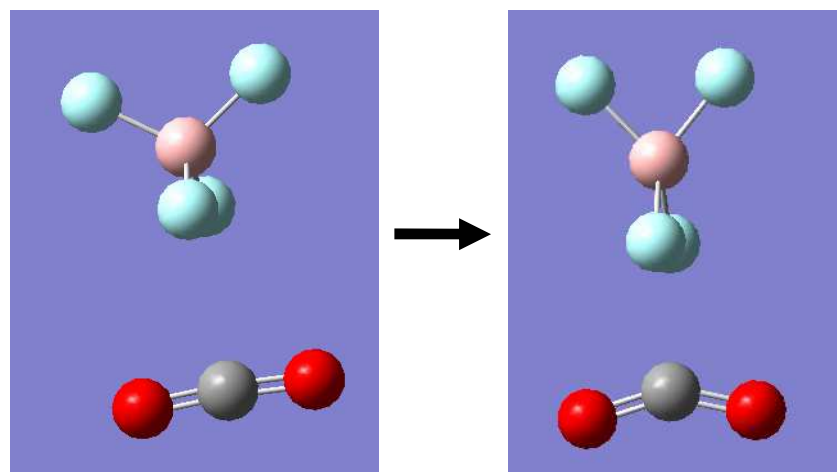
# Investigative Method (cont.): *Ab initio* Computation



- Treatment of electron distribution and energy “from first principles”
  - Enables analysis of molecular structure

$$\hat{H}\Psi = E\Psi$$

## Geometry Optimization

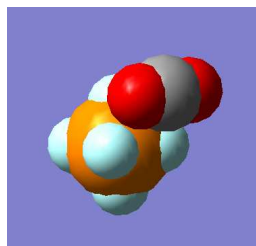


- Spartan '02 / GAUSSIAN 03
  - Computational chemistry software
  - Commercial (pre-existing) code
- cc-PVTZ / aug- cc-PVTZ

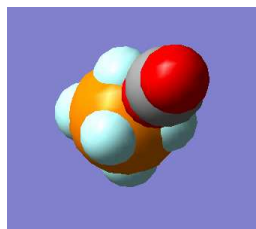
# PF<sub>6</sub><sup>-</sup>/CO<sub>2</sub> PES Results



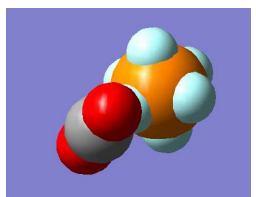
a. [111] <-1,1,0>  
"Tangential"



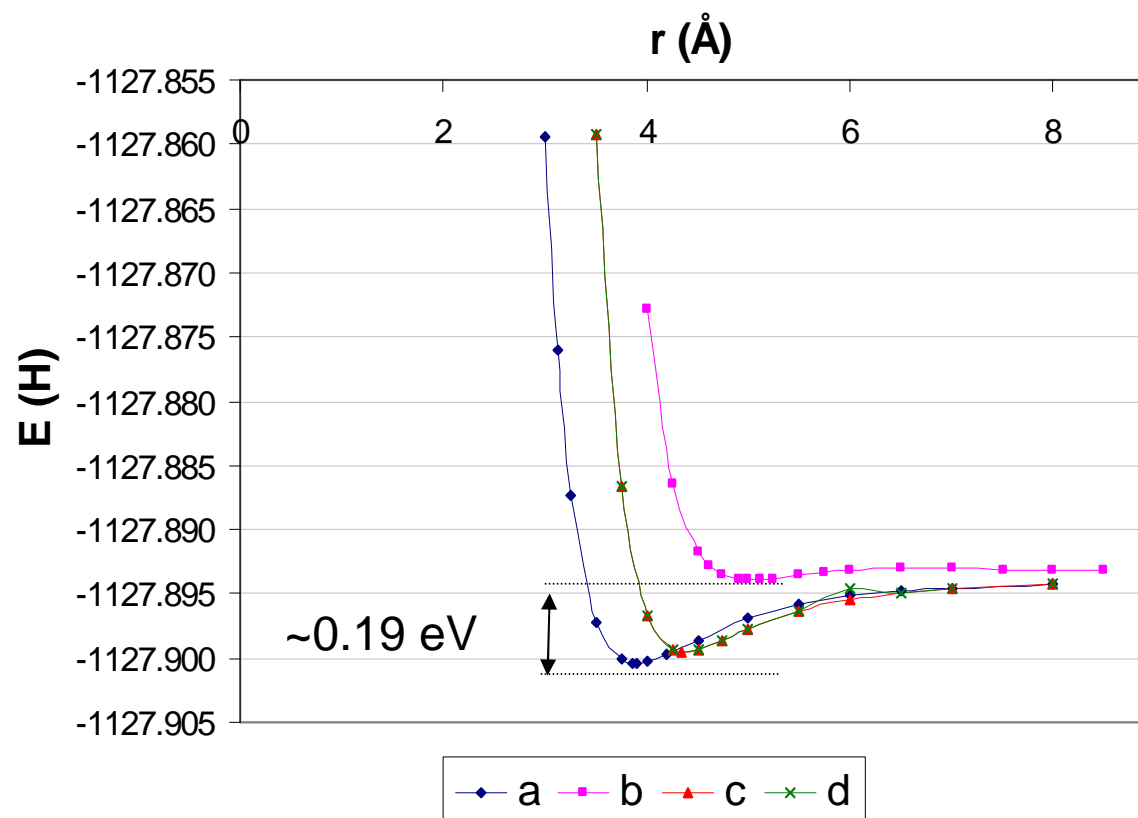
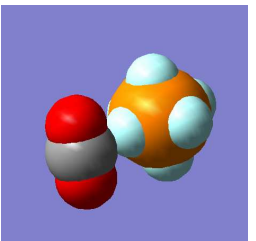
b. [111] <1,1,1>  
"Penetrating"



