Evaluation of Ionic Liquids in Post-Combustion CO_2 Capture

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DOE CCS Targets

- Carbon capture and sequestration key tool for greenhouse gas mitigation
- DOE focus areas
  - Separation and capture
  - Sequestration & storage
  - Monitoring, mitigation, & verification
- Current technology does not meet goals
  - Solvents (amines, ammonia)
  - Sorbents, membranes

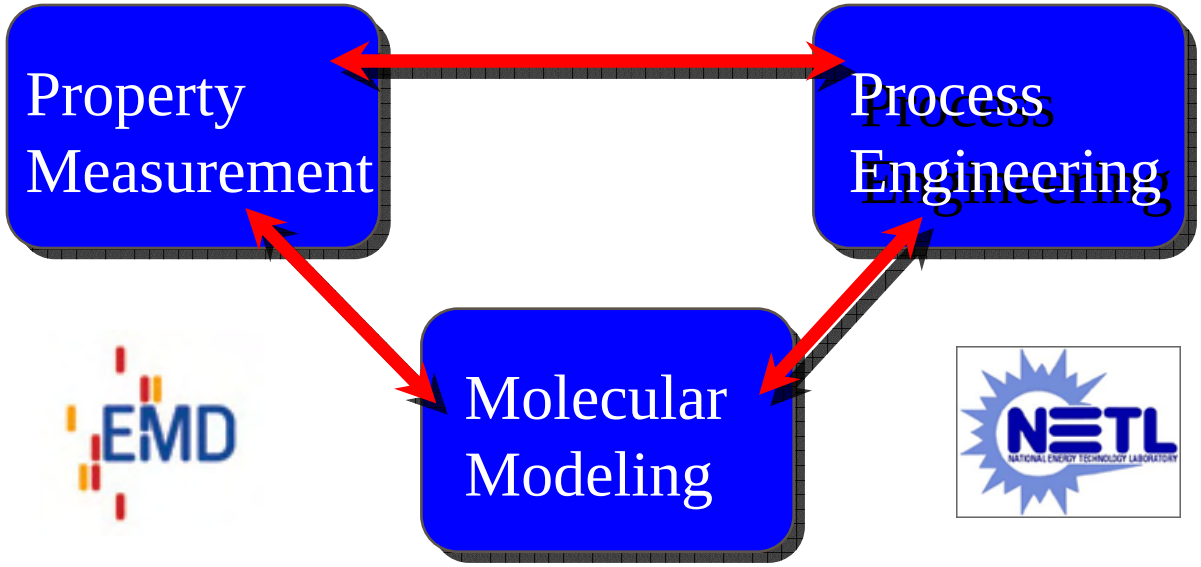
Cost Performance Goals

Year	COE Penalty IGCC Plants (% Increase)	COE Penalty PC Plants (% Increase)
2002	30	80
2007	20	45
2012	10	20
2015	<10	10

Sean Plasynski
NETL, 6/5/07

Research Goal

- Develop *new solvents* based on *ionic liquids* that are *cheaper* and more *energy efficient* than competing technologies
- 3-year project supported by DOE NETL
- Strategy: integrated approach involving molecular modeling, experimental property measurement and process engineering



B&W

EMD

NETL
NATIONAL ENERGY TECHNOLOGY LABORATORY

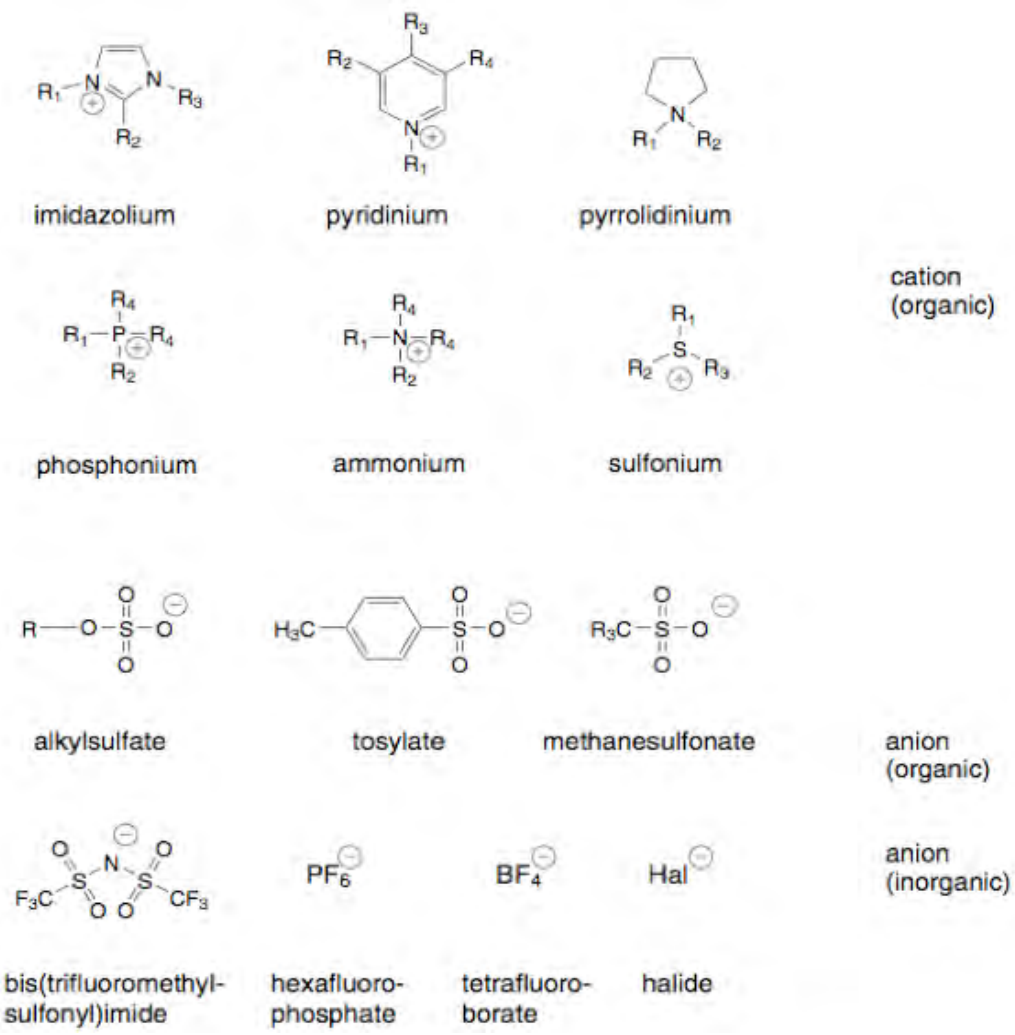
Trimeric

DEPARTMENT OF ENERGY
UNITED STATES OF AMERICA

UNIVERSITY OF NOTRE DAME

AIR PRODUCTS

What are ionic liquids?



