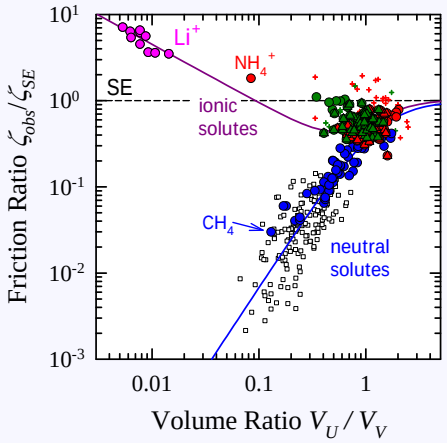
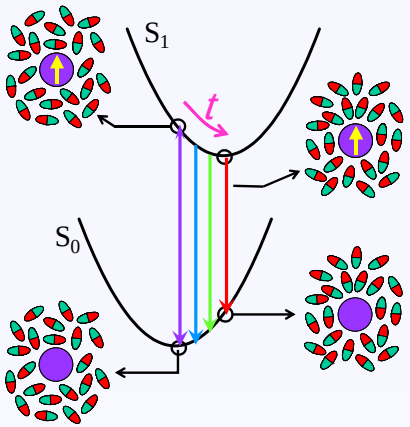
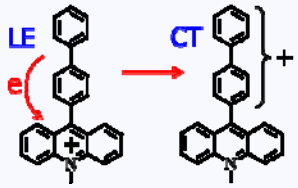
Solvation & Solute Dynamics in Ionic Liquids

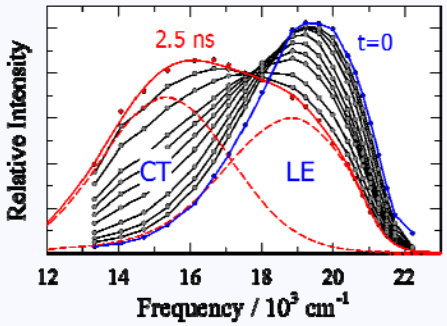
Mark Maroncelli, Penn State

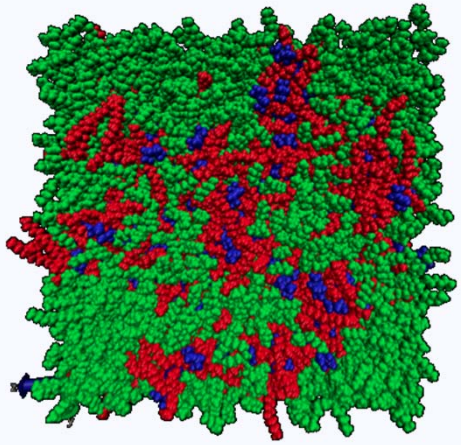
1. Translation & Rotation
2. Solvation Dynamics
3. Reaction Kinetics & Heterogeneity
4. Effect of Nanostructure?





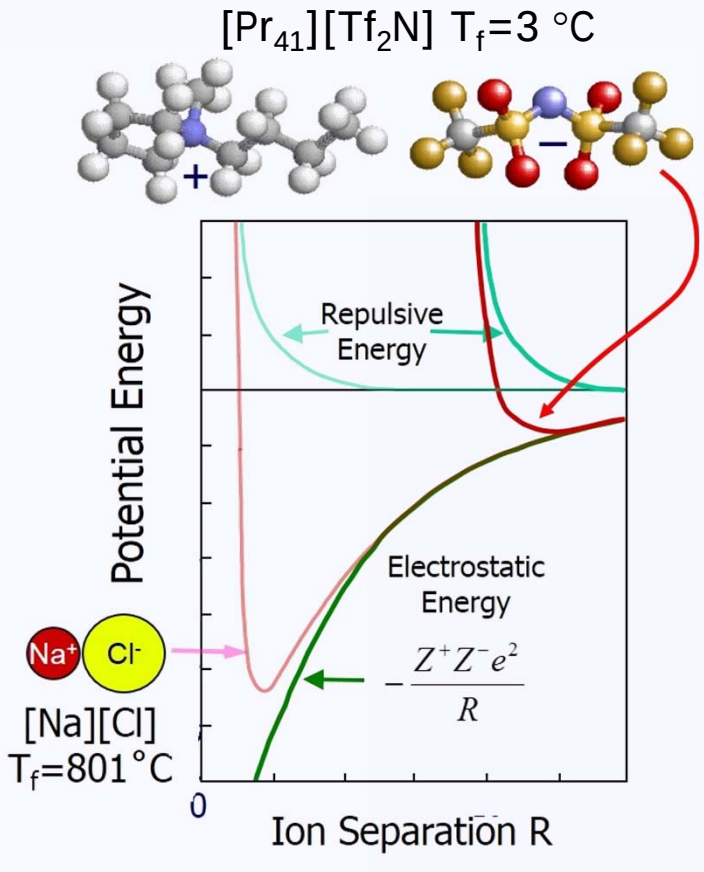




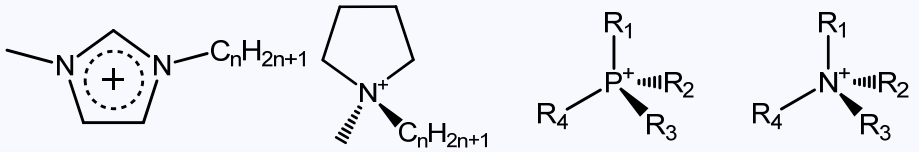


Office of Basic Energy Sciences
Serving the Present, Shaping the Future

(Room Temperature) Ionic Liquids



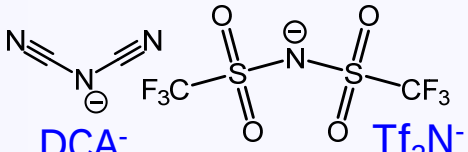
Cation Families:



imidazolium Im_{n1}^+ | pyrrolidinium Pr_{n1}^+ | phosphonium P_{1234}^+ | ammonium N_{1234}^+

Common Anions:

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



DCA$^-$ Tf_2N^-

Typical Properties:

- Low Volatility
- High Thermal Stability
- Intrinsically Conductive
- Wide Electrochemical Window
- Solubility/Phase Control

Lowering T_f:

- charge delocalization
- size mismatch
- low symmetry
- conformational disorder

Our Interests:

- Distinctive solvation/chemistry?
- New lessons to be learned?

1. The Simplest Dynamics: Solute Translation & Rotation

Anne Kaintz

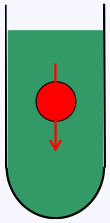
Juan Carlos Araque

Chris Rumble

Ion Self-Diffusion Coefficients & Friction

Stokes-Einstein (Sutherland) Hydrodynamic Prediction:

$$D_{SE} = \frac{k_B T}{6\pi\eta R} \quad \zeta_{SE} = \text{friction on sphere of radius R}$$



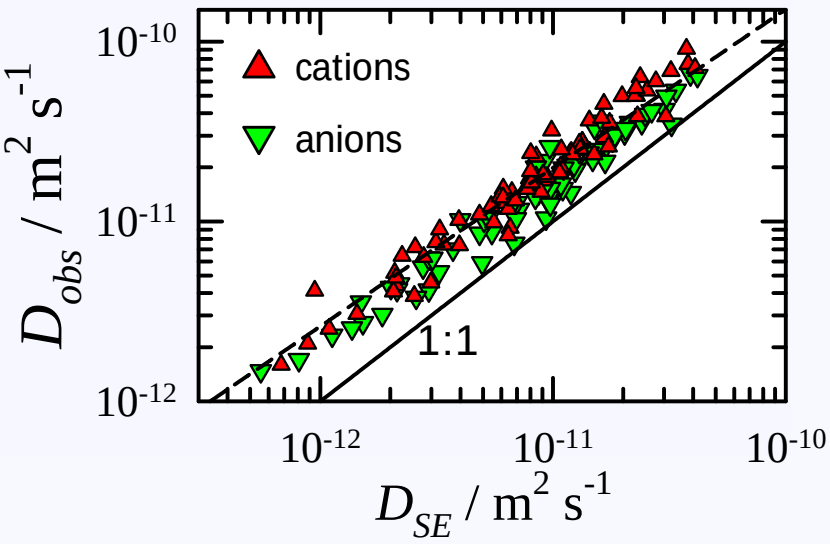
Friction Ratio:

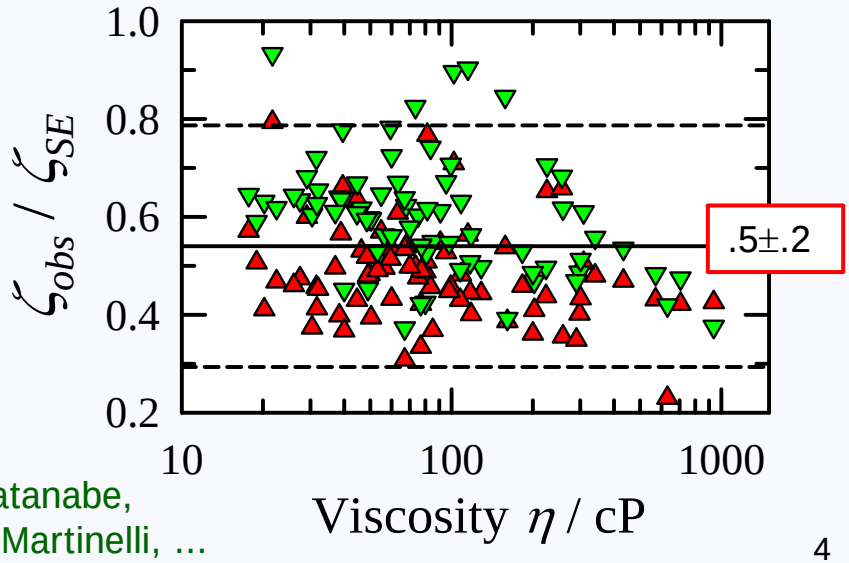
$$\frac{\zeta_{obs}}{\zeta_{SE}} = \frac{D_{SE}}{D_{obs}}$$

measure of the coupling between the diffusor and solvent bath

- SE predictions are reasonably accurate for estimating ion self diffusion in ILs
- nearly identical situation exists in conventional solvents

Ion D in 32 ILs (298 K)

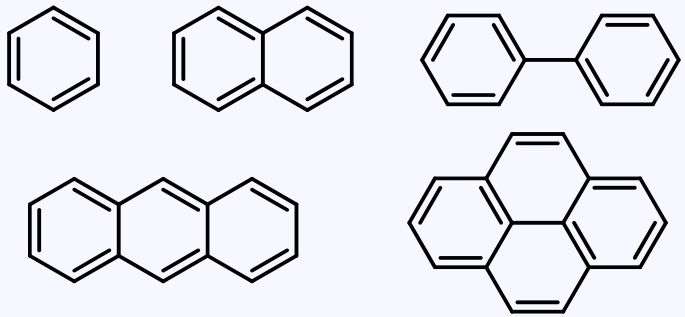




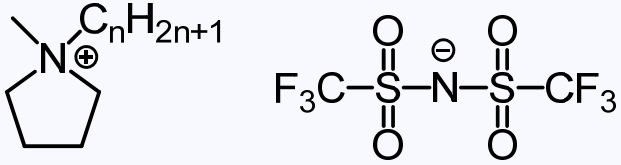
data from Watanabe, Matsumoto, Martinelli, ...

