Ionic Liquids: Breakthrough Absorption Technology for Post-combustion CO_2 Capture

Project NT43091

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Trimeric

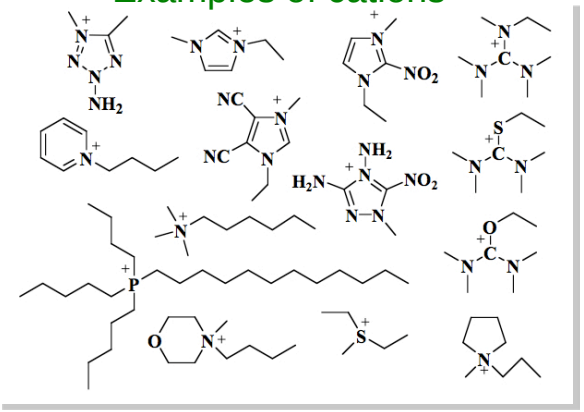
Project status

- Project funding:
  - DOE Share: $2,535,471
  - Non-DOE share: $1,289,808
- Performance dates:
  - March 1, 2007- October 31, 2011
- Project participants:
  - University of Notre dame (lead)
  - Babcock and Wilcox
  - DTE Energy
  - EMD Chemicals / Merck
  - Koei Chemical
  - Trimeric Corp.
- Project objectives:
  - Develop ionic liquid solvents that can be used as a cost effective post-combustion CO_2 capture solvent

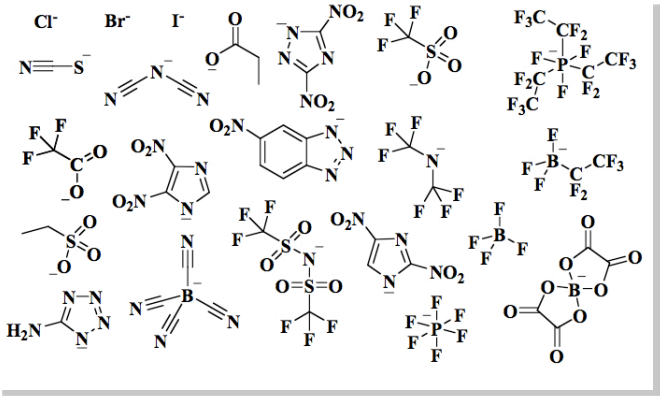
Ionic Liquids and Their Potential as CO_2 Sorbents

- 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_2 solubility and selectivity

Examples of cations



Examples of anions



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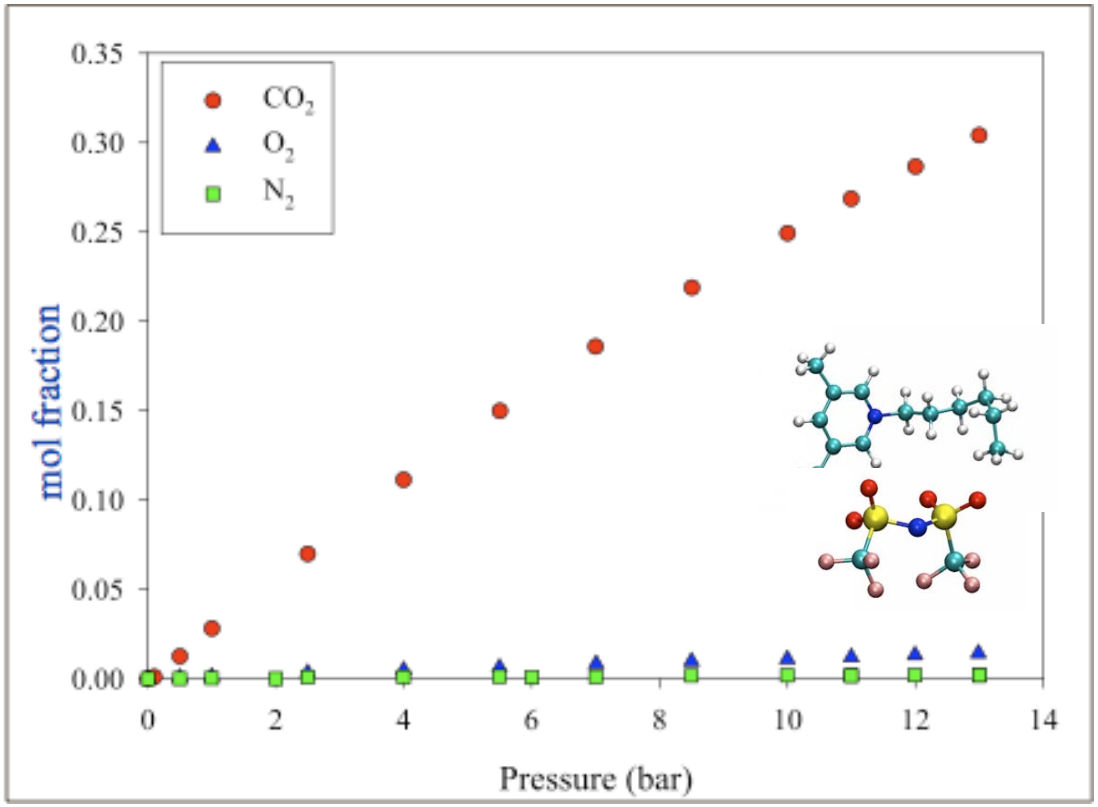
Use of ILs for CCS?



J. Phys. Chem. B, 108, 20355 (2004)

- Process modeling: physical CO_2 solubility *not high enough* to be practical for post-combustion capture
  - Need to add chemical functionality to increase capacity

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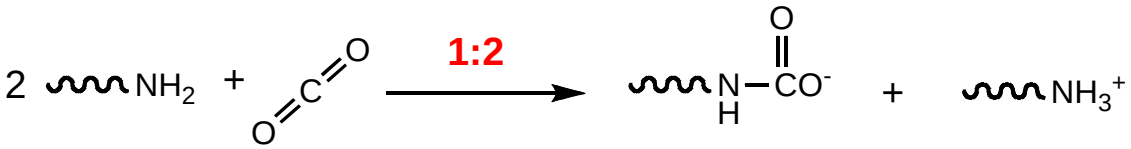
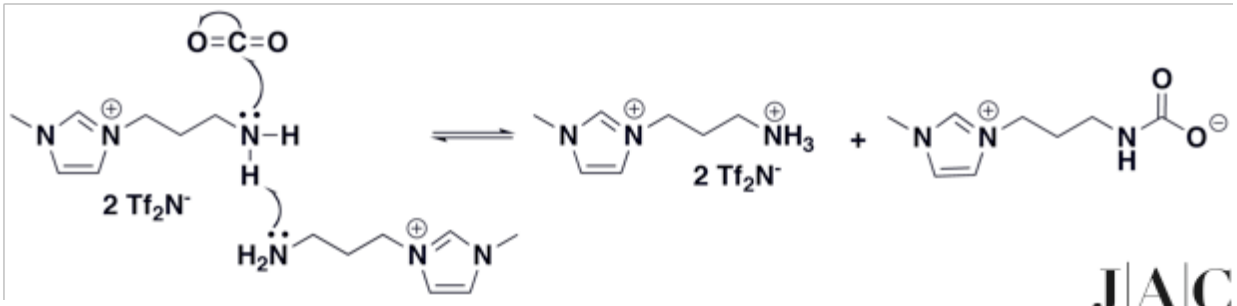
Adding reactive groups to ionic liquids increases capacity

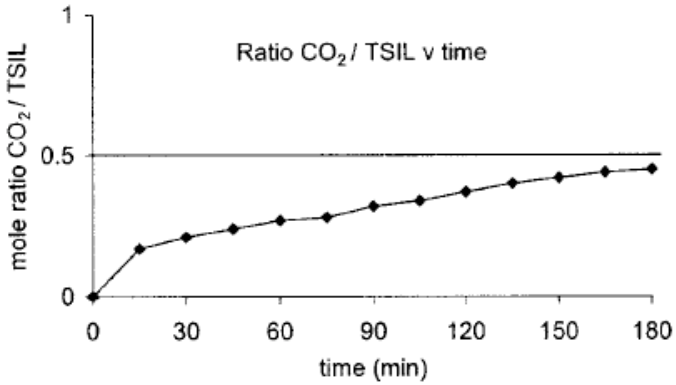
- Build on aqueous amine chemistry:



TSIL CO_2 reaction mechanism



1 atm CO_2
Room temp.



