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# Molecular Engineering of New Ionic Liquid Sorbents for CO<sub>2</sub> Capture

**Edward Maginn, Joan Brennecke,  
William Schneider and Mark McCreedy**  
*Dept. of Chemical and Biomolecular Engineering  
University of Notre Dame*  
ed@nd.edu

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**DTE Energy**

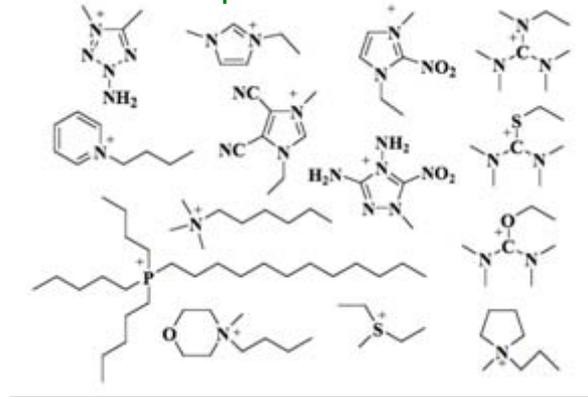


# Ionic Liquids and Their Potential as CO<sub>2</sub> Sorbents

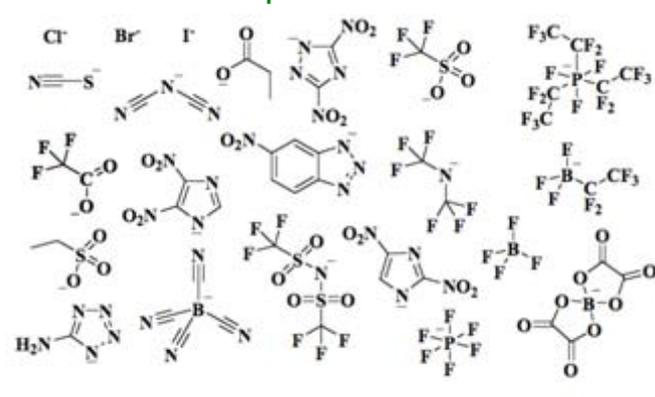
- Pure salts that are liquid around ambient temperature
  - Not simple salts like alkali halides
- Many favorable properties
  - Nonvolatile
  - Anhydrous
  - High thermal stability
  - Huge chemical diversity
  - High intrinsic CO<sub>2</sub> solubility and selectivity