Diffusion of Aromatic Hydrocarbons in ILs

PFG-NMR measurements of simple aromatic hydrocarbons



in a homologous series of ILs

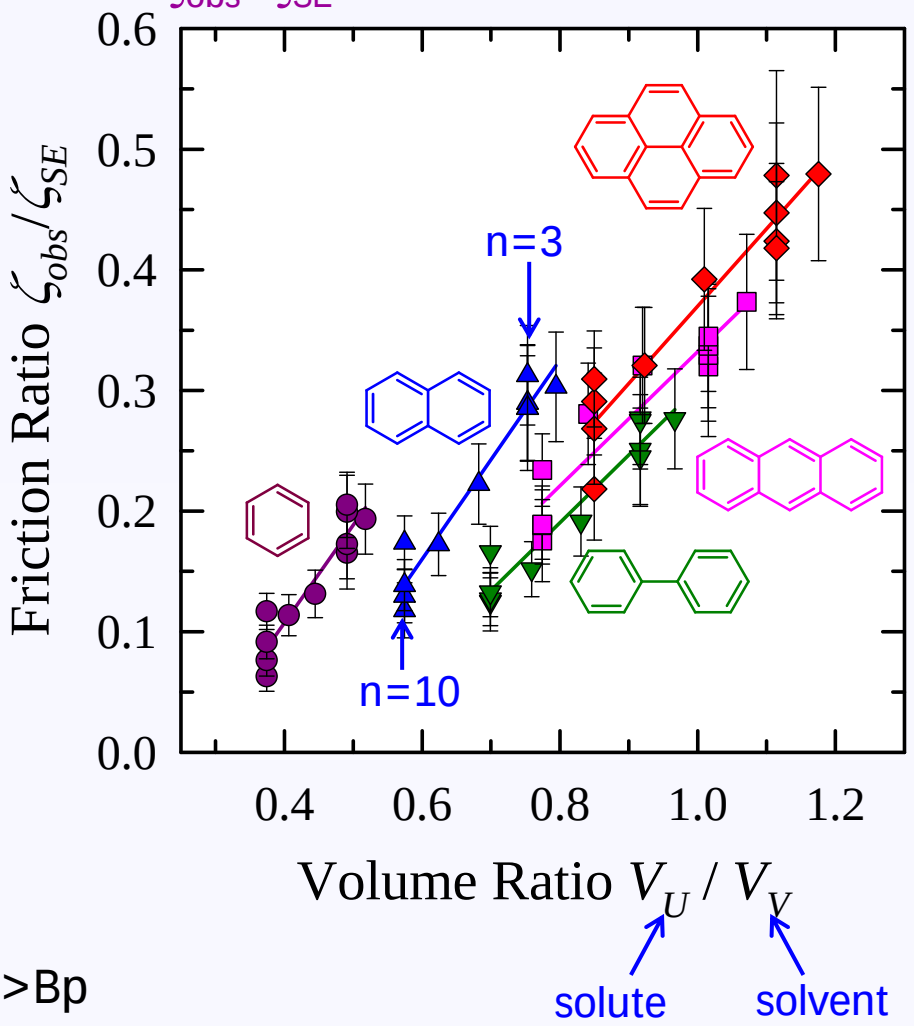


$[Pr_{n1}][Tf_2N]$ n=3, 4, 6, 8, 10

- departure from SE predictions increases with decreasing solute and increasing solvent size
- shape is also a factor Bz>Na>Py>An>Bp

oblate ~prolate

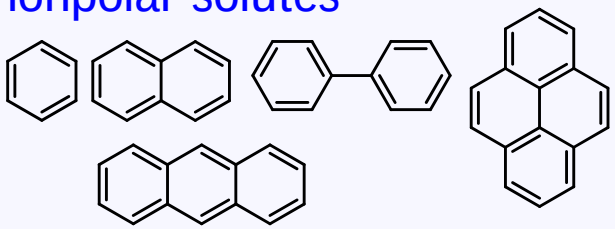
ζ_{obs}/ζ_{SE} vs. Solute/Solvent Size



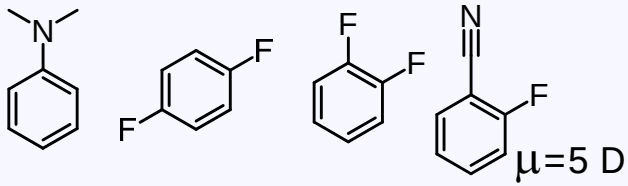
Kaintz et al., *J. Phys. Chem. B* **117**, 11697 (2013).

Neutral Solutes Diffusing in ILs

- nonpolar solutes

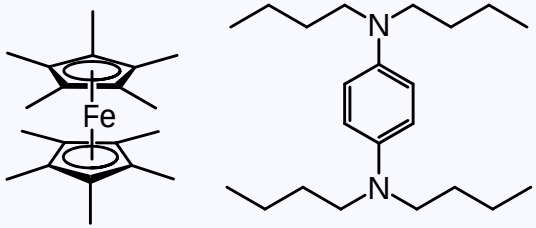


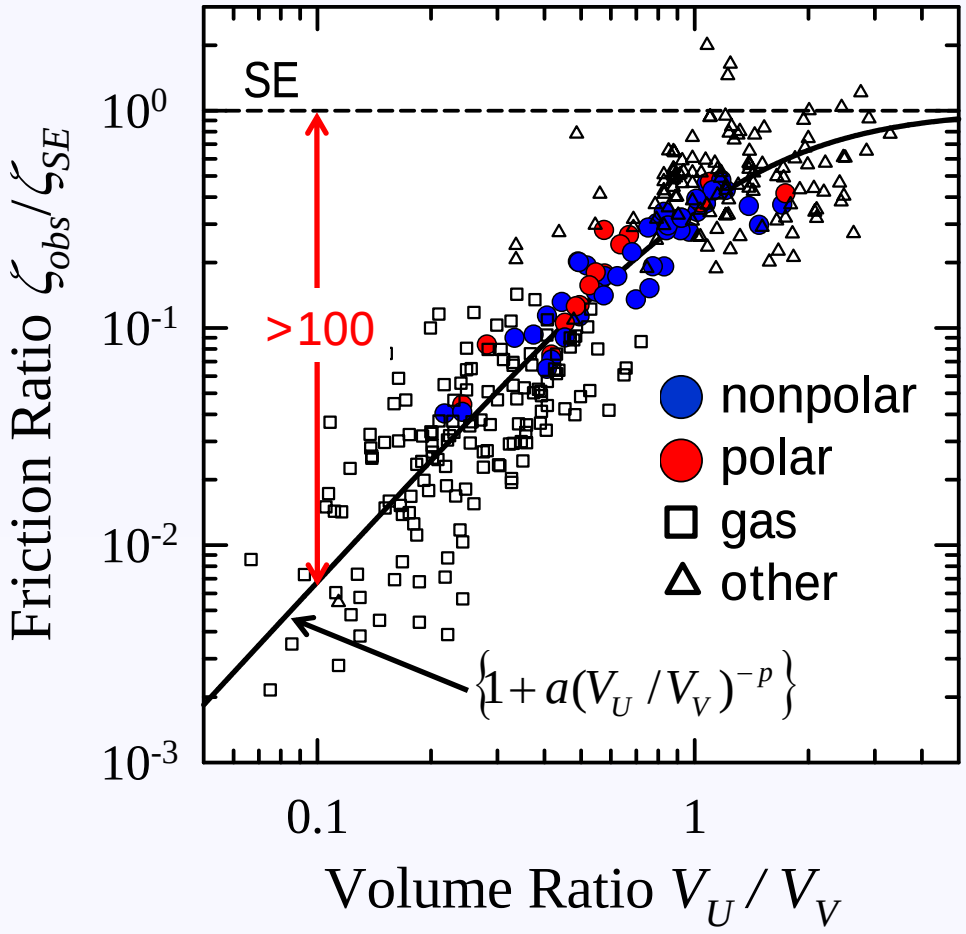
- polar solutes



- literature data:
  323 solute/solvent pairs, 37 solutes, 56 ILs
- small gaseous solutes:

  CO, CO_2, C_2H_4, C_4H_{10}, …
- large solutes:

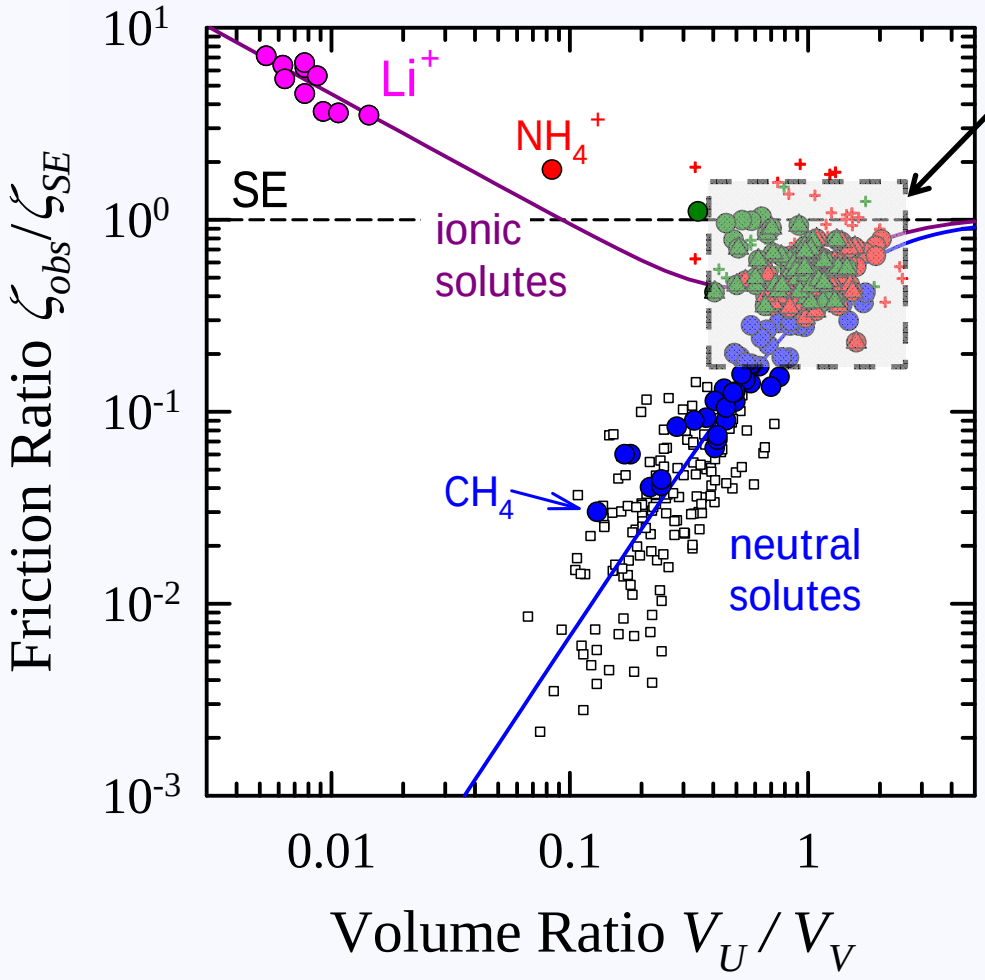




- marked departures from SE predictions
- primary determinant is U/V size ratio

lit. data from: Noble, Baltus, Scovazzo, Kimura, Hardacre, Compton, License, Halpiot, Lagroste, Hussey, …

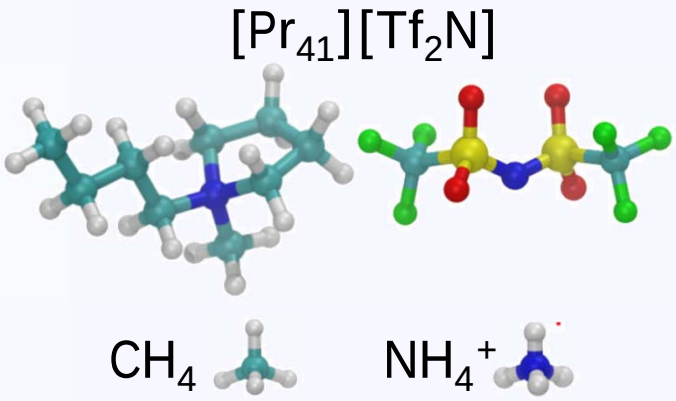
Charged (±1e) Solute Diffusion in ILs

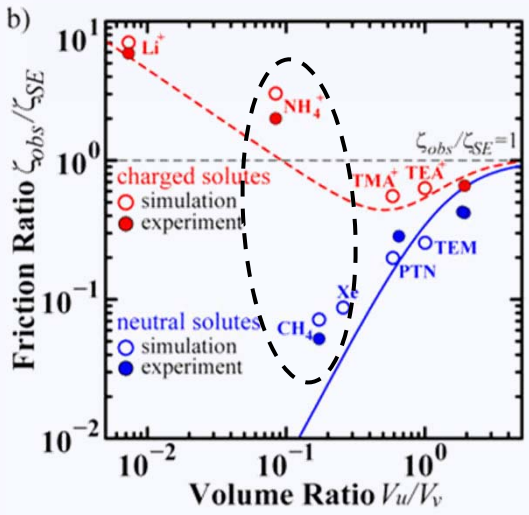


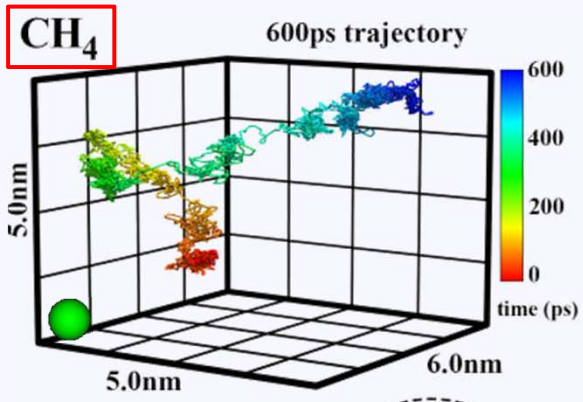
- ζ_{obs}/ζ_{SE}~1 for ions (helpful for $\Lambda\eta$ interpretations)
- large difference in ζ_{obs}/ζ_{SE} for small ions compared to neutral solutes
- the "solventberg" limit well-documented for Li^+

