Development of New Post-Combustion Carbon Dioxide Capture Solvents: Are Ionic Liquids the Answer?

ACS Award in Industrial Chemistry:
Symposium in Honor of T. J. Wallington: Greenhouse Gases Sequestration: Technology and Economics

April 7, 2008

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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 insufficient
  - 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

Need for new technology

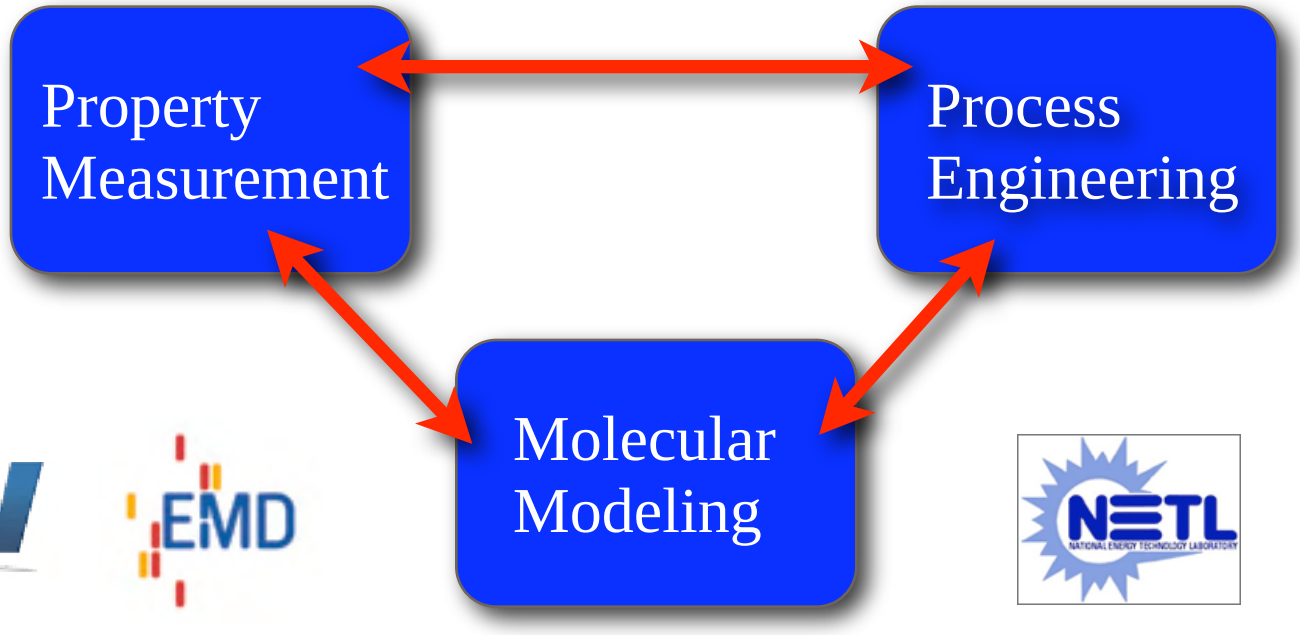
Energy Penalty due to CO_2 Capture	10%	20%	30%	40%
Target Market, GW	184	184	184	184
Fleet CO_2 Reduction, %	50.2	49.2	47.9	46.3
New Capacity Req'd, GW	25.5	57.5	98.5	153.3
Additional Coal Req'd., tons x 10^3	79,940	179,864	308,338	479,637
Cost of New Capacity, MM$	45,975	103,444	177,332	275,850
Cost of CO_2 Retrofits, MM$	91,950	91,950	91,950	91,950
Total New Cost, MM$	137,925	195,394	269,282	367,800

Need for further R&DD to minimize the cost and externalities impact due to CO_2 Capture and Storage.

Current Energy Penalty of CO_2 BACT MEA Absorption System

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 Trimeric

DEPARTMENT OF ENERGY UNITED STATES OF AMERICA

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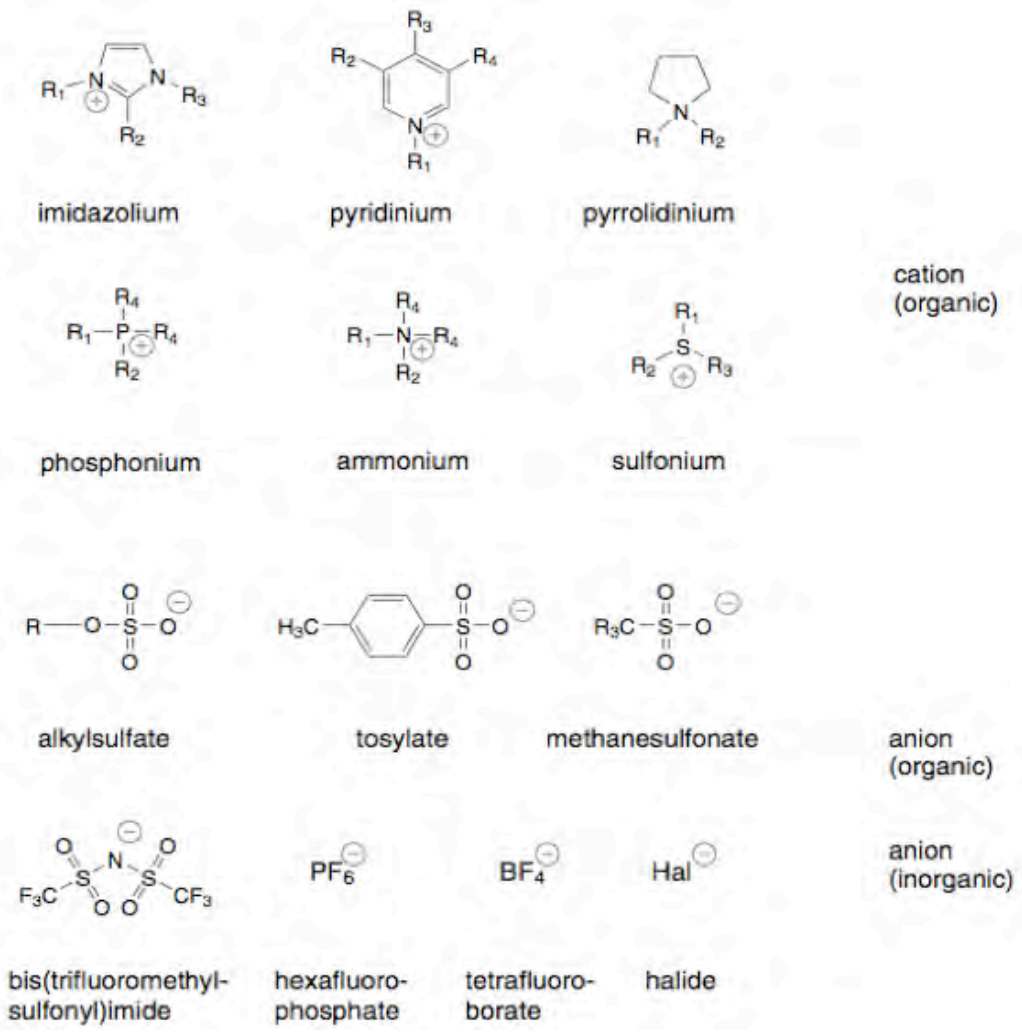
AIR PRODUCTS

What are 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

Some examples of commercially available ionic liquids

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

Targets determined by process modeling

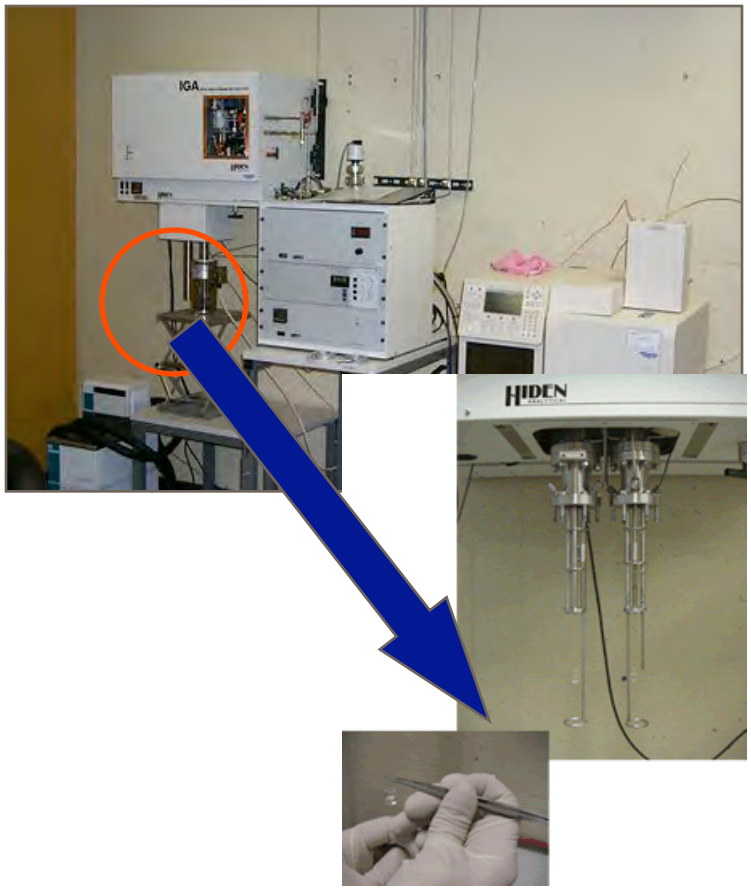
Assumes conventional absorption process

Other processes possible?