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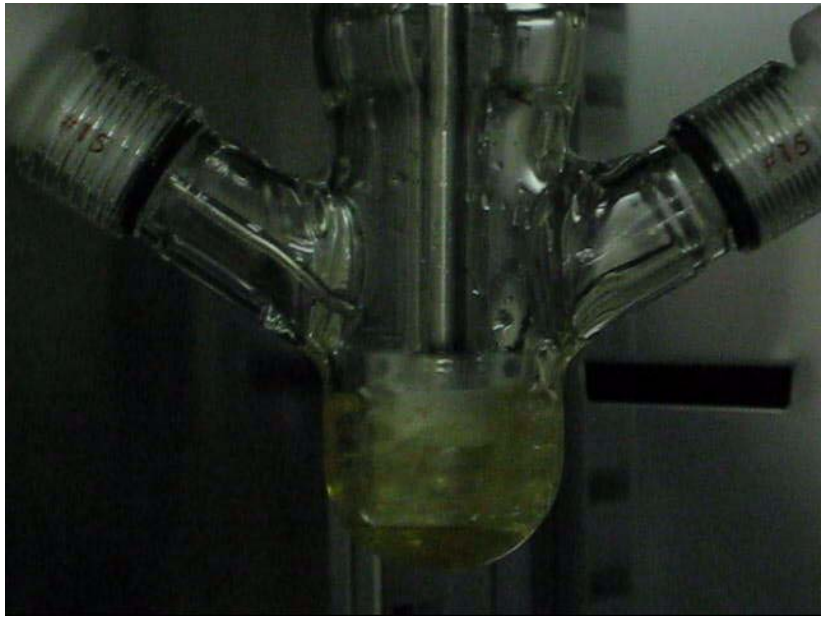
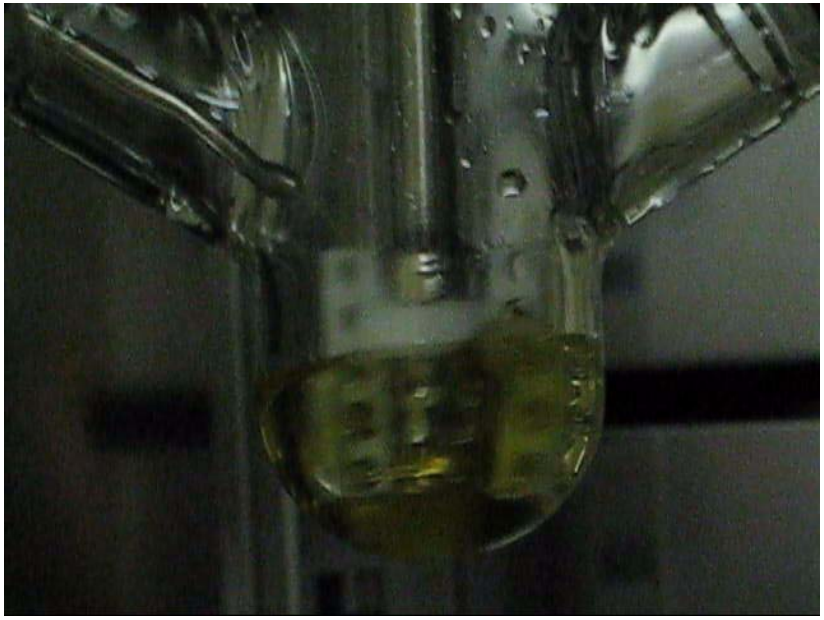
Problems with conventional TSILs



No CO_2



17 mbar CO_2

- Liquid becomes extremely viscous upon CO_2 contact
- Why? Can we eliminate this?
- Can we tune other physical and chemical properties for optimal CCS?

Use molecular modeling + experiments to design ILs for CO_2 capture

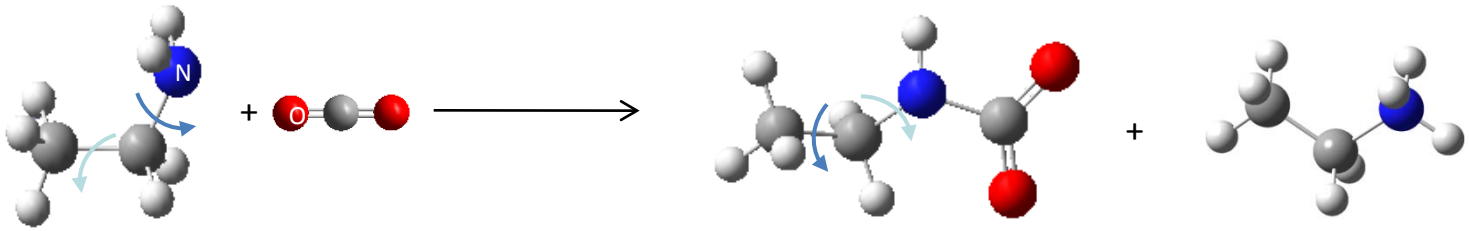
Solvent design targets

- Understand and then eliminate viscosity increase upon CO_2 complexation
- Optimize process economics (using key parameters identified by process modeling)
  - Enthalpy of reaction
  - Stoichiometry of reaction
  - Reaction kinetics

- Approach: combination of molecular-level modeling, process simulation and experimental synthesis and characterization

Molecular-level Modeling Approach

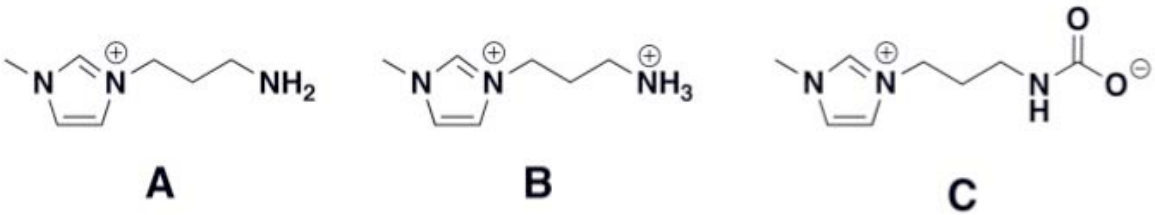
- Electronic structure calculations: evaluate structural and energetic properties of potential absorbents

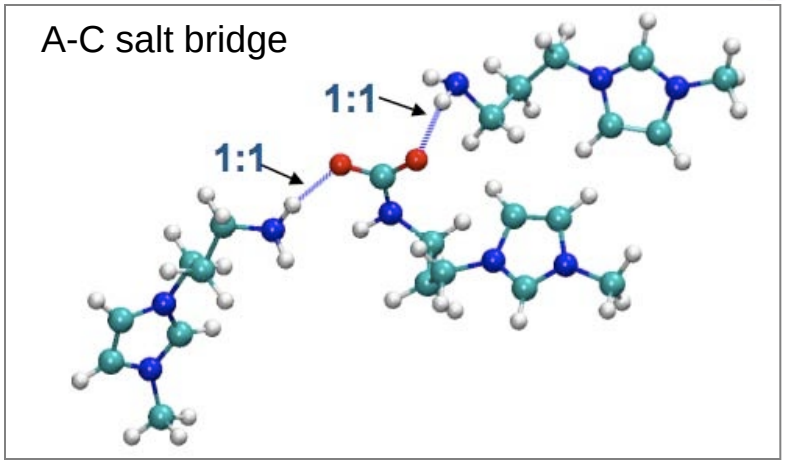


- Examine relative energies for different binding mechanisms
- Investigate how substituent groups affect reaction enthalpy
  - Possible to computationally screen a huge number of candidates
- Condensed phase molecular dynamics simulations
  - Enable calculation of bulk properties (heat capacities, densities, dynamics and physical gas solubility)