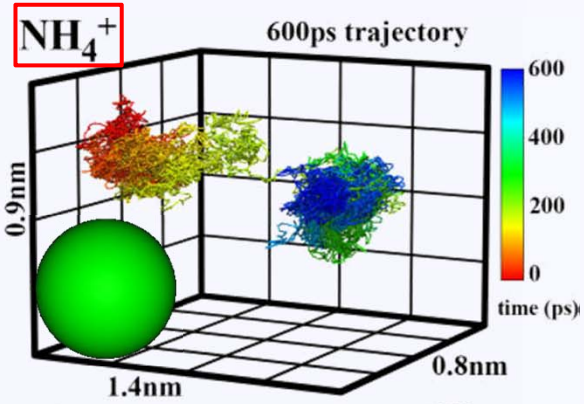
- analogous but weaker trends also seen in conventional solvents
- mismatch between solute and solvent in size or interactions responsible for marked departures from SE predictions

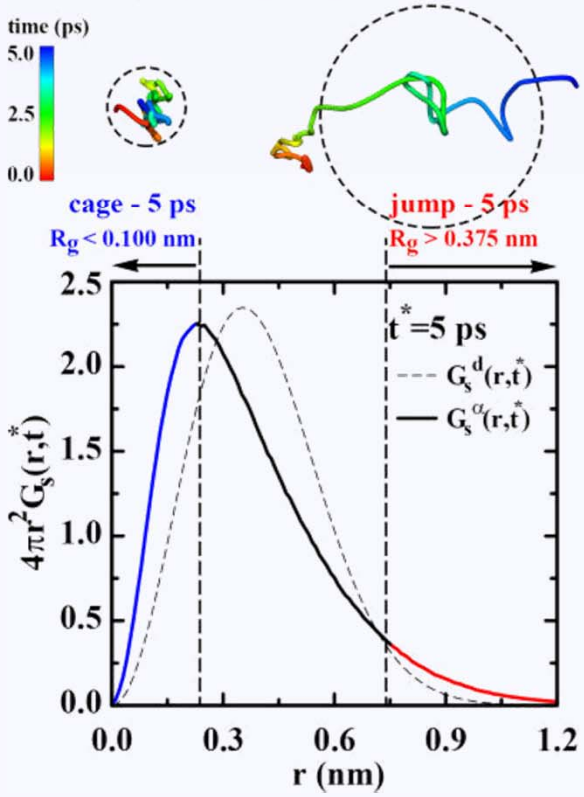
Transport Mechanisms from MD

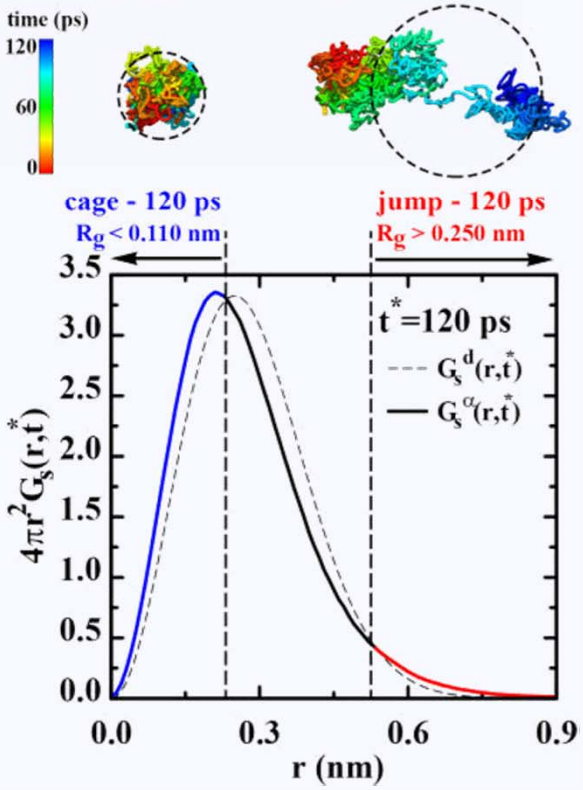










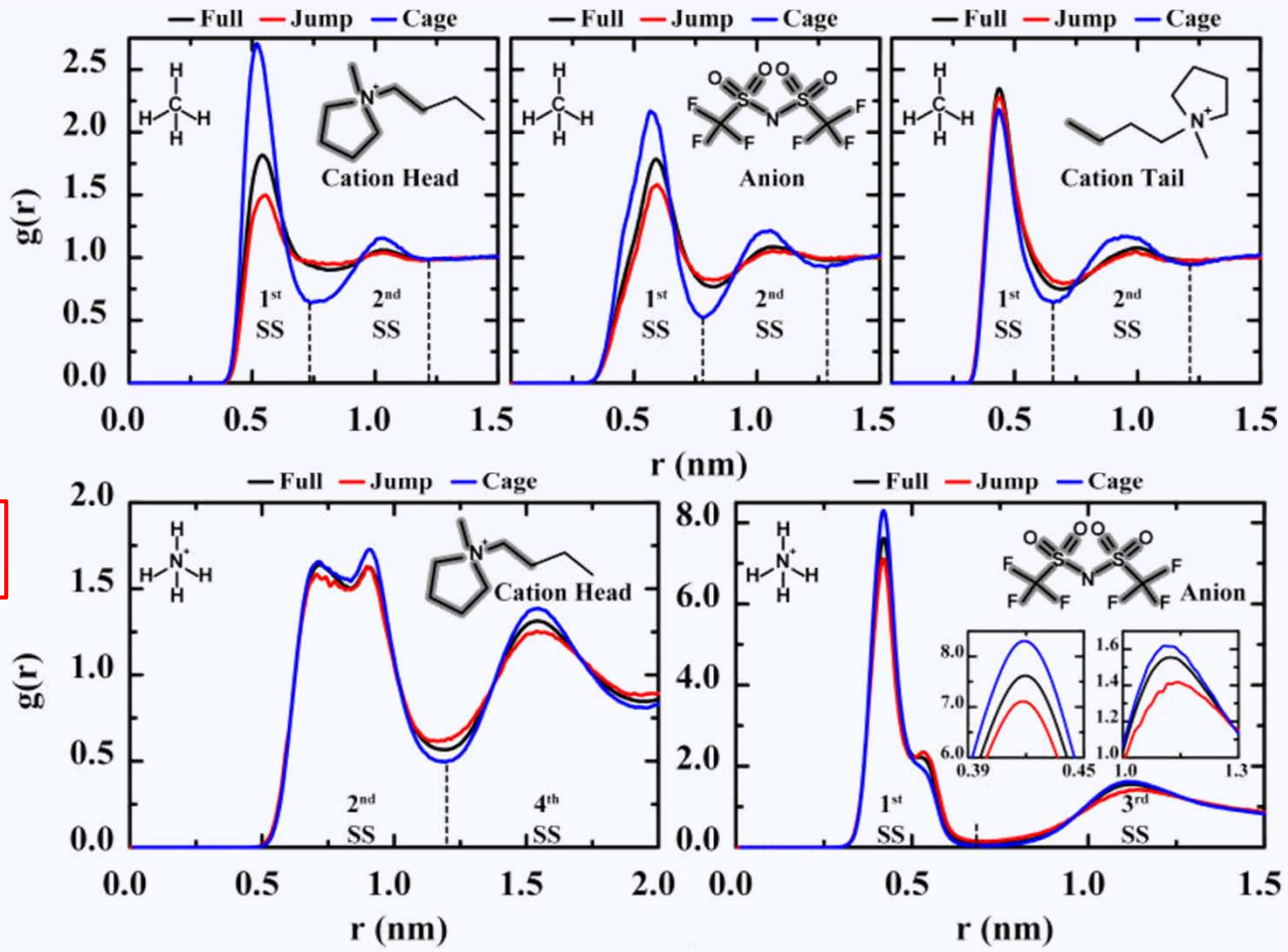


Araque, Margulis et al., *J. Phys. Chem. B* **119**, 7015 (2015).

Trajectory-Resolved Structure

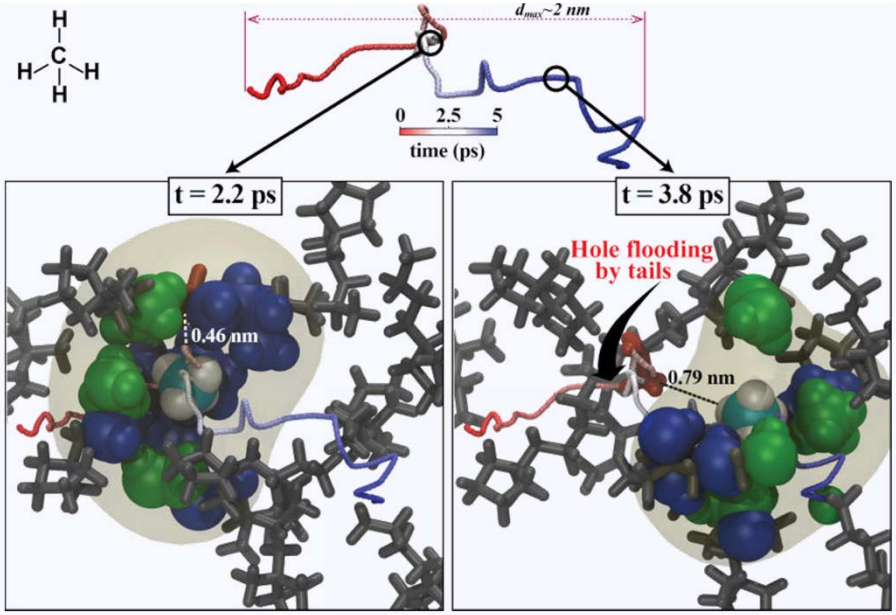
CH_4

NH_4^+



- jumps are associated with low density (and low polarity = "soft") and caging with high density (and polarity = "stiff") regions of the liquid
- CH_4 explores both regions more effectively than NH_4^+

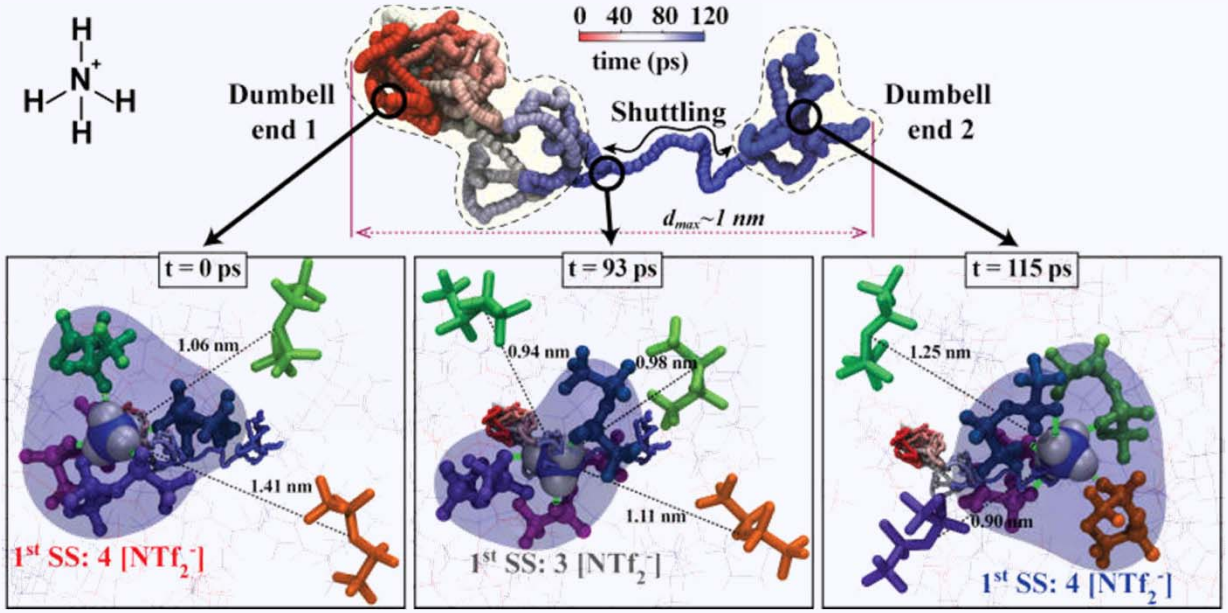
CH_4



blue = cation heads

green = cation tails

NH_4^+



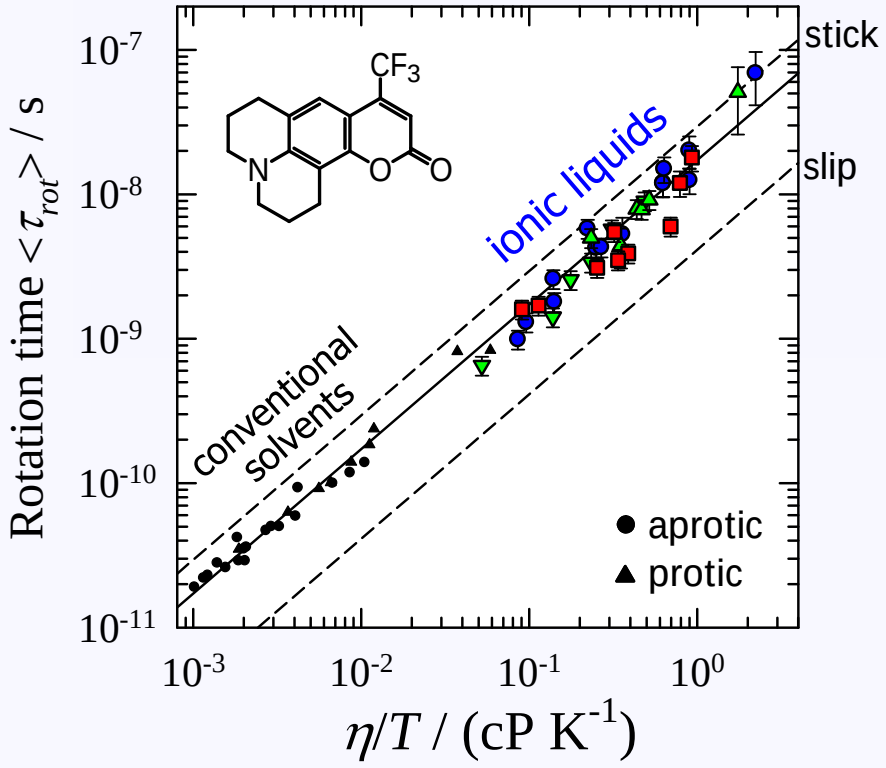
(only anions depicted)