Experimental solubility measurements

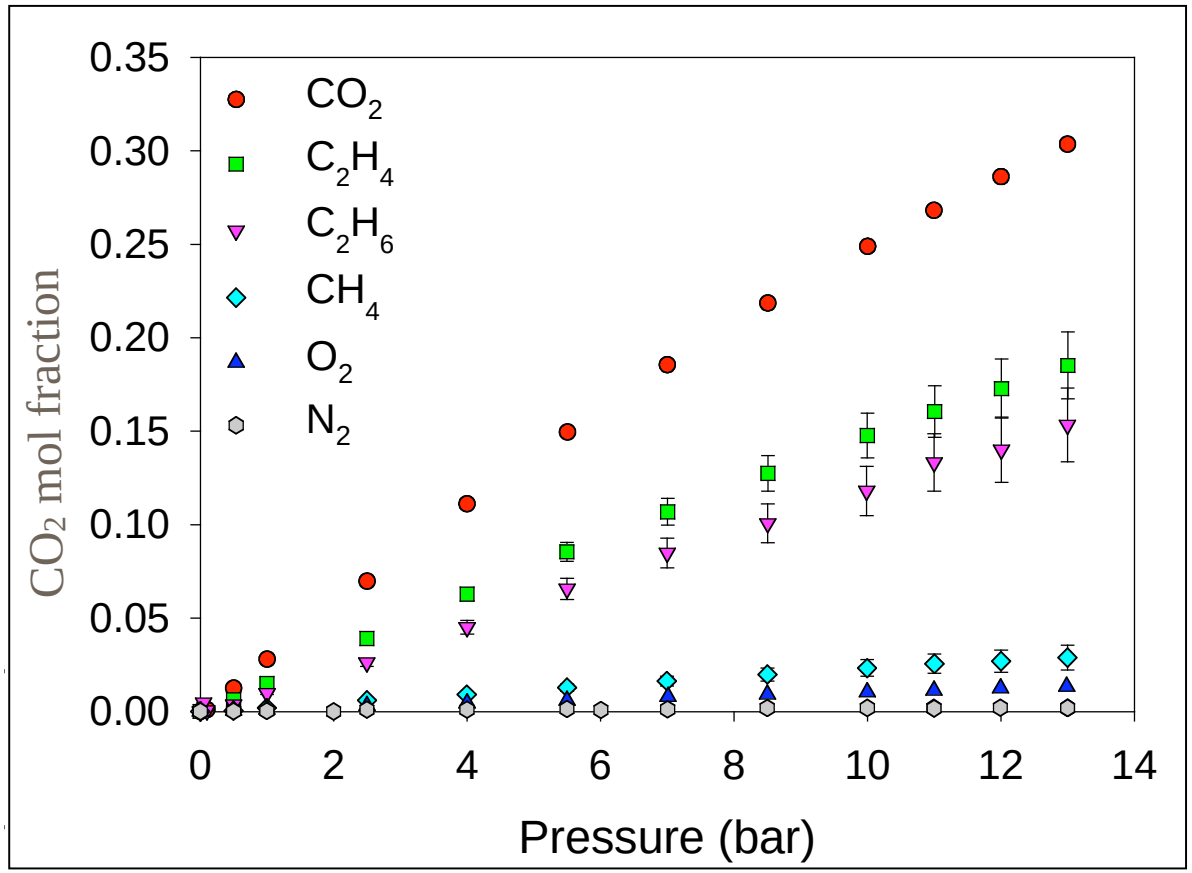
Measure gas uptake in liquid gravimetrically

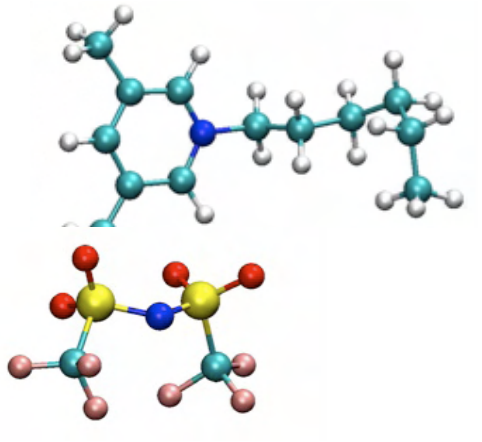
Semi-manual balance capable of measuring SO_2 uptake; requires ~100 mg ionic liquid

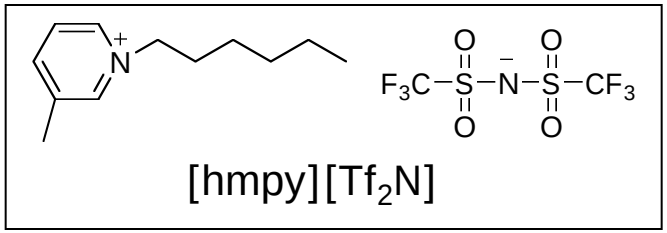


Very sensitive automated balance, used for CO_2 experiments; requires mg quantities of ionic liquid

CO_2 is very soluble in ionic liquids



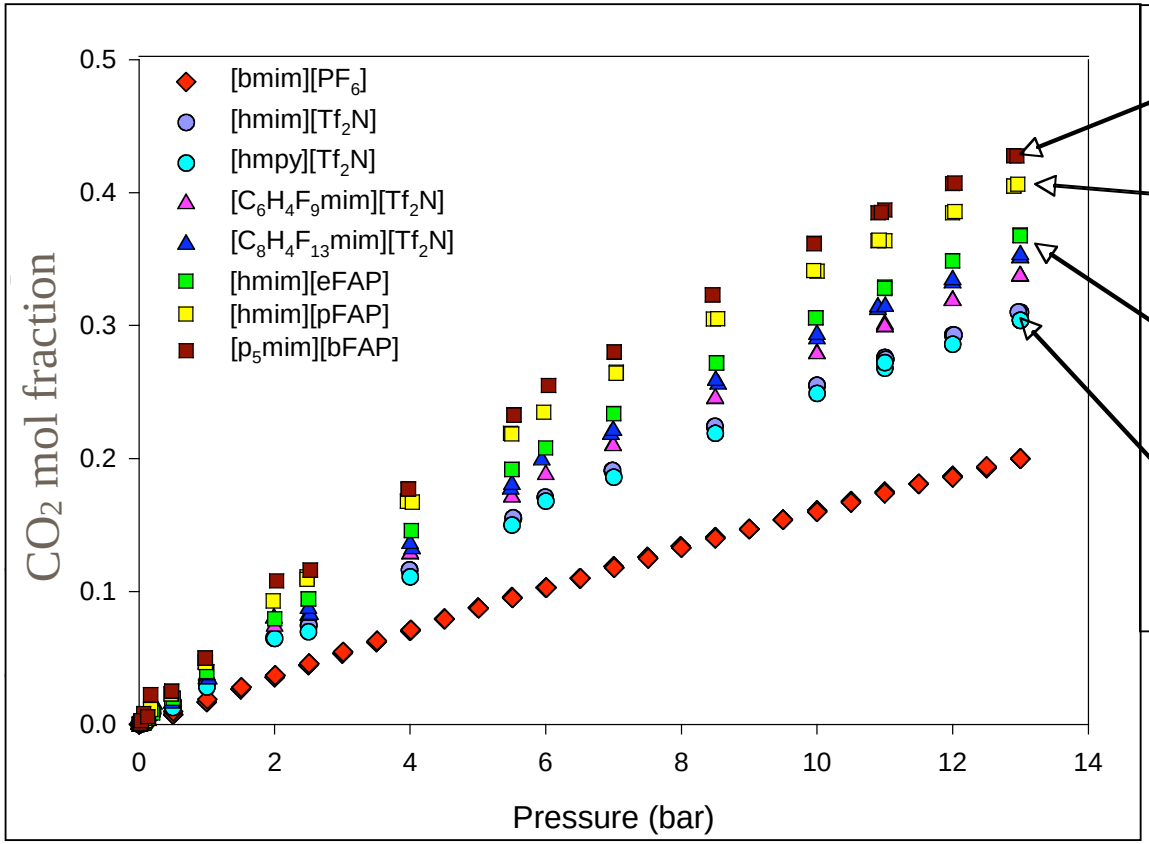


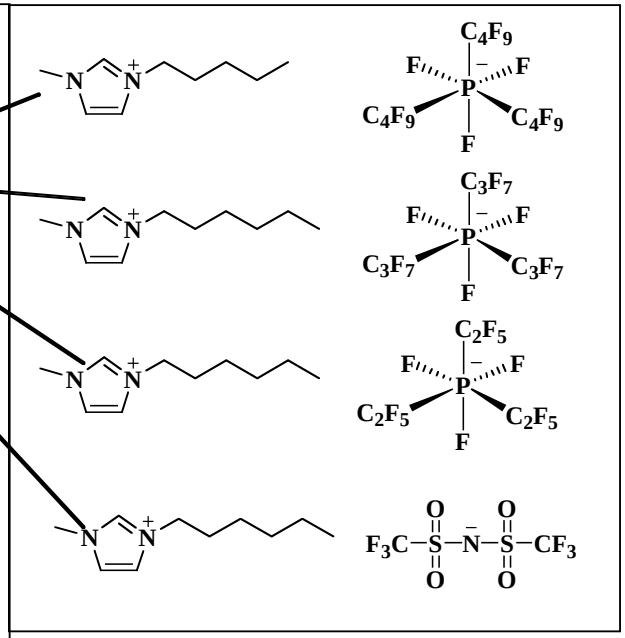


Potential for CO_2 removal from flue gas?

