Ionic Liquids for Fun & Profit

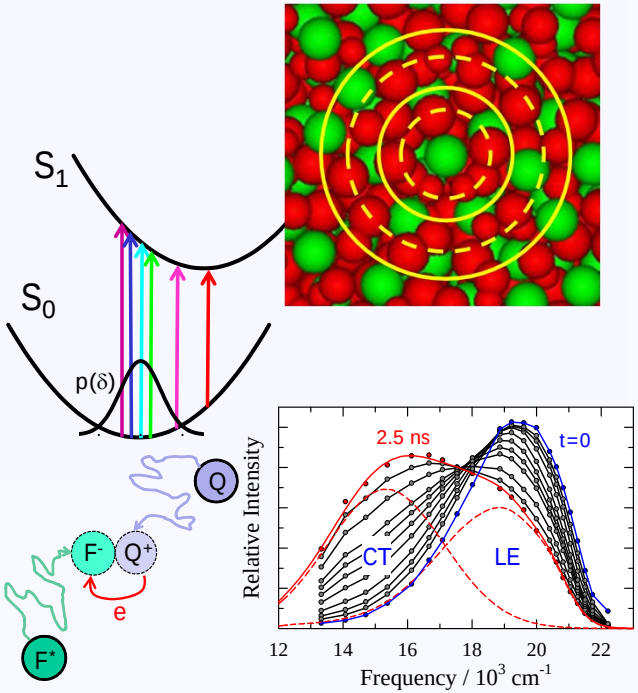
What are Ionic Liquids?

I – Some Applications:

- biomass conversion
- gas chromatography
- astronomy

II – Solvation in Ionic Liquids:

- spectroscopy & solvation
- ultrafast spectroscopy
- computer simulation



Mark Maroncelli
Penn State

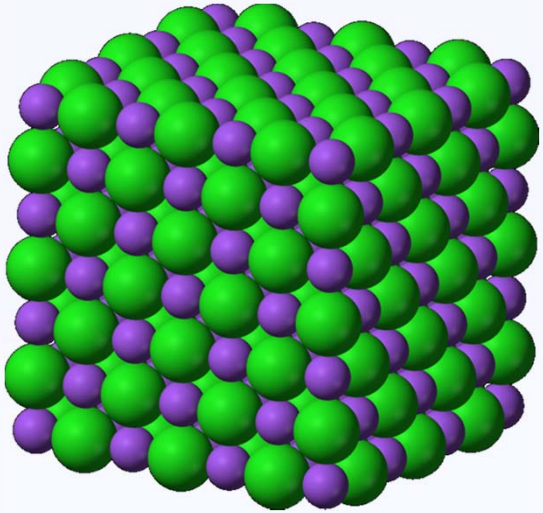
Franklin & Marshall College 4/02/13

What is an Ionic Liquid?

- (room temperature) ionic liquid = a salt that melts below 100 °C

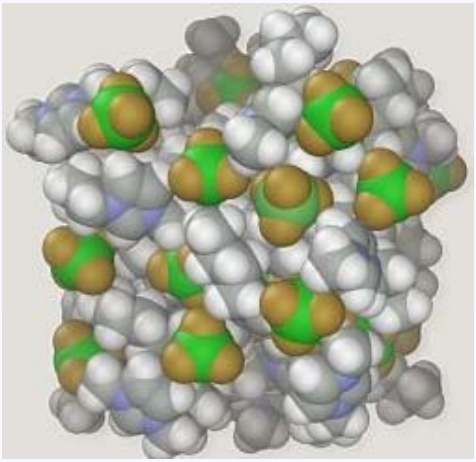
Inorganic Salt - NaCl

T_m=1074 K



Ionic Liquid $[Im_{41}][BF_4]$

T_m=~280 K



http://en.wikipedia.org/wiki/Sodium_chloride

Iolitec Inc.

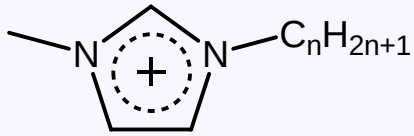
Why Such Low Melting Points?

$$LatticeEnergy = const \times \frac{Q_+ Q_-}{R_+ + R_-}$$

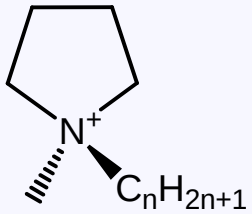
ion charge

ion separation

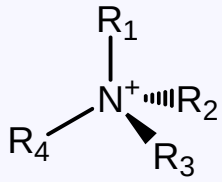
Cation Families:



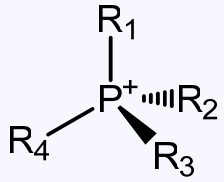
imidazolium



pyrrolidinium



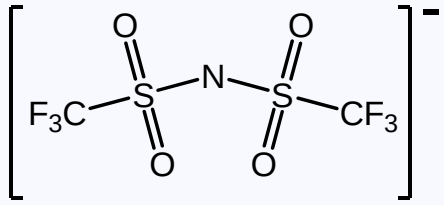
ammonium



phosphonium

Common Anions:

BF_4^-, PF_6^-, $CF_3SO_3^-$, ...