- CH_4 exchanges with nonpolar tails -- Coulomb lattice unperturbed
- NH_4^+ exchanges anions in its 1st shell -- Coulomb lattice must rearrange

Solute & Ion Rotation

$$\tau_{rot}^{(L)} = \frac{6\eta V_{hyd}}{L(L+1)k_B T}$$

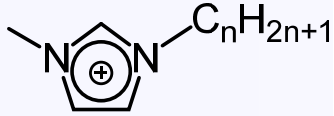
Fluorescence Measurements



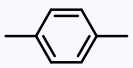
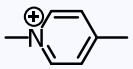
Jin *et al.*, *JPCB* **111**, 7291 (2007)

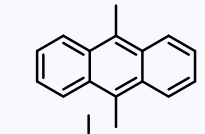
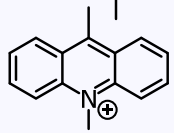
V_{vdW}/V_{hyd} from Dielectric Measurements

Cat/An	DCA^-	BF_4^-	PF_6^-
Im_{21}^+	220	200	
Im_{41}^+	83	310	110



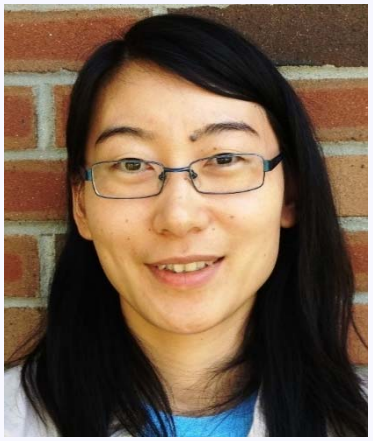
Recent NMR & Fluorescence Data

	V_{vdW}/V_{hyd}
	65
	22
	25

	V_{vdW}/V_{hyd}
	4
	2

- rotation of large solutes not unusual
- Im^+ cations and other small molecules may show more interesting dynamics

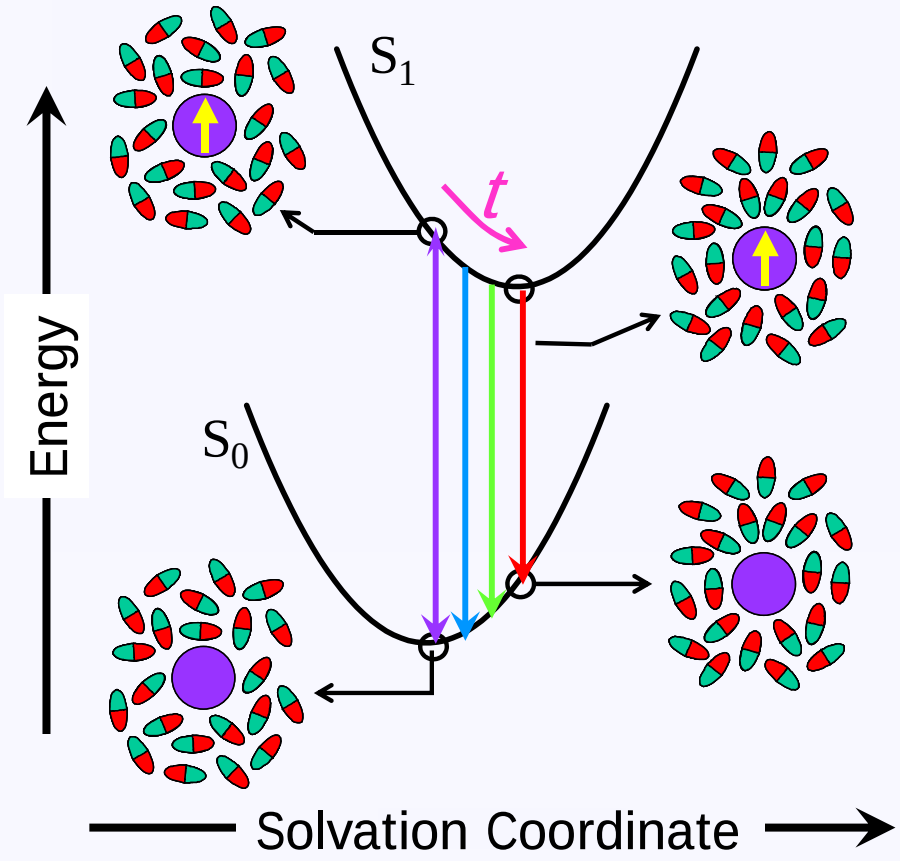
2. More Complicated Dynamics: The Solvation Response



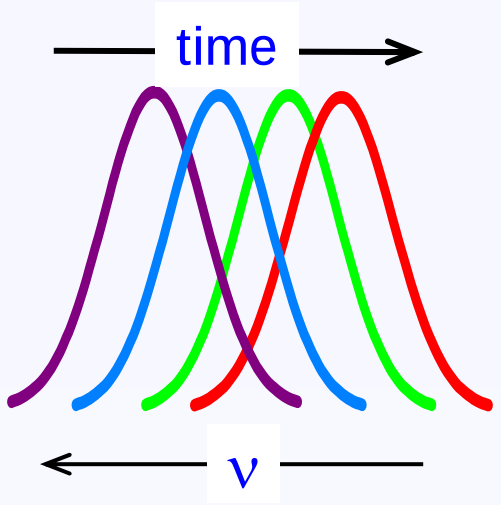
Min Liang

Xin-Xing Zhang

The Spectral / Solvation Response



"Dynamic Stokes Shift"
of Emission Spectra



$\nu(t)$ peak frequency

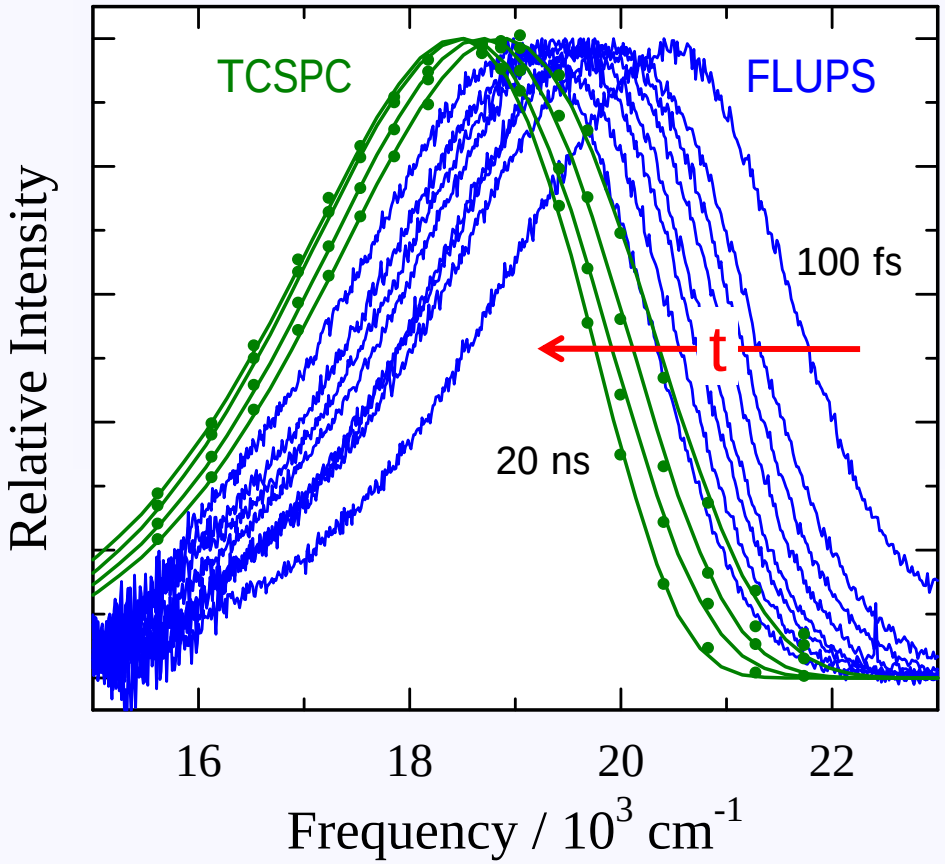
$$S_\nu(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

spectral or solvation response function

- basic property of polar liquids
- determines friction on charge motion

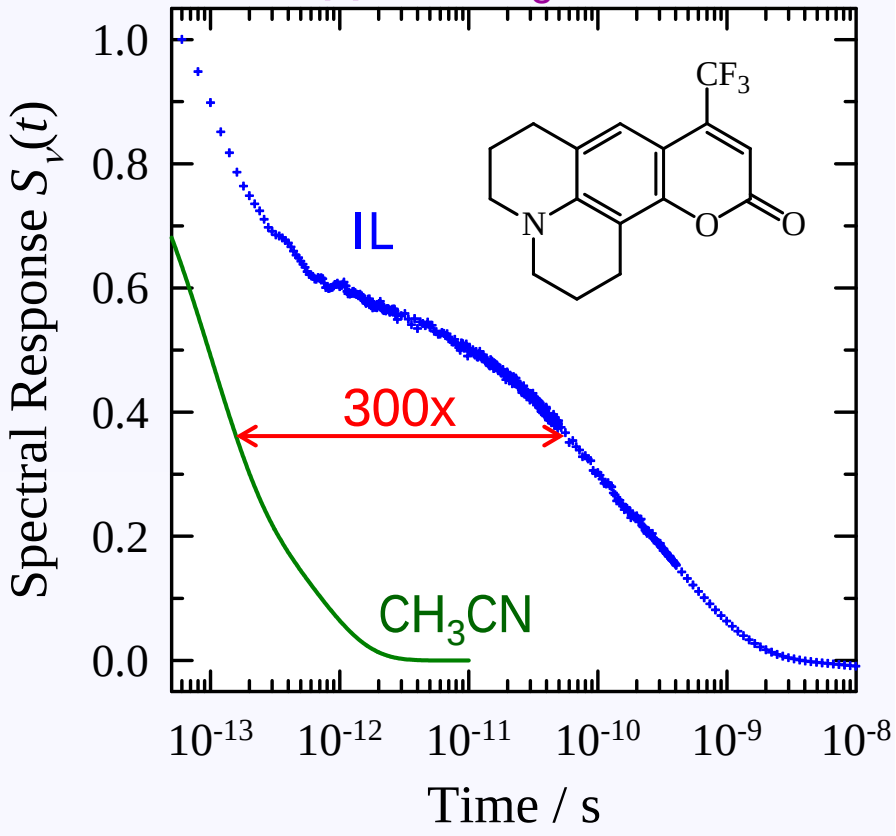
S(t) in Ionic Liquids

Emission Spectra in $[Im_{41}][PF_6]$



- upconversion (FLUPS) & time-correlated single photon counting (TCSPC) experiments combined to capture the full response over 80 fs – 40 ns

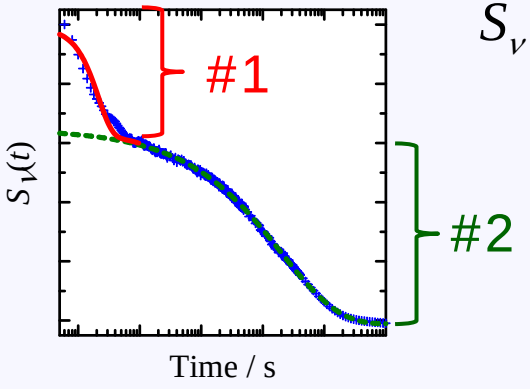
S(t) in CH_3CN & IL



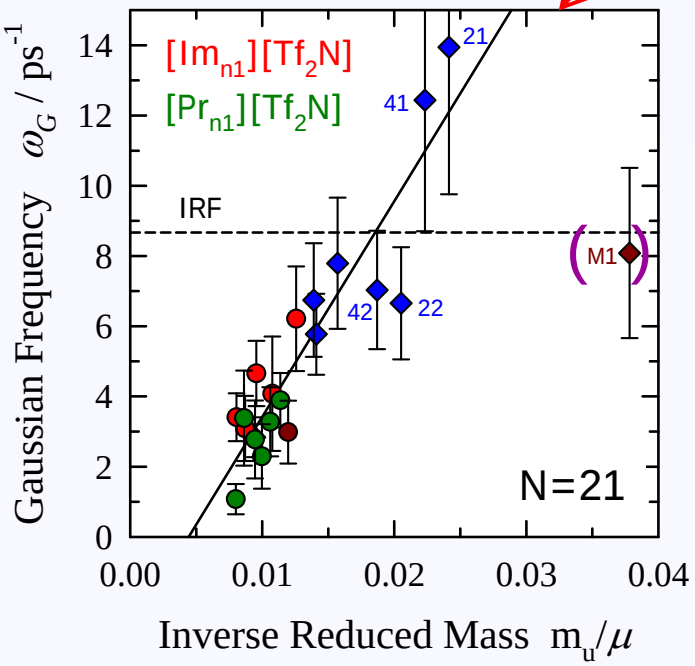
- ~100-fold slower than dipolar solvents (η also 100-fold larger)
- strongly bimodal decay
- broadly distributed in time