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

Widely varying CO_2 solubility

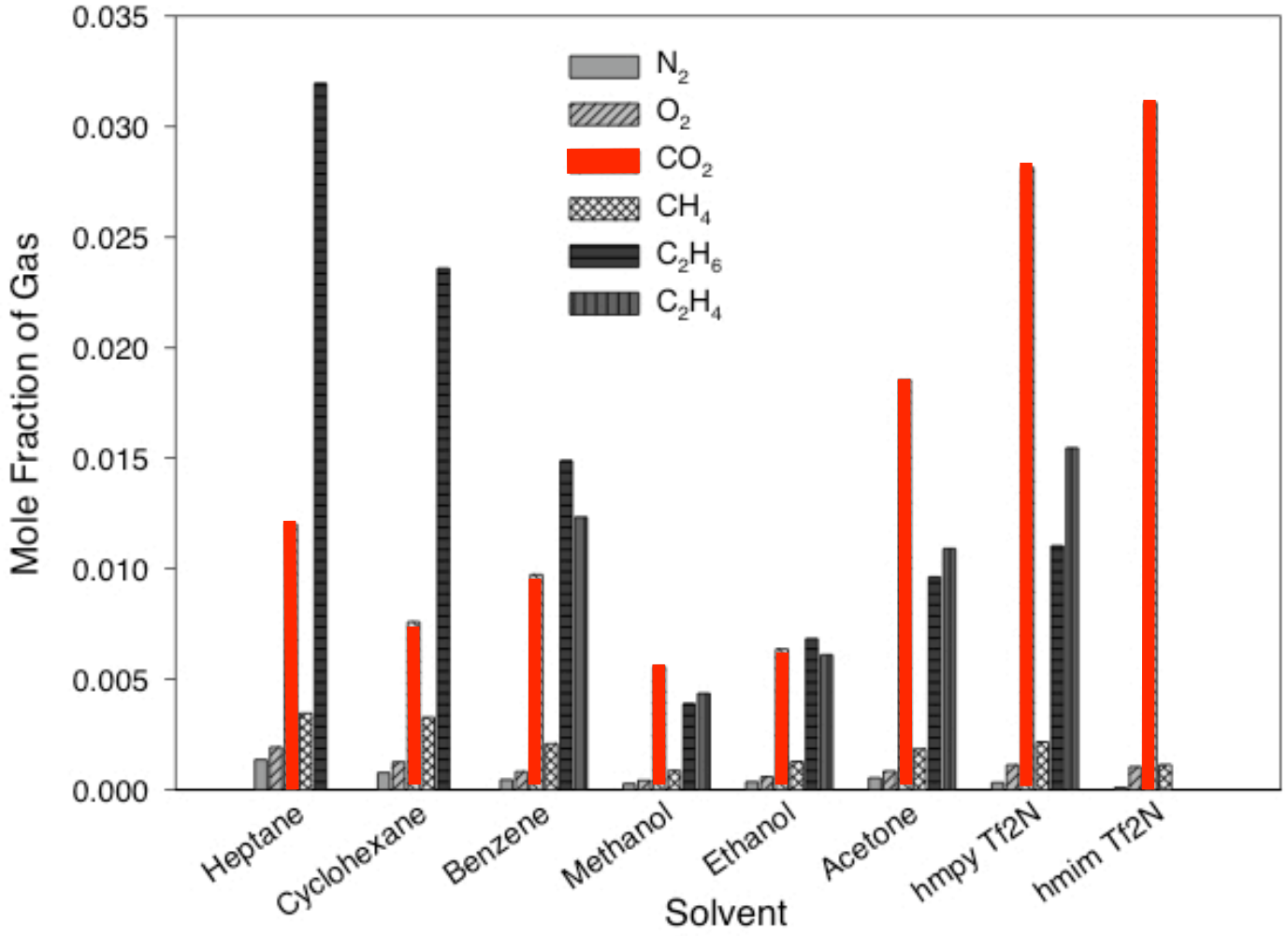




Anion has largest effect on physical CO_2 solubility

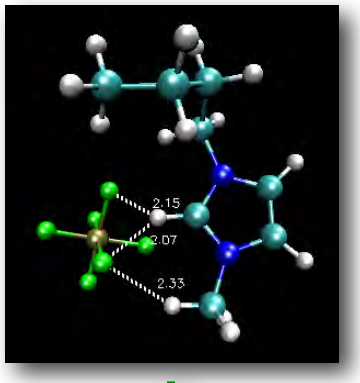
Journal of the American Chemical Society, ***2004****,* 126, 5300-5308*; Journal of Physical Chemistry B,* **2007**, 11, 9001-9009

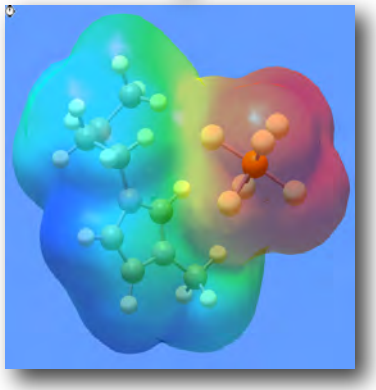
Comparison to other physical solvents



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

Using molecular modeling to compute properties





ab initio calculations

$$V_{bond} = k_x \left(x - x_o\right)^2$$

$$V_{angle} = k_\theta \left(\theta - \theta_o\right)^2$$

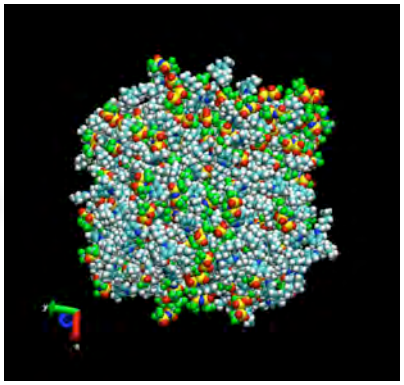
$$V_{dihedral} = k_\phi \left[1 + \cos\left(n\phi - \phi_o\right)\right]$$

$$V_{improper} = k_\psi \left(\psi - \psi_o\right)^2$$

$$V_{LJ} = \varepsilon_{ij}\left[\left(\frac{r_{\min,ij}}{r_{ij}}\right)^{12} - 2\left(\frac{r_{\min,ij}}{r_{ij}}\right)^{6}\right]$$

$$V_{el} = \frac{q_i q_j}{4\pi\varepsilon_0 r_i r_j}$$

Classical force field

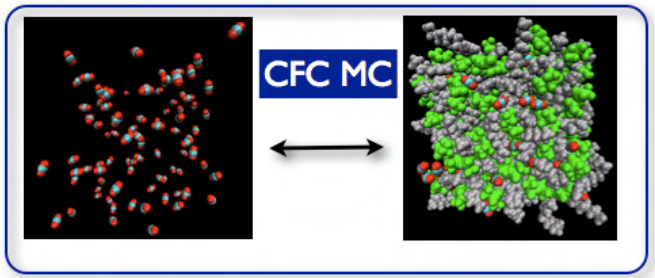


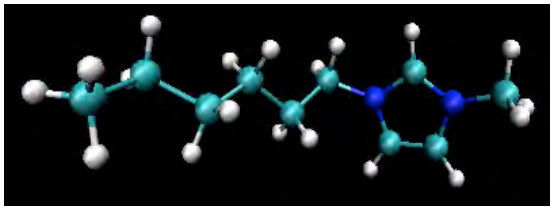
Condensed phase simulations (MD, MC)

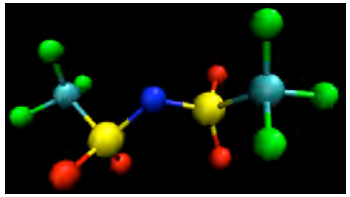
Statistical mechanics

Properties

Calculating gas solubility



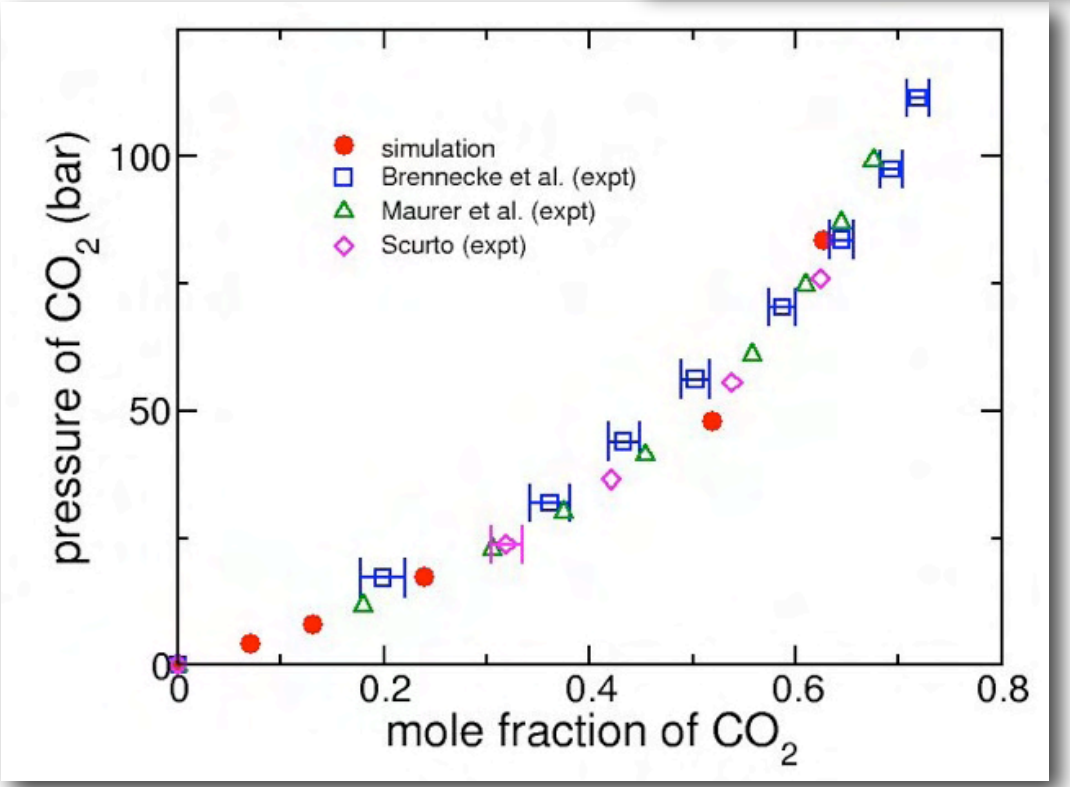




Continuous fractional component Monte Carlo

[C_6mim] [Tf_2N]