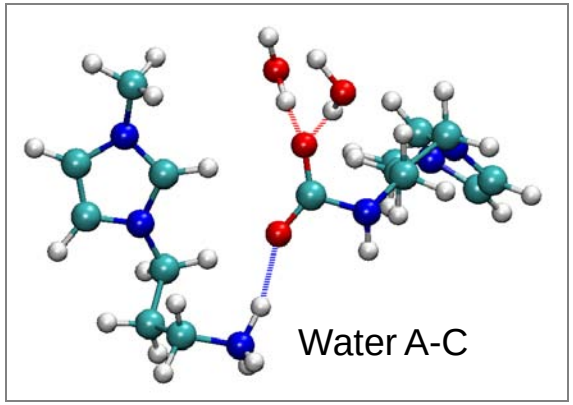
Goal: virtual screening of solvents to speed discovery

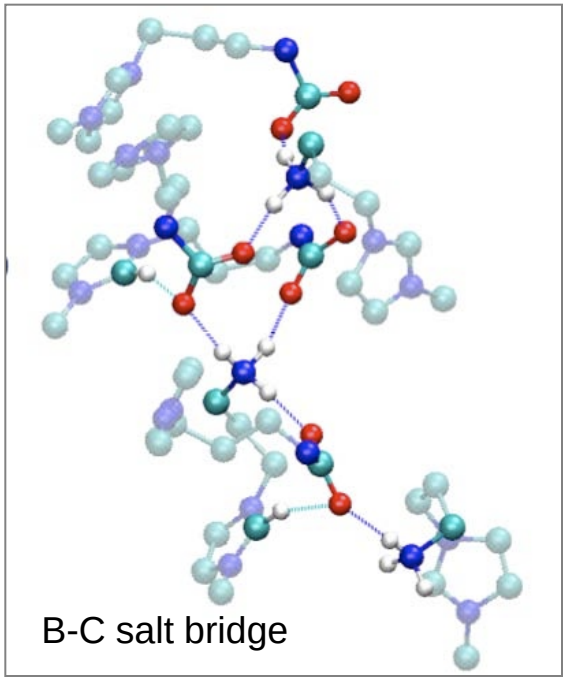
Explanation for viscosity increase





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





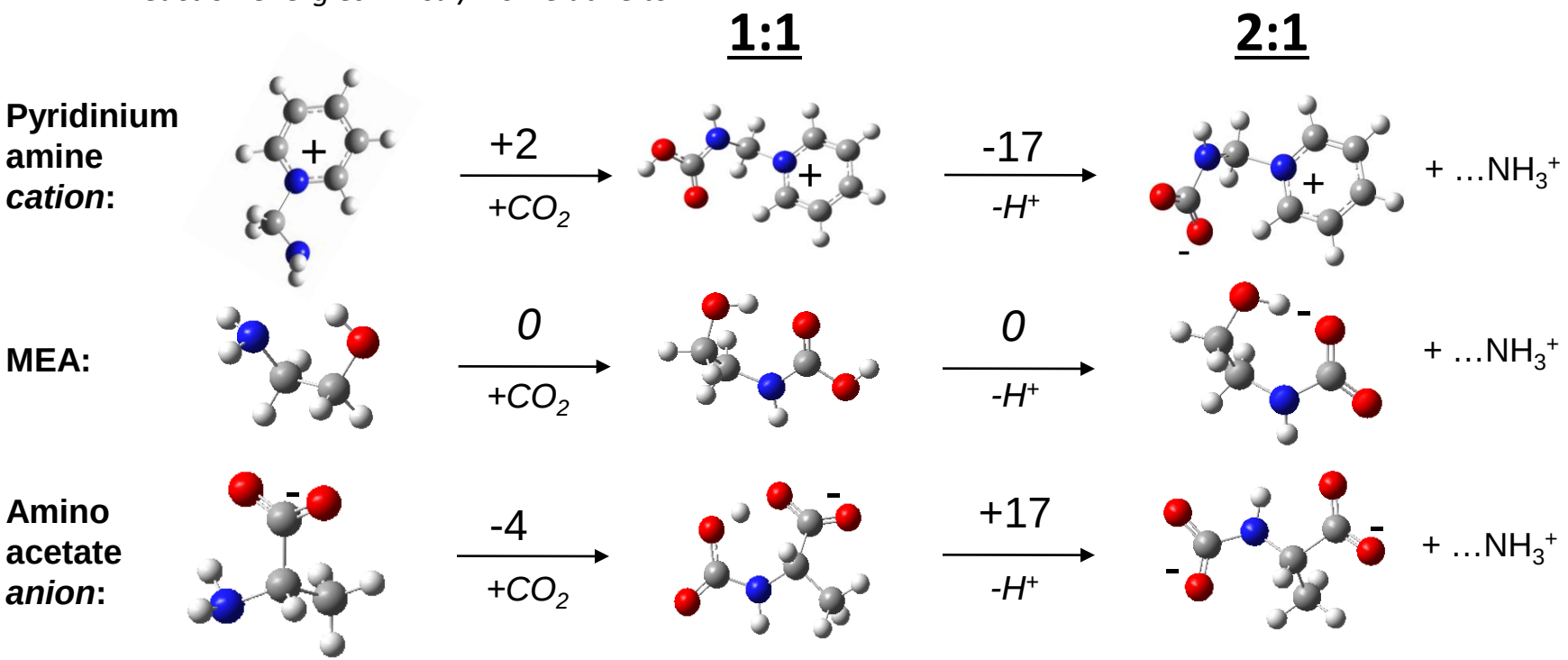
Atomistic MD simulations show an increase in viscosity upon reaction with CO_2 just like experiments.

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

Reaction stoichiometry

Reaction energies in kcal/mol relative to MEA



- Local cation tethering favors 2:1 binding
- Local anion tethering disfavors 2:1 binding, favors 1:1
- Tethering ion and tethering point as important as functional groups in controlling CO_2 reactions
  - DOF unique to ILs!!

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

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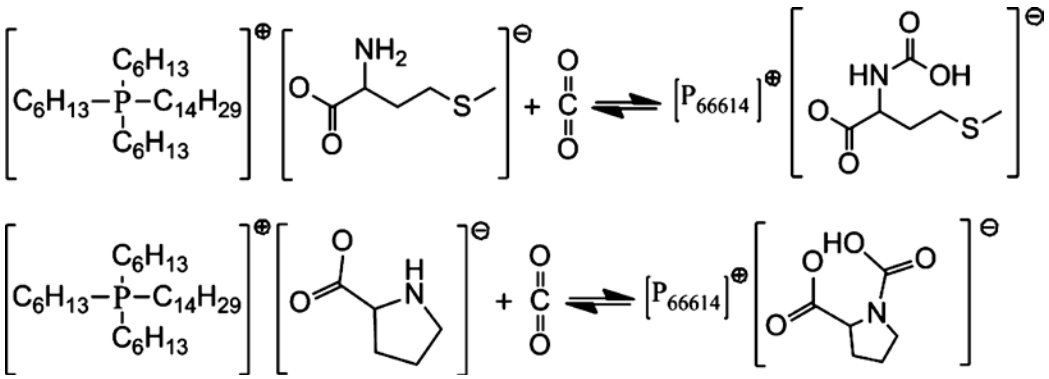
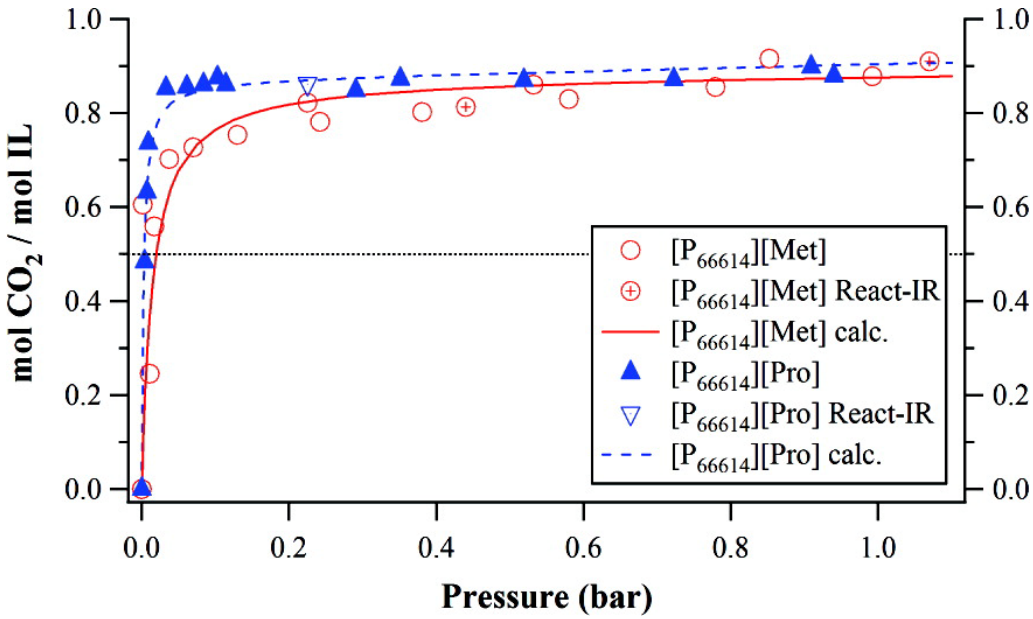
1:1 binding for anion functionalized IL confirmed