Some examples of commercially available ionic liquids

- Ionic liquids are molten salts that are molten near ambient conditions
  - Not ionic solutions
- Many useful properties
  - Solvation properties
  - Very low volatility
  - Thermal stability
- Molecular design
  - Vary cation, anion
  - Functional groups

Key properties for CO_2 capture

- High CO_2 capacity
- High CO_2 selectivity
- Ease of regeneration
  - Low enthalpy of solution
  - Low solubility with water
  - Low heat capacity
- Stability
  - Thermal
  - Other gases (SO_2)
- Low viscosity
- Inexpensive

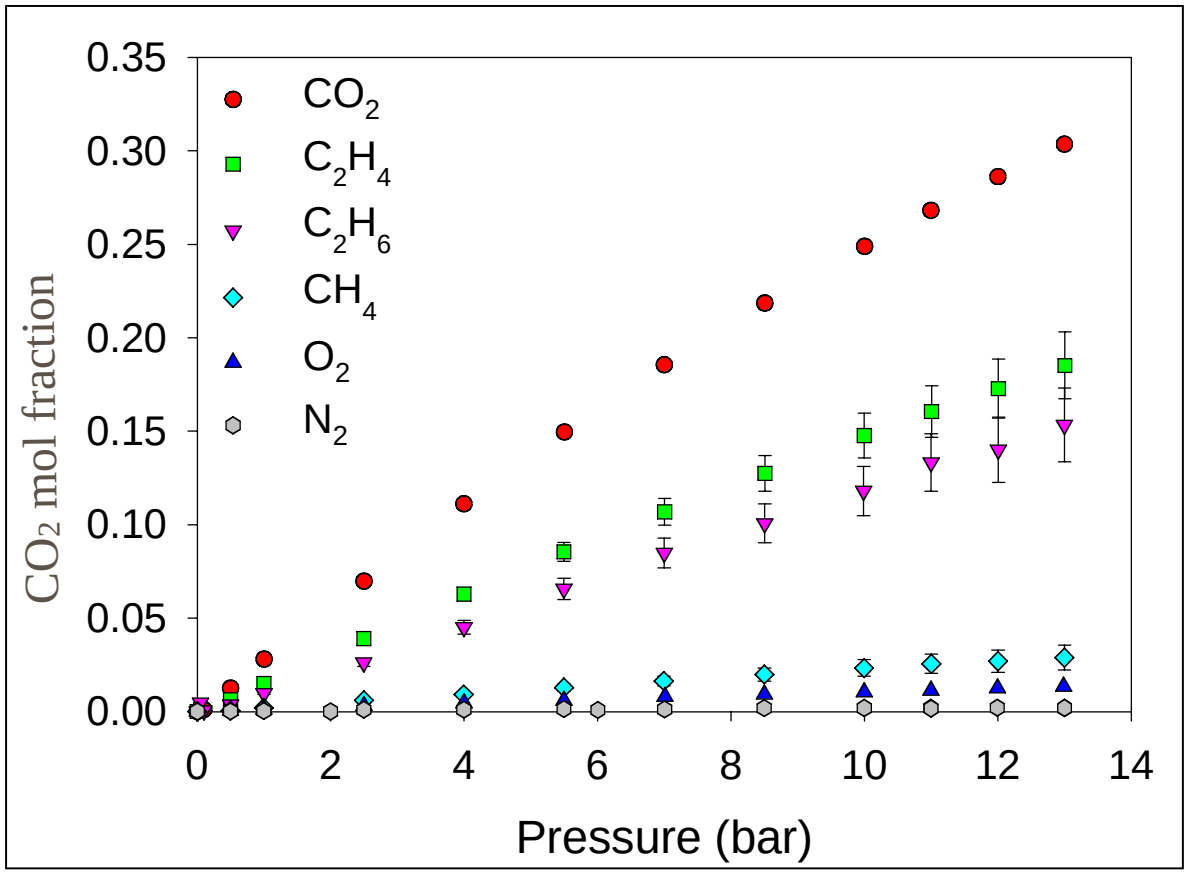
Experimental solubility measurements

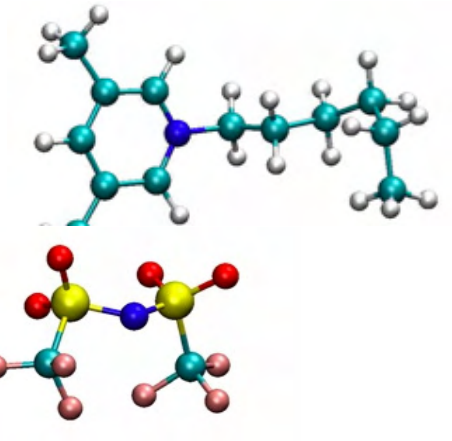
Targets determined by process modeling

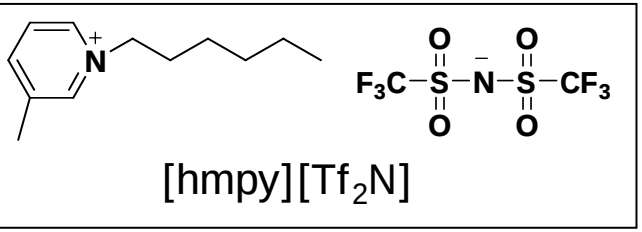
Assumes conventional absorption process

Other processes possible?