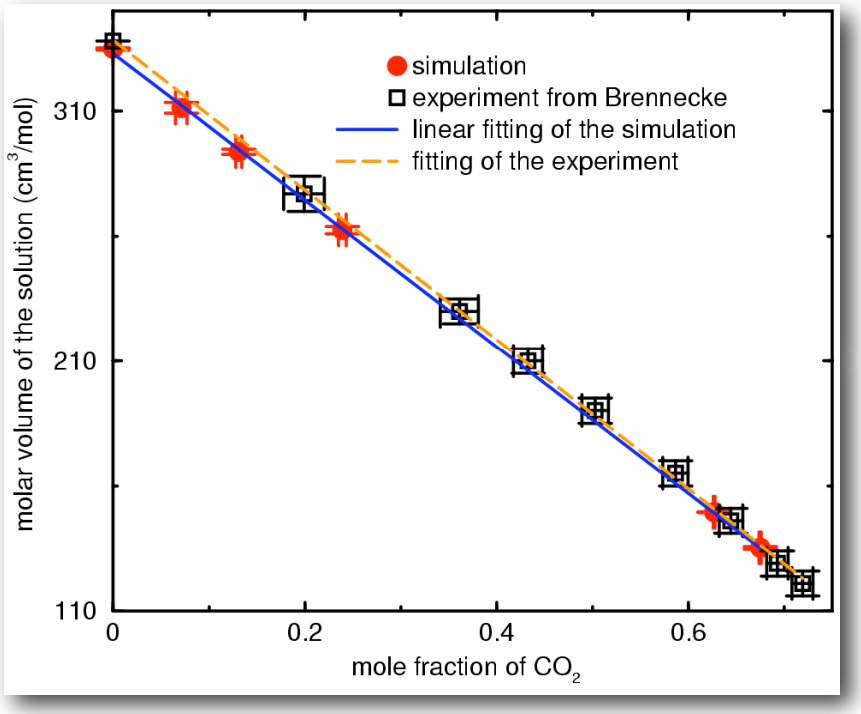
Quantitative agreement between simulations and experiment

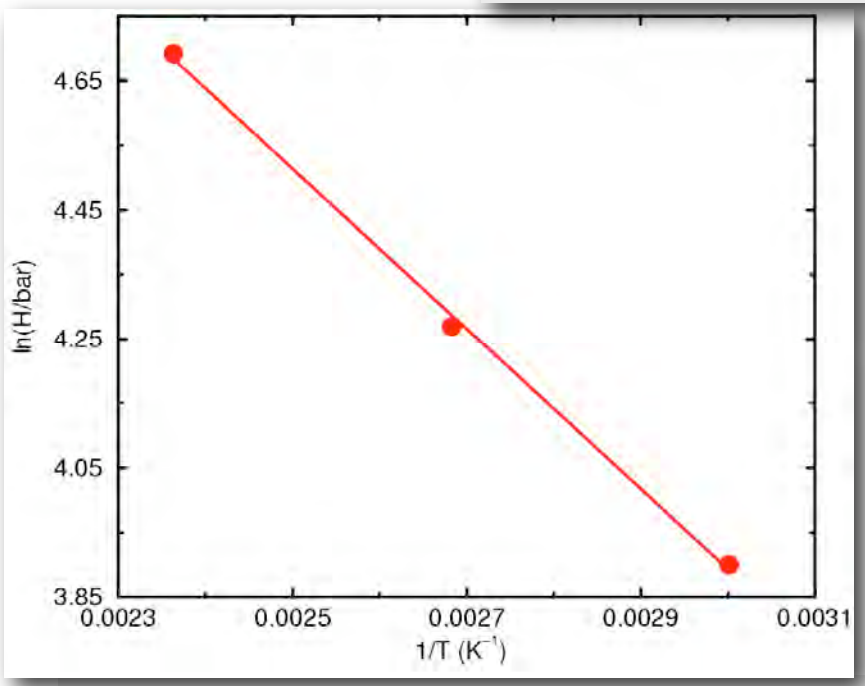


Journal of Chemical Theory and Computation, **2007**, 3, 1451-1463; *Journal of Physical Chemistry B*, **2008**, 112, 2045-2055.

Molar volumes and enthalpies

[C_6mim] [Tf_2N]





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

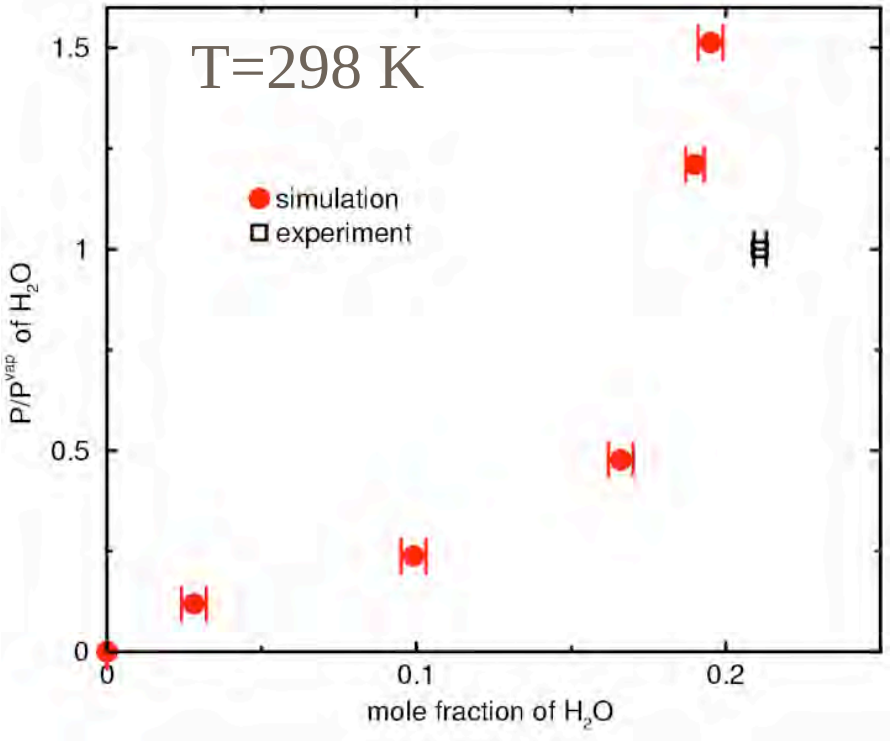
-13.2 (0.15) kJ/mol

Simulation: -10.3 (0.5) kJ/mol

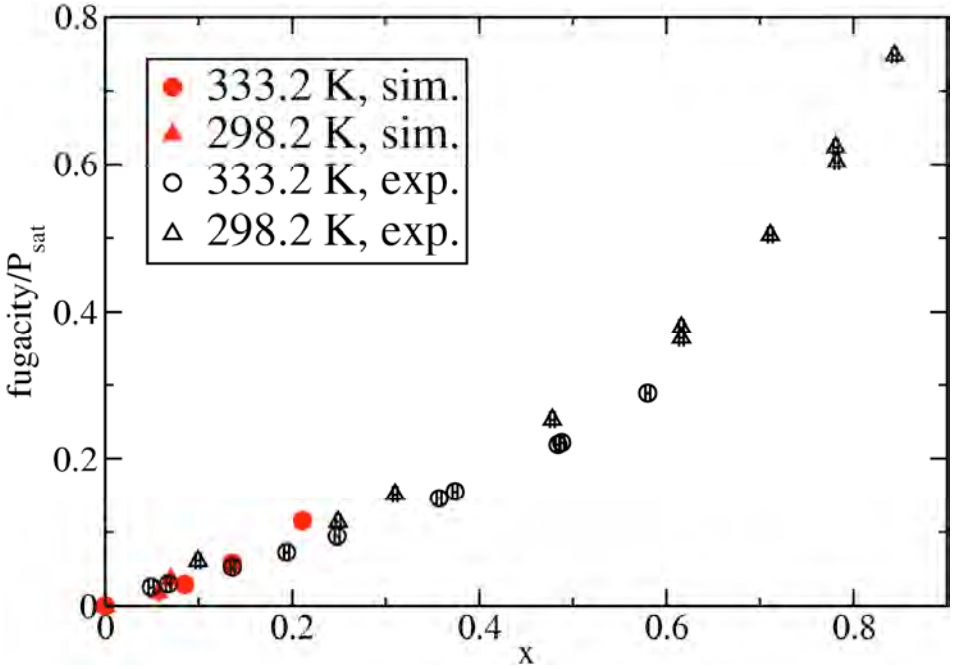
Small enthalpies typical of physical absorption.
Low regeneration cost, but also relatively low capacity