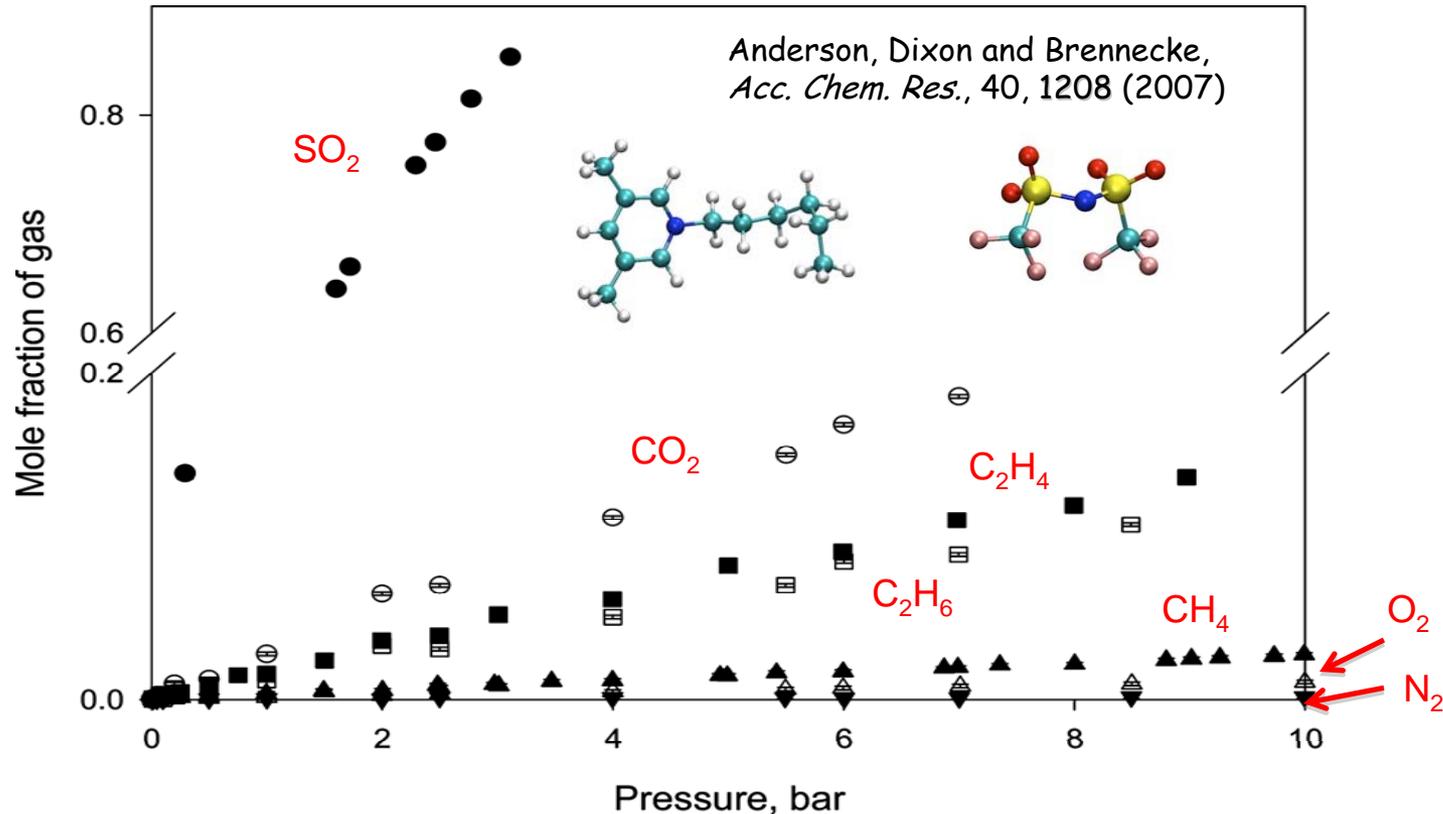
Examples of cations



Examples of anions



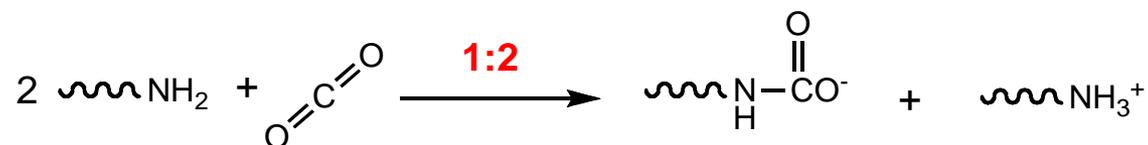
# SO<sub>2</sub> and CO<sub>2</sub> solubility high...



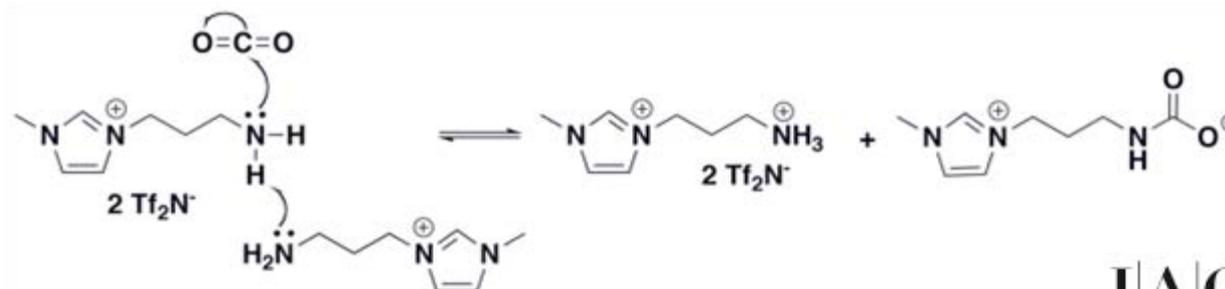
- Process modeling indicates physical CO<sub>2</sub> solubility still not high enough to be practical for post-combustion capture
  - Need to add chemical functionality to increase capacity

# Adding reactive groups to ionic liquids increases capacity

- Build on aqueous amine chemistry:



## TSIL CO<sub>2</sub> reaction mechanism



**J|A|C|S**  
COMMUNICATIONS

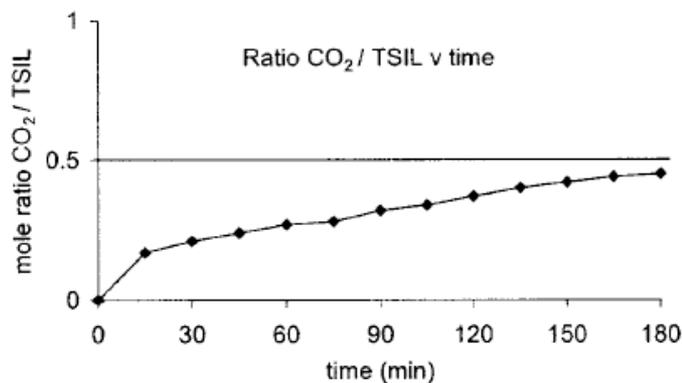
Published on Web 01/19/2002

### CO<sub>2</sub> Capture by a Task-Specific Ionic Liquid

Eleanor D. Bates, Rebecca D. Mayton, Ioanna Ntai, and James H. Davis, Jr.\*  
Department of Chemistry, University of South Alabama, Mobile, Alabama 36688

926 VOL. 124, NO. 6, 2002 ■ J. AM. CHEM. SOC.

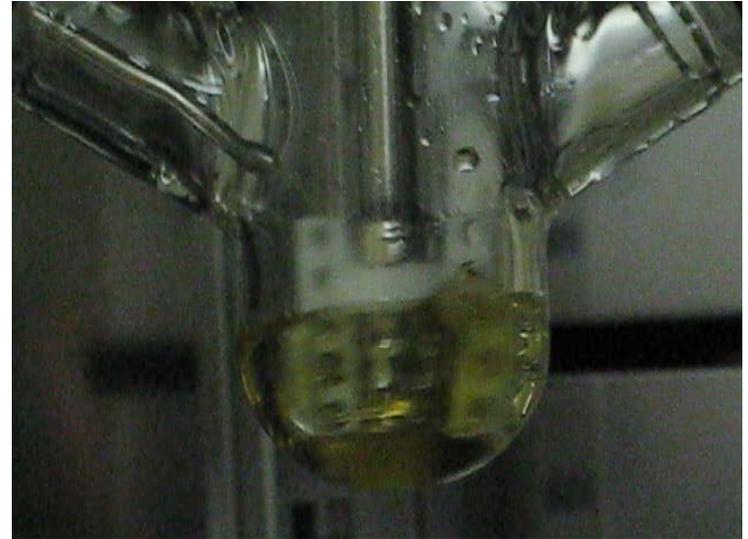
1 atm CO<sub>2</sub>  
Room temp.