- Simulations predict prolinate (–71 kJ mol^{-1}) stronger 1:1 absorber then methionate (–55)
- Experimental RT isotherms consistent with this ranking and with ~1:1 reaction stoichiometry
- Excellent agreement with calorimetric experiments

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

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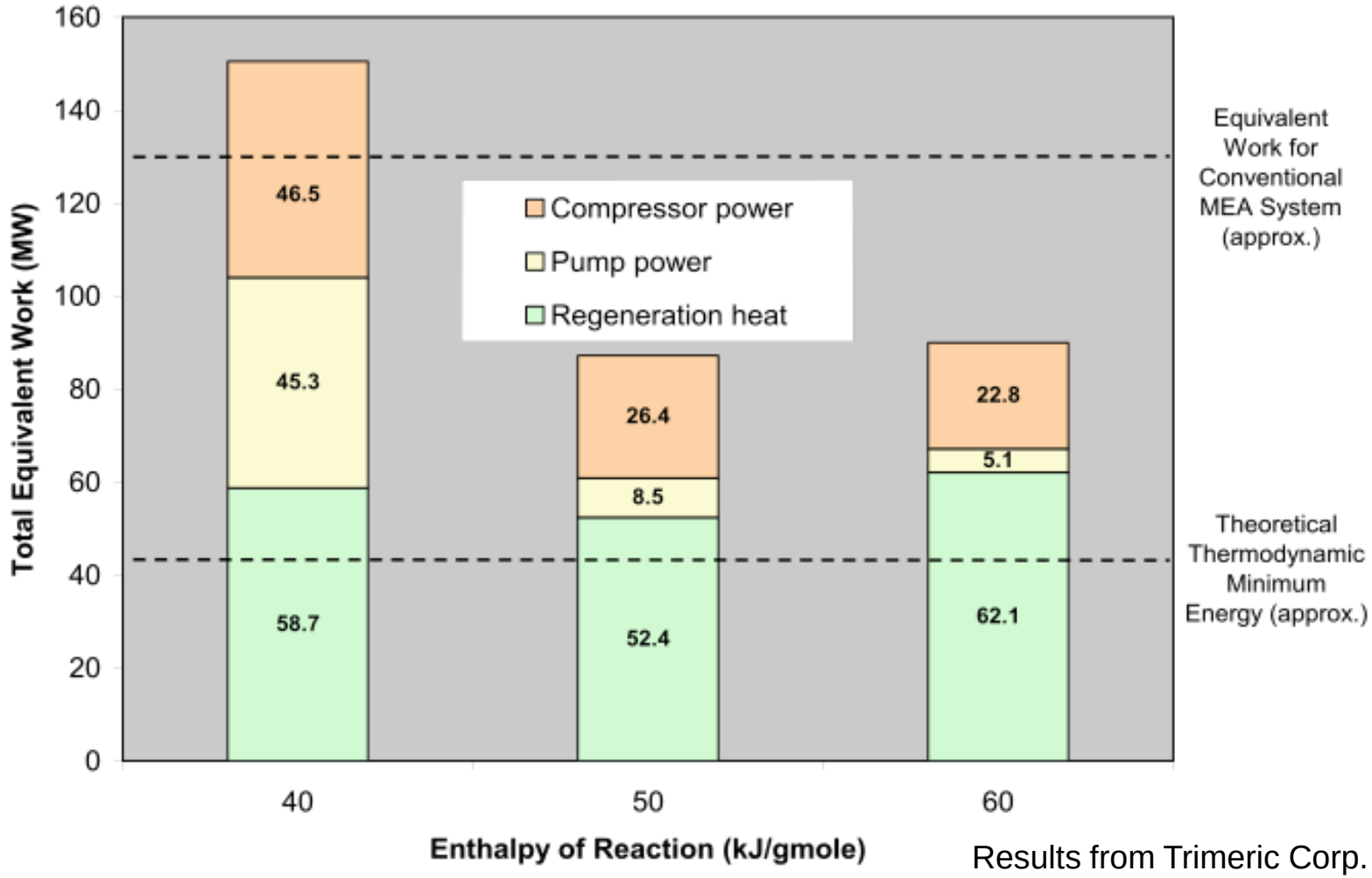
Optimal binding energy from process modeling



Results from Trimeric Corp.

Can ILs be designed with optimal CO_2 reaction enthalpy?

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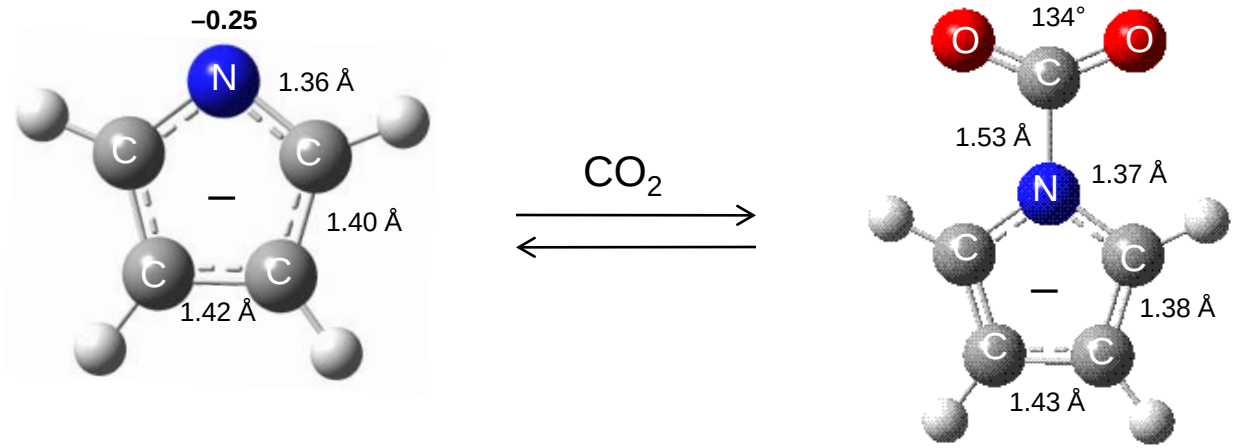
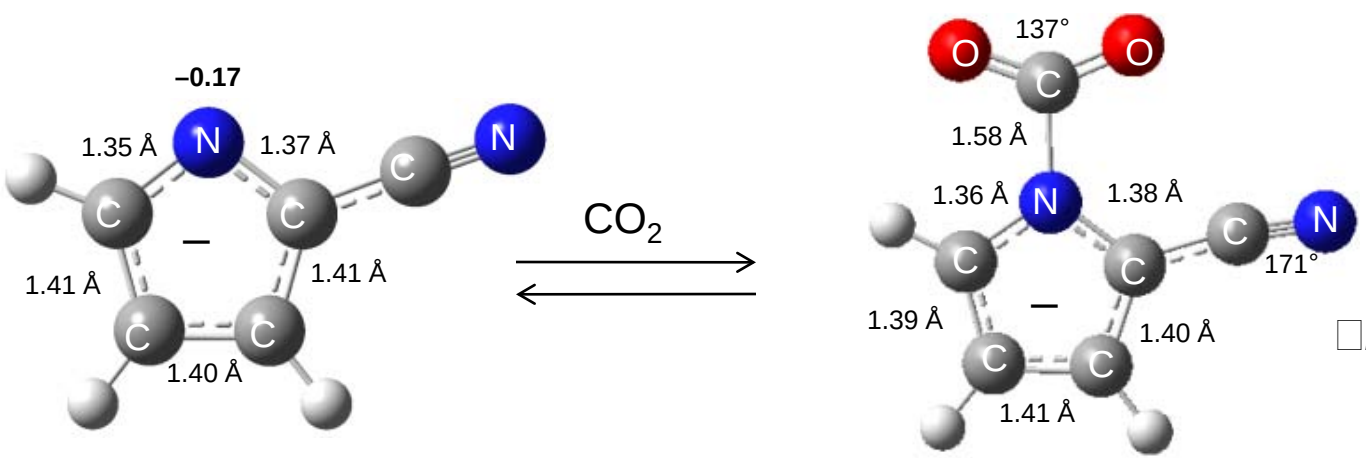
Tuning reaction enthalpy using substituent groups