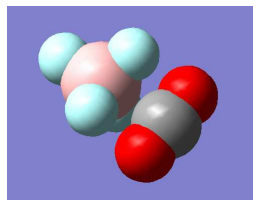
c. [100] <0,1,1>  
"T staggered"



d. [100] <0,0,1>  
"T aligned"

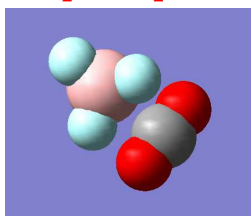


cc-PVTZ Energy vs r [PC] Selected Conformations

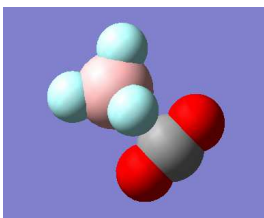


# BF<sub>4</sub><sup>-</sup>/CO<sub>2</sub> PES Results

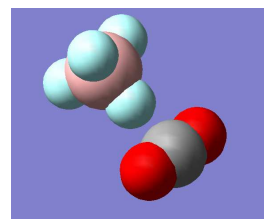
a. [111] <Non-Aligned  
Tangential>



b. [111] <Aligned  
Tangential>

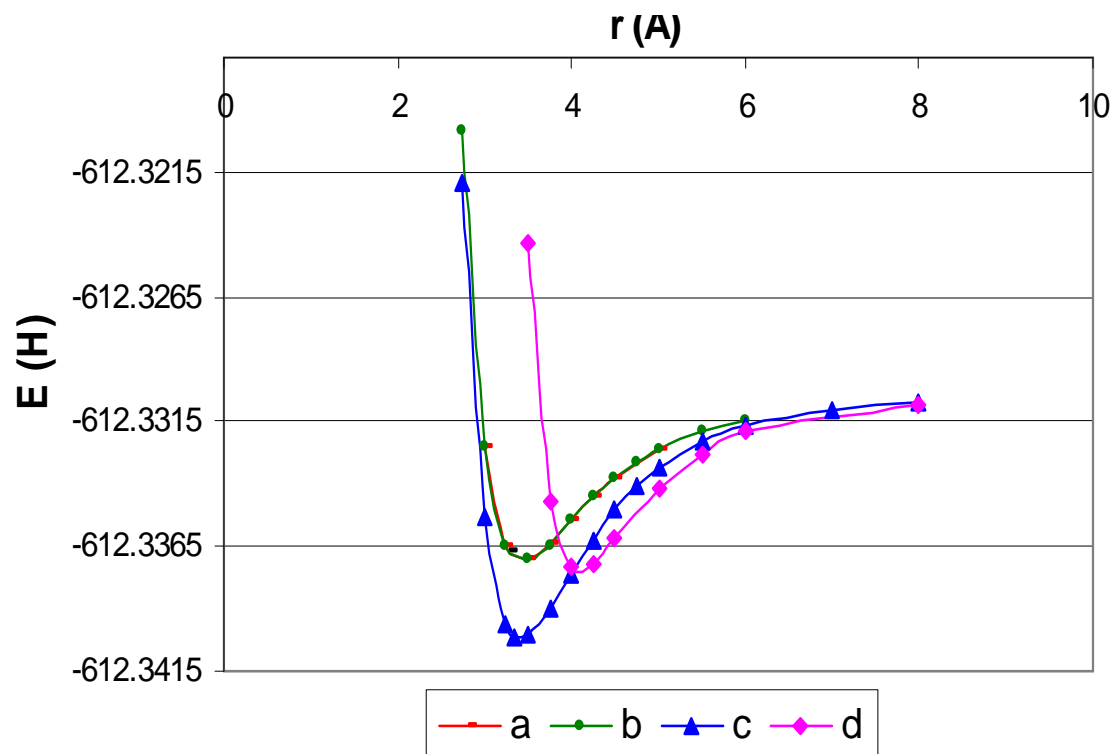


c. [110] <Tangential>



d. [100] <T Aligned>

MIDN W. EUCKER

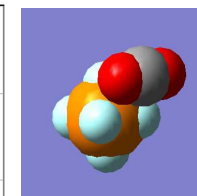
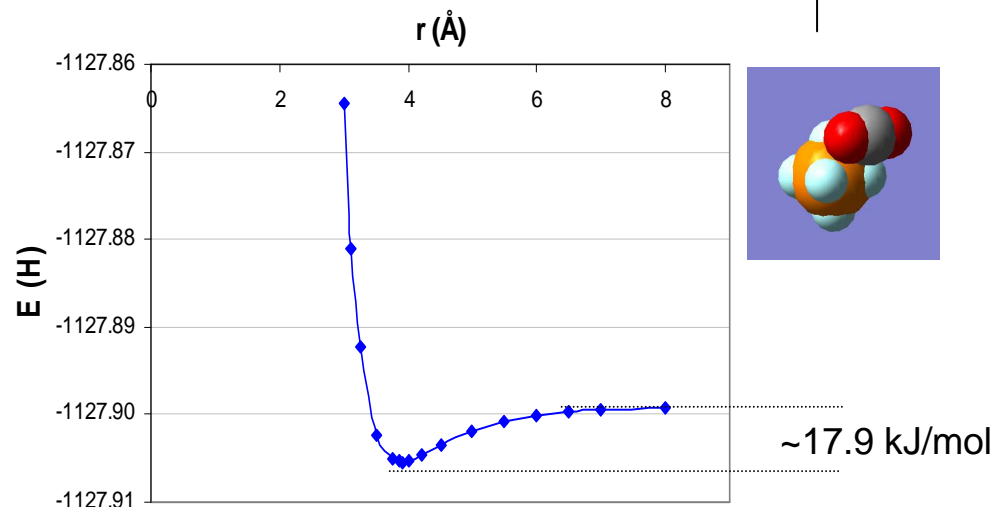


cc-PVTZ Energy vs  $r$  [BC] Selected Conformations

# Energetics vs. Solubility



- $\text{BF}_4^-$  interacts with  $\text{CO}_2$  more strongly than  $\text{PF}_6^-$ 
  - Greater binding energy to the global minimum site