# Problems with conventional TSILs



No CO<sub>2</sub>

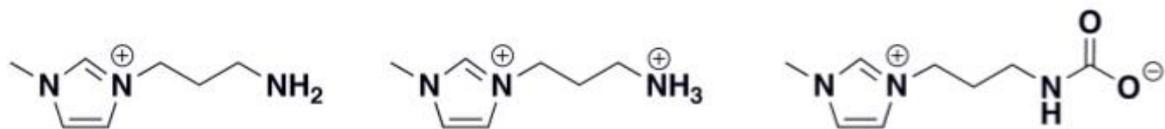


17 mbar CO<sub>2</sub>

- Liquid becomes extremely viscous upon CO<sub>2</sub> contact
- 2:1 mechanism is inefficient...1:1 mechanism possible?
- How to tune the physical and chemical properties?

Use molecular modeling + experiments to design ILs for CO<sub>2</sub> capture

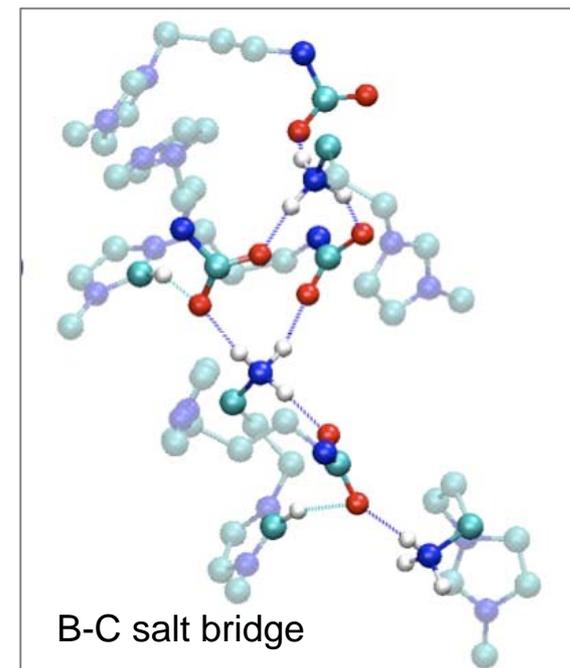
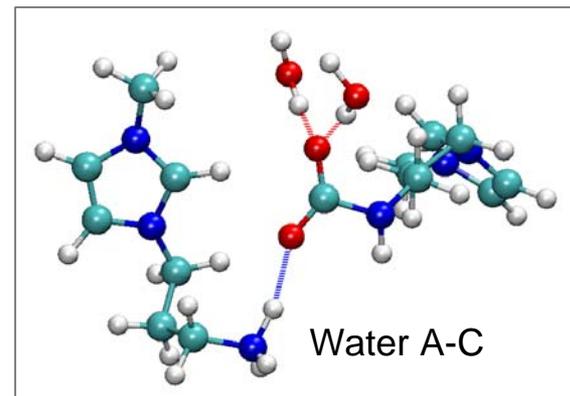
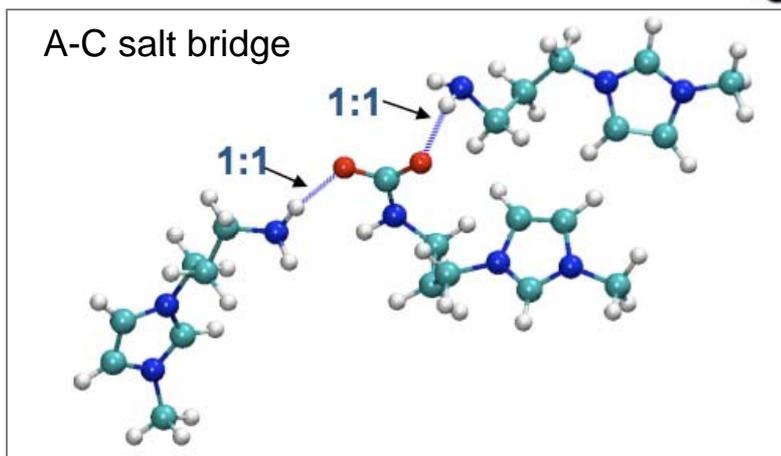
# Explanation for viscosity increase