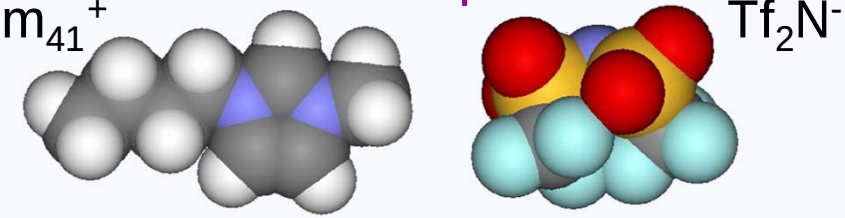
Inorganic Salt

Na^+ Cl^-

V_m=38 cm^3/mol

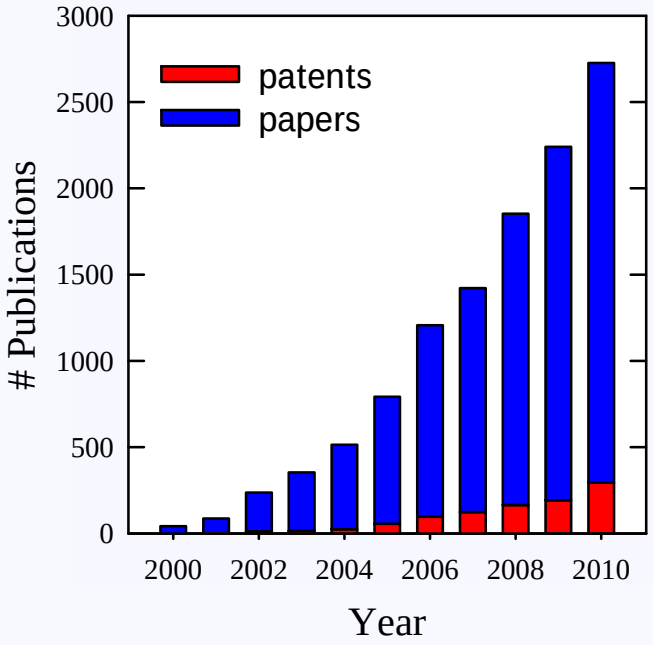
Ionic Liquid

Im_{41}^+ Tf_2N^-



V_m=295 cm^3/mol

A Hot Topic in Chemistry



Some Reasons Why

Thermal and chemical stability

Low melting point

High ionic conductivity

Solubility (affinity) with many compounds

Negligible volatility

Flame retardancy

Moderate viscosity

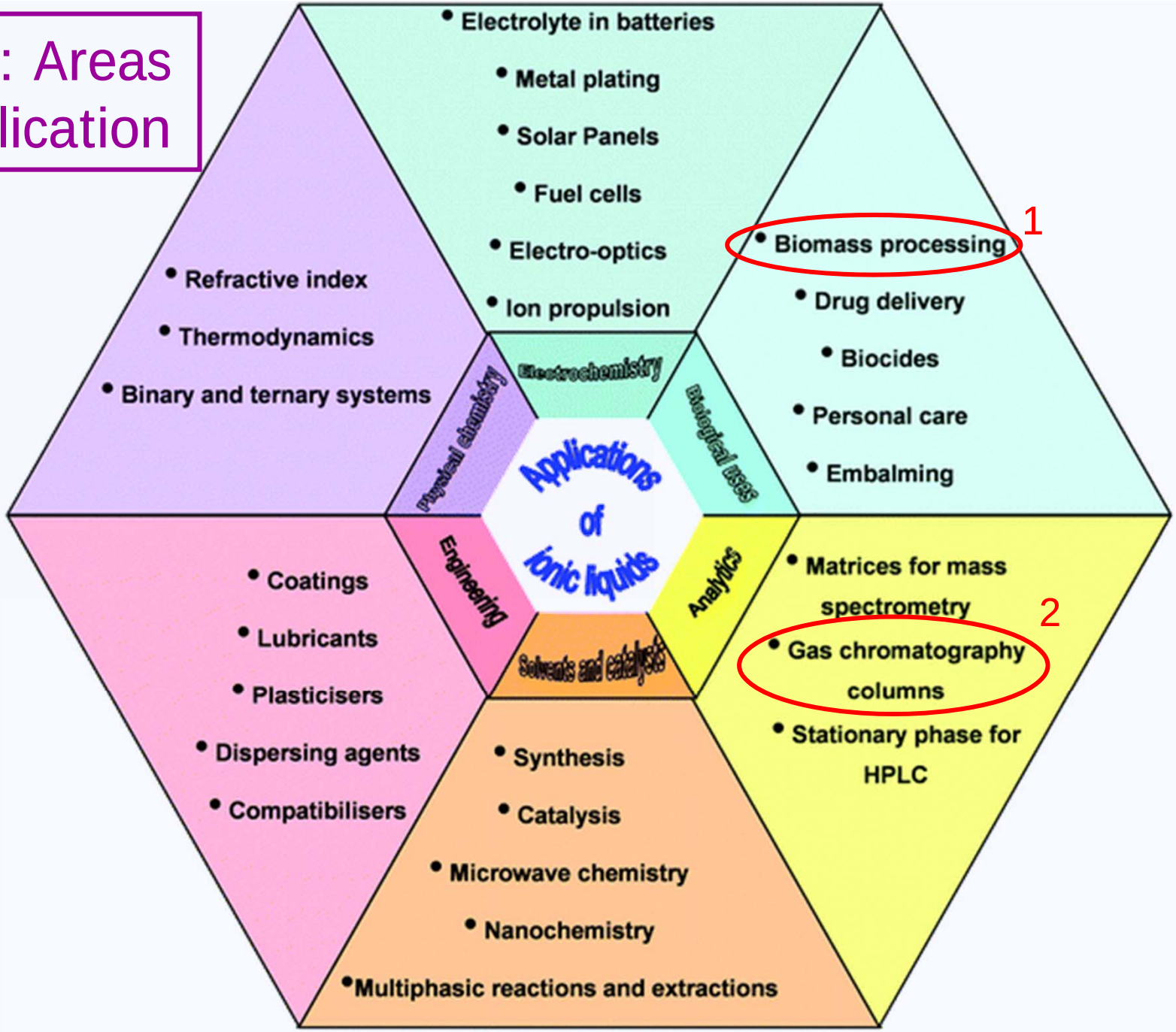
High polarity

Variation of ion structure (10^6)

- Ion conductive materials for electrochemical devices
- Solvents for chemical reaction
- Solvents for bioscience

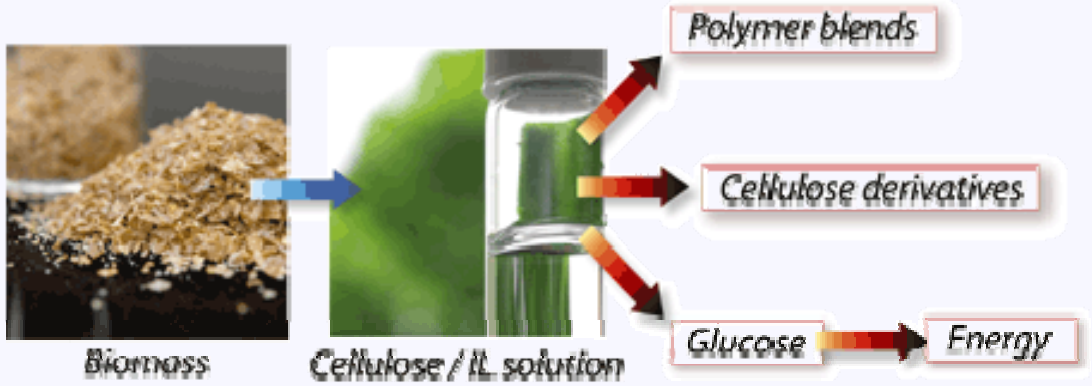
Armand et al., *Nature Materials* 8, 621 (2009)

For Profit: Areas of IL Application



Plechkova & Seddon, *Chem. Soc. Rev.* 37, 123 (2008).

1. ILs in Biomass Processing

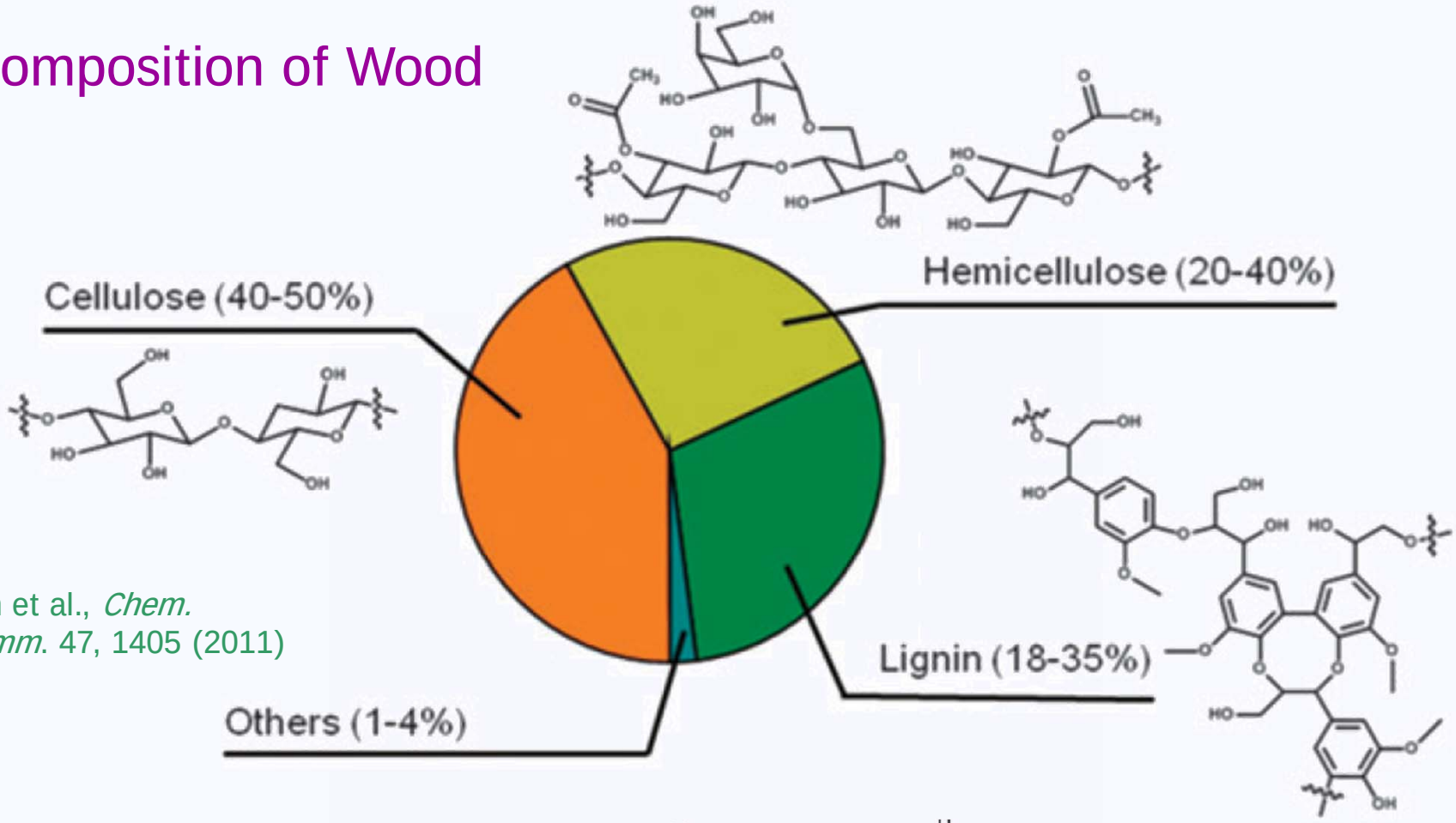


Ohno & Kukaya, *Chem. Lett.* 38, 2 (2009)

- DOE Grand Challenge: clean separation of the major components of lignocellulosic biomass, without loss of quality of the products, using an environmentally friendly method
- "biomass" – bagasse, corn stover, wheat & rice straw, wood chips...
- some ILs solubilize cellulose and even wood much better than conventional solvents

➢ ILs present a unique solvation environment

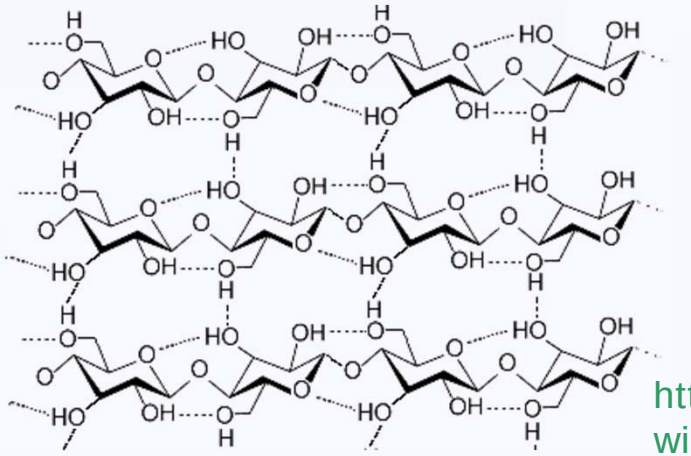
Composition of Wood



Sun et al., *Chem. Comm*. 47, 1405 (2011)

Cellulose:

uses: paper, cellophane, rayon, & related polymers, feedstock for small molecules & fuels



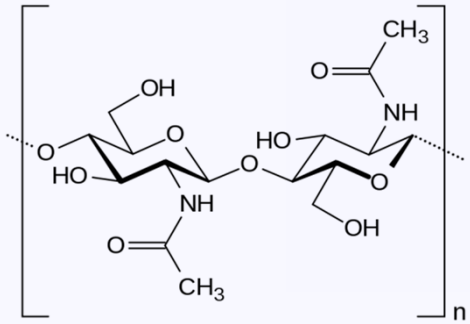
http://en.wikipedia.org/wiki/Cellulose

A Closely Related Use: Chitin from Crustacean Shells

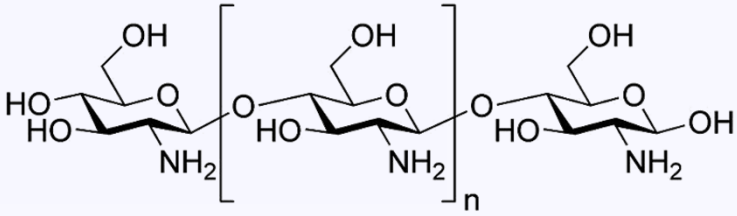
"chitin fibers can be spun from a solution resulting from direct dissolution of shrimp shells in a one-pot process"