CO_2 is very soluble in ionic liquids



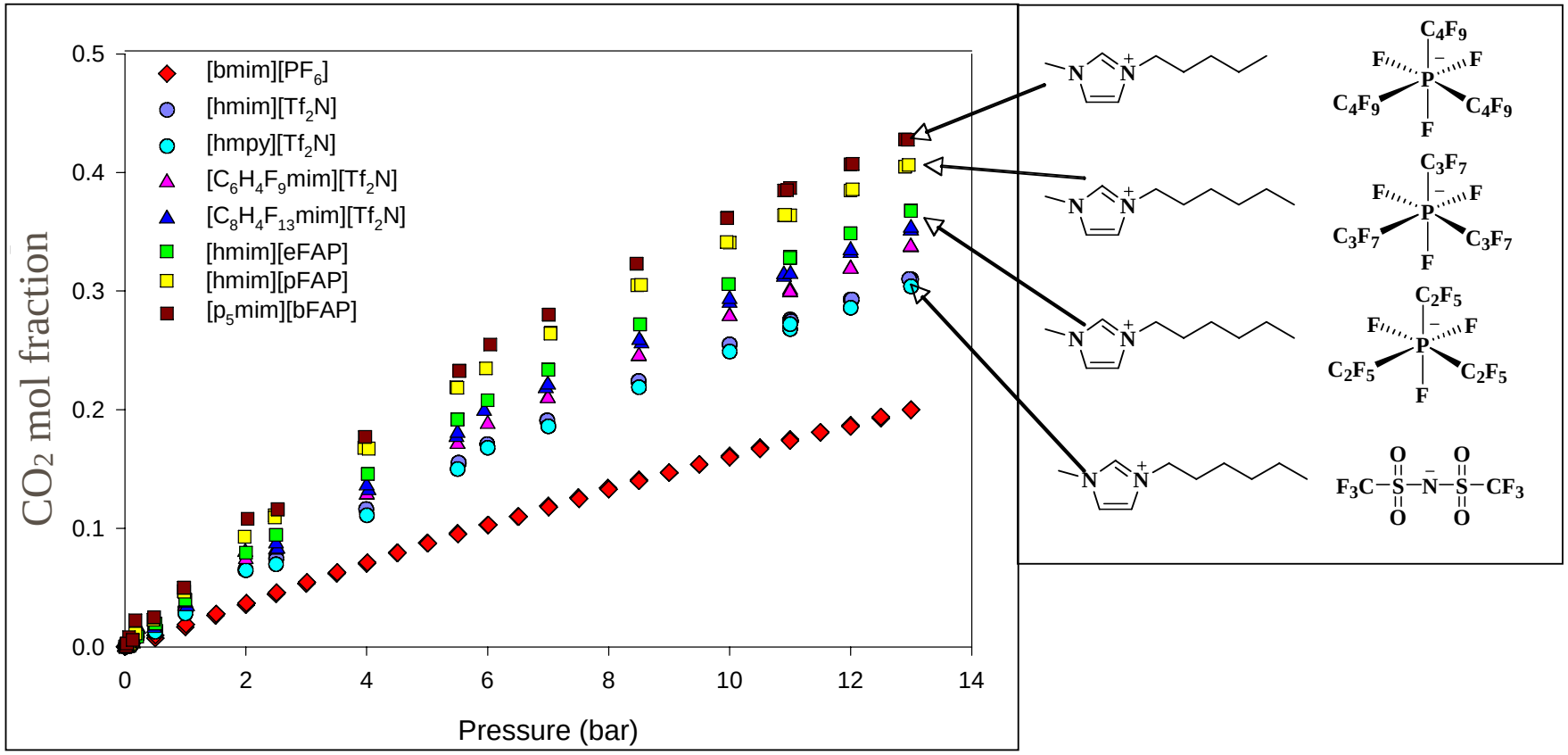




Potential for CO_2 removal from flue gas?

Accounts of Chemical Research, **2007**, 40, 1208 1216

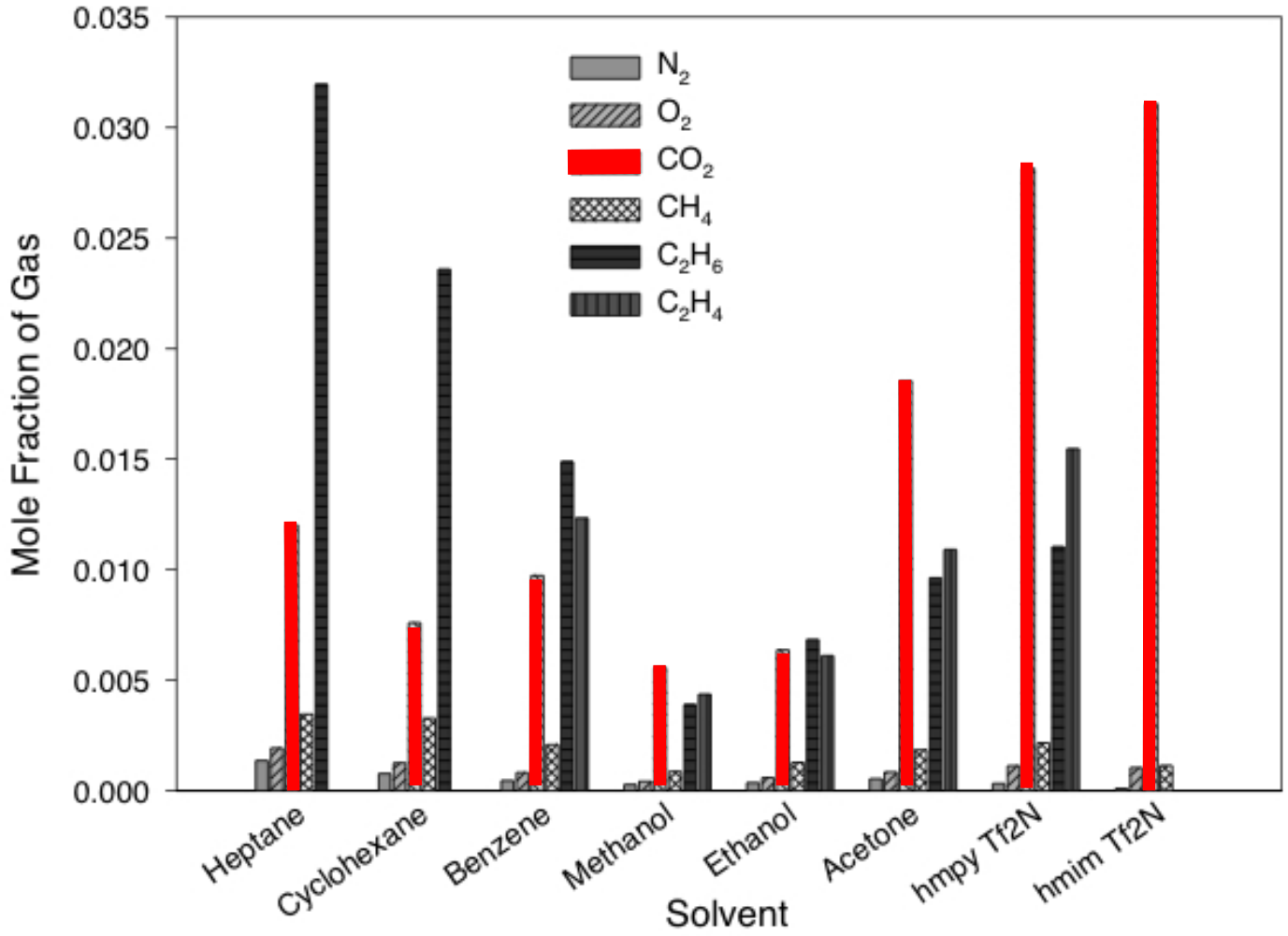
Widely varying CO_2 solubility



Anion has largest effect on physical CO_2 solubility

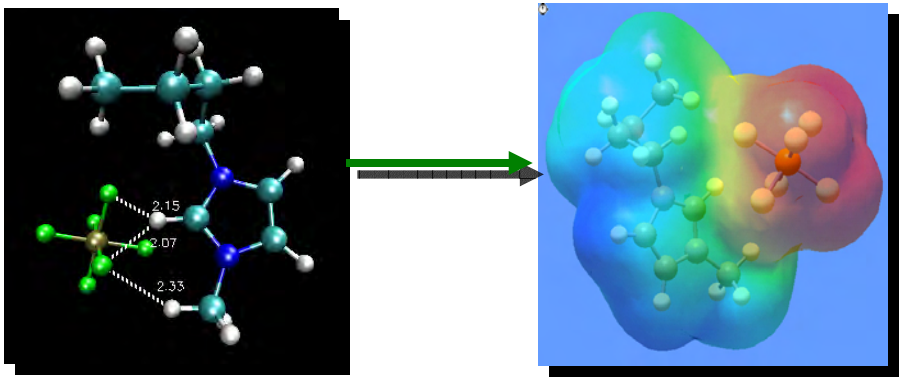
Journal of the American Chemical Society, ***2004***, 126, 5300 5308; *Journal of Physical Chemistry B*, **2007**, 11, 9001 9009