  - More numerous, deep well active sites surrounding  $\text{BF}_4^-$
- Agrees with Kazarian (in situ ATR-IR spectroscopy) (1)
- **BUT:**  $[\text{PF}_6^-/\text{bmim}^+]$  better solvent than  $[\text{BF}_4^-/\text{bmim}^+]$

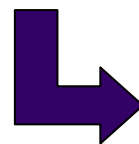


Anion	[Orientation] <Alignment>	$E_{\min}$ (Global) (a.u.)	R (Å)	B (kJ/mol)	$\theta$ (°)	$k_{(\text{CO}_2)}^{(2)}$ (atm)
$\text{PF}_6^-$	[111] <-110>	-1127.9004	3.90	17.87	177.0	$53.4 \pm 0.4$
$\text{BF}_4^-$	[110] <n-tan>	-612.3401	3.35	25.24	175.0	$56.5 \pm 0.4$

Energy comparisons:

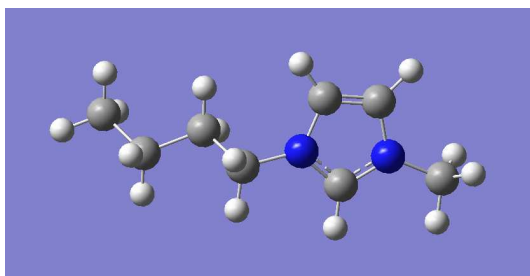
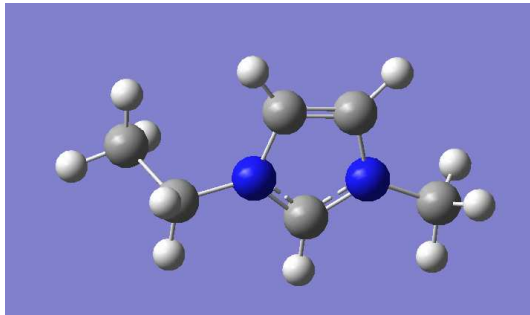
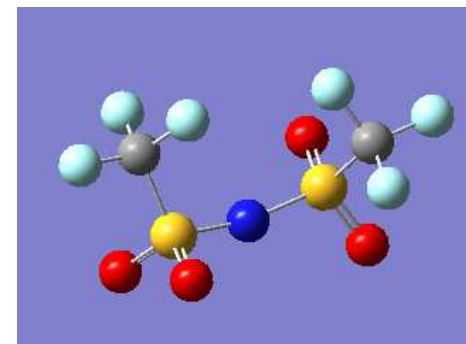
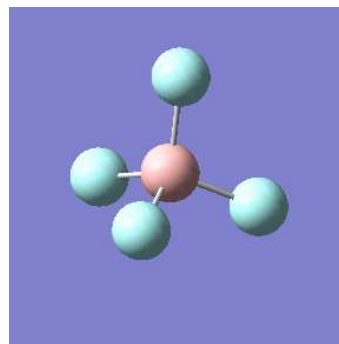
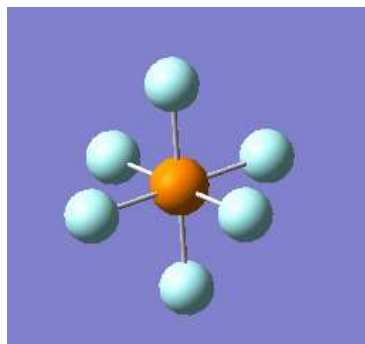
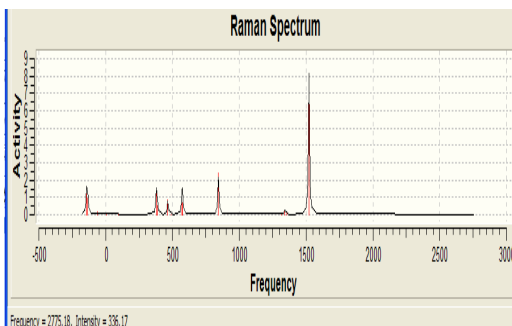
$$\Delta H_{\text{fus}}^{\circ}(\text{H}_2\text{O}) = 6.009 \text{ kJ/mol}$$