A

B

C



Gutowski and Maginn, *JACS* **2008**, 130, 14690

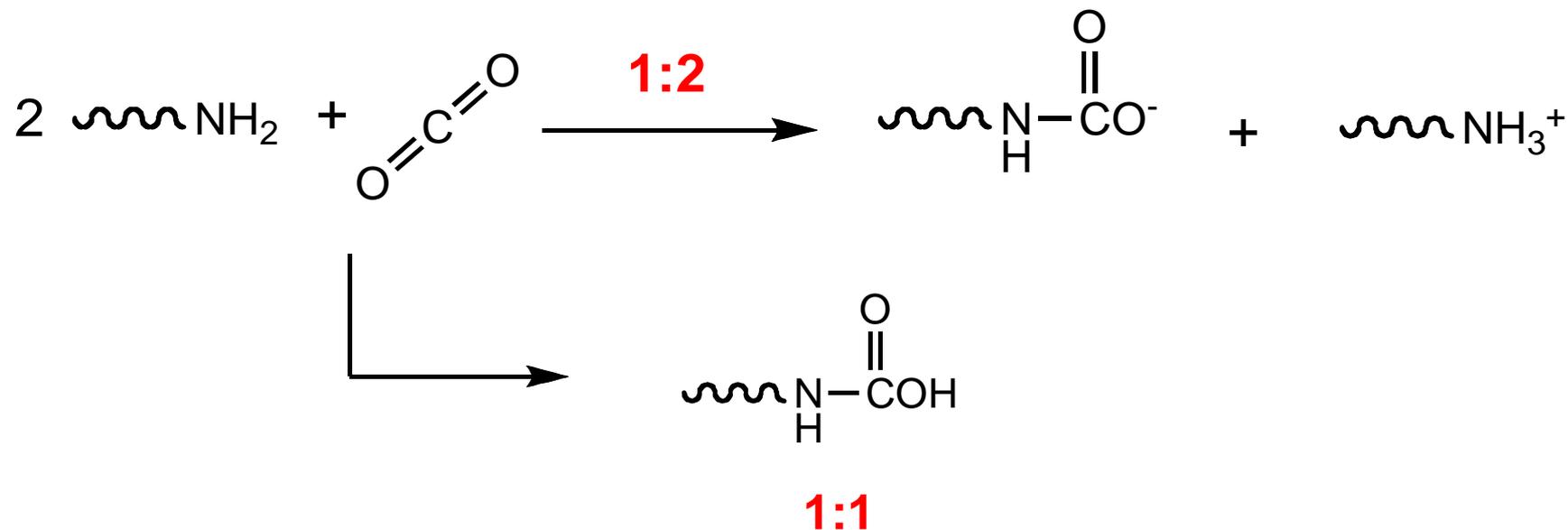
Atomistic MD simulations show an increase in viscosity upon reaction with  $\text{CO}_2$  just like experiments.

Why? Formation of a pervasive network of salt bridges between carbamate and ammonium / unreacted species.

**Solution:**  
design *aprotic* molecules that do not form salt bridges

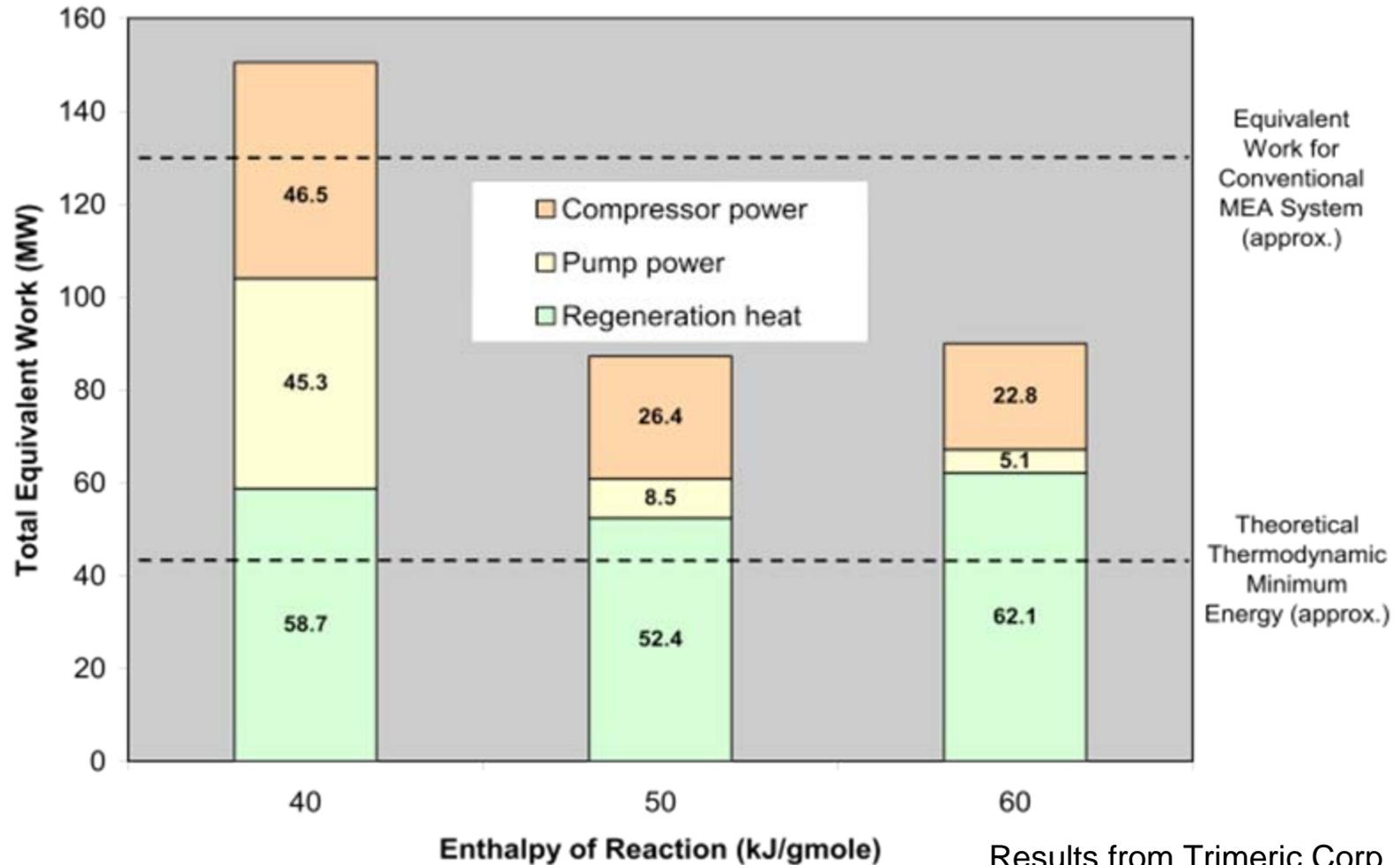
# Achieving 1:1 binding stoichiometry?