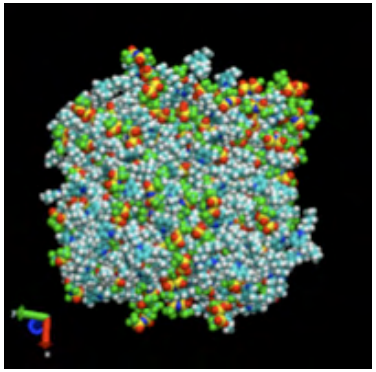
Comparison to other physical solvents



Accounts of Chemical Research, **2007**, 40, 1208 1216

Using molecular modeling to develop new solvents

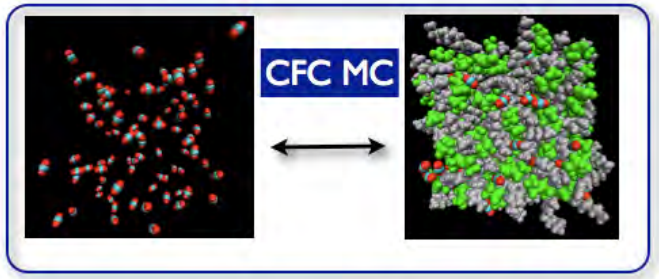


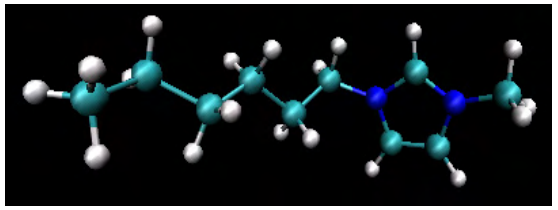


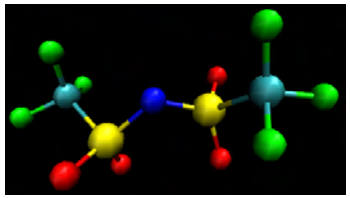
- First-principles simulations
  - Systematic screen intrinsic reactivity
  - Tethering strategies
  - Uptake mechanisms and kinetics
  - Parameterize condensed-phase classical simulations
- Computational approach
  - B3LYP/6-311++G(d,p)
  - Systematic exploration of local conformations and electronic effects
  - Boltzmann averaged energies over conformations

- Classical simulations
  - Condensed phase
  - Thermodynamic properties
  - Transport properties
- Computational approach
  - First-principles derived cassical potential
  - Molecular dynamics
  - Monte Carlo

Calculating gas solubility



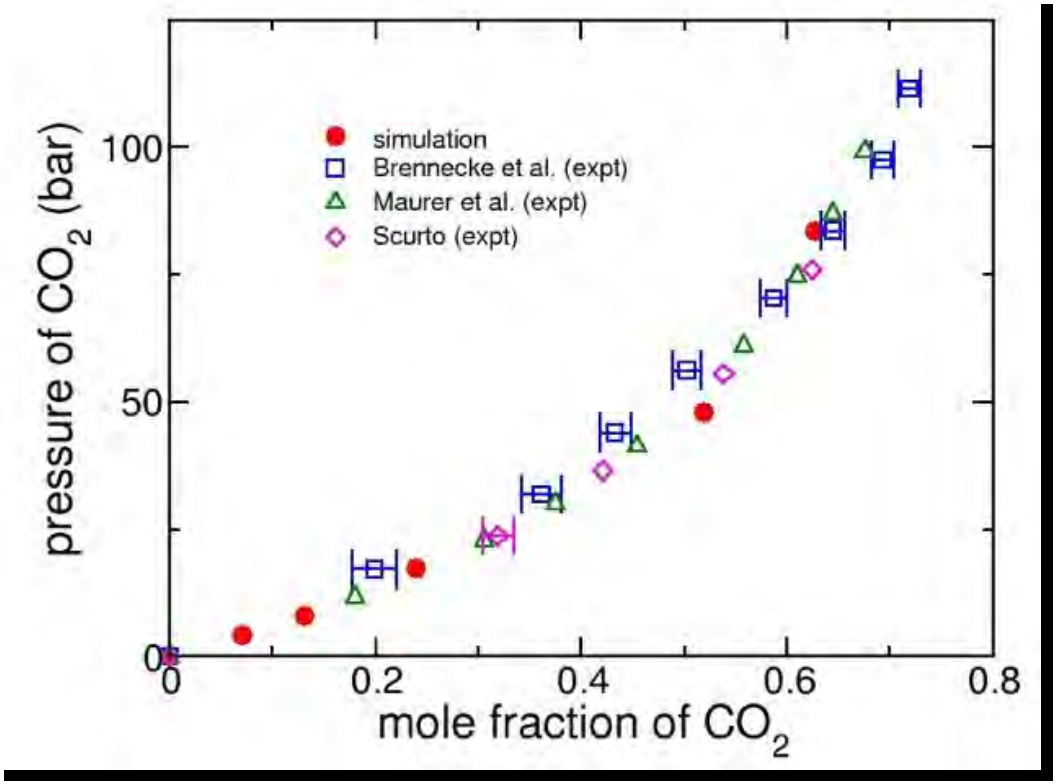




[C6mim] [Tf2N]

Continuous fractional component Monte Carlo

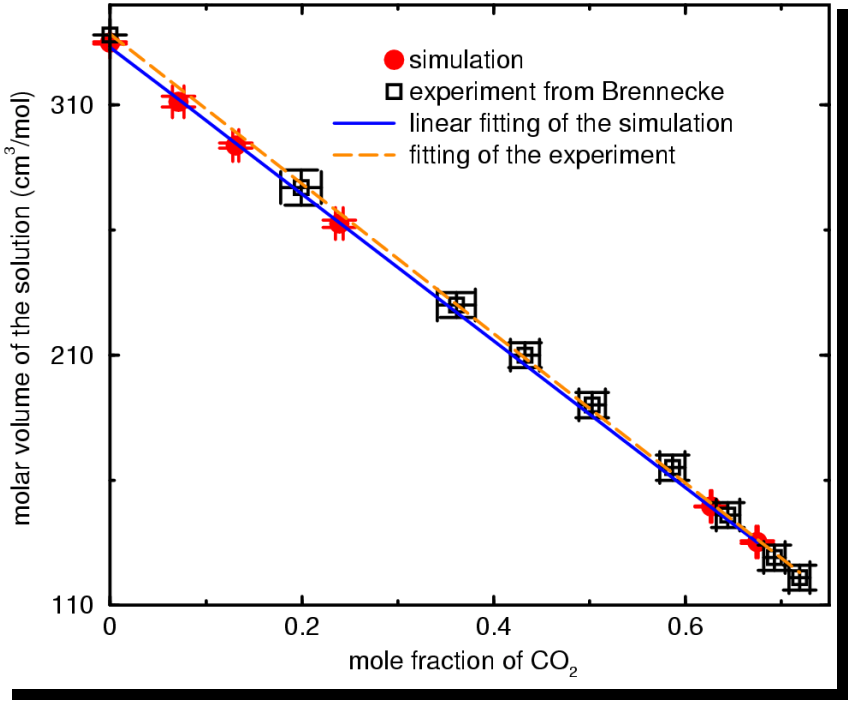
Quantitative agreement between simulations and experiment