$\Delta E_o = -98$ kJ mol^{-1}

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



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

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

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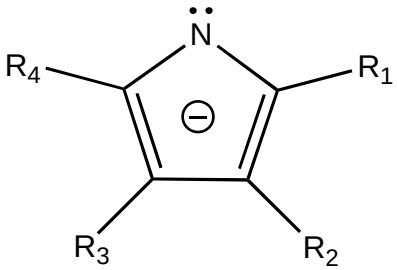
TSIL design targets

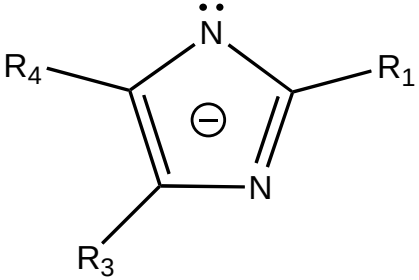
Design targets

- Anion-functionalized IL
  - 1:1 reaction stoichiometry
- Disrupt H-bonding network
  - Aprotic base
- Tunable absorption energy
- Clean, reversible kinetics

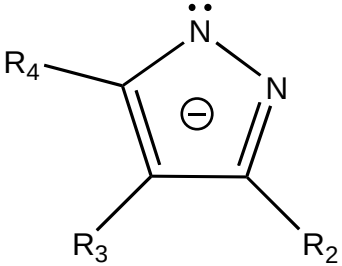
- **Aprotic heterocyclic anions ("AHA"s)**
  - Simple, tunable Lewis bases
  - Takes advantage of intrinsic nucleophilicity of anions



"Pyrrolide"



"Imidazolide"



"Pyrazolide"

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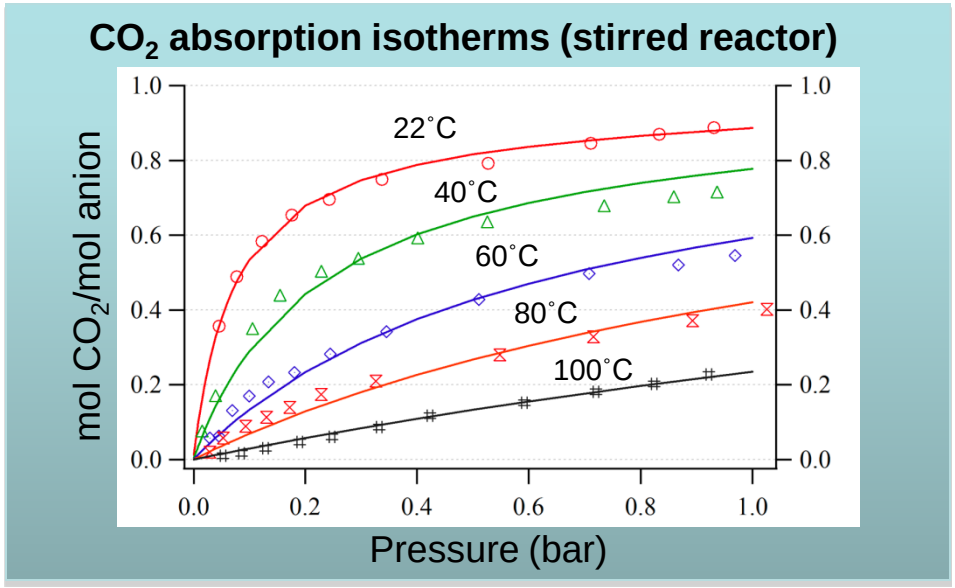
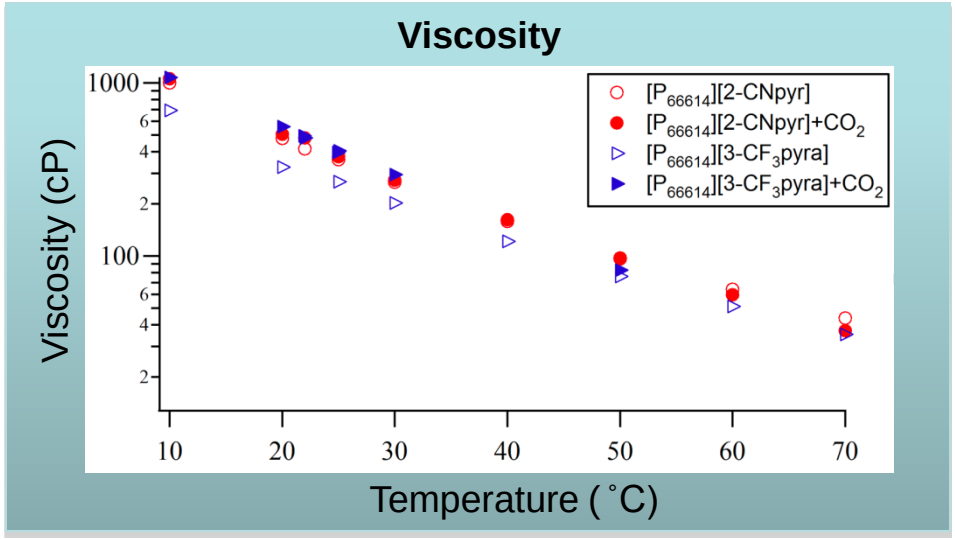
$[P_{66614}]$[2-CNpyrrolide] experiments

- AHAs readily form room-temperature ionic liquids
- CO_2 isotherms consistent with 1:1 reaction
- Isotherms fit with Langmuir + Henry's Law model
  - $\Delta H_{rxn} = -43$ kJ mol^{-1}
  - $\Delta S_{rxn} = -130$ J mol^{-1} K^{-1}
- Virtually no change in viscosity!