Qin et al., *Green Chem.* 12, 968 (2010)

Chitin



Chitosan



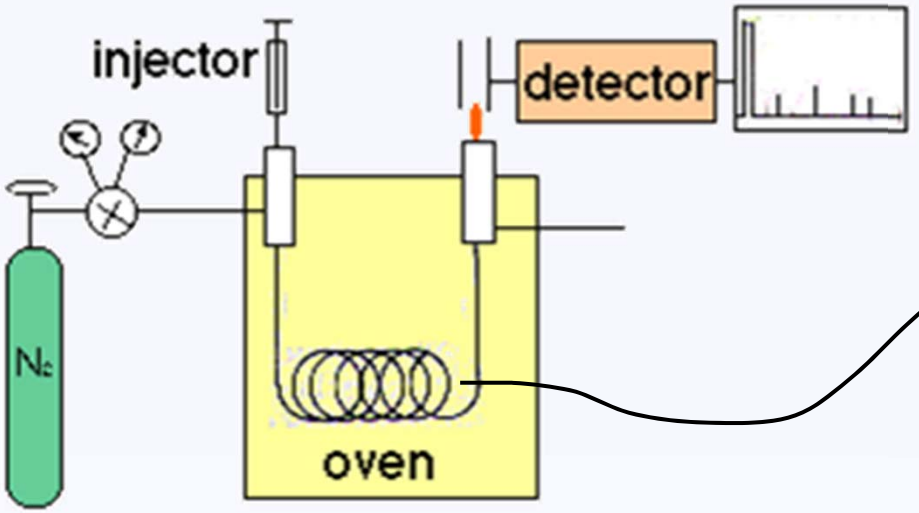
- 2nd most plentiful biopolymer
- surgical thread
- controlled drug release

- biopesticide, biocontrol agent
- filtration processes
- bandages

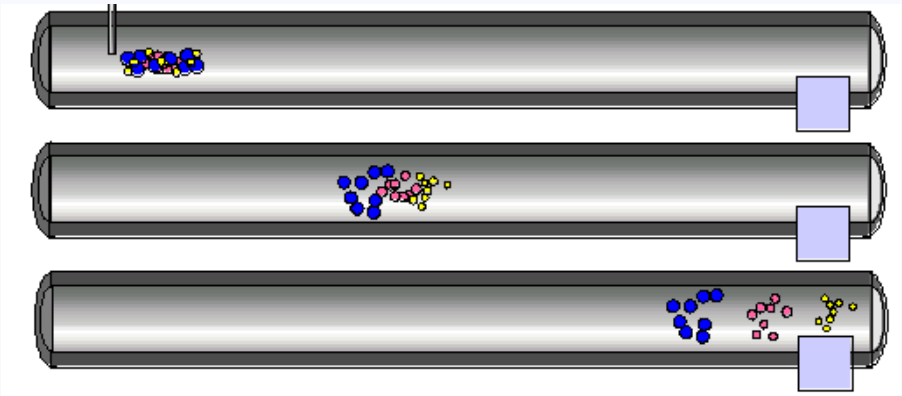
http://en.wikipedia.org/wiki/Chitin

2. Materials for Gas Chromatography

Gas Chromatography



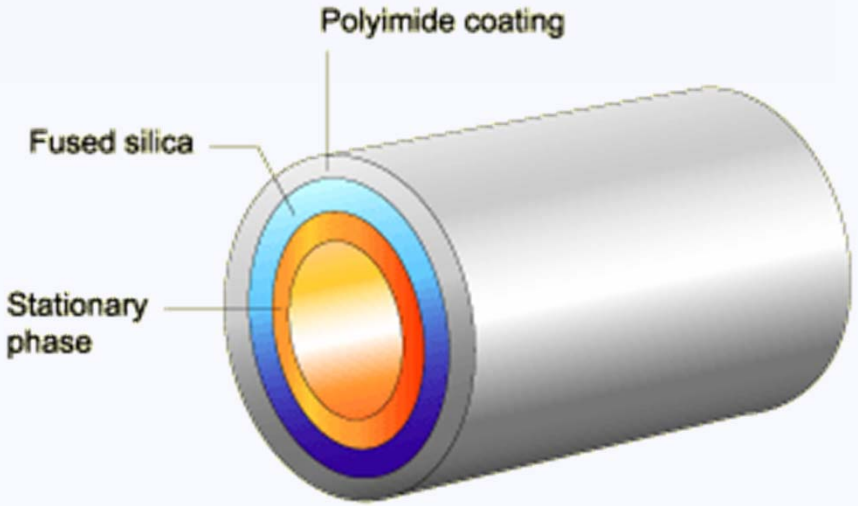
http://www.sfu.ca/bisc/bisc-429/GLC.html



http://chemsite.lsrhs.net/Intro/chromatography.html

The Capillary Column

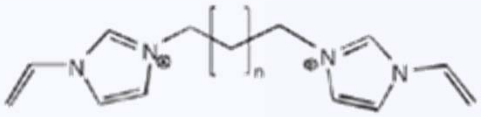
50 m, 200μm

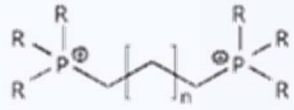


http://toolboxes.flexiblelearning.net.au/demosites/series5/508/laboratory/studynotes/snTheGCColumn.htm

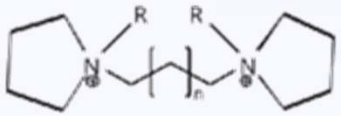
- in GC differential solubility is key; ILs offer a new range of interactions
- huge potential for tailor-making ILs for specific separations
- almost negligible volatility
- high viscosity
- high thermal stability

Cations

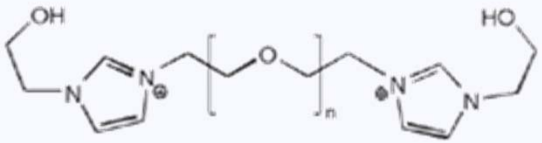




(R = alkyl or aryl)

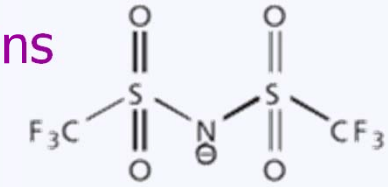


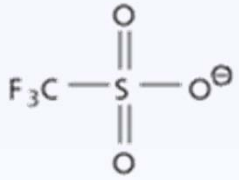
(R = alkyl or aryl)



Armstrong et al. LCGC North Am. 27, 596 (2009)