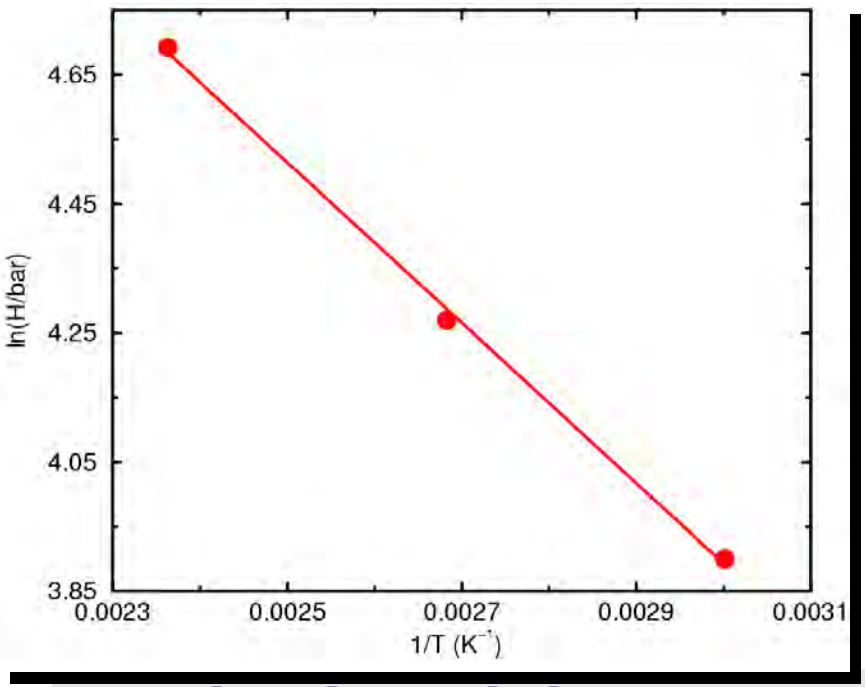


Journal of Chemical Theory and Computation, **2007**, 3, 1451-1463; *Journal of Physical Chemistry B*, **2008**, 112, 2045-2055.

Molar volumes and enthalpies

[C6mim] [Tf2N]





Partial molar volumes

Experiment: 39.2 (0.7) cm^3/mol

Simulation: 40.7 (1.0) cm^3/mol

Partial molar enthalpy

Experiment: -12.1 (0.2) kJ/mol

-13.2 (0.15) kJ/mol

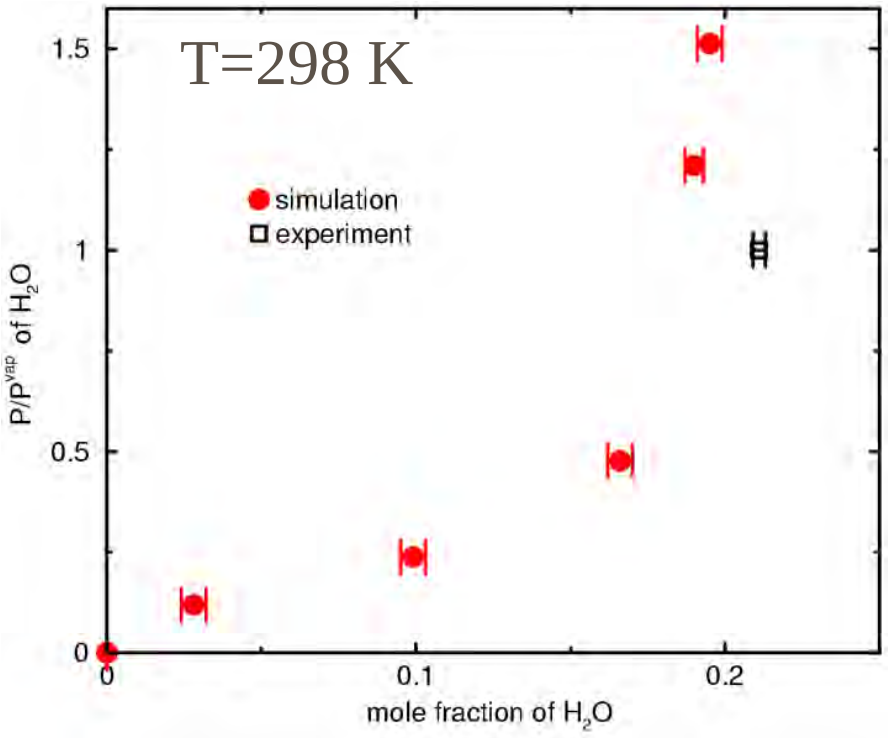
Simulation: -10.3 (0.5) kJ/mol

Small enthalpies typical of physical absorption.

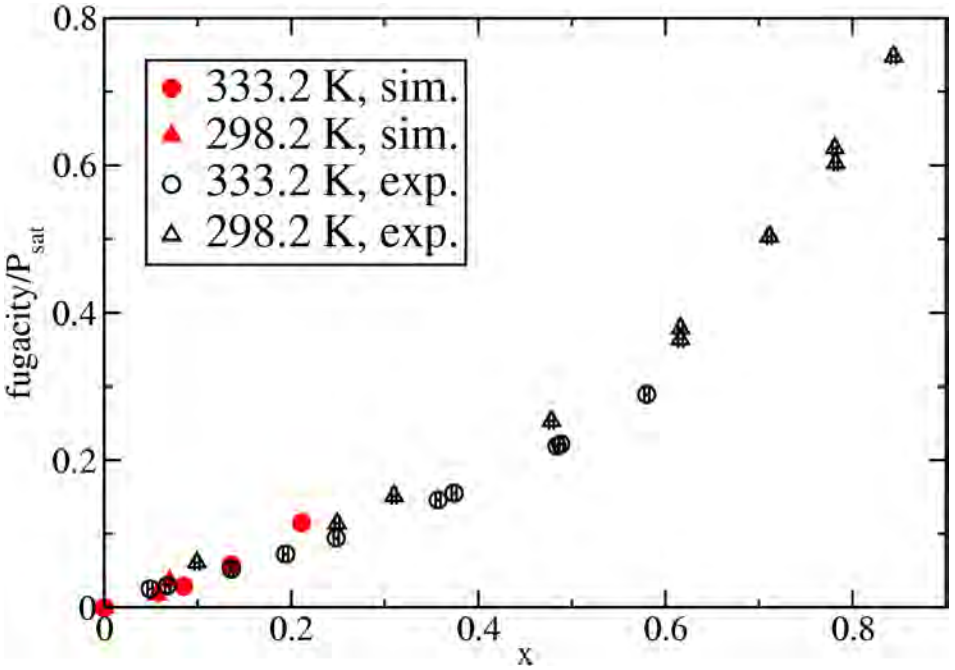
Low regeneration cost, but also relatively low capacity