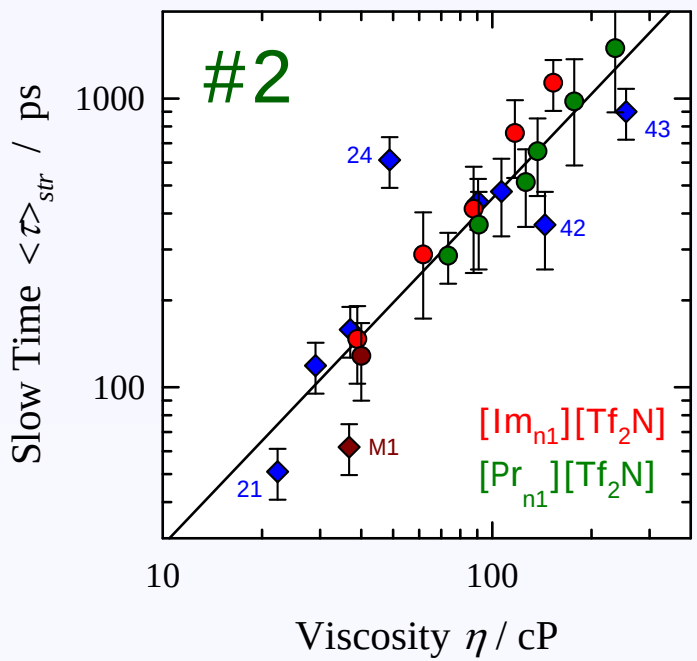
Dissecting the Solvent Response

$$S_\nu(t) = f_G \exp\{-\tfrac{1}{2}\omega_G^2 t^2\} + (1-f_G)\exp\{-(t/\tau)^\beta\}$$



#1



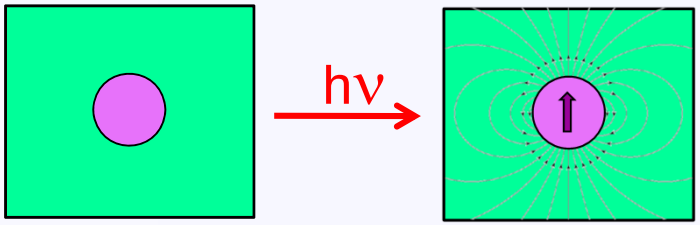


- mechanism is primarily solvent translation
- #1: 30-40% inertial motions
  ⇒ displacements of 1st shell ions
- #2: the rest is overdamped & highly coupled ion motions
  ⇒ subtle displacements of ions over <1σ

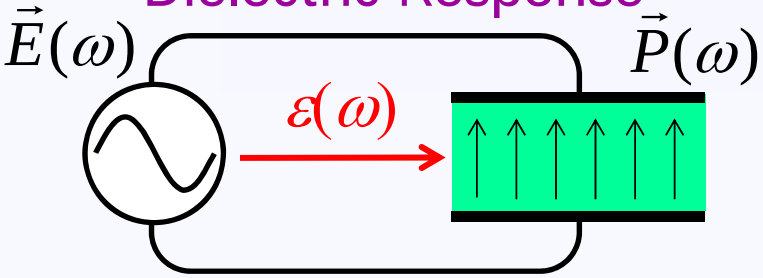
Zhang et al., *JPCB* **117**, 4291 (2013).

Solvation & Dielectric Relaxation

Solvation Dynamics

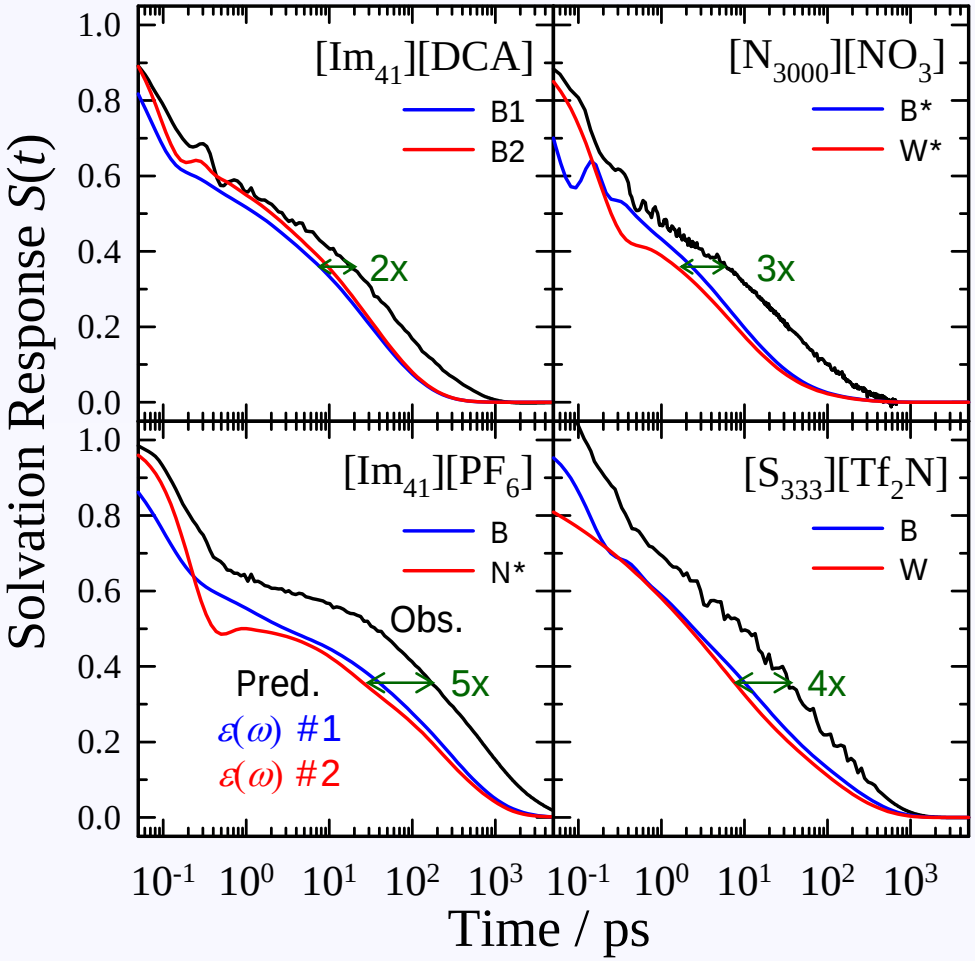


Dielectric Response



- dielectric continuum predictions are qualitatively correct in ILs
- but too fast by factors of 3-4
- similar results in IL + dipolar solvent mixtures

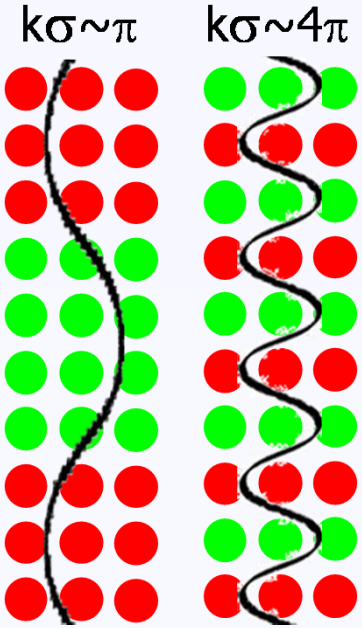
Some S(t) Comparisons



Zhang et al., *JPCB* **117**, 4291 (2013).

Why Continuum Predictions are too Fast

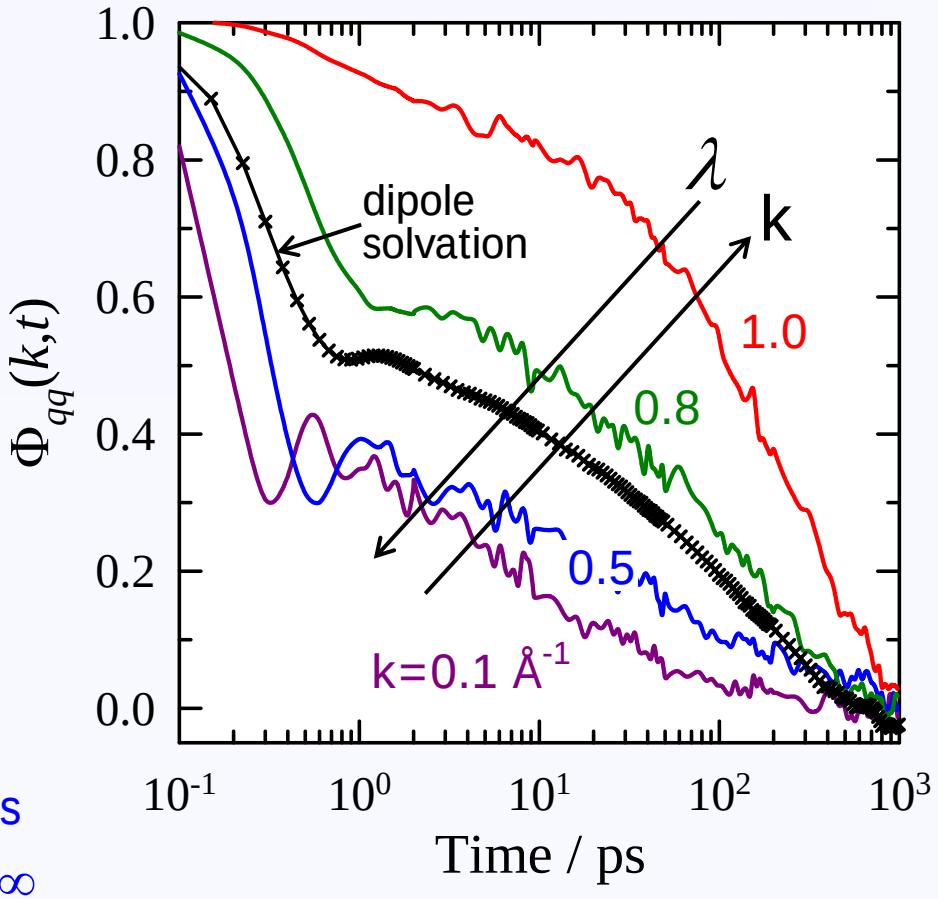
- molecular solvation entails charge redistribution in response to non-uniform fields; basic dynamics captured in Φqq(k,t) of the neat solvent



(k=2π/λ; σ=ion size.)

Charge Density Correlation Function

$$\Phi_{qq}(k,t) \propto \left\langle \rho_q(\vec{k})\rho_q(-\vec{k},t) \right\rangle$$



- ε(ω) captures only k=0 (λ=∞) dynamics
- solvation involves entire spectrum k=0-∞
- solvent response is slower at k>0 thus dielectric predictions are too fast

Maroncelli et al., *Faraday Discuss.* **154**, 409 (2012).