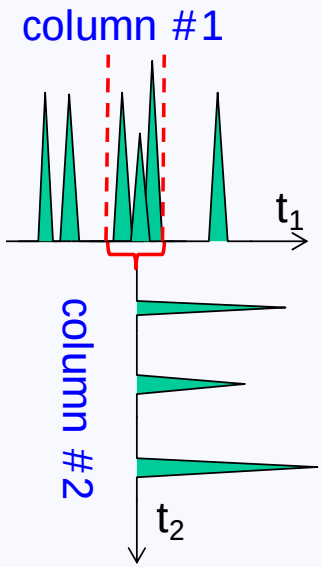
Anions

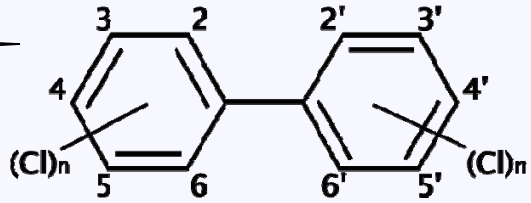




Supelco currently sells 7 IL GC columns

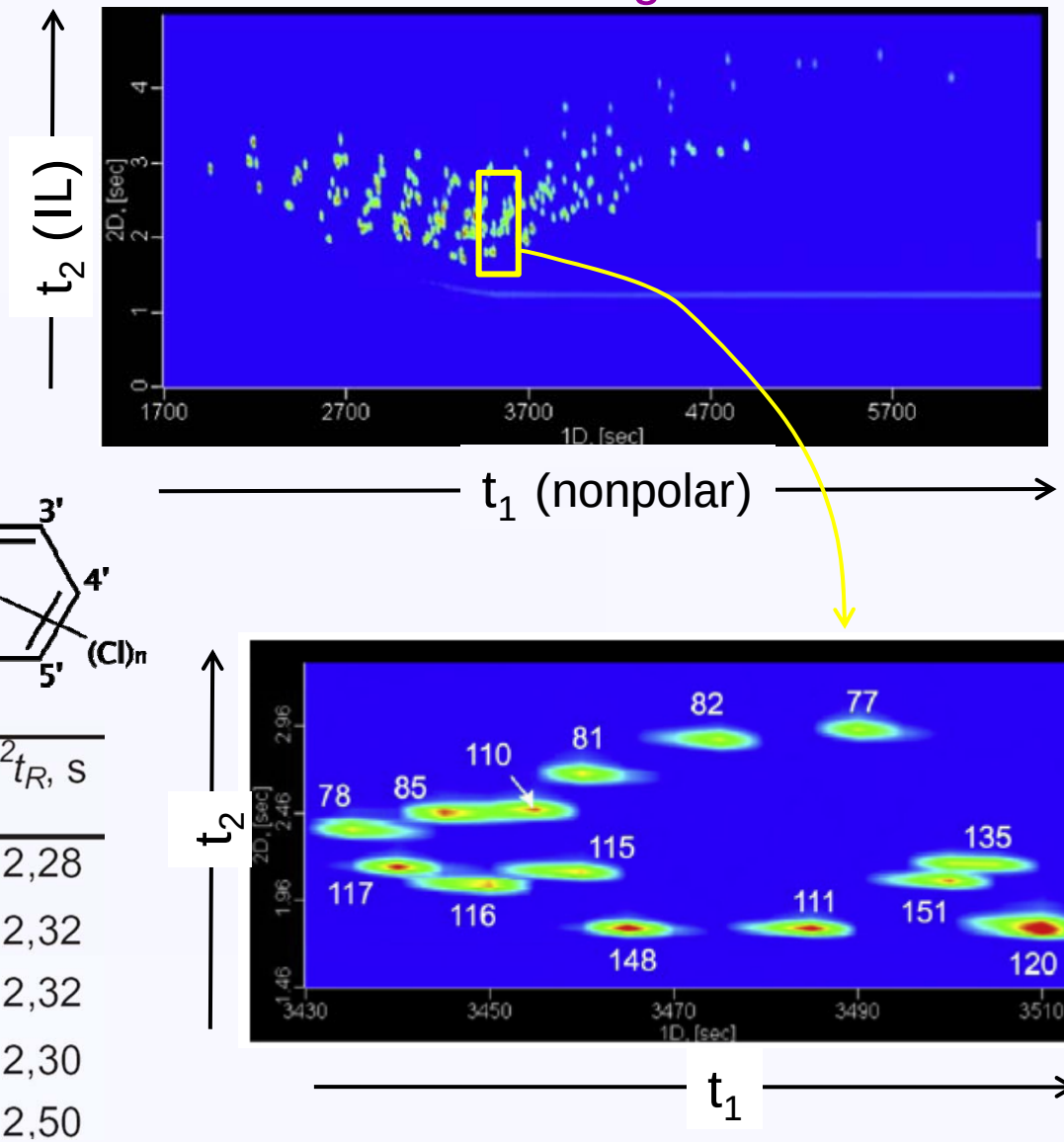
ILs in 2-Dimensional Gas Chromatography





IUPAC No	Cl position	^1t_R, s	^2t_R, s
79	3,3',4,5'	3405	2,28
97	2,2',3',4,5	3405	2,32
125	2',3,4,5,6'	3405	2,32
86	2,2',3,4,5	3410	2,30
87	2,2',3,4,5'	3410	2,50

2D-GC of 209 PCB Congeners



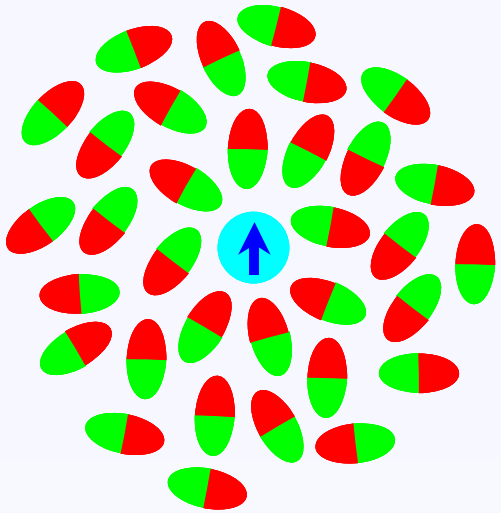
➢196 of 209 congeners resolved (the record to date)

Zapadlo et al., *J. Chromatogr. A* 1218, 746 (2011)

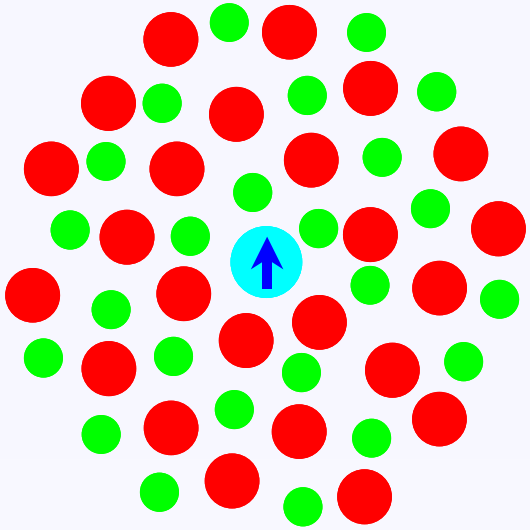
II. Now for Fun:
Solvation in Ionic Liquids

Ionic vs. Dipolar Solvents

The Old Dipolar World



The Ionic World



Intermolecular Interactions

- H-bonding
- dispersion
- dipole-dipole
- induction

ion-ion

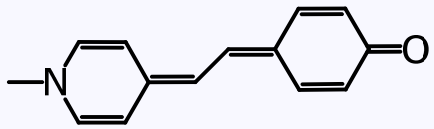
ion-dipole

The Spectroscopy of Solvation

acetone acetic acid DMF 2-propanol THF

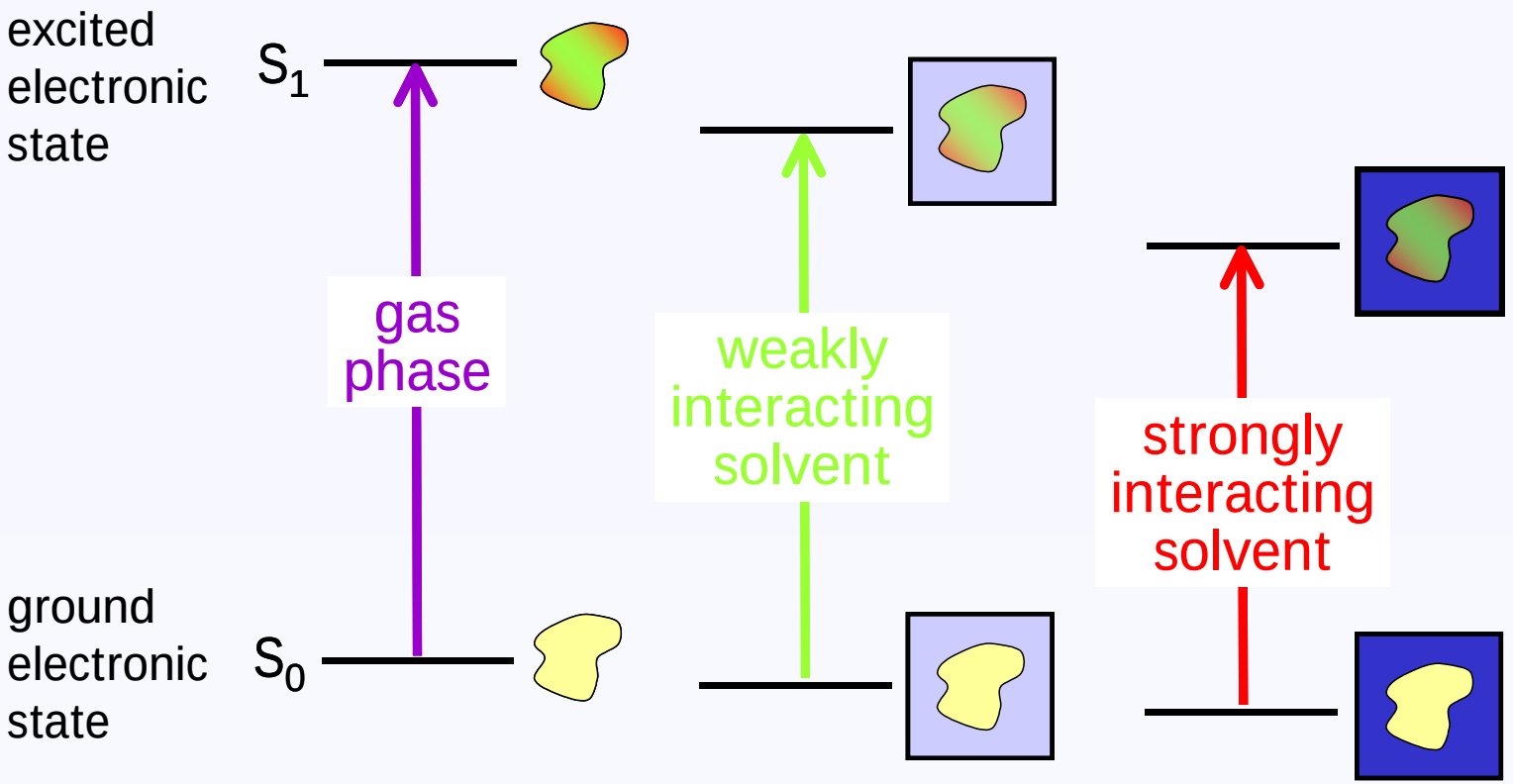
ethanol water acetonitrile methanol DMSO

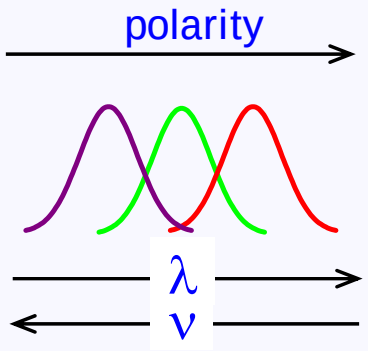
Brooker's Merocyanine



http://en.wikipedia.org/wiki/User:Brutulf/Brooker%27s_Merocyanine

Why the Color Changes?

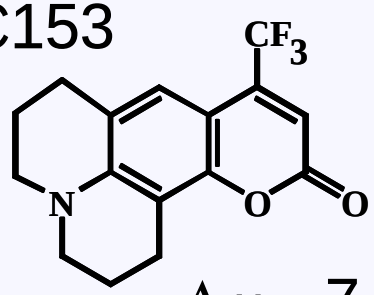




How Polar are Ionic Liquids?