Water and SO_2 - $[C_6mim][Tf_2N]$

Water



SO_2

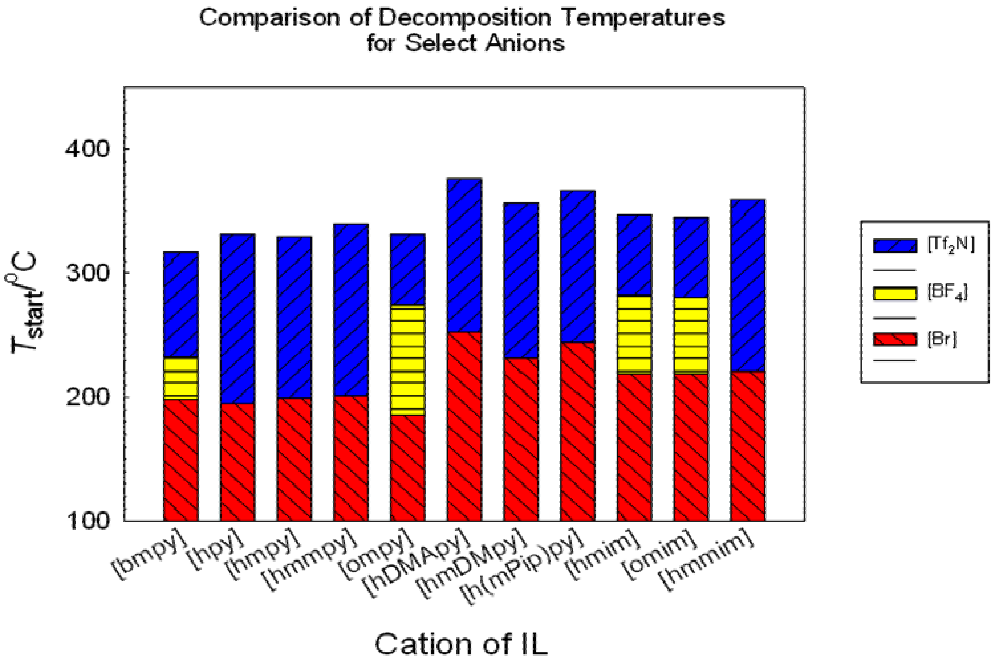


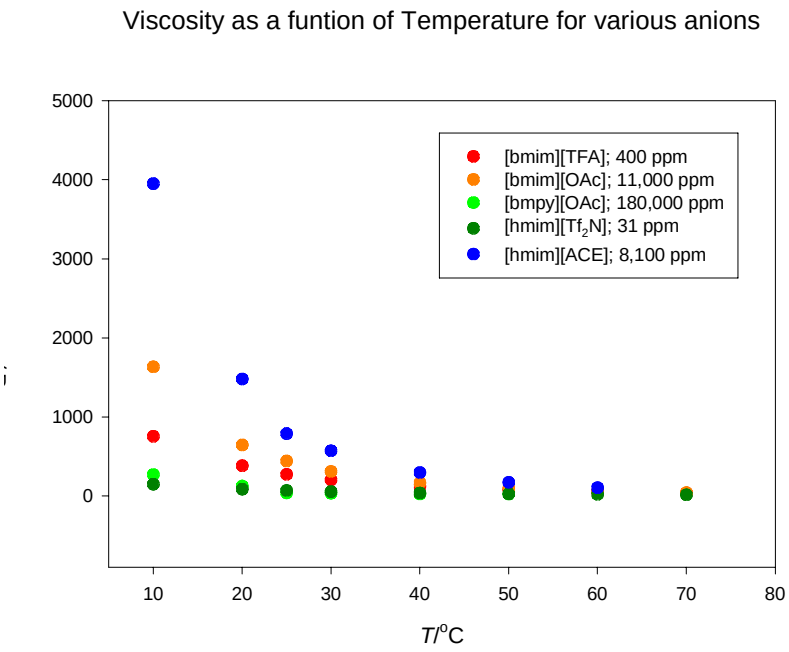
Water saturates at x~0.2; SO_2 is highly soluble: SO_2 removal?

Journal of Physical Chemistry B, **2008**, 112, 2045-2055.

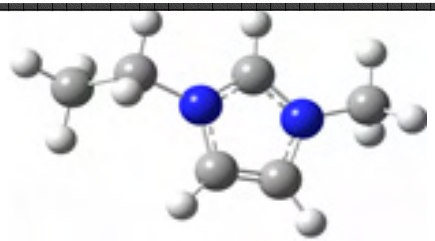
Journal of Physical Chemistry B, **2006**, 110, 15050-15062.

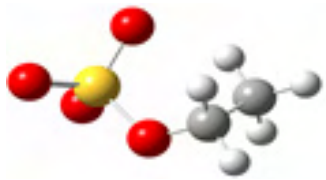
Many other properties measured...





Example comparison with simulations: [C_2mim][$EtSO_4$]



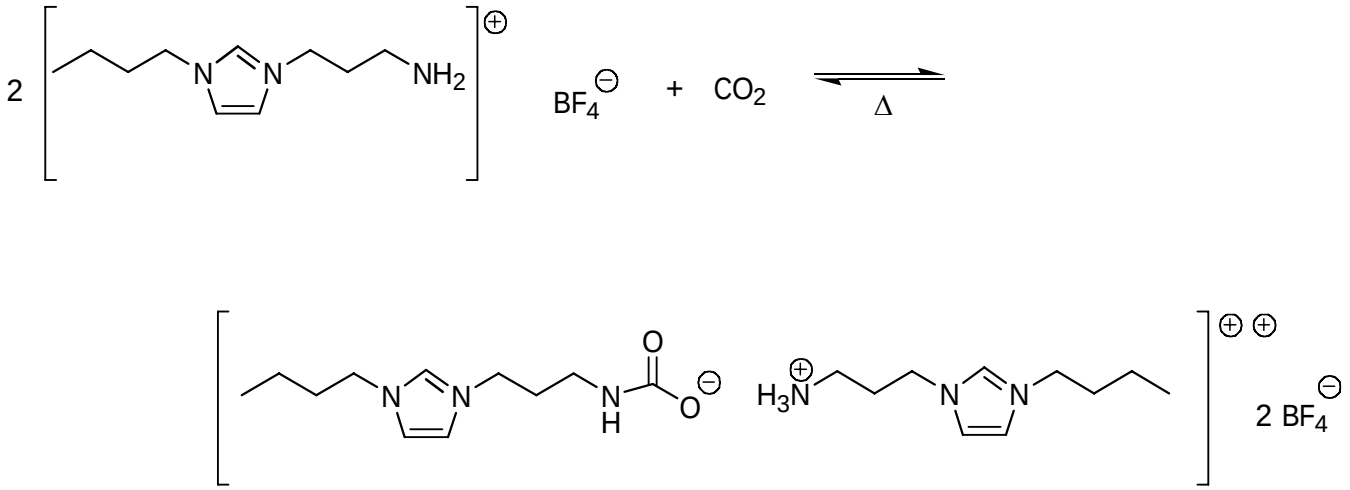


QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Conclusions for physically absorbing ILs