Conventional primary amine chemistry requires two active groups for every one molecule of CO<sub>2</sub>



*Is it possible to design molecules that bind CO<sub>2</sub> 1:1?*

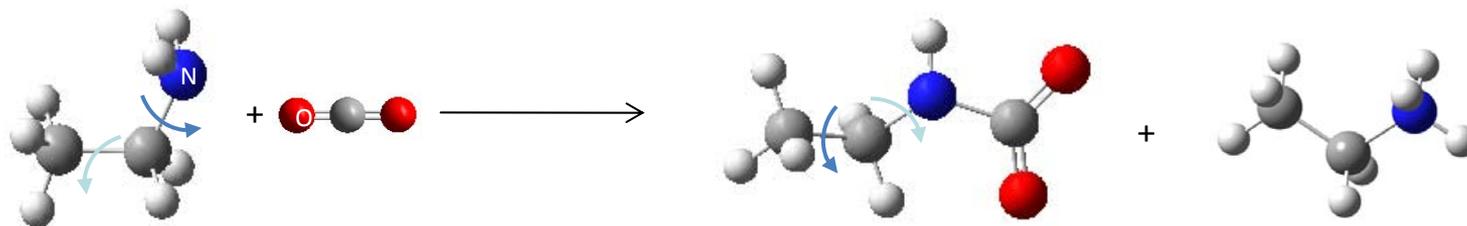
# Optimal binding energy from process modeling



*Can ILs be designed with optimal CO<sub>2</sub> reaction enthalpy?*

# Approach: electronic structure calculations

- Evaluate structural and energetic properties of potential absorbents



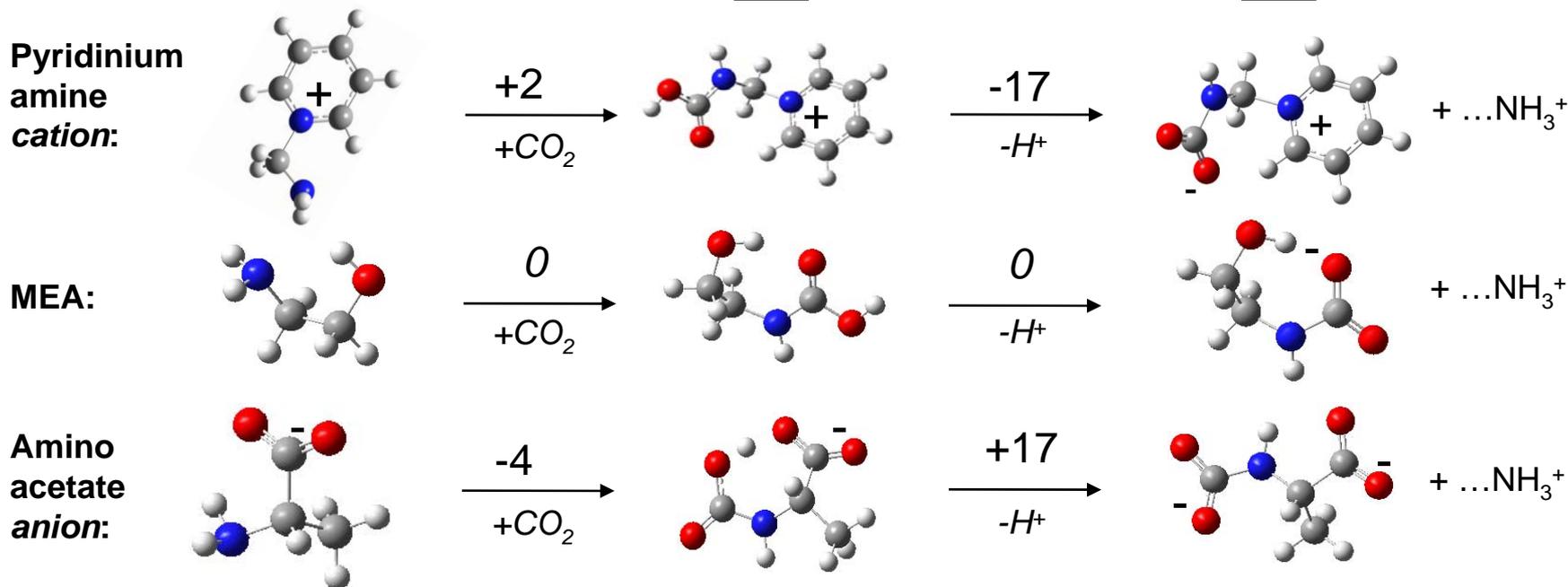
- Examine relative energies for different binding mechanisms
- Investigate how substituent groups affect reaction enthalpy
  - Possible to computationally screen a huge number of candidates
- Hybrid-DFT calculations implemented in Gaussian
  - B3LYP/6-311++G(d,p)
  - Harmonic frequency analysis
  - Standard ZPE and gas-phase free energy analysis
  - Boltzmann averaged reaction energies