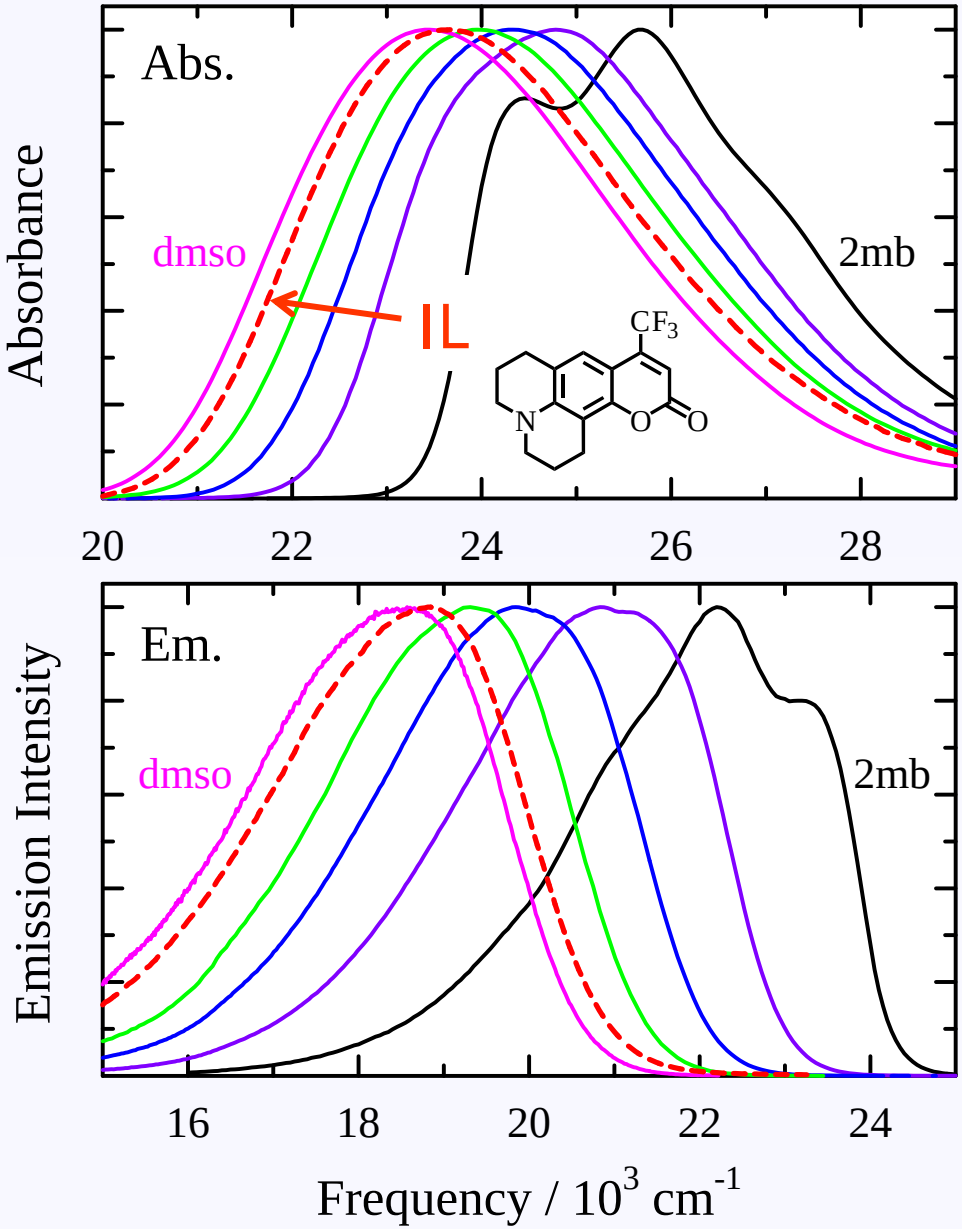
Probe of Generic Polarity

C153

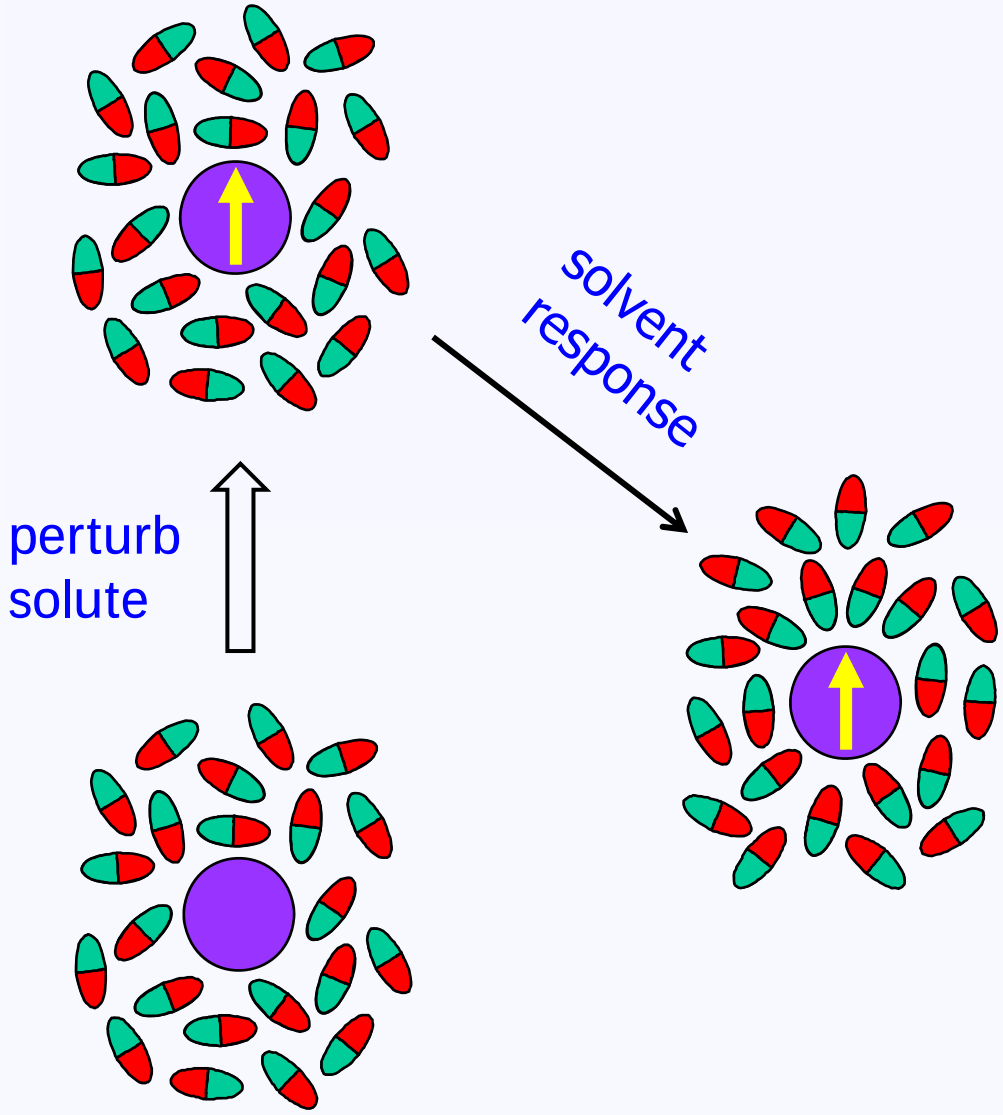


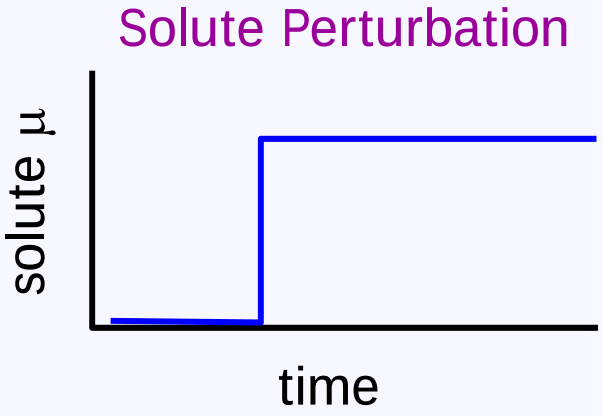
$\Delta\mu \sim 7$ D

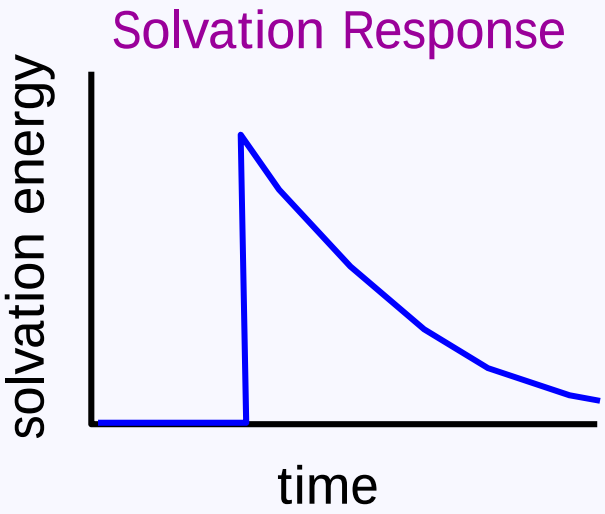
- spectra in ILs are not distinctive
- "polarity" is similar to CH_3CN, DMSO, MeOH



How Fast is Solvation?