- CO_2 capacity probably too low
  - How to increase CO_2 capacity?
  - How to maintain low regeneration energy?
    - What is optimal balance?
- Add chemical functionality
- Molecular design strategy
  - Quantum simulations: target functional groups, mechanisms
  - Classical simulations: condensed phase properties
  - Synthesis, experimental property measurement
  - Iterate, using process modeling in feedback

Amine-tethered Cations (TSILs)

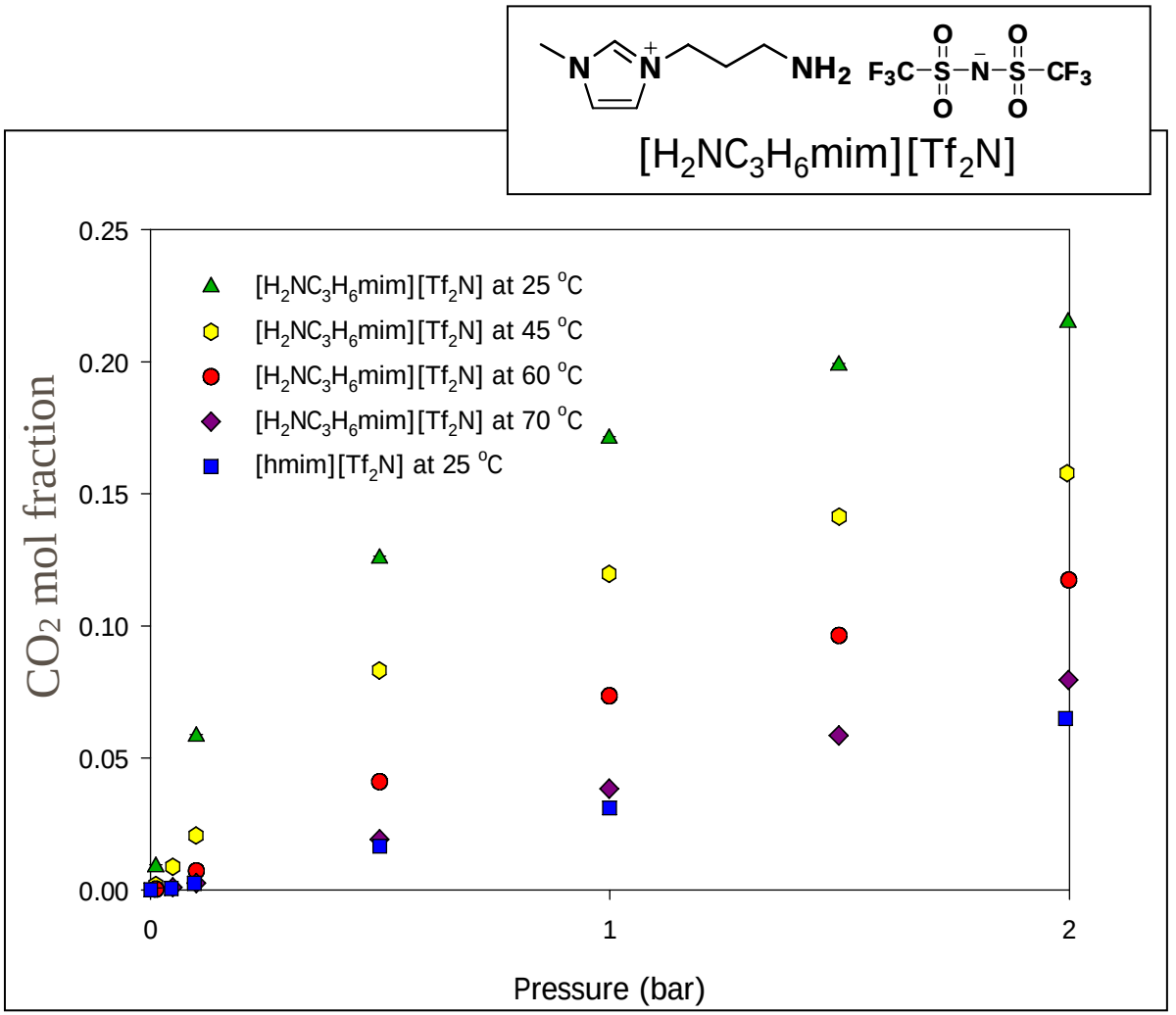


- ^{13}C NMR evidence of carbamate formation
- Reversible under vacuum with heating

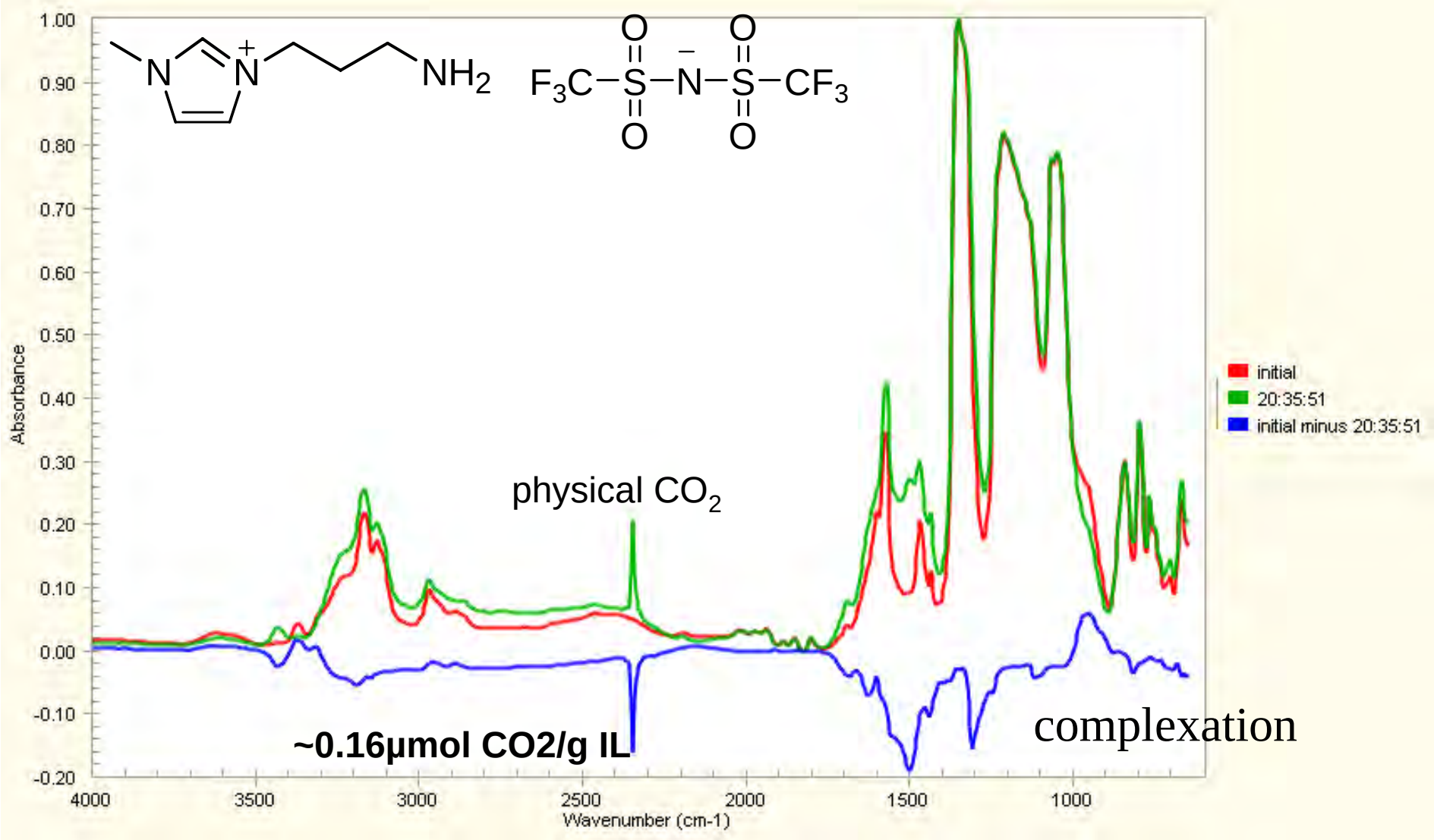
Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., *J. Am. Chem.*, **2002**, *124*, 926.