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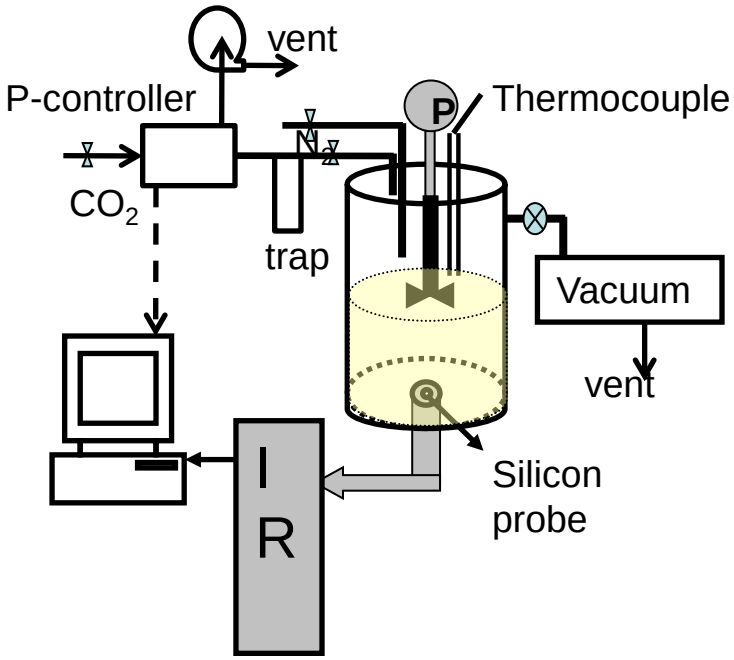
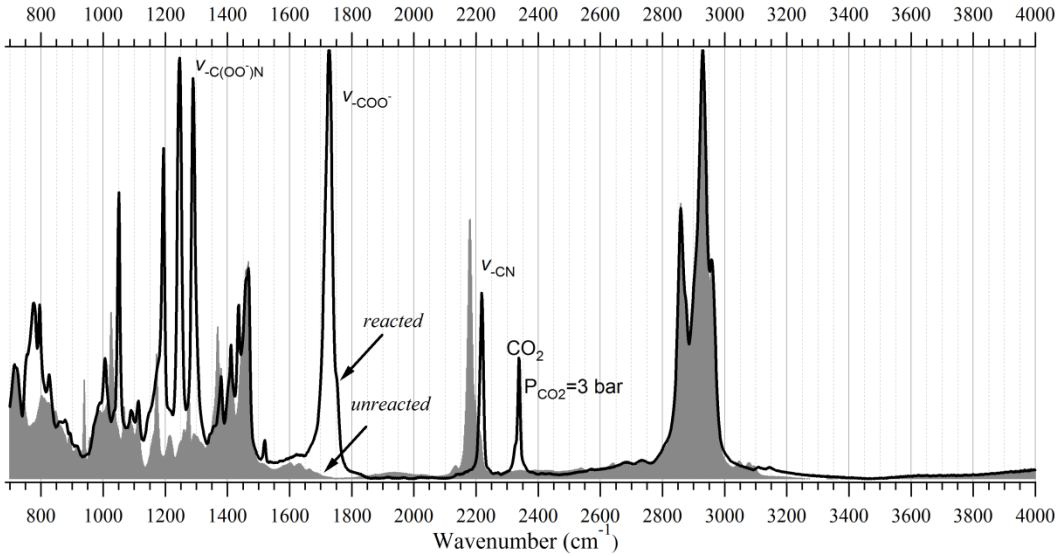
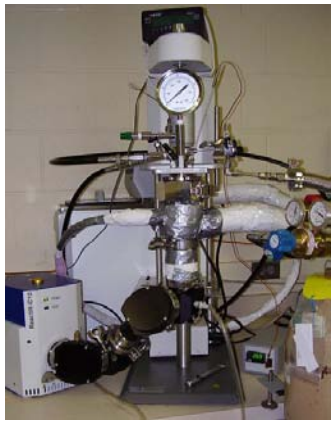
In situ vibrational spectroscopy







- IR distinguishes physically and chemically absorbed CO_2
- Confirms 1:1 reaction stoichiometry
  - Ammonium peaks absent
  - Carbamic acid peaks appear

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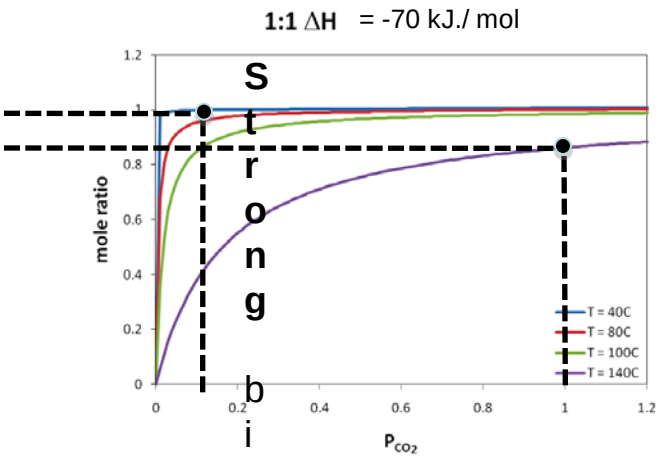
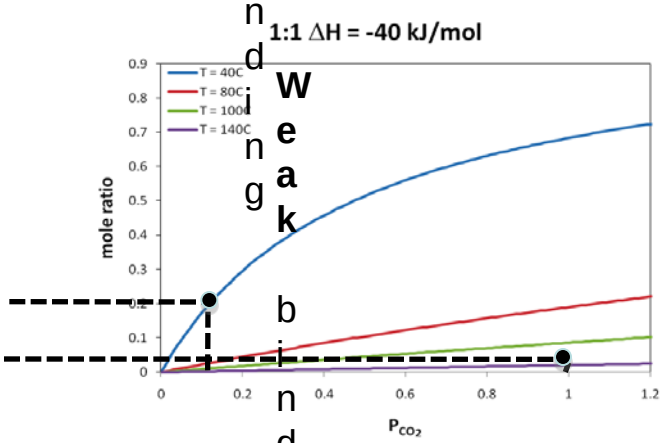
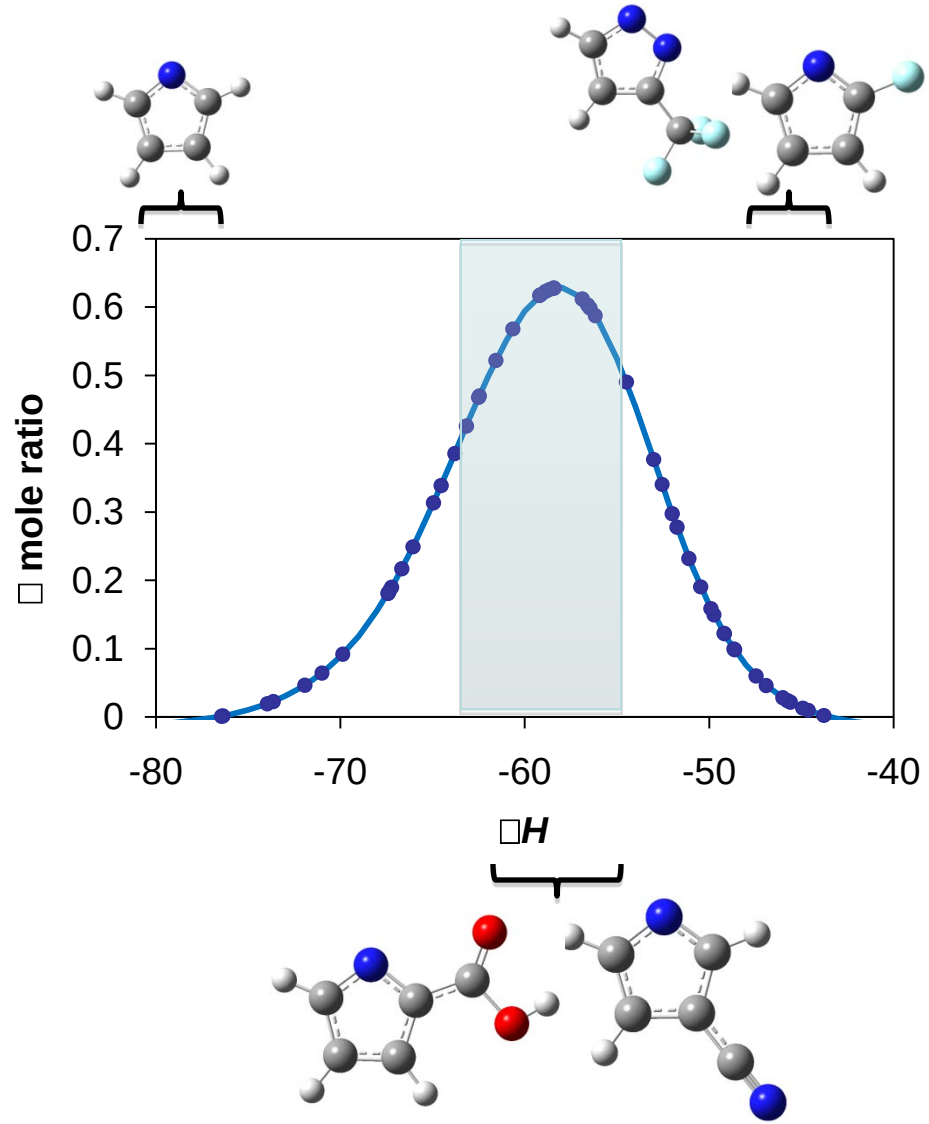
Absorption optimization