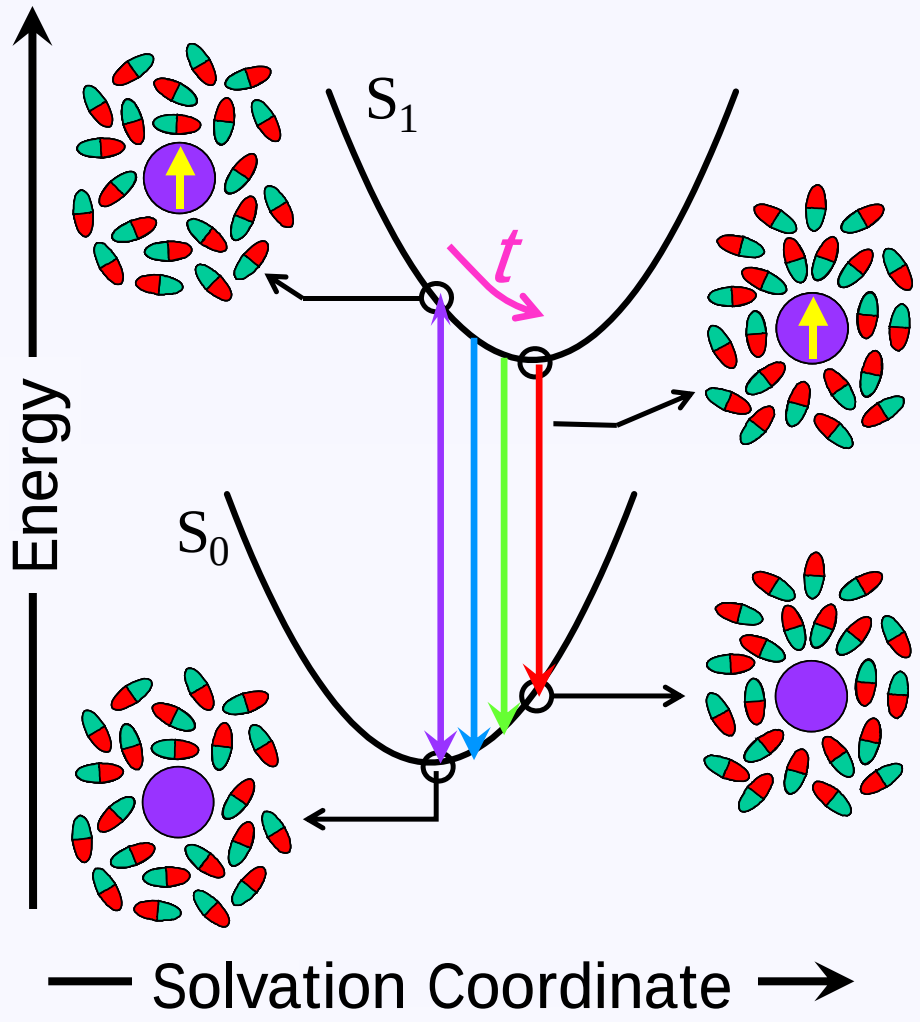




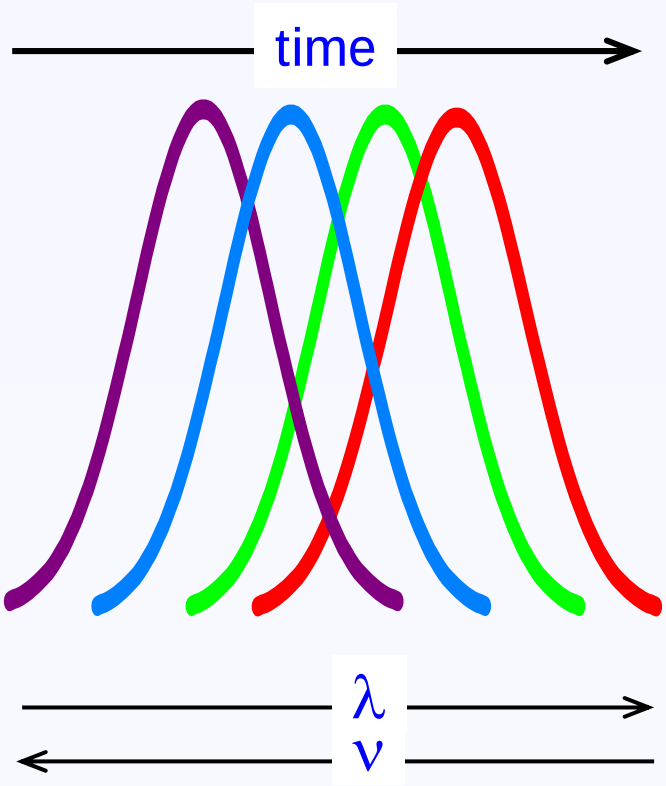


Solvation & Time-Resolved Emission

Solvation Dynamics

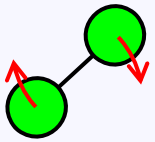


Time-Resolved Emission Spectra

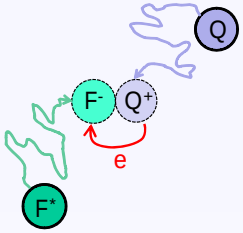


Typical Molecular Timescales

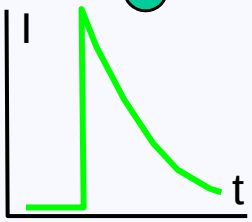
vibrational period 10^{-14}-10^{-13} 10-100 fs



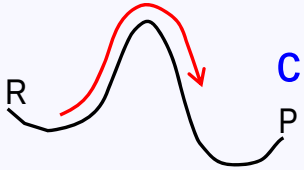
rotation time 10^{-12}-10^{-10} 1-100 ps



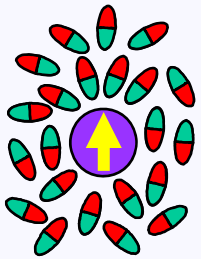
diffusion time (at 1 M) 10^{-10}-10^{-9} 0.1-1 ns



fluorescence lifetime 10^{-9}-10^{-11} 1-100 ns



chemical reaction 10^{-14}- 10 fs-∞

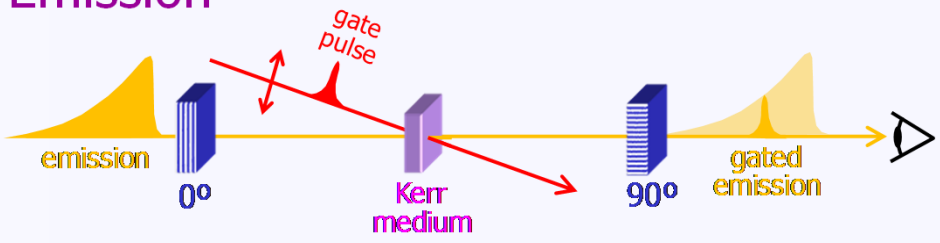


solvation 10^{-13}-10^{-11} 0.1-10 ps

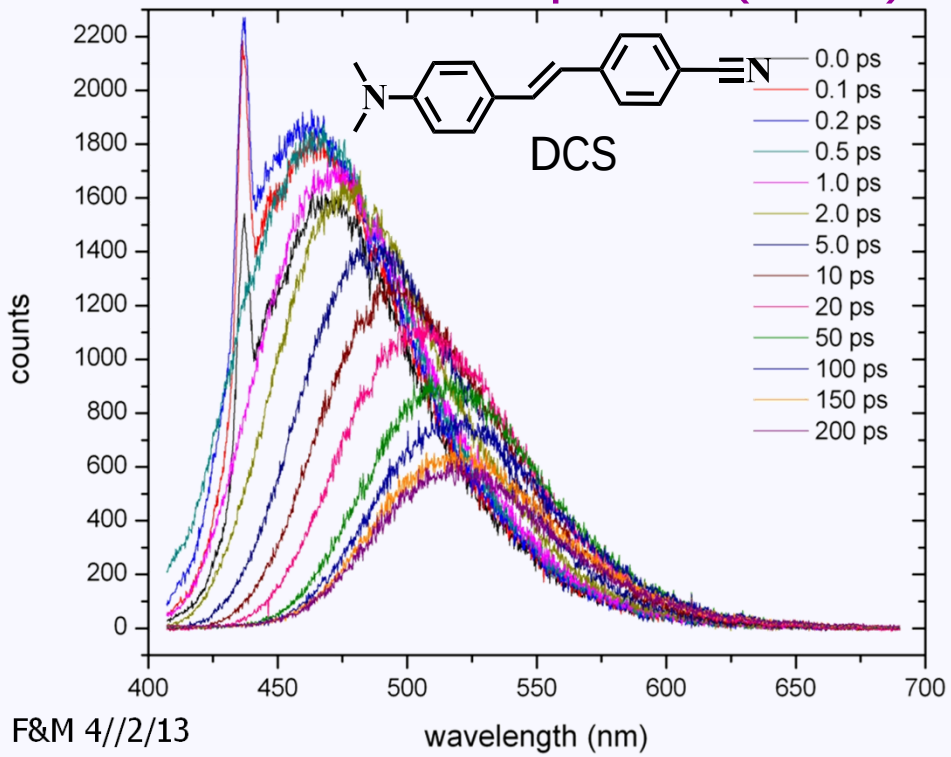
Some Experimental Results

Kerr Gating Emission

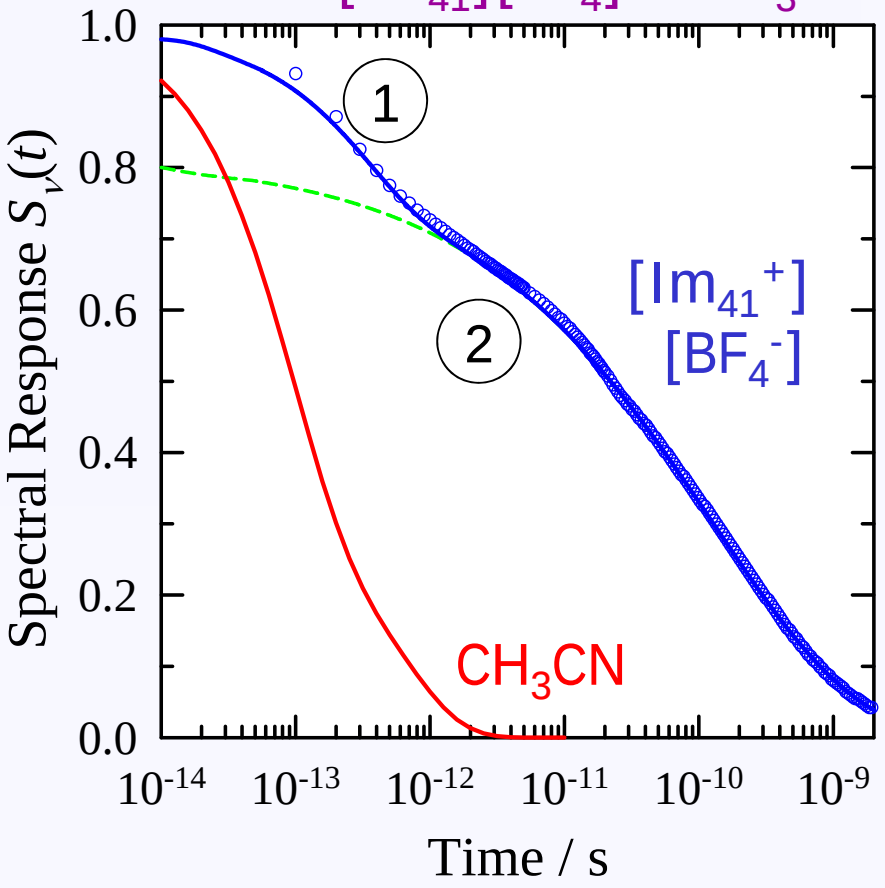
~300 fs IRF



KGE Emission Spectra (EtOH)