# MEA vs. cation- vs. anion-tethered amines

Reaction energies in kcal/mol relative to MEA

1:1

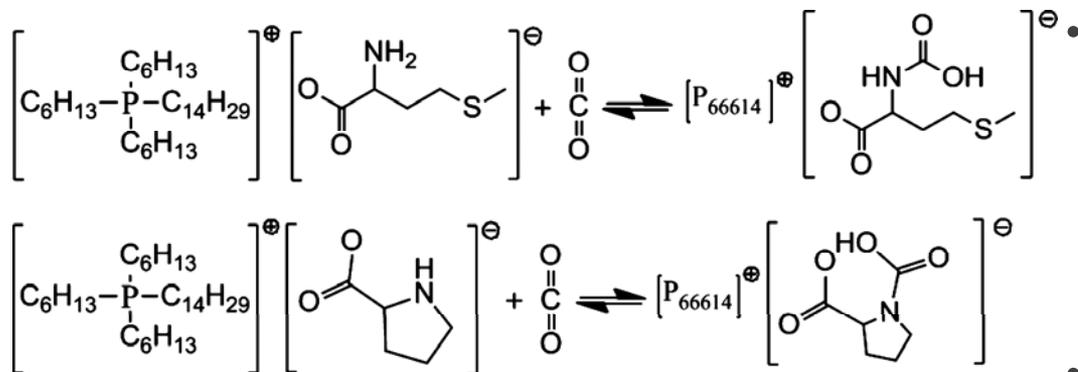
2:1



- Local cation tethering favors 2:1 binding
- Local anion tethering disfavors 2:1 binding
- Tethering ion and tethering point as important as functional groups in controlling CO<sub>2</sub> reactions
  - DOF unique to ILs!!

Mindrup and Schneider, *ACS Symp. Series* **2010**

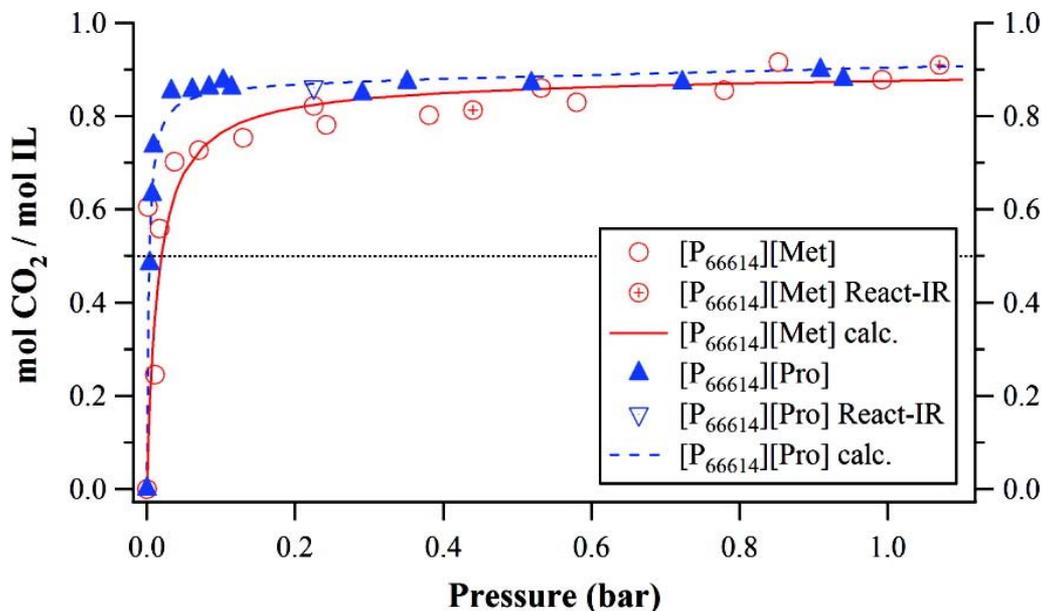
# 1:1 stoichiometry for anion functionalized IL



• Simulations predict proline ( $-71 \text{ kJ mol}^{-1}$ ) stronger 1:1 absorber than methionate ( $-55$ )

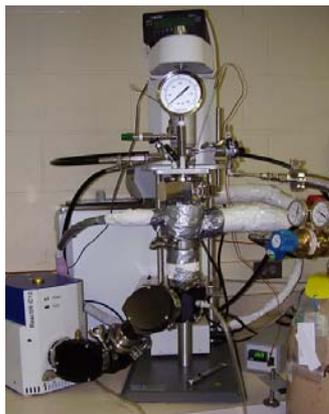
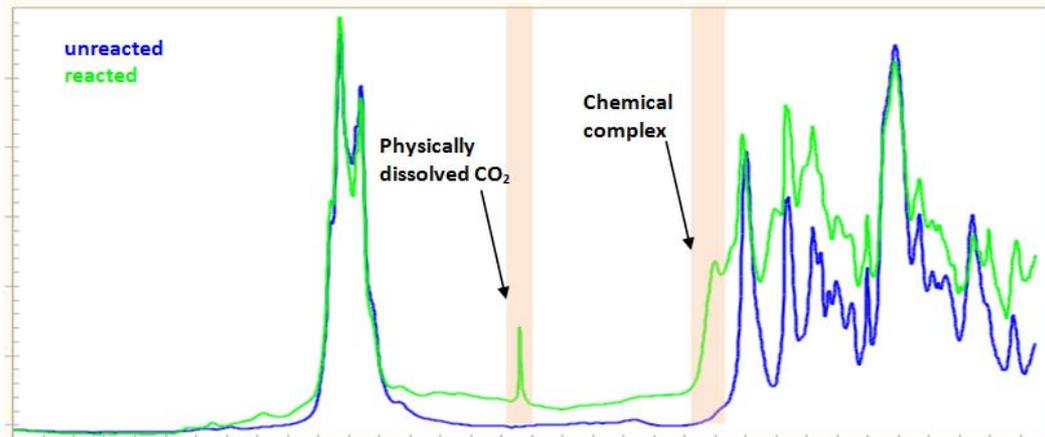
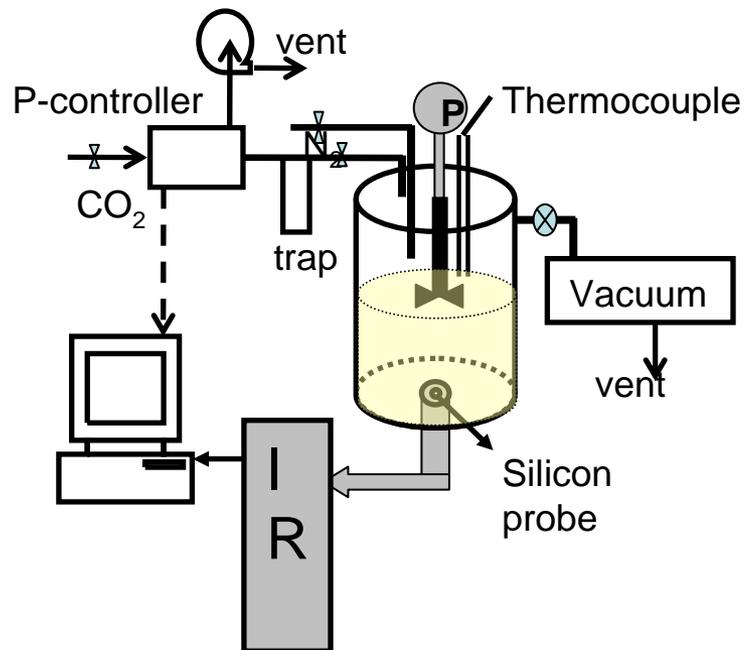
• Experimental RT isotherms consistent with this ranking and with  $\sim 1:1$  reaction stoichiometry