$$\Delta H_{\text{vap}}^{\circ}(\text{H}_2\text{O}) = 40.646 \text{ kJ/mol}$$



Anion-Cation interaction must also contribute to solubility mechanism

# Continuing Project Plan: Experiment + Computation

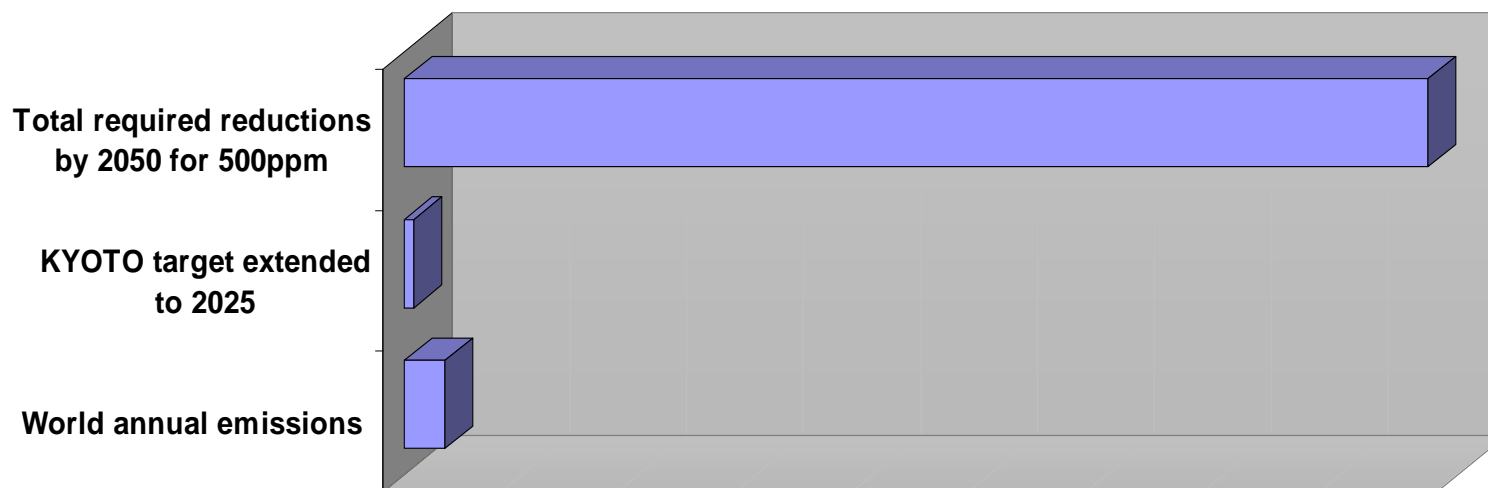


Explore RTIL structural, spectroscopic and thermophysical properties varying **temperature** and ambient **CO<sub>2</sub>**, **N<sub>2</sub>**, and **O<sub>2</sub>** partial pressures



# Conclusions

**Conjecture:** Fossil fuels will continue to be the primary global fuel and chemical feedstock sources for some years to come.