Preliminary results: enhanced CO_2 solubility *is* observed

- Questions / issues
  - Thermal stability
  - Viscosity increase
  - Uptake kinetics
  - Mechanism



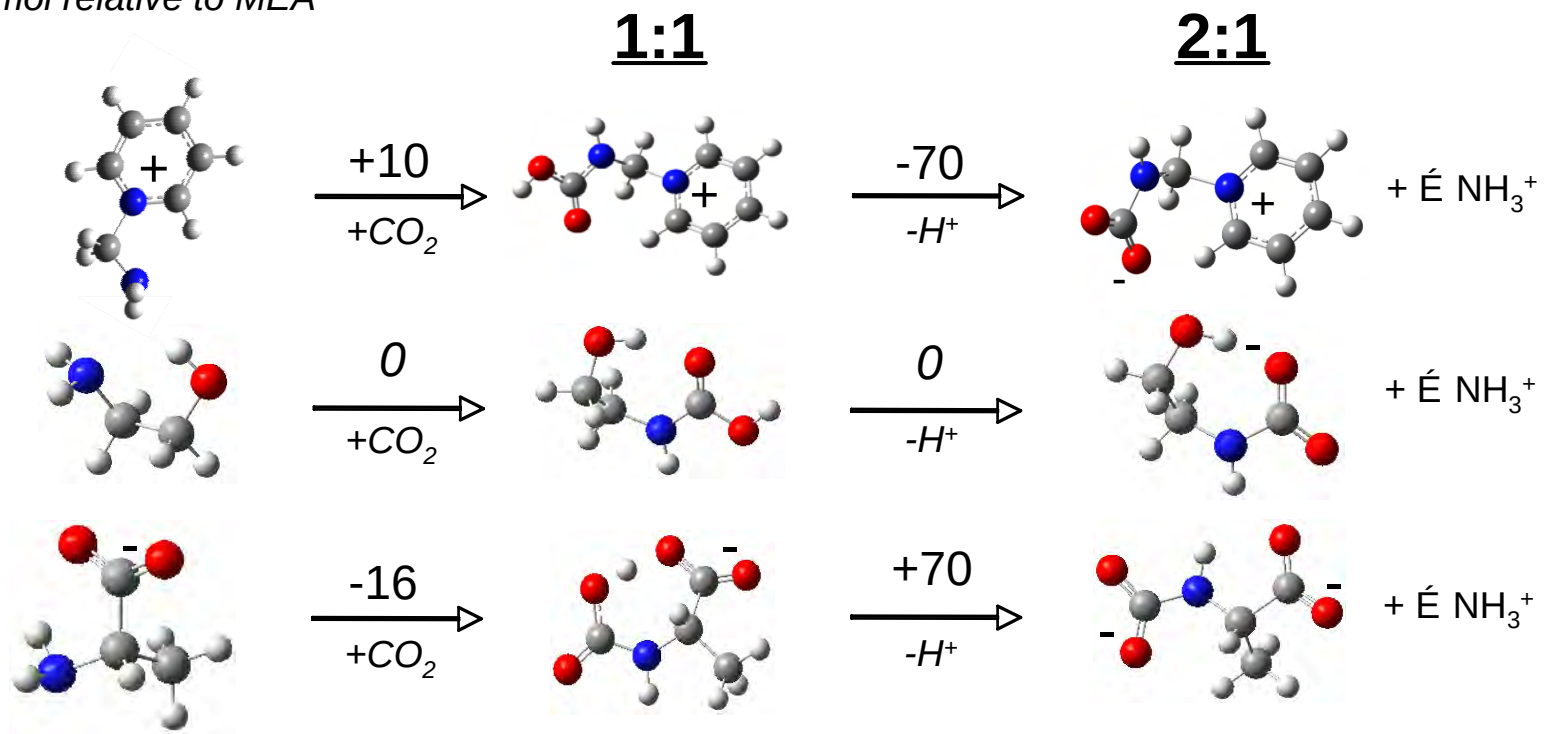
CO_2 in TSIL



IR confirms ~ 2X less physical dissolution in TSIL

MEA vs Cation- vs Anion-Tethered Amines

Reaction energies in kJ/mol relative to MEA



- Local cation tethering *favors* 2:1 binding
- Local anion tethering *disfavors* 2:1 binding
- Opportunities / challenges
  - Functional group / framework design
  - Incorporate influence of condensed phase

Summary

- Ionic liquids promising platform for CO_2 capture
- Solvent design - modeling and experiment
  - Thermodynamic and transport properties
  - Physical solubility governed mainly by anion
  - Chemical complexation
    - Amine-tethered cation
    - Functionalized anion
    - Other functional groups
- Optimal design determined via feedback from process modeling (underway)

Project Team

- Notre Dame
  - Prof. Edward Maginn
  - Prof. Joan Brennecke
  - Prof. Bill Schneider
  - Dr. JaNeille Dixon
  - Dr. Zulema Lopez-Castillo
  - Dr. Keith Gutowski
  - Dr. Wei Shi
  - Dr. Jindal Shah
  - Dr. Manish Kelkar
  - Dr. Erica Price
  - Jes Anderson
  - Elaine Mindrup
  - Burcu Gurkan
  - Devan Kestal
- Industrial Partners
  - DTE Energy
  - Trimeric Inc.
  - Babcock and Wilcox
  - Air Products
  - EMD Chemicals / Merck KAaG
- U.S. Department of Energy, National Energy Technology Laboratory, Award Nos. DE-FC26-04NT42122 and DE-FC26-07NT43091