• Excellent agreement with calorimetric experiments



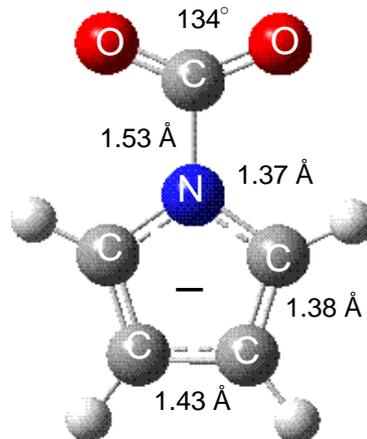
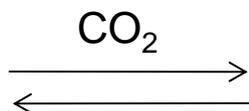
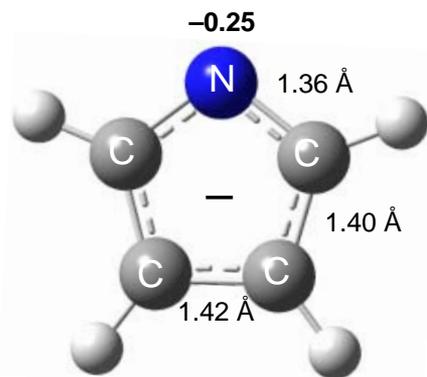
Gurkan et al., *JACS* **2010**, 132, 2116-2117

# *In situ* vibrational spectroscopy



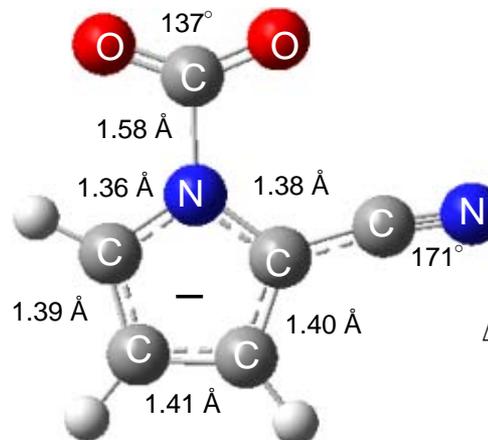
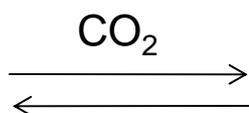
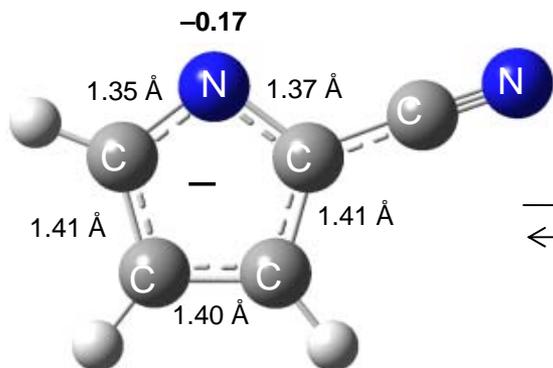
- IR distinguishes physically and chemically absorbed CO<sub>2</sub>
- Confirms 1:1 reaction stoichiometry
  - Ammonium peaks absent
  - Carbamic acid peaks appear

# Tuning reaction enthalpy using substituent groups



$$\Delta E_o = -96 \text{ kJ mol}^{-1}$$

B3LYP/6-311++G(d,p)



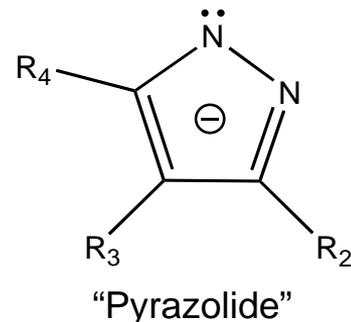
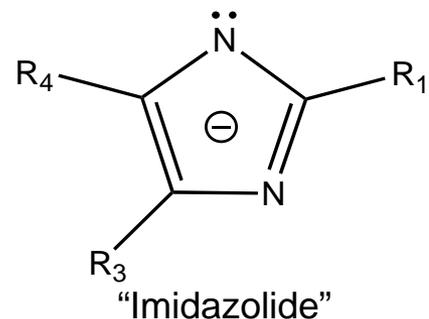
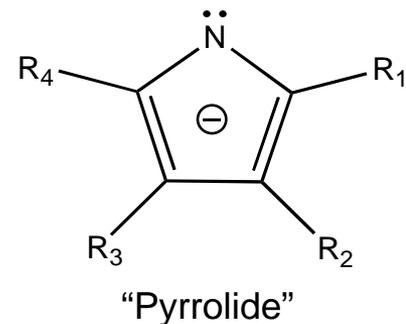
$$\Delta E_o = -35 \text{ kJ mol}^{-1}$$