**Recommendation:** Develop carbon-capture technologies as a wedge in the stabilization triangle.

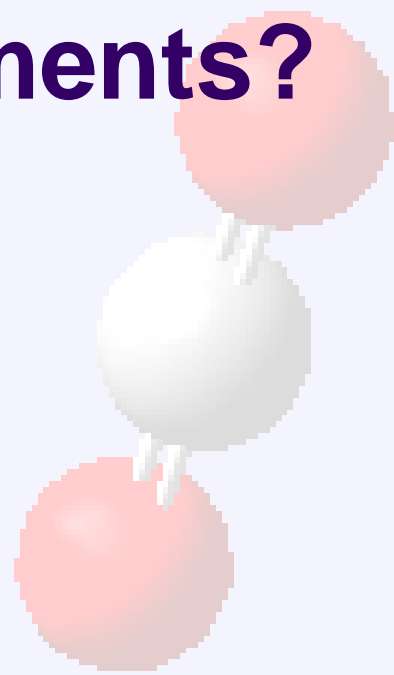
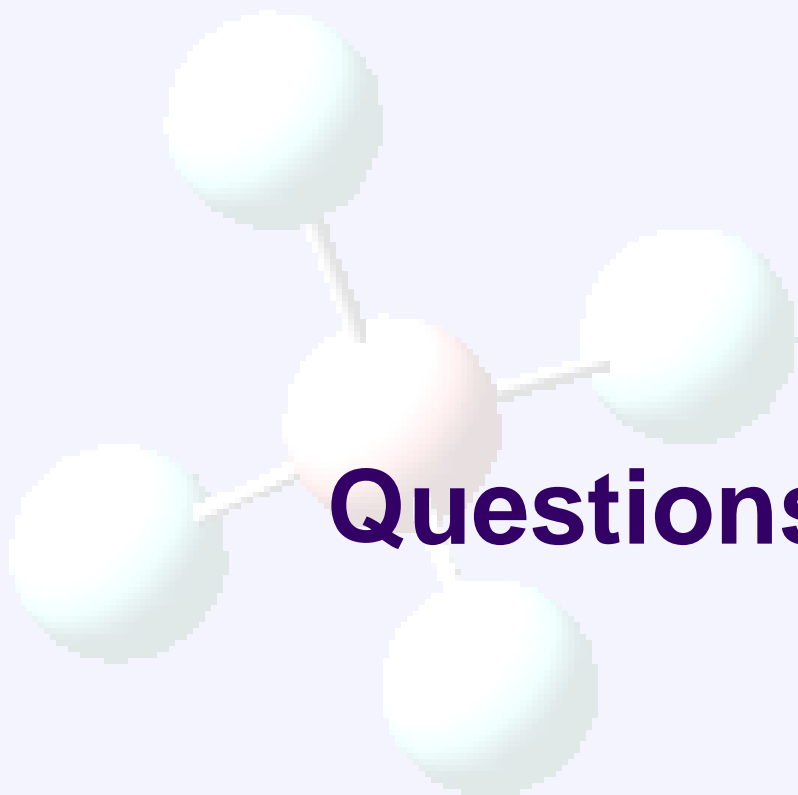
# Acknowledgements



- Physics Department, USNA
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- Chemistry Department, USNA
  - Asst. Prof. Dr. Wesley Henderson
  - Assoc. Prof. Paul Trulove
  - Assoc. Prof. Joe Urban
- Chalmers University of Technology
  - Dr. Patrik Johansson
- Division of Mathematics and Science, USNA
  - CAPT Kathy Shanebrook, USN ('80)
- Center for Research and Academic Development, USNA
  - Prof. Reza Malek-Madani
  - Prof. Joyce Shade
- ONR-Global
  - CAPT David Comis, USN ('77)
  - Dr. Vijay Kowtha



**Questions, Comments?**





# Why Regulate CO<sub>2</sub> ?

- Produced via metabolic respiration
  - 24 L per hour per person → 5.2 kg CO<sub>2</sub>/hour !
- Chemically inert asphyxiant
- High CO<sub>2</sub> partial pressures cause:
  - heavy breathing (1%)
  - impaired vision
  - dizziness (2-3%)
  - impaired judgment
  - impaired muscular coordination
  - unconsciousness (6%)
  - death
- Pressurized hull is isolated system
  - → need to self-regulate CO<sub>2</sub> partial pressures (<0.6 % of total)

# FutureGen



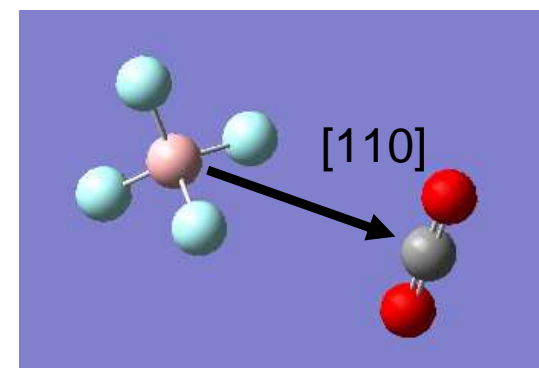
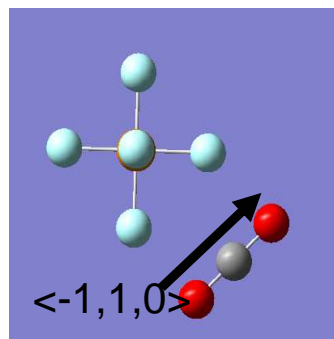
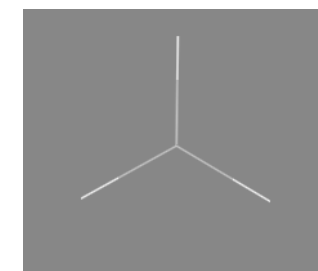
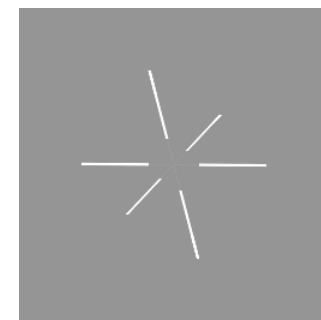
"Today I am pleased to announce that the United States will sponsor a \$1 billion, 10-year demonstration project to create the world's first coal-based, zero-emissions electricity and hydrogen power plant..."