Solvation & Conductivity

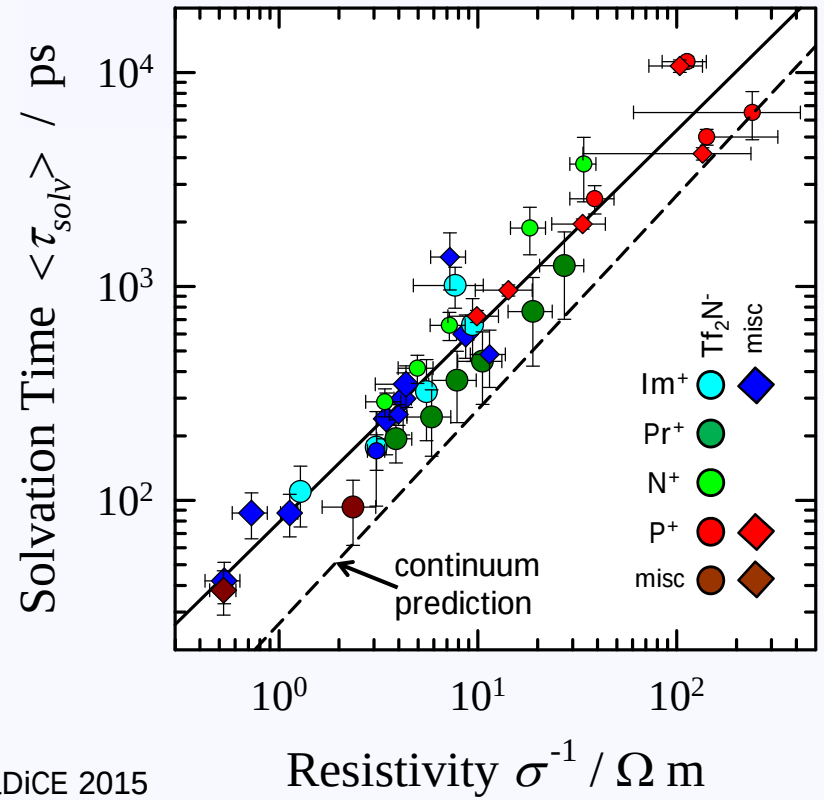
The D.C. model predicts integral solvation times $\langle\tau_{solv}\rangle$ to be inversely proportional to conductivity σ_0

$$\left\langle \tau_{solv} \right\rangle \equiv \int_0^\infty S(t)dt = \frac{(\varepsilon_\infty + \frac{1}{2}\varepsilon_c)}{4\pi\sigma_0}$$

~const.

- as predicted, $\langle\tau_{solv}\rangle$ and σ_0 are strongly correlated
- prediction is an average of 3-fold too fast
- (σ is easy)

C153 in 34 Ionic Liquids



The $\varepsilon(\omega) \leftrightarrow \sigma_0$ Connection:

$$\hat{\varepsilon}(\omega) = \hat{\varepsilon}_{corr}(\omega) + i\frac{4\pi\sigma_0}{\omega}$$

expts. report — divergence removed

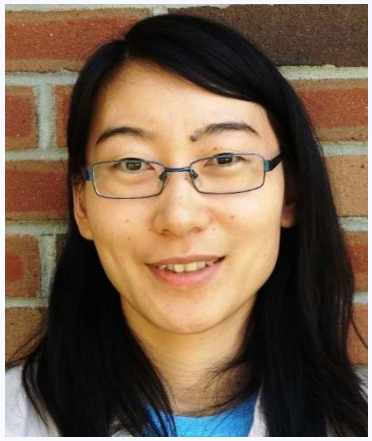
conductivity & permittivity reflect identical dynamics

$$\hat{\sigma}(\omega) = i\omega\frac{\hat{\varepsilon}(\omega)}{4\pi} \leftarrow \left\langle \vec{M}\cdot\vec{M}(t)\right\rangle$$

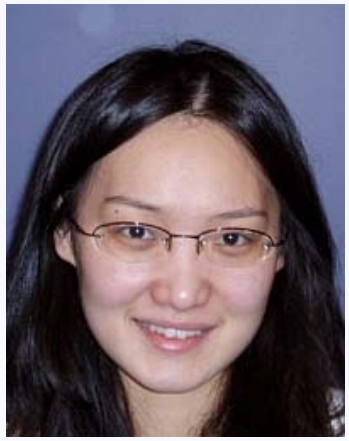
$$\uparrow \left\langle \vec{J}\cdot\vec{J}(t)\right\rangle$$

Zhang *et al.*, *JPC Lett.* **4**, 1205 (2013).

3. Even More Complicated: Reaction Kinetics



Min Liang

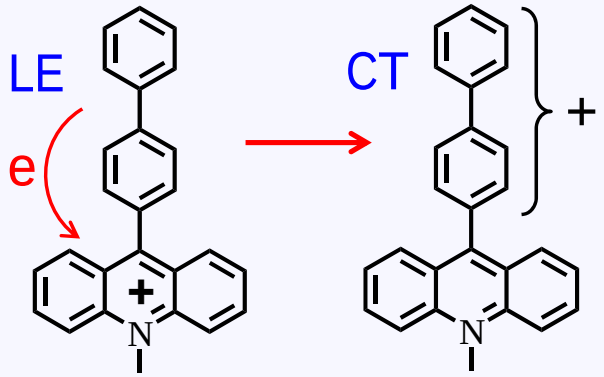


Lillian Li

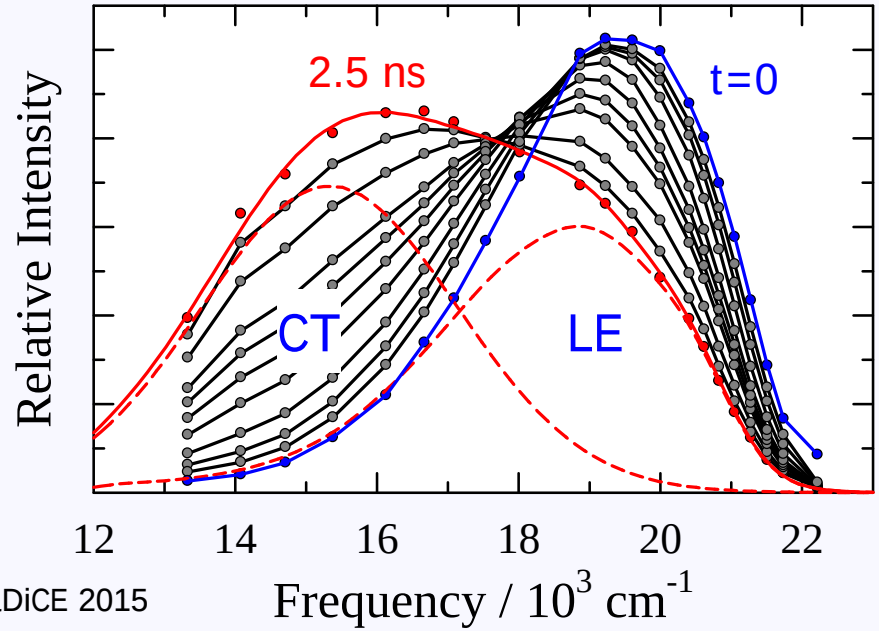
Minako Kondo

1. Intramolecular Charge Transfer

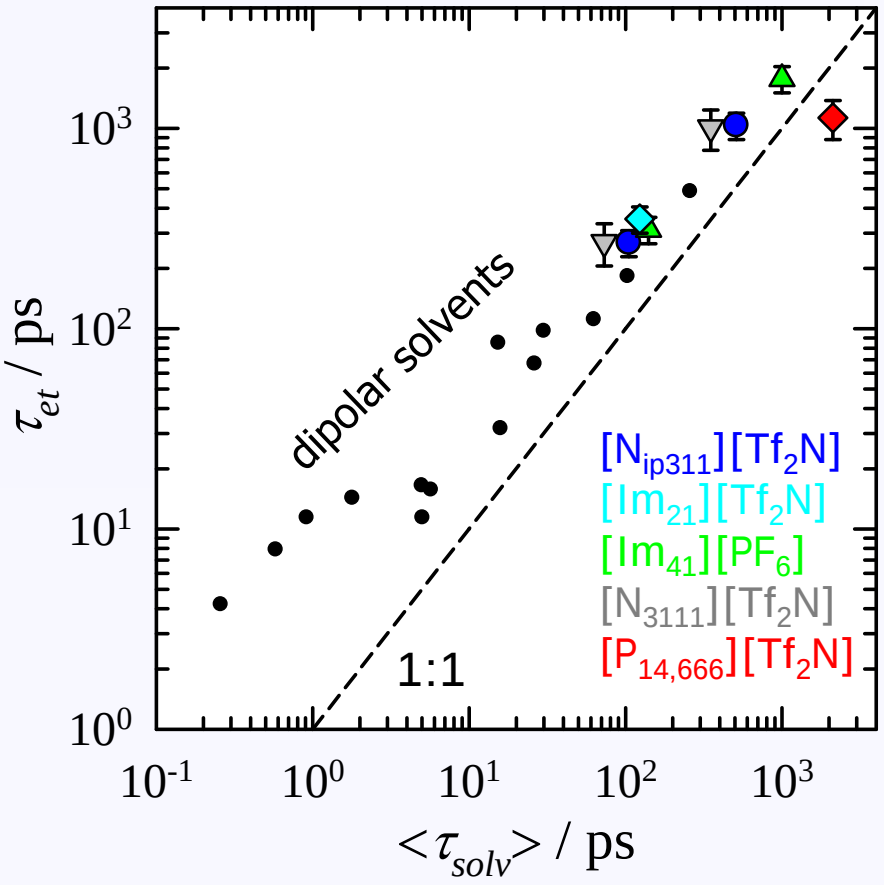
Biphenyl Acridinium ($BPAc^+$)



TR Emission in $[N_{3111}][Tf_2N]$



Reaction and Solvation Times

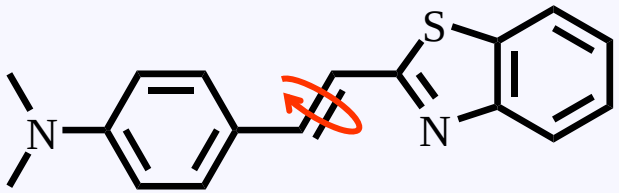


- reaction in ILs continues trend established by dipolar solvents

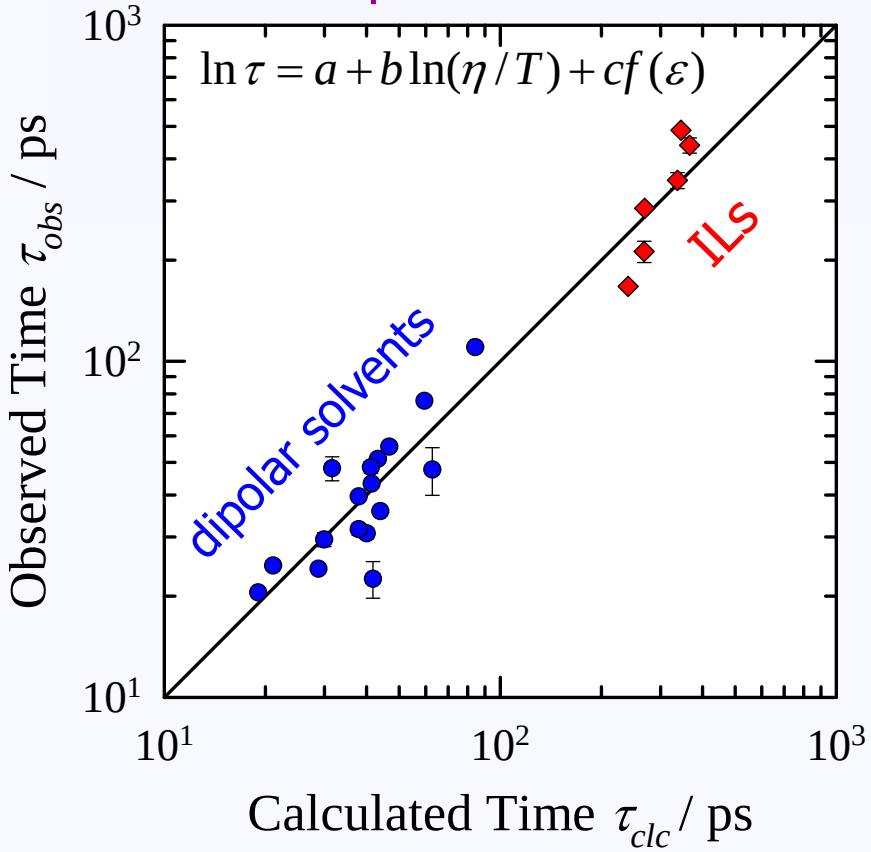
Li et al., *JPCB* **115**, 6592 (2011).