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

Water



SO_2

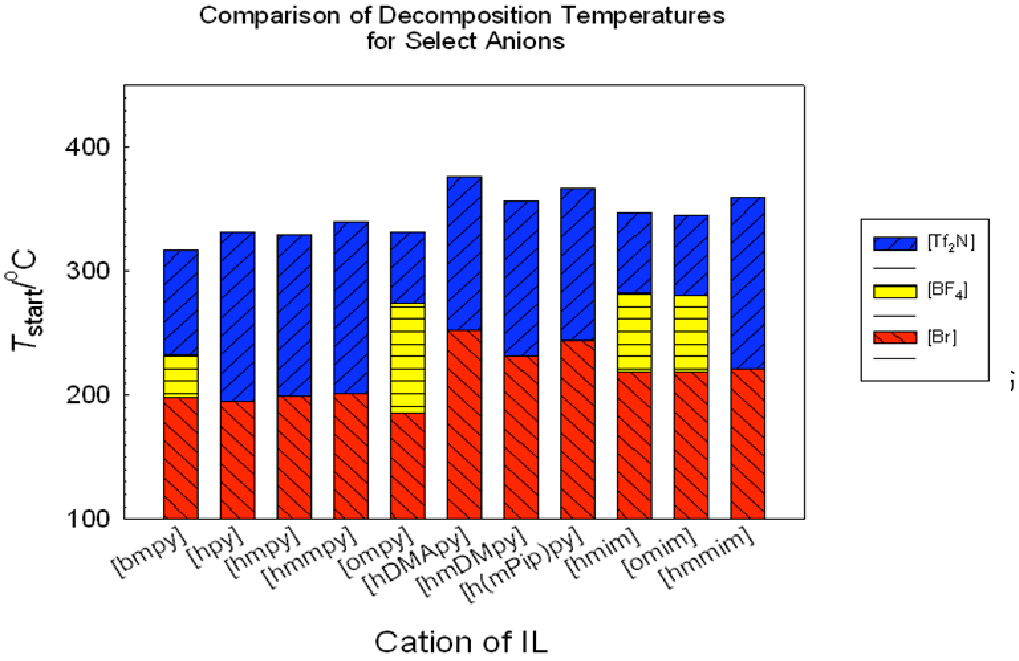


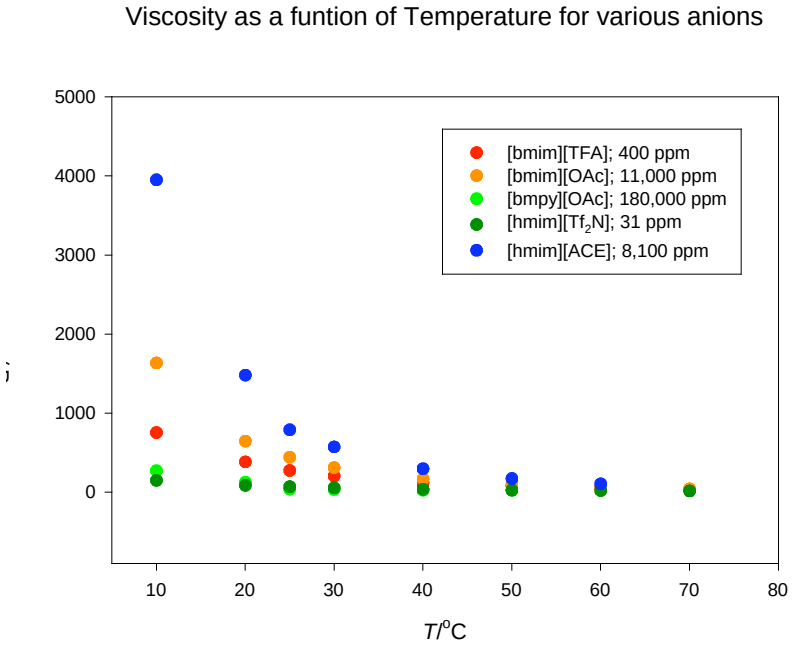
Water saturates at x~0.2; SO_2 is highly soluble: SO_2 removal?

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

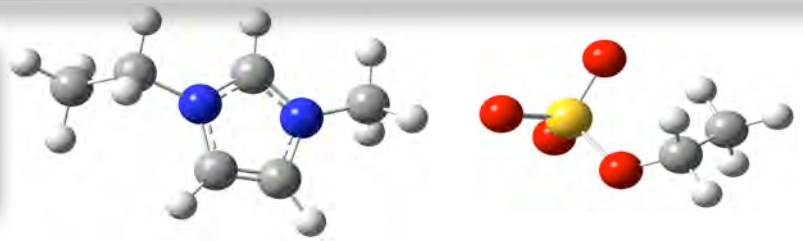
Journal of Physical Chemistry B, **2006**, 110, 15050-15062.

Many other properties measured...





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

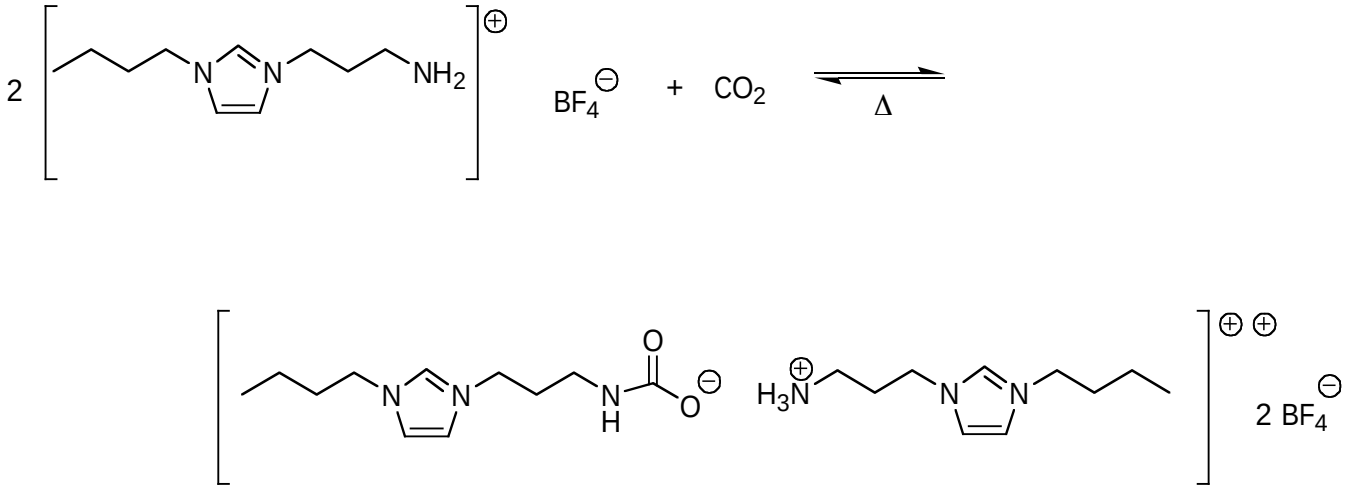


Property (units)	Simulation	Experiment	% Deviation
Density $[\rho(T)]$ (gm/cc)	1.19	1.204	1.2
Volume expansivity $[\alpha]$ $(1/K)$	6.26×10^{-4}	5.37×10^{-4}	16.5
Heat capacity $[C_v]$ $(J/mol-K)$	445.99	405.66	9.9
Heat of vaporization $[\Delta H_{vap}]$ (kJ/mol)	183.7	–	–
Viscosity $[\eta(T)]$ (cP)	18.5	16.7	10.8
Thermal conductivity $[\kappa(T)]$ $(W/m-K)$	0.167	–	–

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)

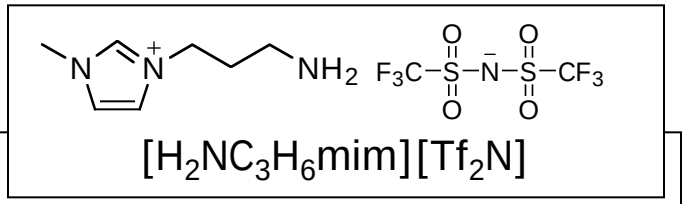


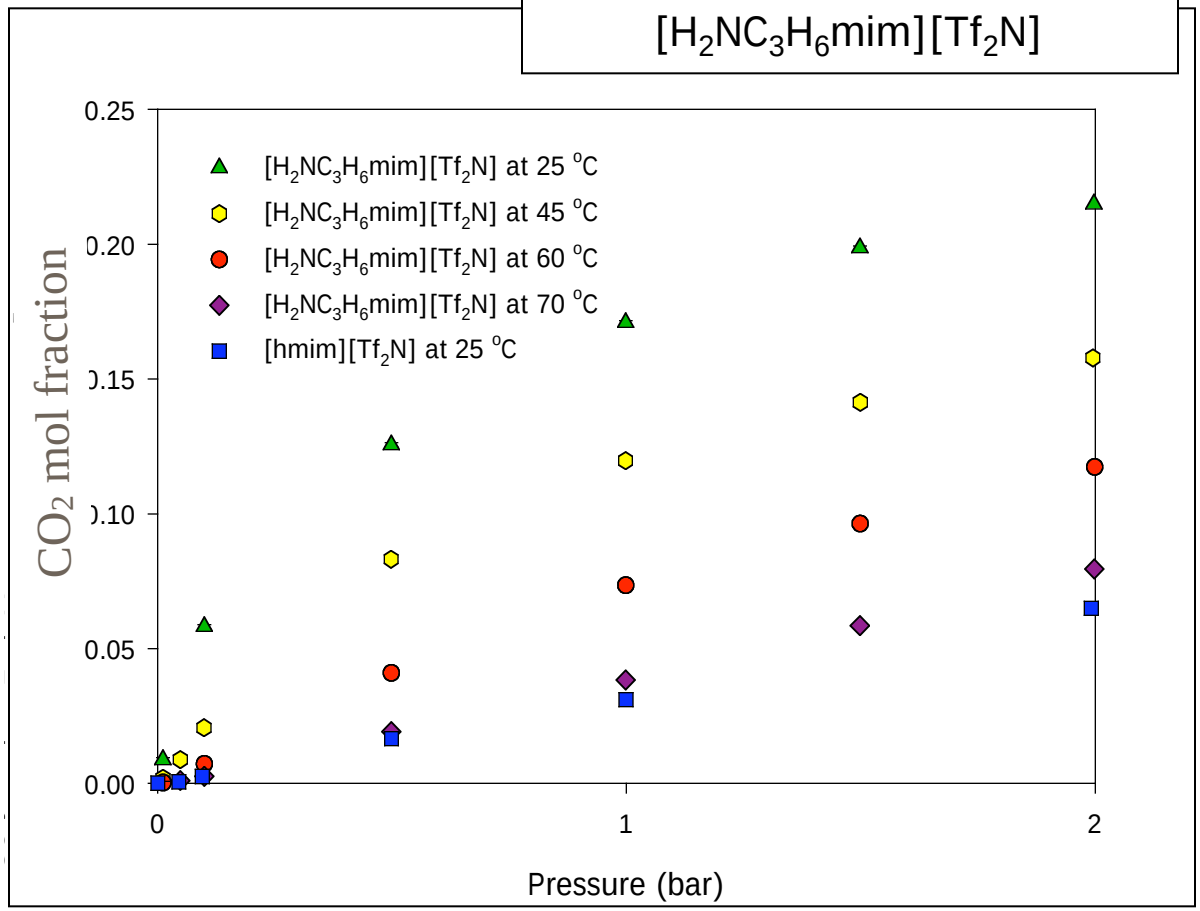
- ^{13}C NMR evidence of carbamate formation
- Reversible under vacuum with heating

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

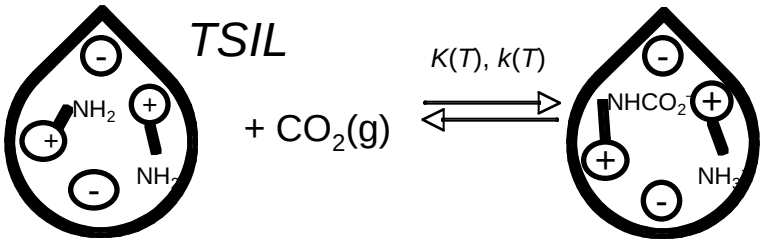
- Questions / issues
  - Thermal stability
  - Viscosity increase
  - Uptake kinetics
  - Mechanism