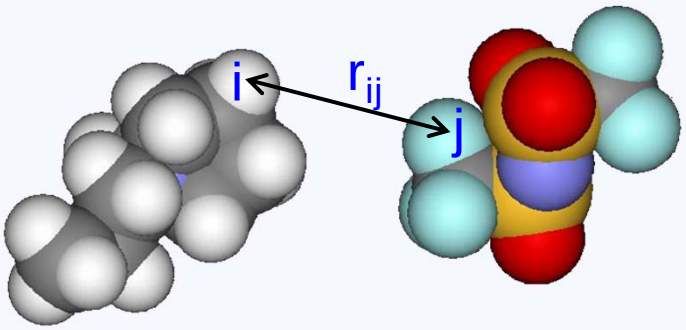


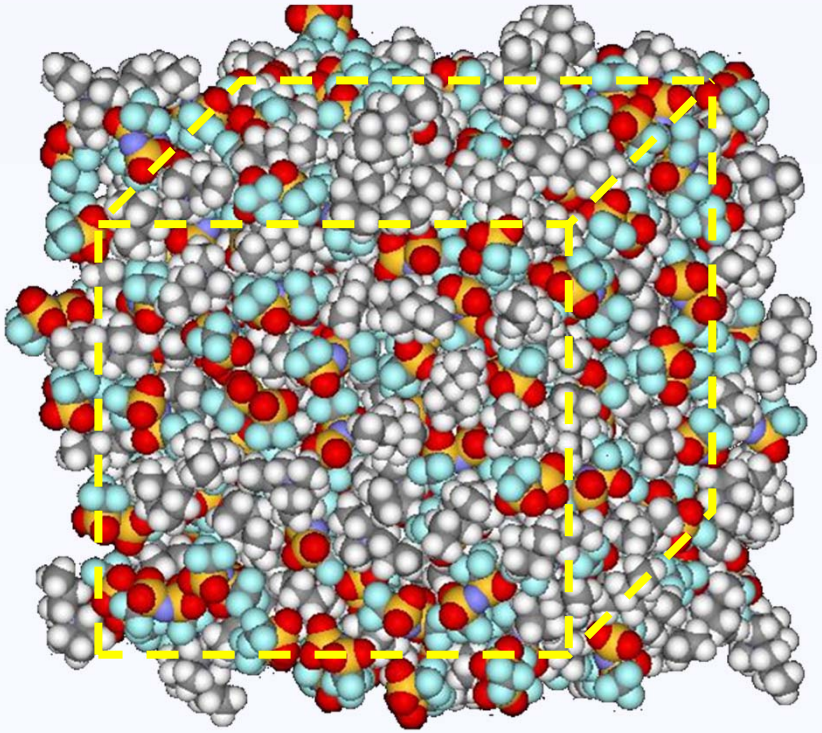
DCS in $[Im_{41}][BF_4]$ & CH_3CN



- ILs ~100x slower (like η)
- dual character
- spans 100 fs – 10 ns

Computer Simulations





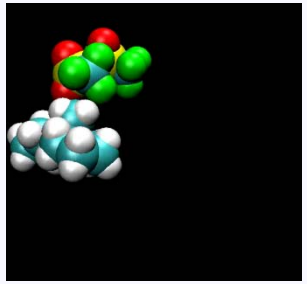
- choose interaction model

$$V_{ij}(r_{ij}) = \frac{q_i q_j}{r_{ij}} + 4\varepsilon\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right\}$$

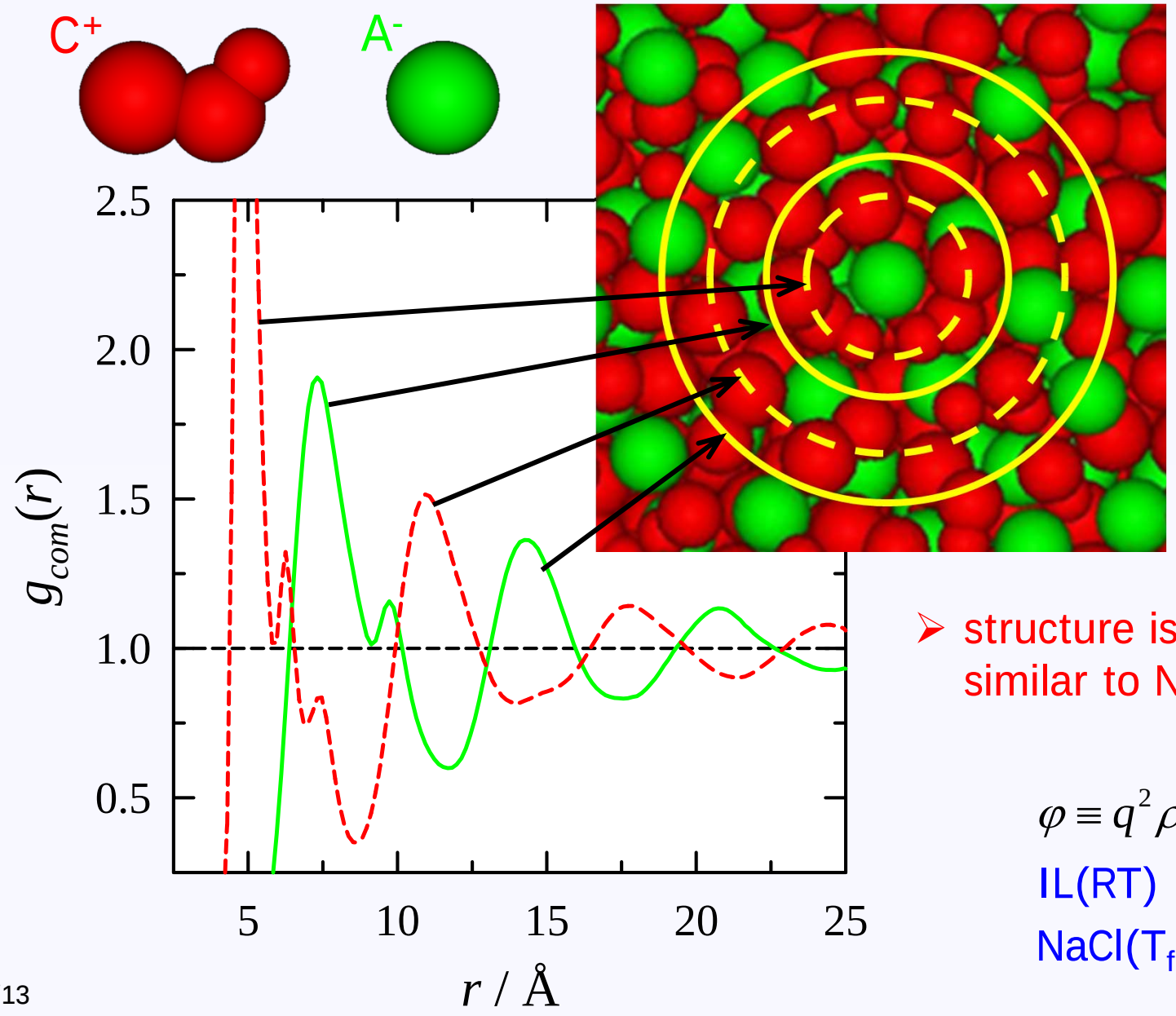
- construct starting point of ~500 ions in a periodic box
- numerically integrate equations of motion (F=ma)

$$\vec{F}_i = -\nabla_i \sum_j V_{ij} \qquad \frac{d^2\vec{r}_i}{dt^2} = \frac{\vec{F}_i}{m_i}$$