2. Isomerization

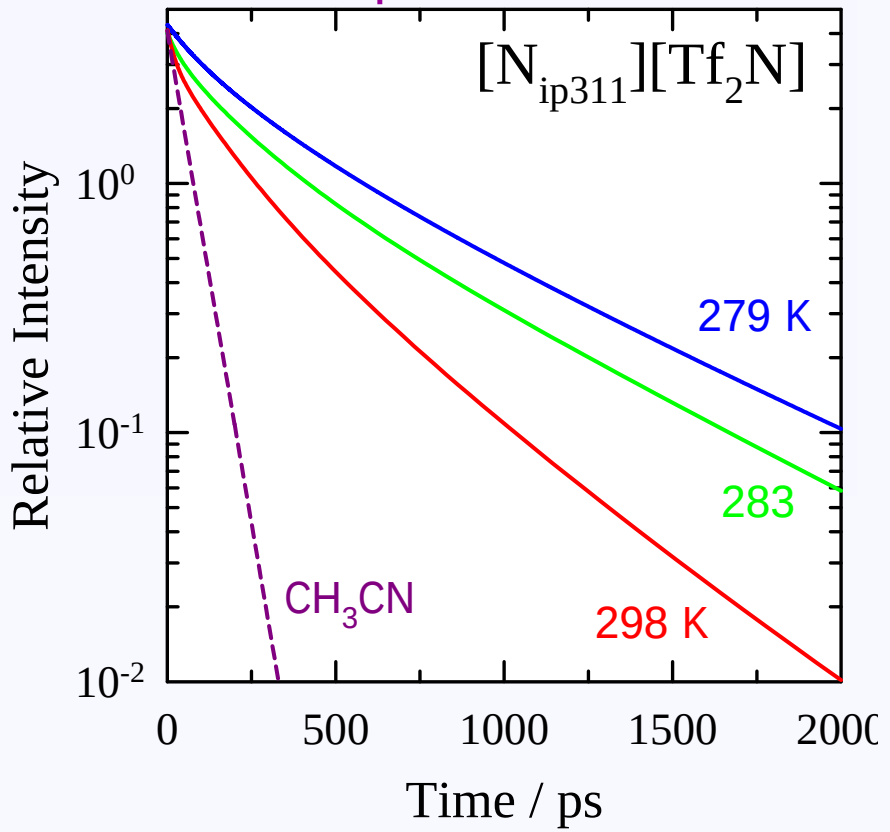
DMASBT



An Empirical Correlation



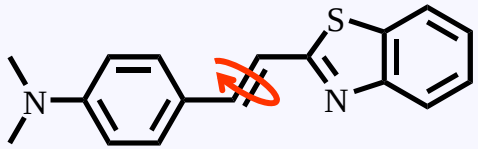
Non-Exponential Kinetics



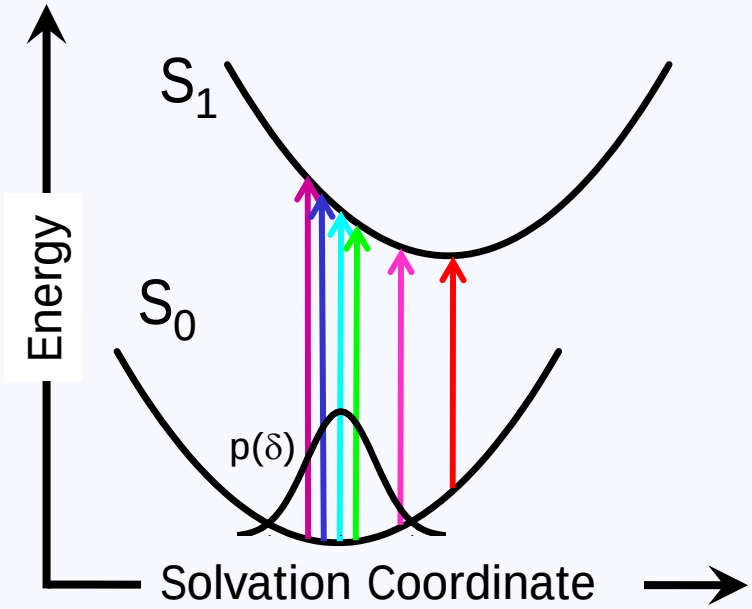
- rates in ILs correlate with those in dipolar solvents
- kinetics more complex

Kondo & Maroncelli, *JPCB* **117**, 12224 (2013).

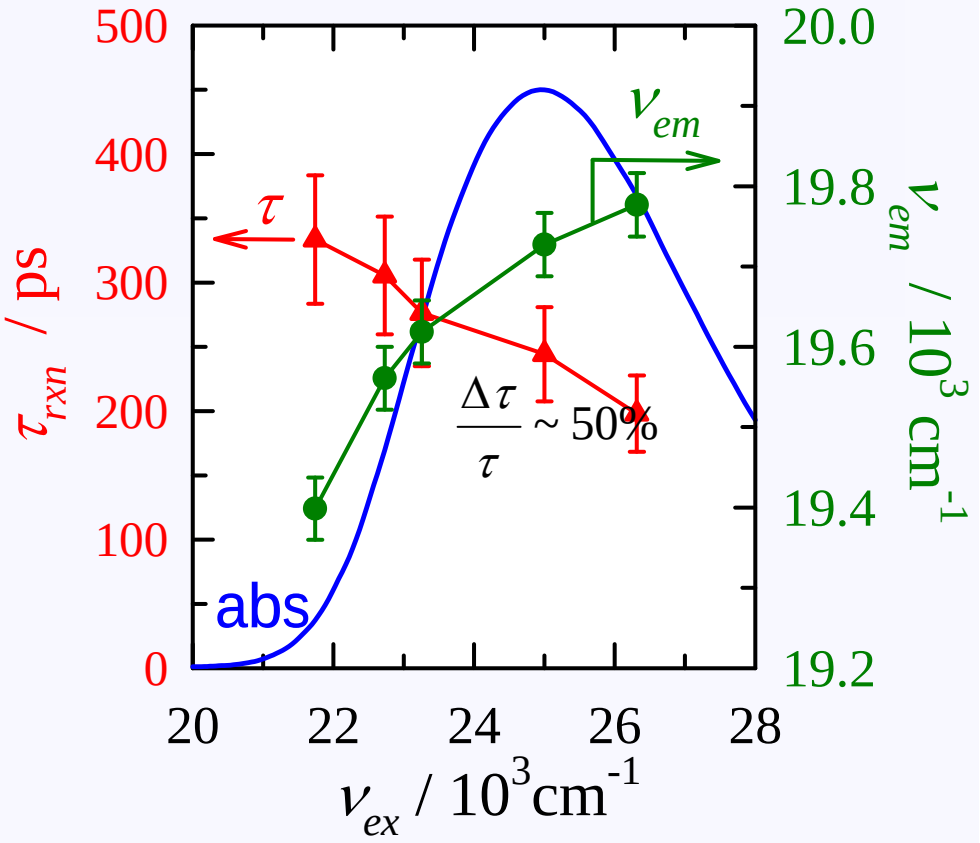
REE & Kinetic Heterogeneity



Red Edge Excitation

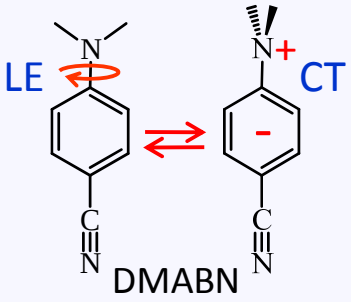


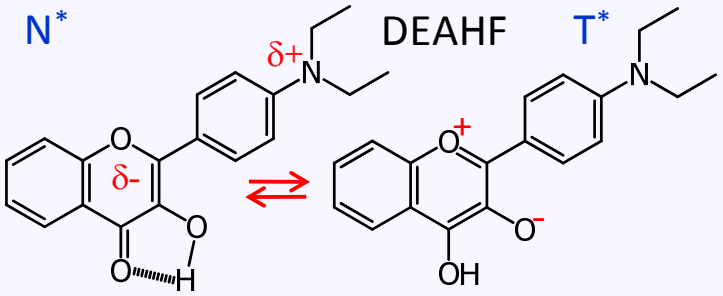
Reaction Time vs ν_{exc}



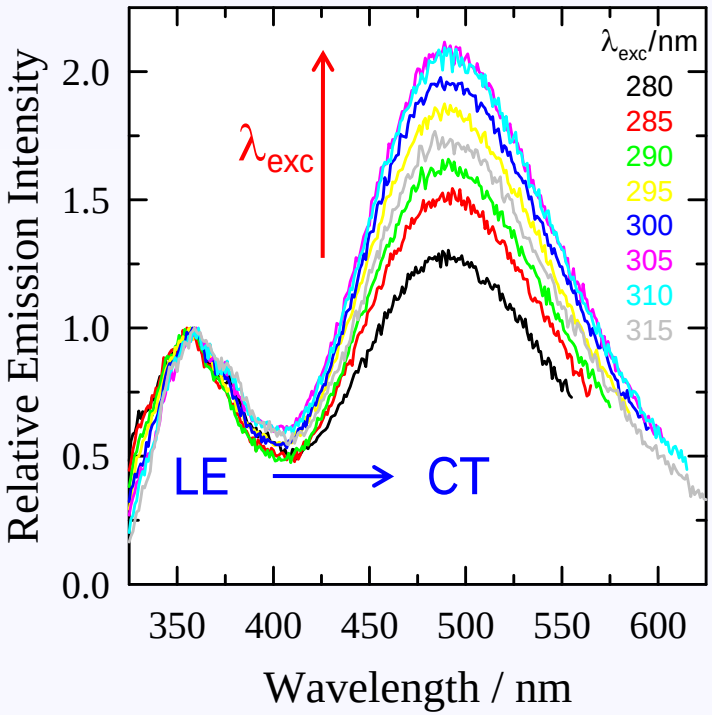
- heterogeneous kinetics should be the norm for ps processes given the slow solvation / structural relaxation times of ILs

Other Examples



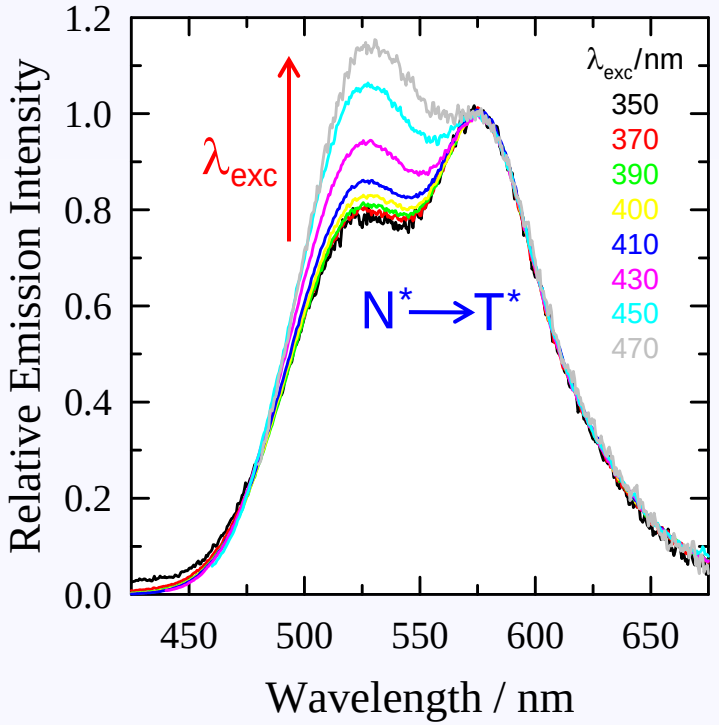


TICT Reaction of DMABN



Samanata & Co., *JPCB* **114**, 1967 (2010).

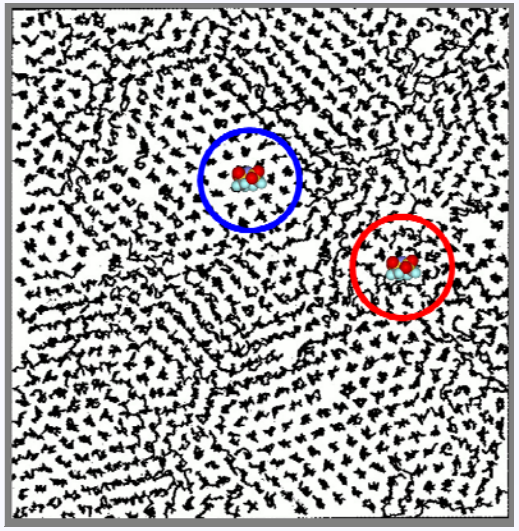
ESPT in DEAHF



Kimura et al., *JPCB* **114**, 11847 (2010); *JPCB* **117**, 6759 (2013).

Possible Interpretations

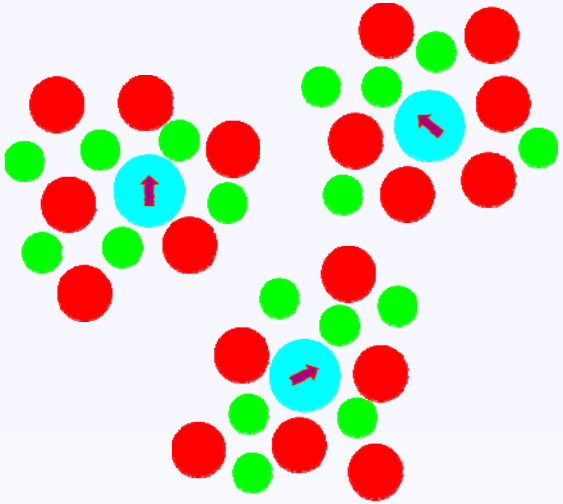
Distinct Local Dynamics



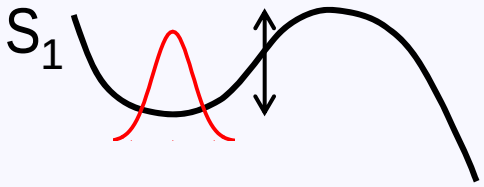
- reaction senses "dynamic heterogeneity" – the fact that local packing effects cause different regions to have different fluidities

Hurley *et al.*, *Phys. Rev. E* **52**, 1694 (1995)

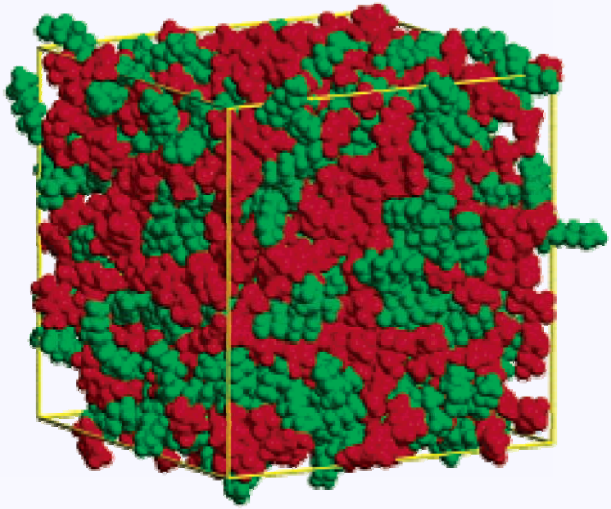
Distinct Local Energies



- different solute-solvent interaction energies affect PES for reaction



Nanoscopic Domains



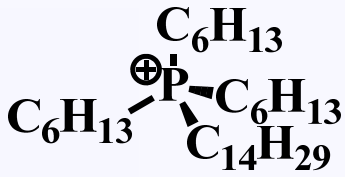
- solutes are distributed among nanoscopic domains of different polarity and/or fluidity

Lopes & Padua, *J. Phys. Chem. B* **110**, 3330 (2006).