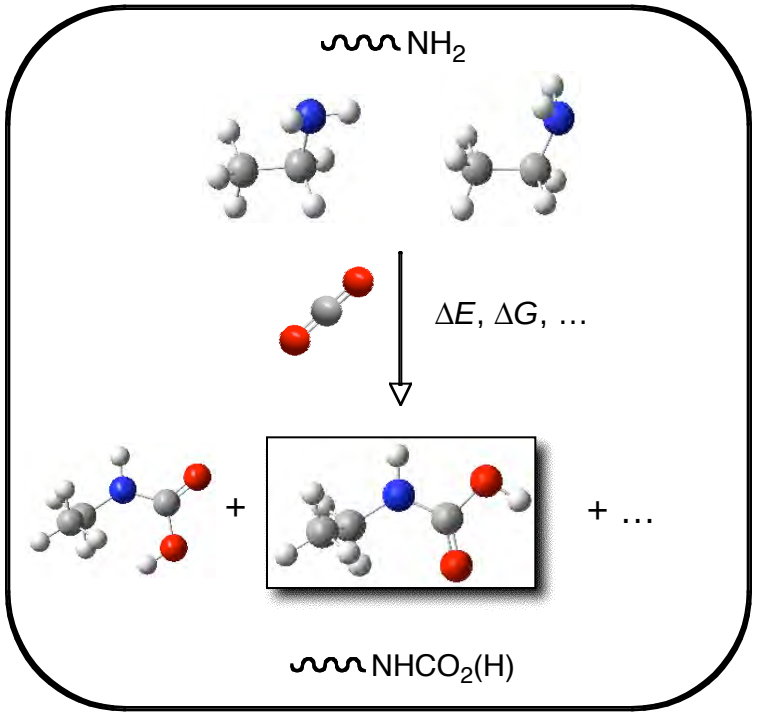




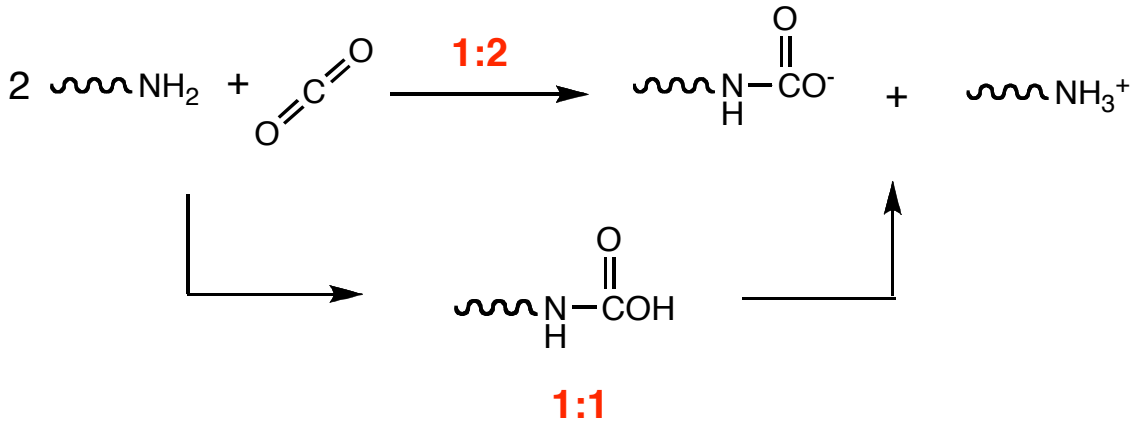
Simulation-Based Rational Design of TSILs

- CO_2 - TSIL reaction characteristics determine efficacy
  - Reaction stoichiometry, mechanism
  - Thermodynamics
  - Kinetics
- 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





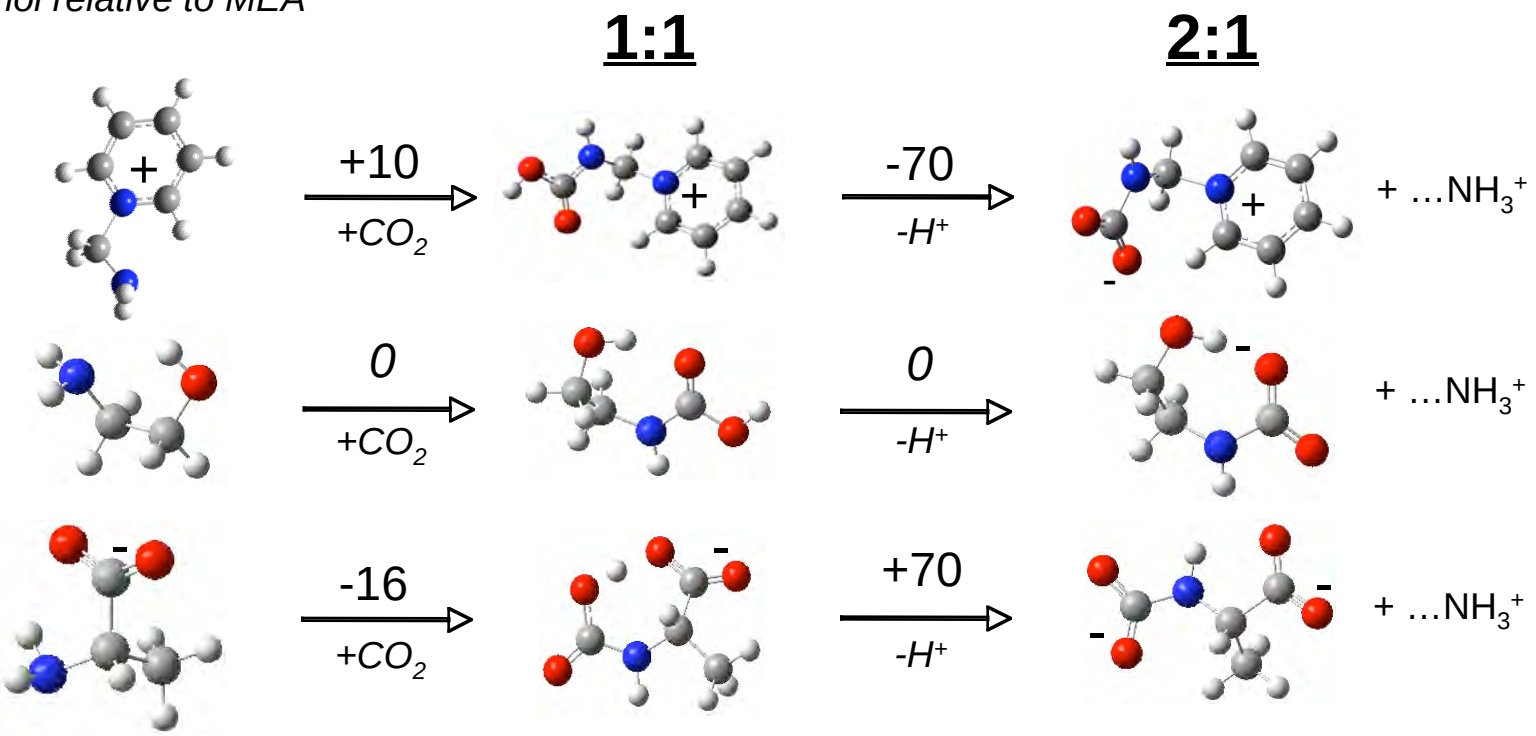
Stoichiometry of CO_2 Reaction with Amines



- Aqueous monoethanolamine (MEA) common CO_2 capture medium
- MEA stoichiometry generally accepted to be 1 CO_2 : 2 MEA
  - 2 amine + CO_2 => carbamate + ammonium
- Ionic liquid functional groups suggest opportunity to promote 1:1 stoichiometry

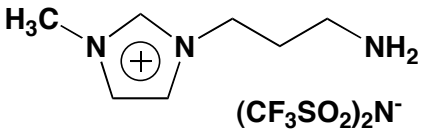
MEA vs Cation- vs Anion-Tethered Amines

Reaction energies in kJ/mol relative to MEA

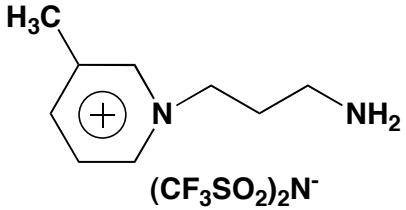


- Local cation tethering *favors* 2:1 binding
- Local anion tethering *disfavors* 2:1 binding
- Opportunities / challenges
  - Functional group / framework design
  - Incorporate influence of condensed phase

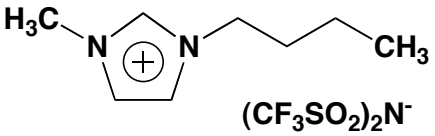
Condensed phase simulation of TSILs



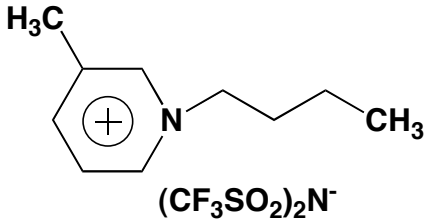
T (ºC)	ρ(calc)*	ρ(exp)*	%diff	V_{molar}(calc)**
298	1.5604	1.5920	-1.99	269
308	1.5561	1.5829	-1.69	270
318	1.5432	1.5738	-1.94	272
328	1.5359	1.5647	-1.84	274
333	1.5309	1.5604	-1.88	275



T (ºC)	ρ(calc)*	ρ(exp)*	%diff	V_{molar}(calc)**
293	1.5139	1.5405	-1.73	285
308	1.5111	1.5269	-1.04	285
323	1.4940	1.5133	-1.27	289
338	1.4817	1.4997	-1.20	291
353	1.4644	1.4861	-1.46	295



T (ºC)	ρ(calc)*	ρ(exp)*	%diff	V_{molar}(calc)**
298	1.4865	1.4360	3.52	282
304	1.4836	1.4336	3.49	283
314	1.4755	1.4247	3.57	284
323	1.4645	1.4142	3.56	286
334	1.4576	1.4054	3.72	288