Strong binding



Weak binding



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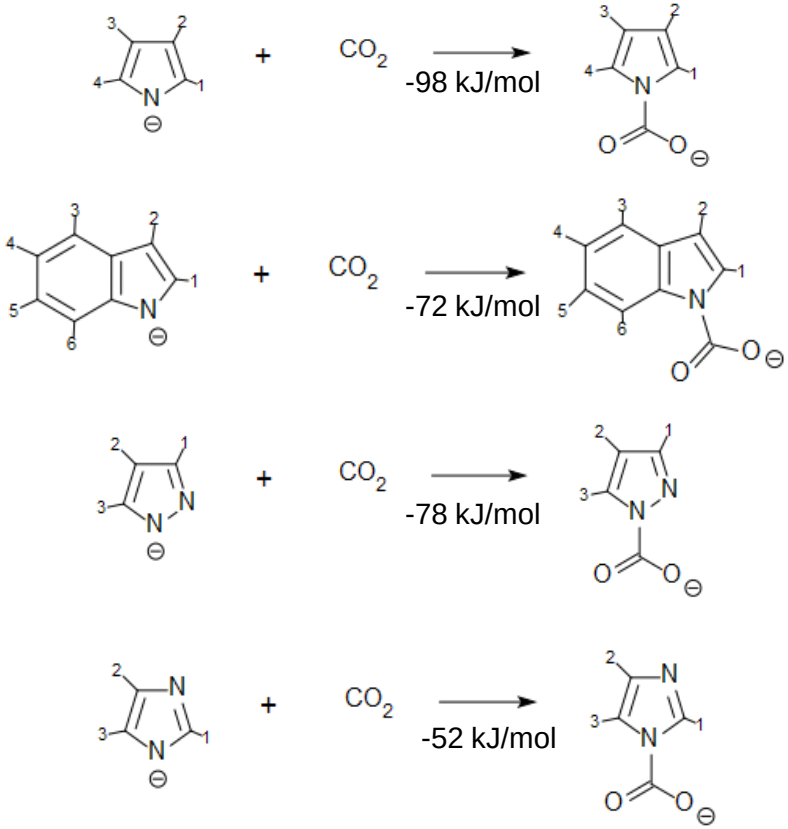
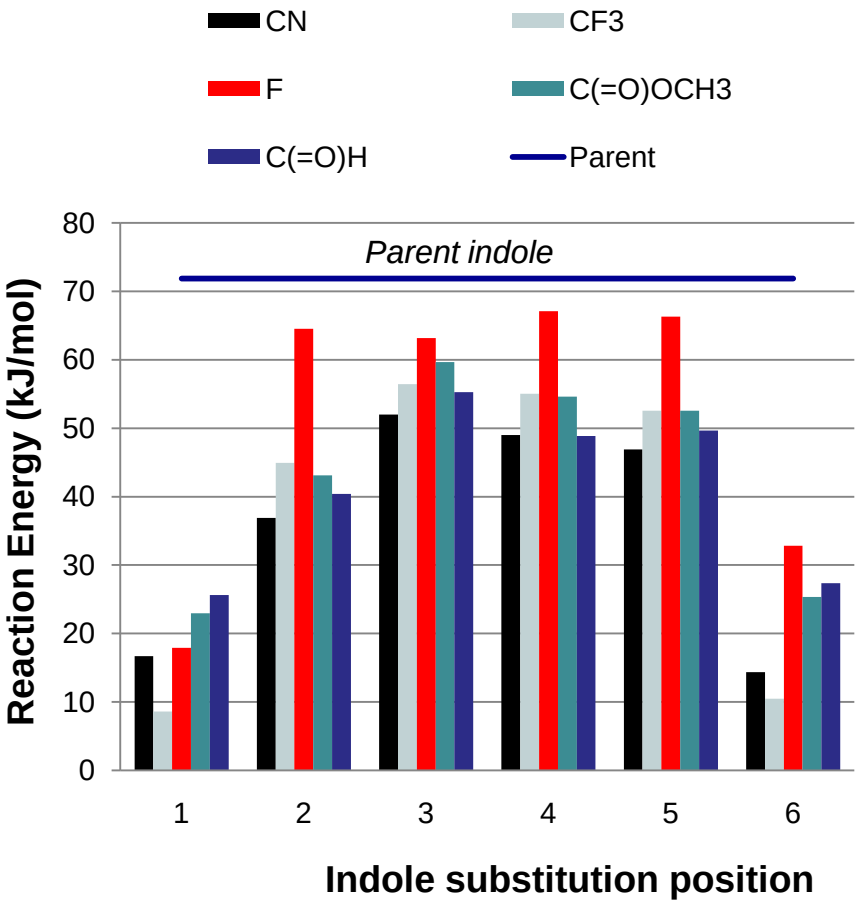
Generalized AHA reactions

- Wide variety of AHAs predicted to combine with CO_2



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

- Substituents offer wide range of reaction tunability



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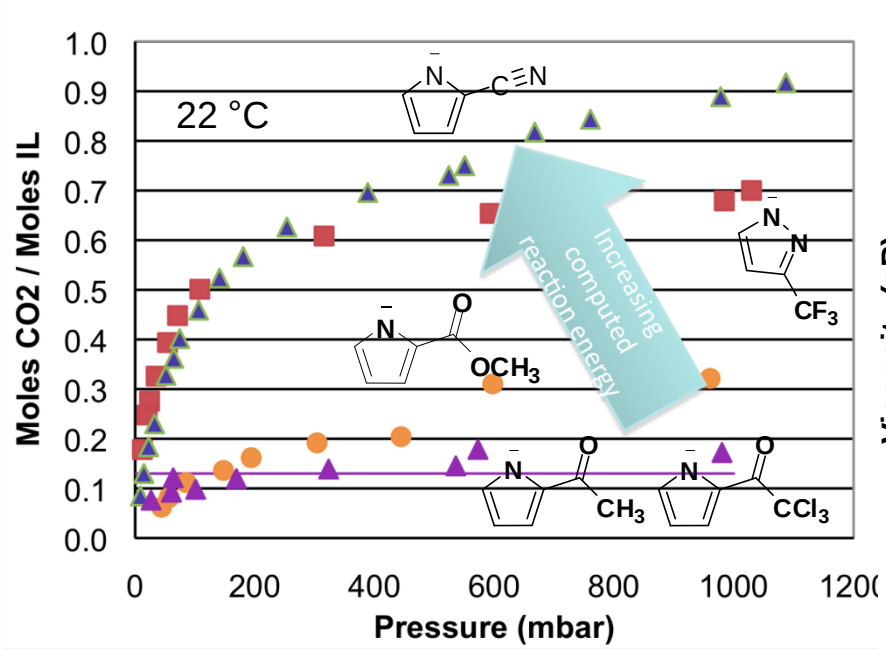
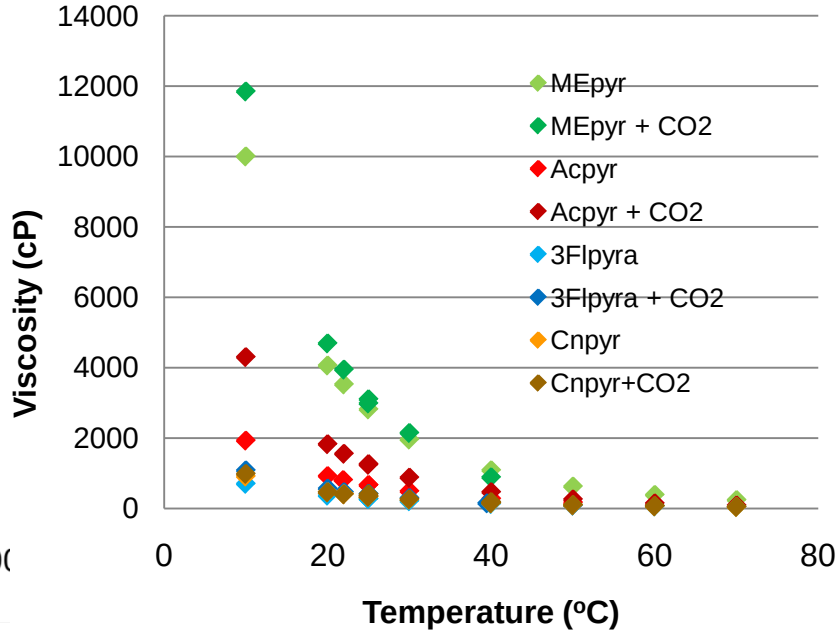
TSIL design targets—realized