*President George W. Bush  
February 27, 2003*

# Systematic Vector Description



- Ensure that all sites be investigated
  - "Bookkeeping method"
- Defining Vectors with Anion Symmetry
  - Octahedral  $\text{PF}_6^-$   
→ orthogonal cartesian x,y,z unit vector basis triplet
  - Tetrahedral  $\text{BF}_4^-$   
→ non-orthogonal unit vector basis triplet
- C orientation from central anionic atom: P, B
  - [ ] vector
- $\text{CO}_2$  alignment vis à vis anion
  - < > vector

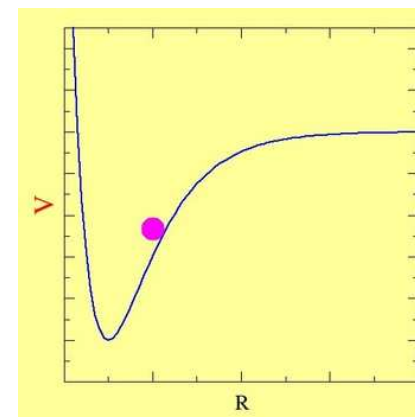




# Potential Surfaces

- Born-Oppenheimer approximation
  - nuclei remain fixed on the scale of electron movement

$$\hat{H}^{elec}\Psi^{elec}(r, R) = E^{eff}(R)\Psi^{elec}(r, R)$$



- $E(R)$  is ground state electronic potential energy surface (PES) for lowest energy eigenvalue
- Local minima on PES signify equilibrium structures—“optimized” or true atomic configurations

# Fundamentals of *ab initio*



- Combine one-electron functions (spin orbitals) to approximate full wavefunction

$$\Psi = (n!)^{-1/2} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \cdots & \psi_{n/2}(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \cdots & \psi_{n/2}(2)\beta(2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_1(n)\alpha(n) & \psi_1(n)\beta(n) & \psi_2(n)\alpha(n) & \cdots & \psi_{n/2}(n)\beta(n) \end{vmatrix}$$

- Spatial orbitals are linear combinations of a finite set of N basis functions

$$\psi_i = \sum_{\mu=1}^N c_{\mu} \phi_{\mu}$$

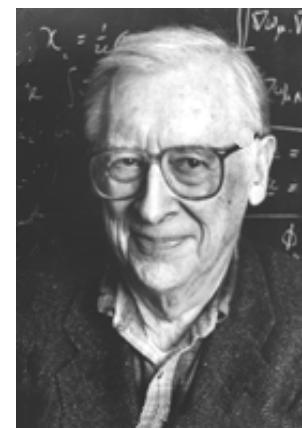
Orthogonal atomic orbitals

- Variational Principle: ground state energy eigenvalue of any anti-symmetric basis function will be greater than the energy of the exact wavefunction
- Core electrons treated as “frozen”

# Gaussian03/GaussView



- Computational suite invented by John A. Pople
- Outline of a Calculation:
  - Read input & calculate a geometry
  - Assign basis set
  - Calculate nuclear repulsion energy
  - Calculate integrals
  - Assign electronic configuration
  - Generate initial guess
  - Perform self-consistent field iterations
    - i.e. calculate the electronic energy
  - Calculate total energy = nuclear repulsion + electronic
    - Calculate potential energy surface (PES)
    - Optimize atomic geometry
  - Perform electron density analysis
  - Carry out further steps...