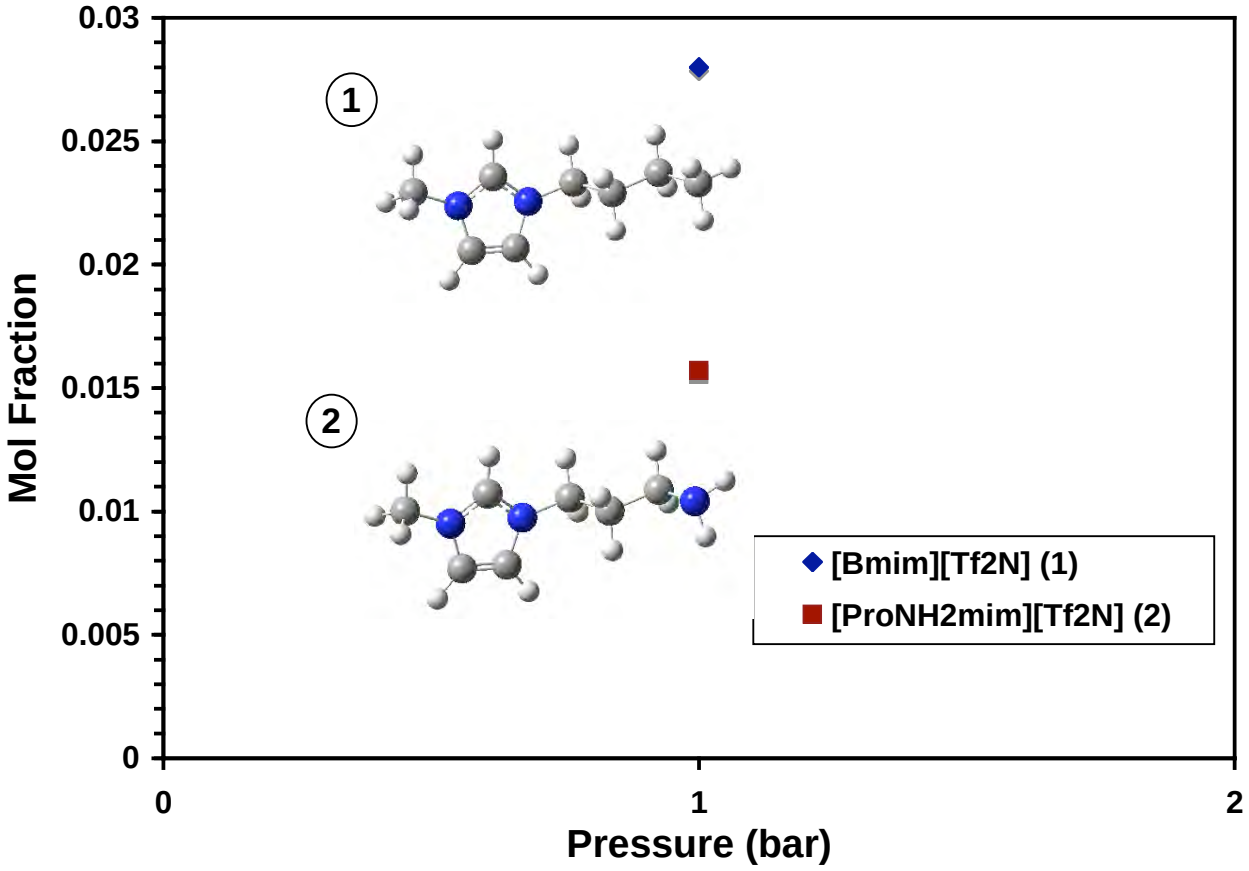
T (ºC)	ρ(calc)*	ρ(exp)*	%diff	V_{molar}(calc)**
293	1.4544	1.4190	2.49	296
308	1.4430	1.4055	2.67	298
323	1.4260	1.3920	2.45	302
338	1.4153	1.3785	2.67	304
353	1.3982	1.3650	2.44	308

* g/cm^3 ** cm^3/mol

Simulations and experiment in good agreement.
Functionalized ILs have smaller molar volume.

Physical absorption in TSIL

Results from Continuous Fractional Component (CFC) calculations:



Henry's constant @ 1 bar:

[Bmim][Tf_2N]

Calc 35.7

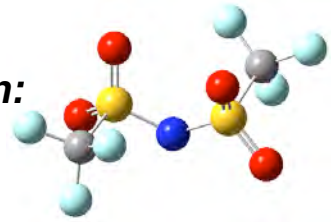
Exp*** 33.0

[ProNH_2mim][Tf_2N]

Calc 63.7

Exp -

Tf_2N^- anion:



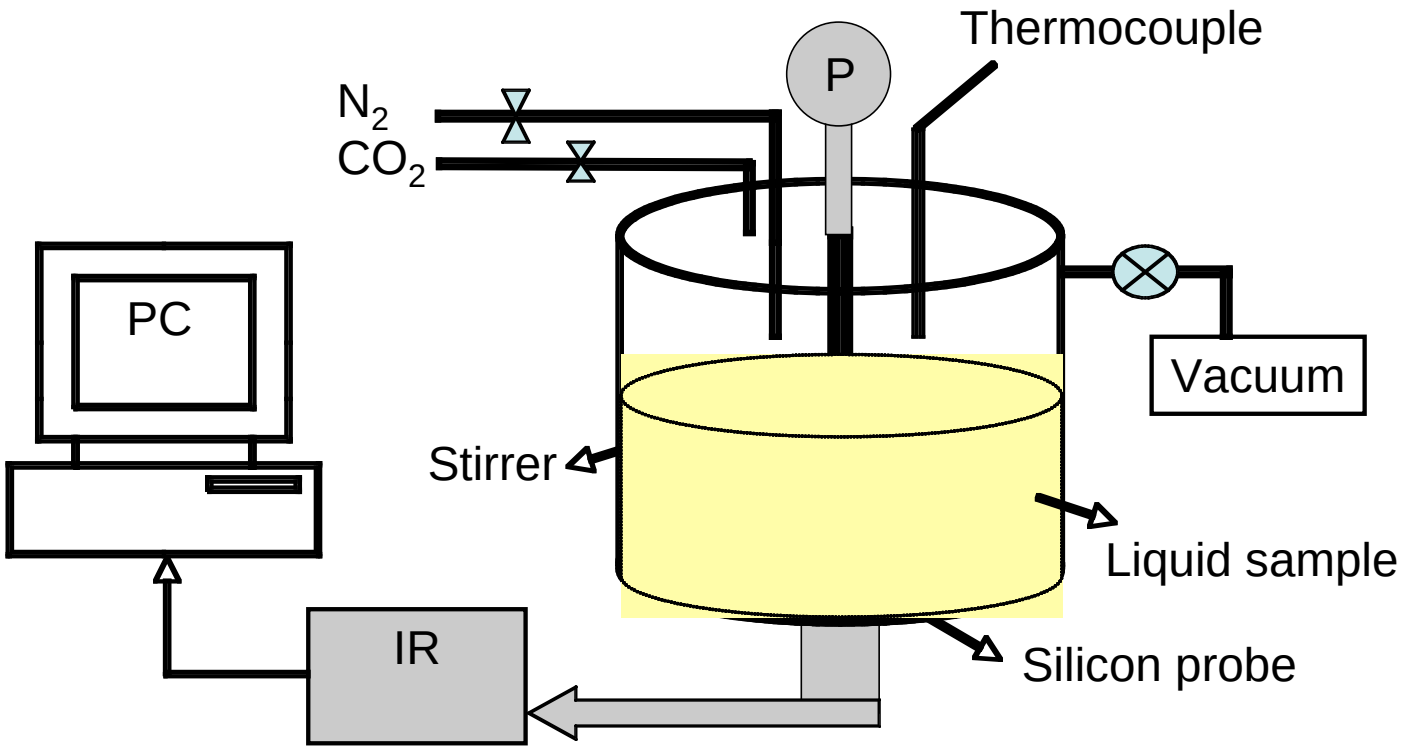
* Preliminary results, 298K

** Chemically complexing

*** Anthony, et al., JPCB 2005, 109, 6366.

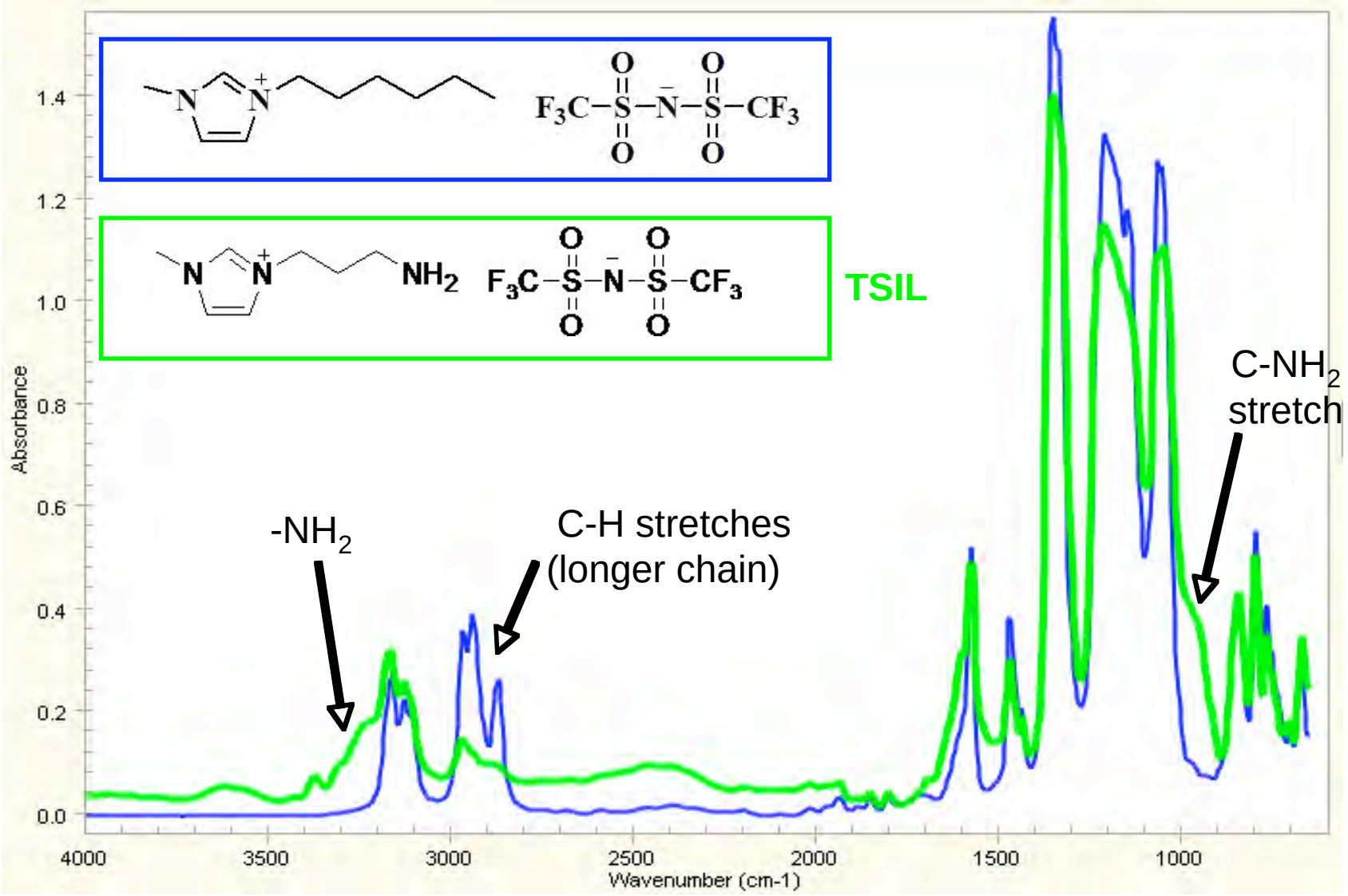
TSIL *physical* solubility ~ 2X lower than normal IL: molar volume