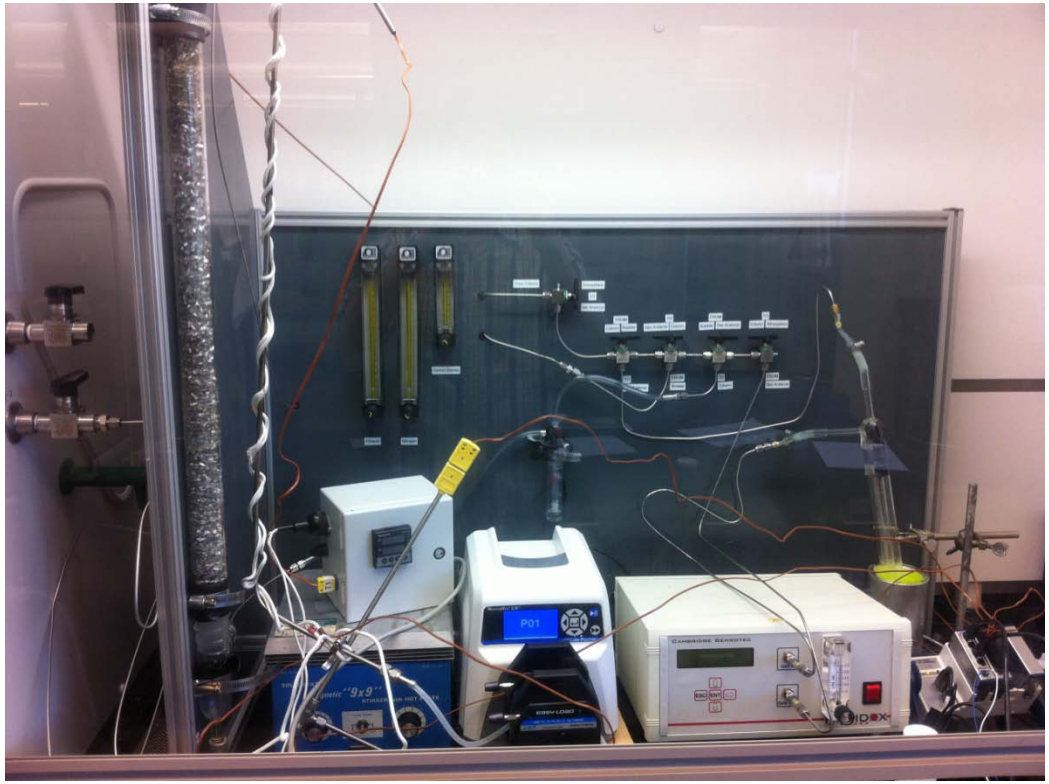




Gen 3 results

- Adsorption uptake tracks computational predictions
- Stoichiometry close to 1:1
  - Atom efficient
- Modest viscosity change upon reaction!

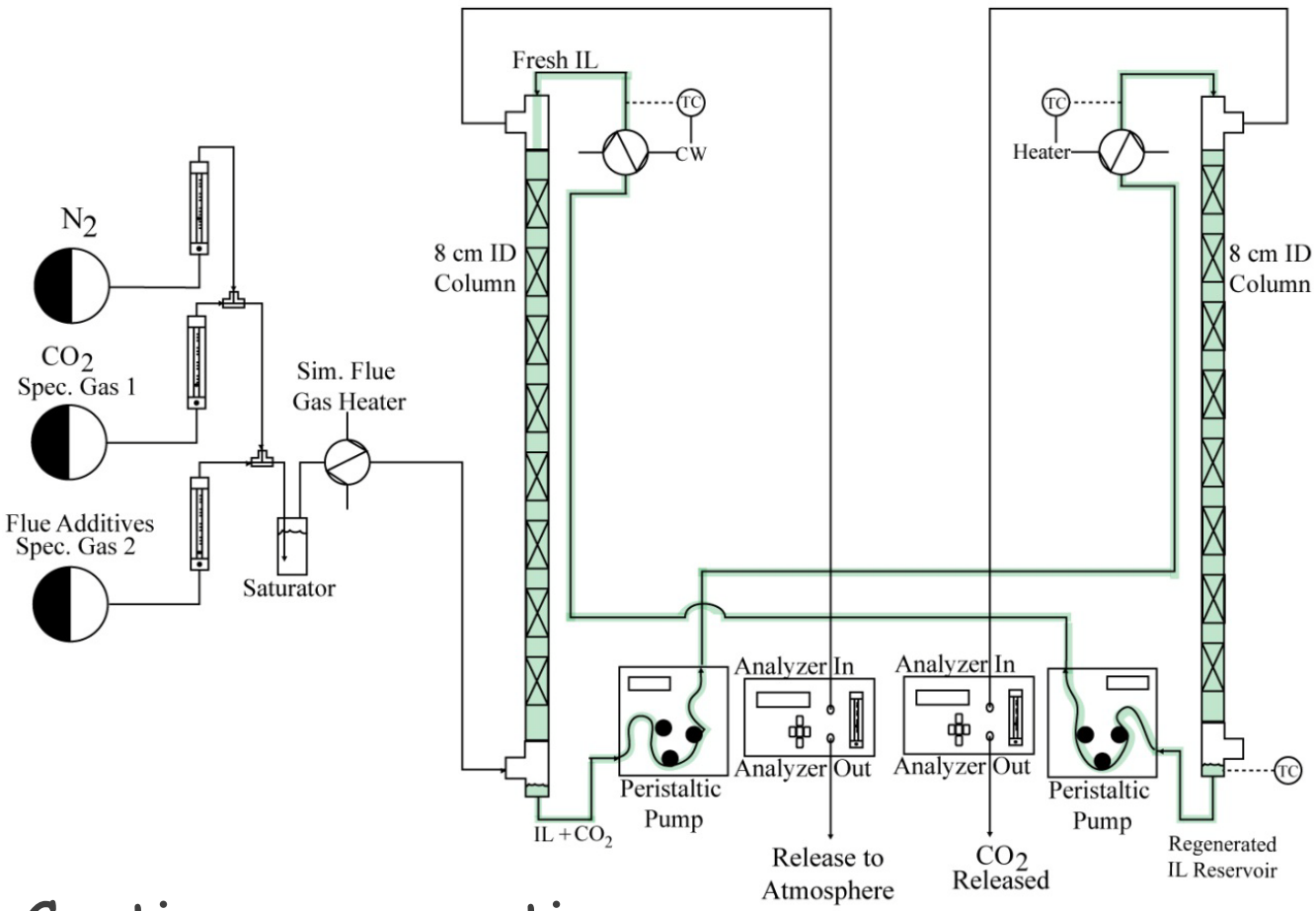
Small-scale batch absorber



Preliminary results

- Mass transfer efficiency (measured by HTU) equal to or better than aqueous MEA
- Successfully captured CO_2
  - several regeneration cycles

Lab-scale Absorption Experiments



- Continuous operation
- 40 liter liquid samples

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Current work

- Continued work on discovering the optimal AHA IL
  - Binding energy
  - Viscosity
  - Other properties
- Perform larger lab-scale tests
  - Gain operational experience
  - Degradation, impurities
- If successful, preparations for moving to larger scale testing

Conclusions

- 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
  - Operation of continuous 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, Dan Pohlman

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the ENERGY lab
Where energy challenges converge and energy solutions emerge

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