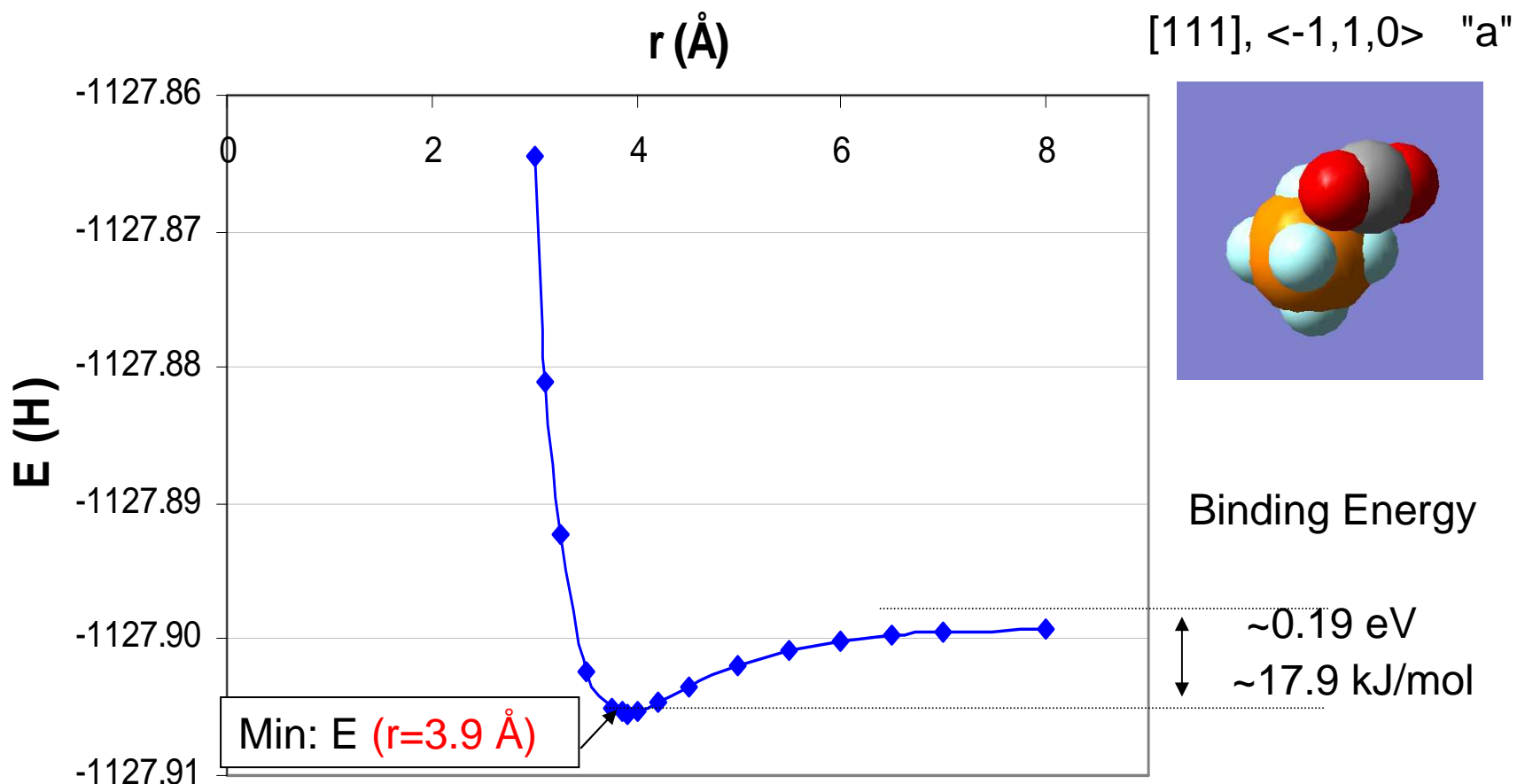


1998 Nobel Prize  
(Chemistry)



# Extracting the Binding Energy

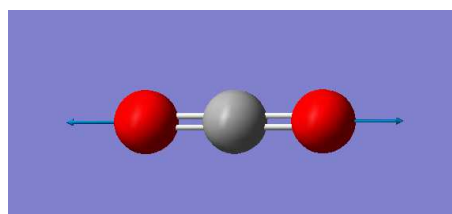
$$B = E_{scf} \left( PF_6^- + CO_2 \middle| cc - pVTZ \right) - E_{scf} \left( PF_6^- \middle| cc - pVTZ \right) - E_{scf} \left( CO_2 \middle| cc - pVTZ \right)$$



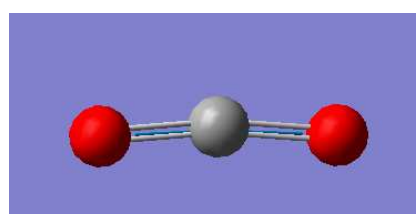


# Raman Analysis

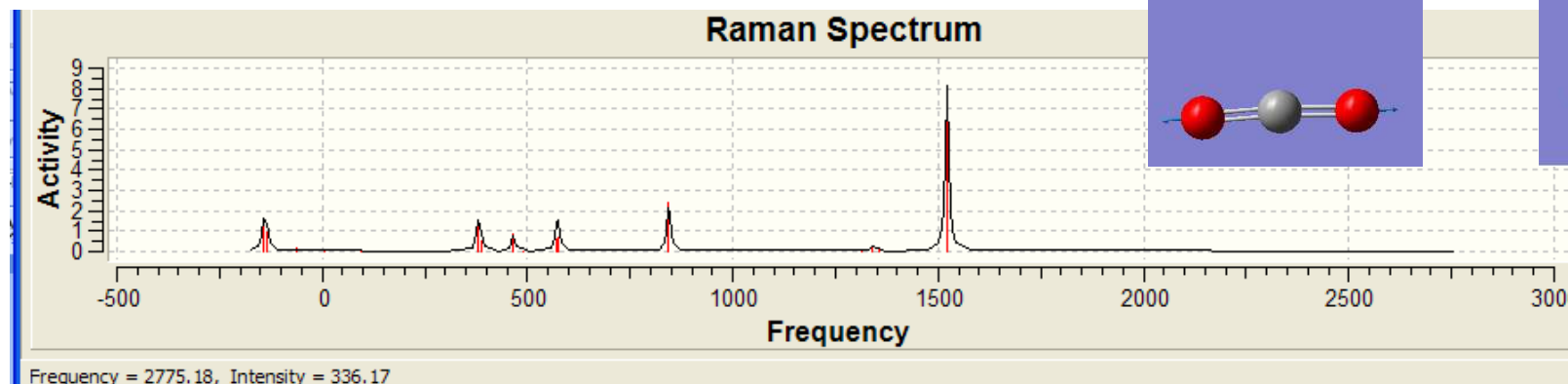
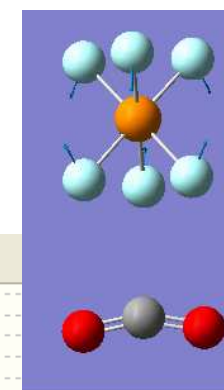
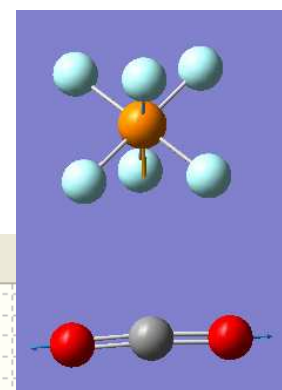
- *Diagnosis peak*: CO<sub>2</sub> stretch mode:  $\gamma_1$