React-IR Setup

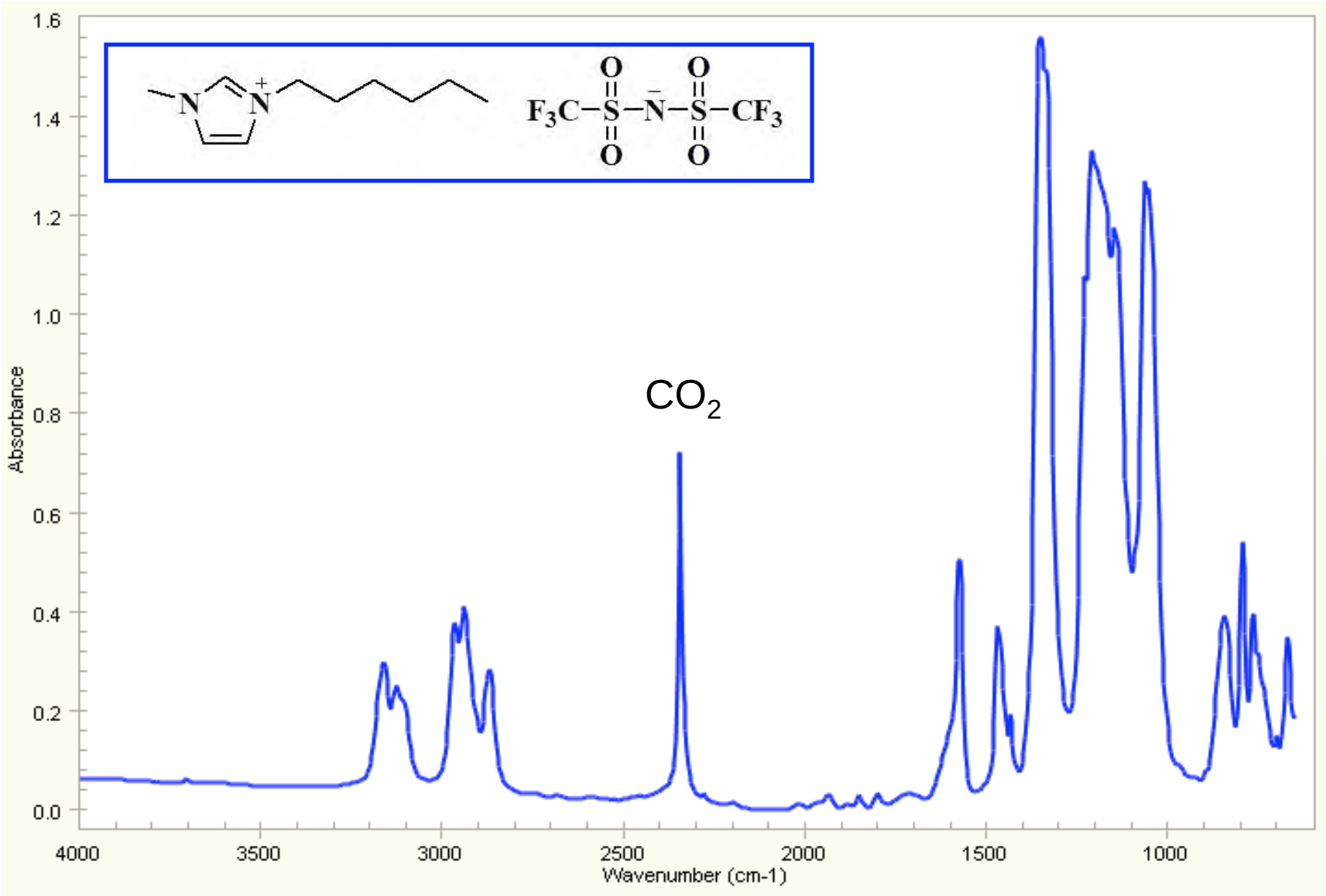


- Study kinetics and mechanism of CO_2 absorption and complexation

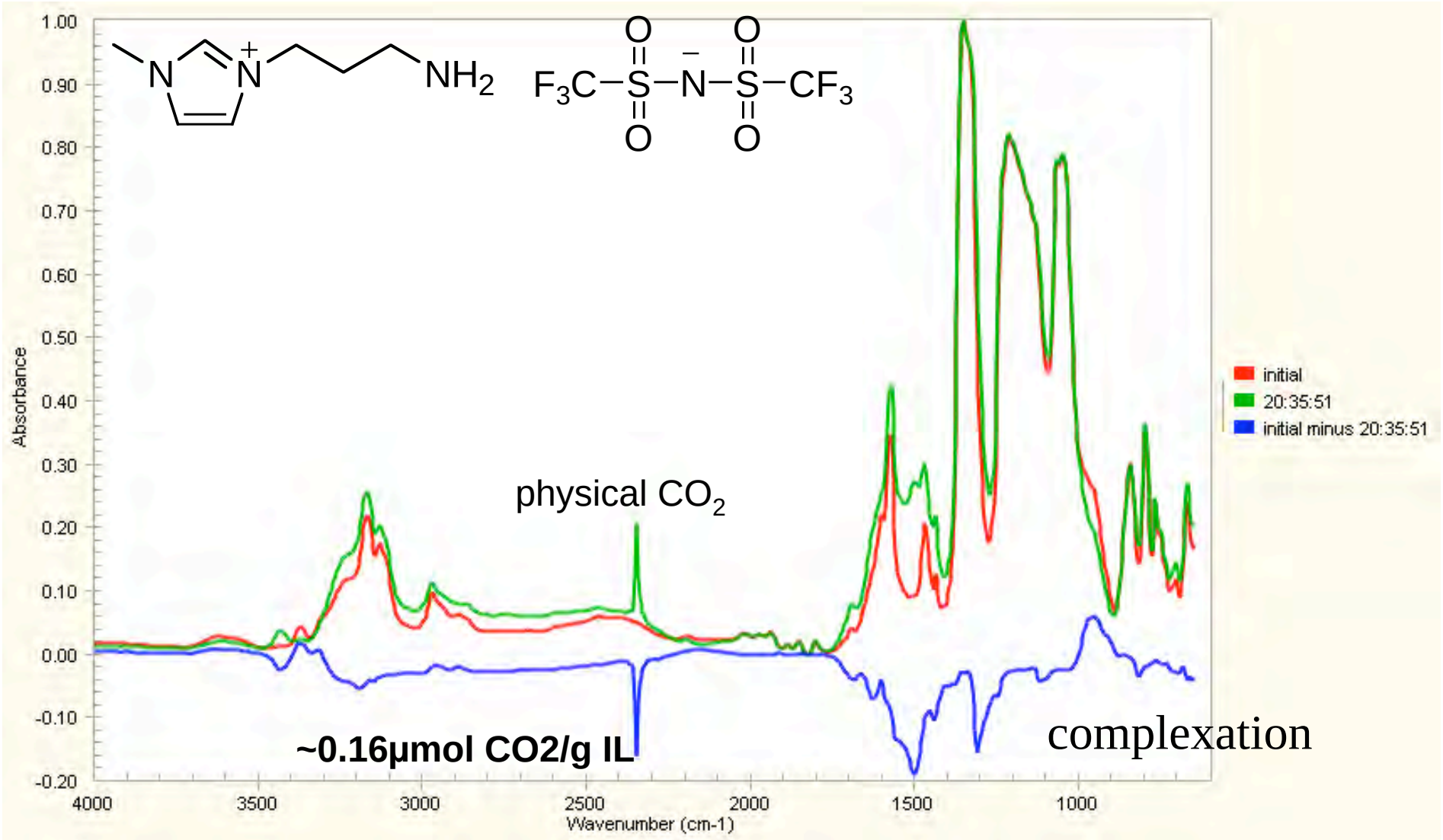
Pure IL Spectra



Physical solubility of CO_2



CO_2 in TSIL



IR confirms ~ 2X less physical dissolution in TSIL

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

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  - Trimeric Inc.
  - Babcock and Wilcox
  - Air Products
  - EMD Chemicals / Merck KAaG

Funding

- U.S. Department of Energy, National Energy Technology Laboratory, Award Nos. DE-FC26-04NT42122 and DE-FC26-07NT43091