- observe the dance



Charge Ordering



- structure is quite similar to NaCl @ T_f

$$\varphi \equiv q^2 \rho^{1/3} / k_B T$$

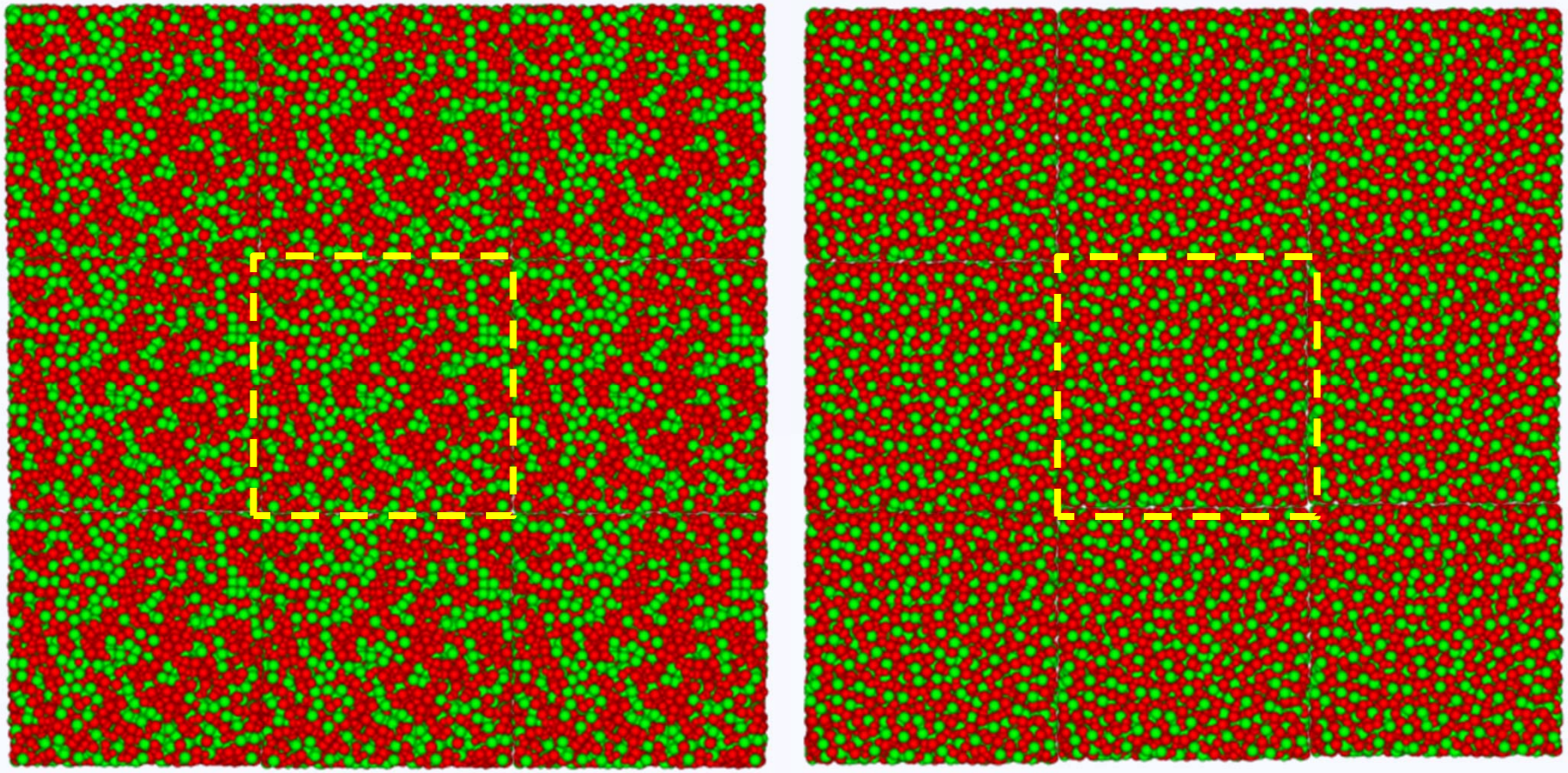
IL(RT) φ=48

NaCl(T_f) φ=50

The Effects of Charge

Neutral Mixture

Ionic Liquid

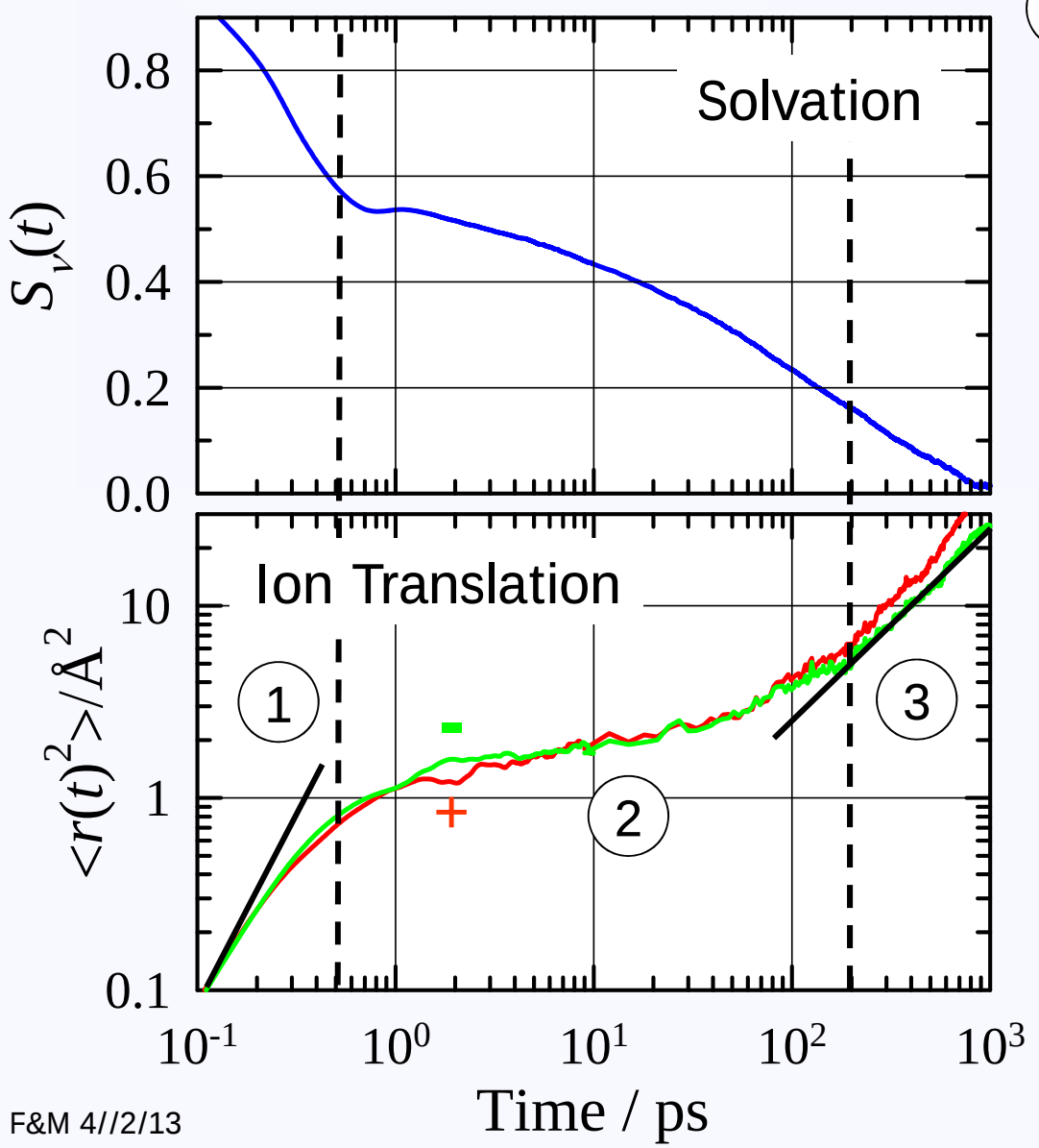


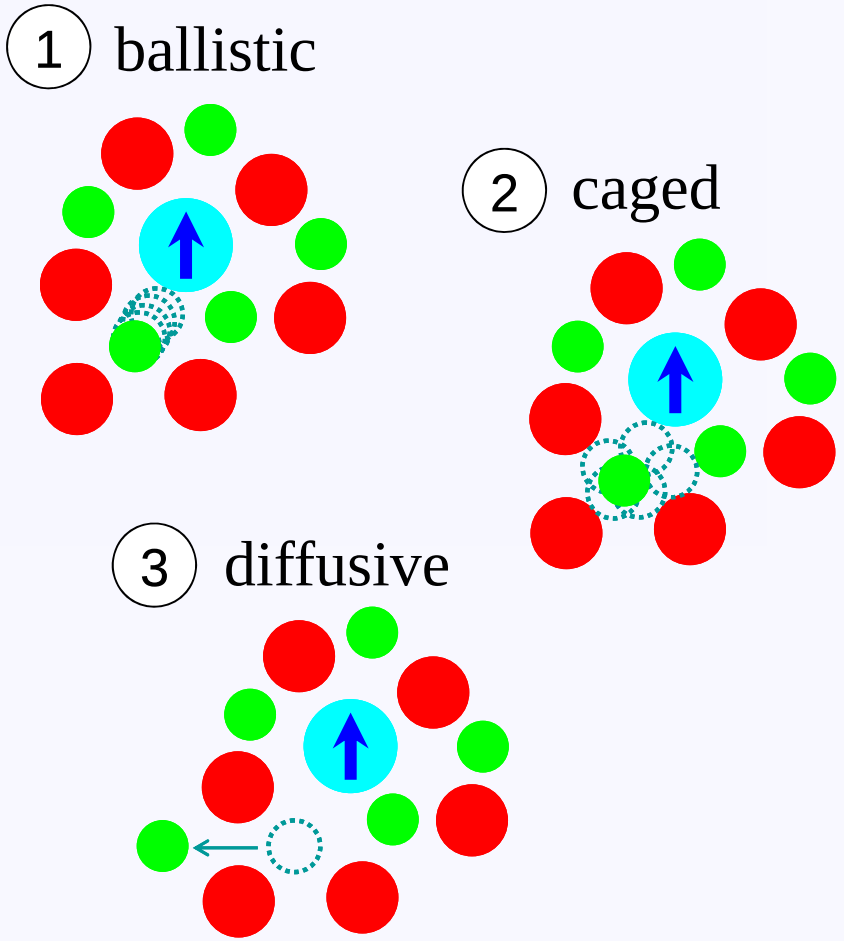
$q_i = 0 \Longrightarrow q_i = \pm 1$

cohesive energy U	↑	5x
molar volume V_m	↓	18%
fluidity $1/\eta$	↓	250x

Solvation "Mechanism"

Simulated Dynamics





- primarily ion translation
- highly collective "vibration"

Summary

- Ionic Liquids – salts that stay liquid below 100 °C
  - large organic cations + organic/inorganic anions
  - unique solvating abilities
  - liquid over wide temperature range
  - good electrolytes
  - essentially nonvolatile
- applications in virtually all areas of chemistry
  - biomass conversion
  - gas chromatography
  - (astronomy)
- physical chemistry research
  - ultrafast spectroscopy of solvation
  - computer simulations

Parting Shots