- Calculations predict reversible carbamate formation
  - *Tunable* reaction energy

# Putting it all together: solvent design targets

## Design targets

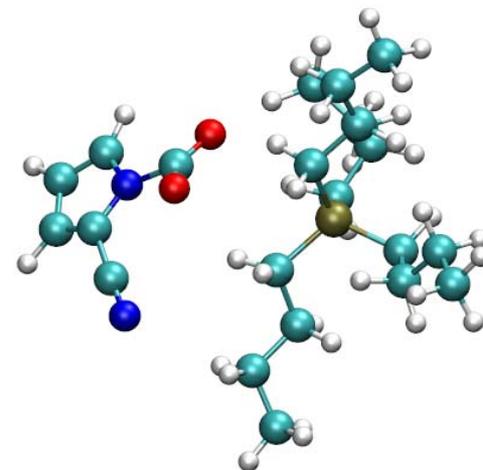
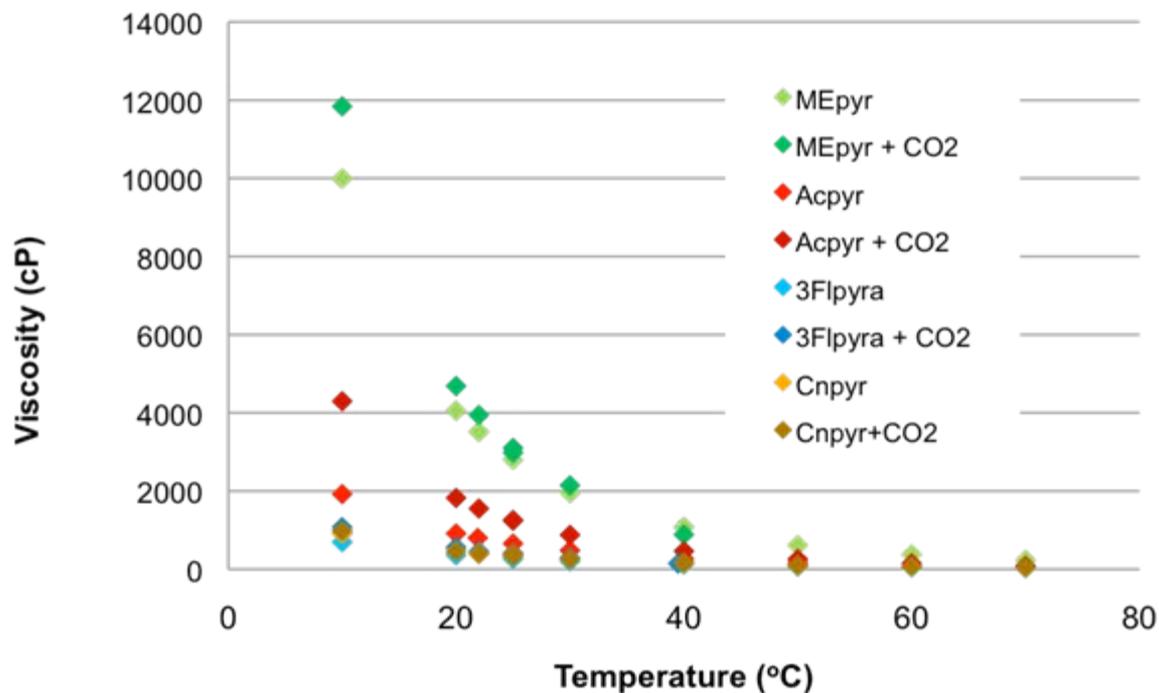
- Disrupt salt bridge network
    - Aprotic base
  - Anion-functionalized IL
    - 1:1 reaction stoichiometry
  - Tunable absorption energy
    - Choice of substituent groups
  - Clean, reversible kinetics
- 
- **Aprotic heterocyclic anions ("AHA"s)**
    - Simple, tunable Lewis bases



*US patent pending, University of Notre Dame*



# As predicted, little viscosity increase upon reaction



Molecular modeling shows that only cation-anion interactions are present; *no salt bridges formed!*

- Modest viscosity change upon reaction!
- Process simulations suggest substantial CO<sub>2</sub> reduction relative to amines (see poster by Trimeric, #1291)

# Conclusions

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- Ionic liquids a promising platform for chemically tailored gas separations
- Molecular simulations have helped design a new class of reactive ionic liquids that
  - Do not increase in viscosity upon reaction
  - Have desired 1:1 binding mechanism
  - Have tunable enthalpies of reaction for process optimization
- In-house synthesis, characterization and testing capability
- Many technical hurdles remain to be overcome
  - Run a lab scale demonstration unit
  - Additional testing, optimization and characterization
- **Students and postdocs**
  - Elaine Mindrup, Mandelle Danser, Thomas Sentfle, Tom Rosch, Hao Wu, Jindal Shah, Marcos Perez-Blanco, Matthew LeMay, Burcu Gurkan, Juan de la Fuente, Erica Price, Devan Kestel, Samuel Seo, Marjorie Massel, Levi Wilson, Michael Glaser, David Zadigan, Brett Goodrich, Lindsay Ficke

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