CO<sub>2</sub>: 1520.8 cm<sup>-1</sup>



CO<sub>2</sub>+ PF<sub>6</sub><sup>-</sup>: 1523.0 cm<sup>-1</sup>



- Anion-cation symmetric vibrational modes

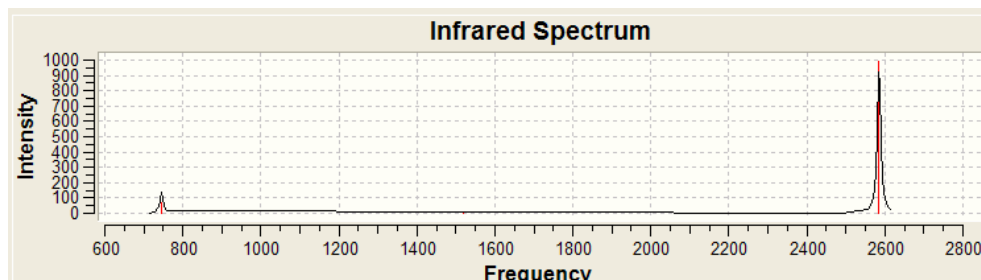
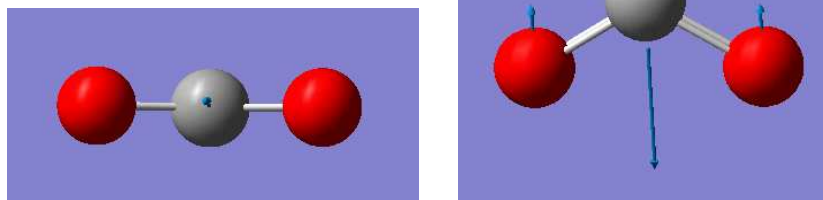


# Vibrational Frequency Data

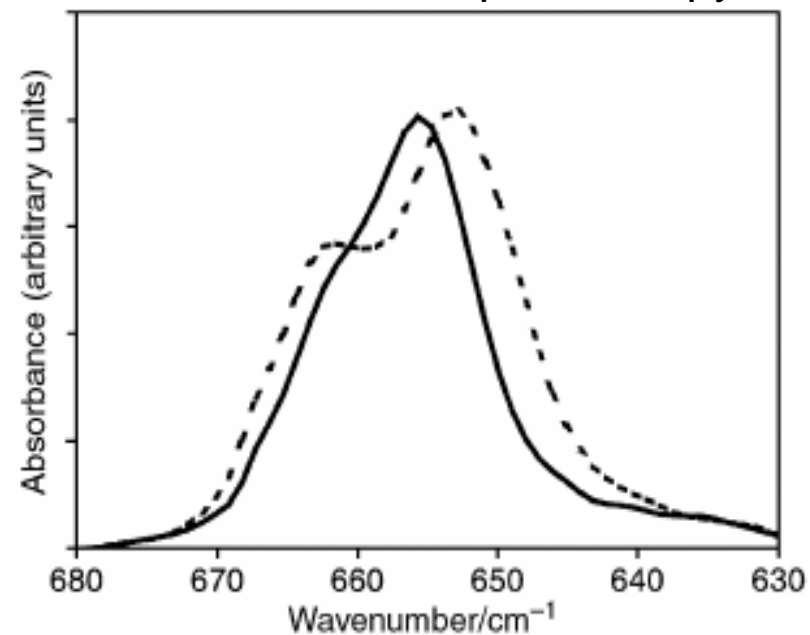
- IR-active
  - (antisymmetric bending mode  $\nu_2$ )
- Molecular deformation:

PF<sub>6</sub><sup>-</sup>:  $\theta=176.97^\circ$

BF<sub>4</sub><sup>-</sup>:  $\theta=175.05^\circ$



In situ ATR-IR spectroscopy



Kazarian et al, *Chem. Commun.*, (2000), 2047.

-- BF<sub>4</sub>, — PF<sub>6</sub>