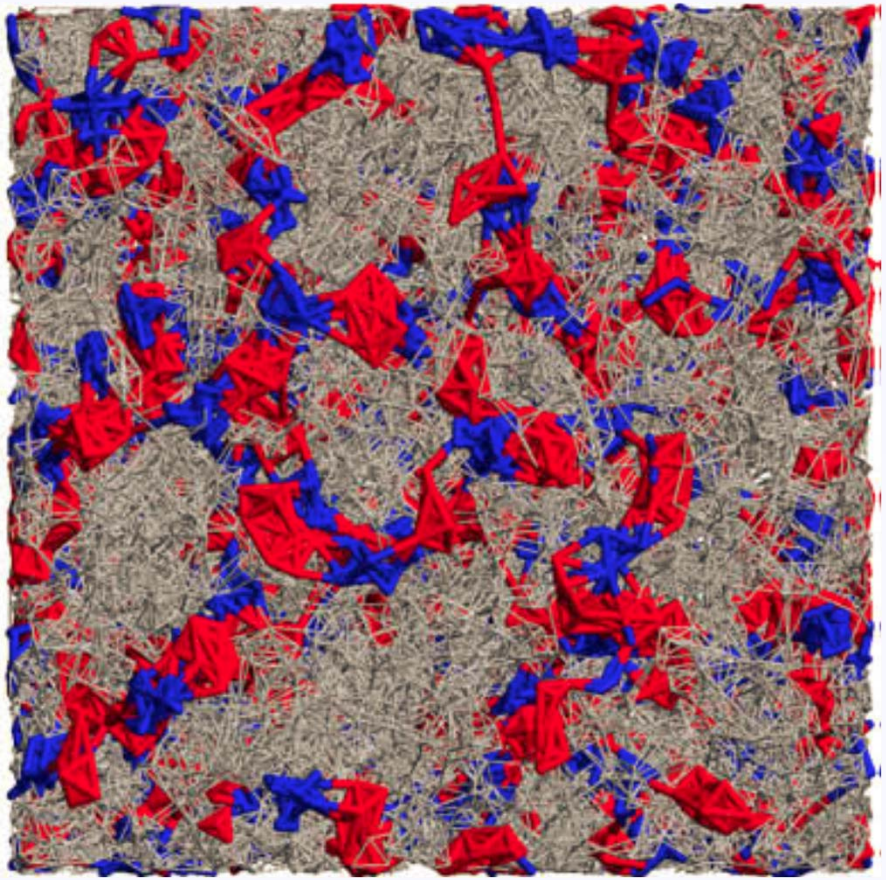
4. Aside: Where's the Effect of Nanoscopic Structure?

Jacob Schesser

Solvation in $[P_{14,666}][X]$ ILs

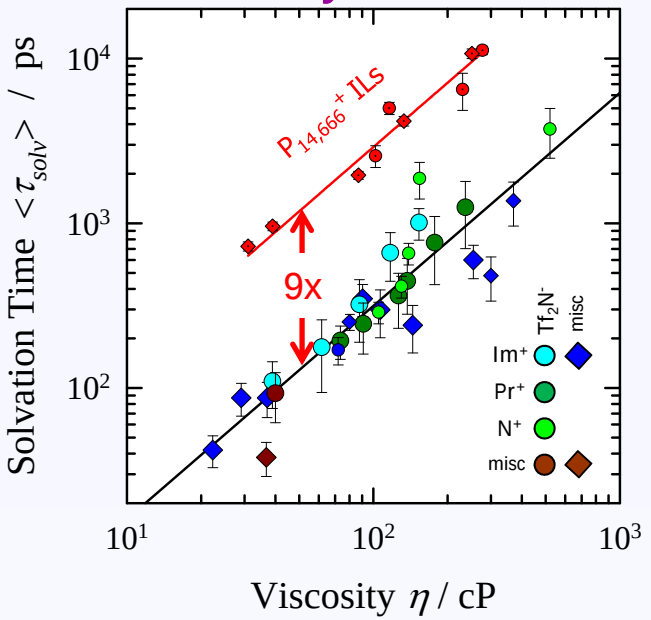


Snapshot of $[P_{14,666}][Tf_2N]$ Simulation

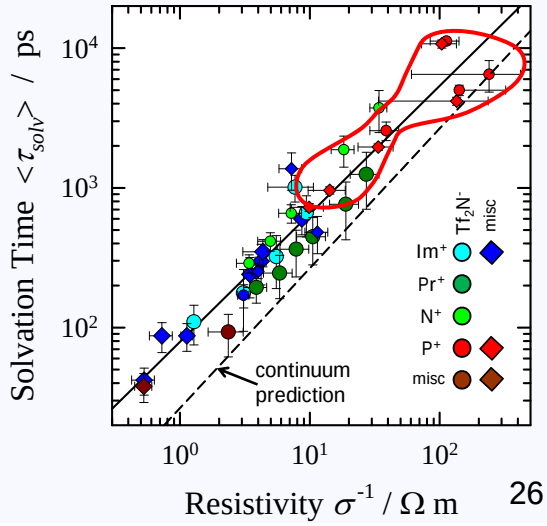


blue=+, red=-, grey=alkane

Viscosity Correlation



Resistivity Correlation

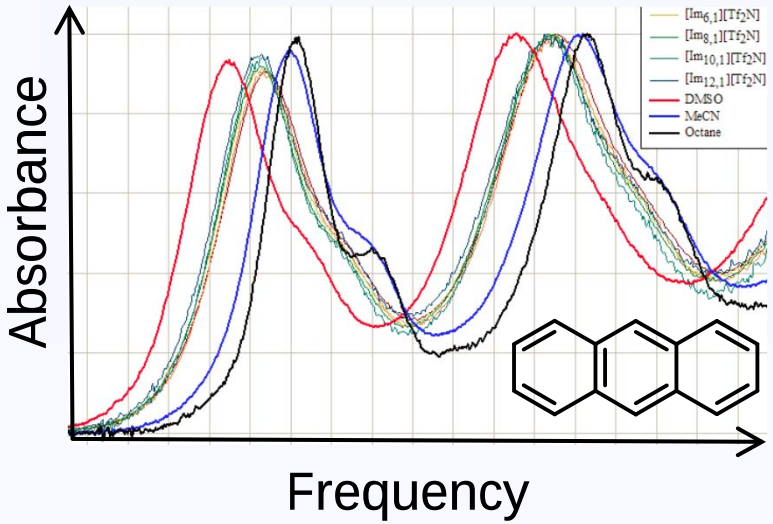


Shimizu, *J. Mol. Struct.* **946**, 70 (2010).

Further Recent Attempts

- anthracene & bianthryl in $[Im_{n1}][Tf_2N]$ (n=2-12), & $[P_{14,666}][Tf_2N]$+n-hexane

Anthracene Absorption Spectra

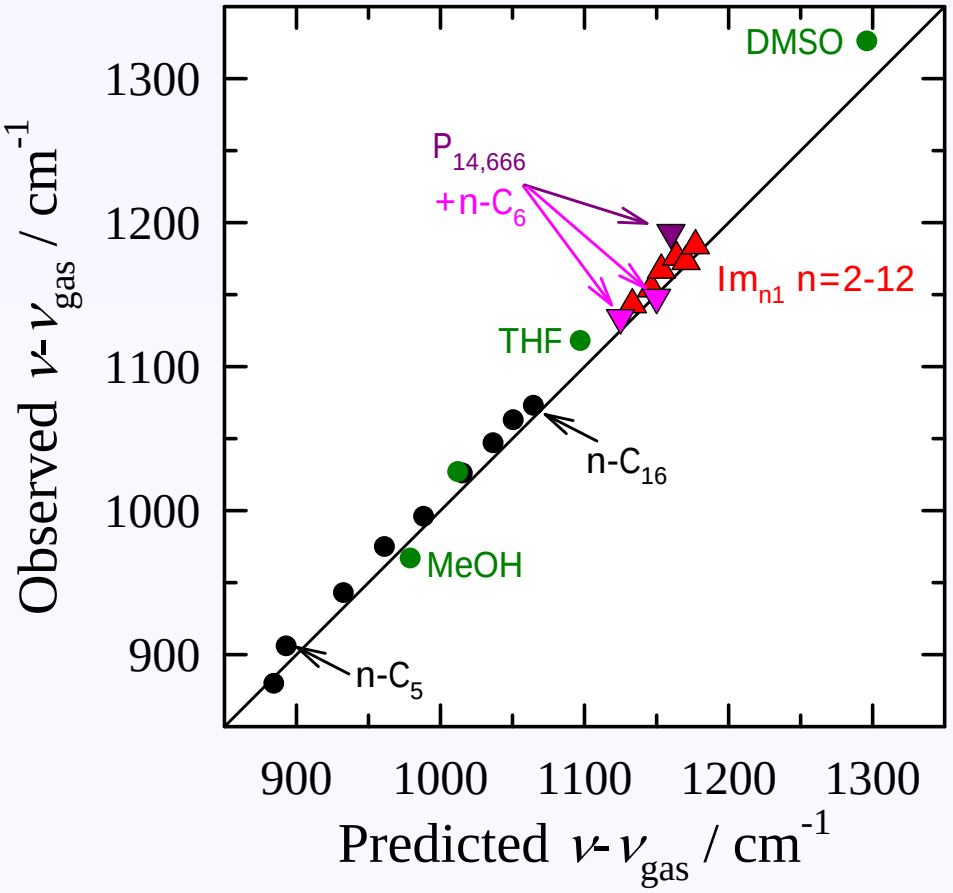


in 74 organic solvents:

$$\nu - \nu_{gas} = \alpha\left(\frac{n^2-1}{n^2+2}\right) + \beta\left\{\left(\frac{\varepsilon-1}{\varepsilon+2}\right) - \left(\frac{n^2-1}{n^2+2}\right)\right\}$$

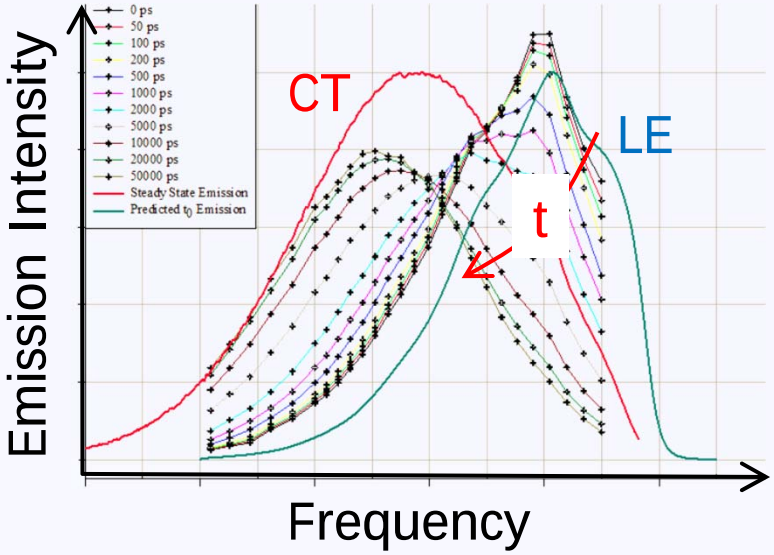
α = 4100 cm^{-1}, β = 170 cm^{-1}

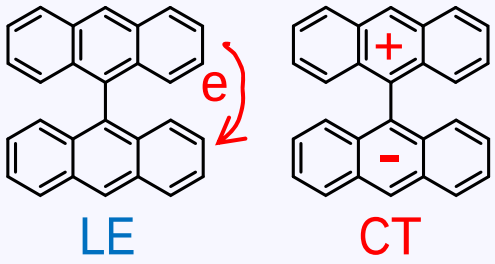
Anthracene Solvatochromic Shifts



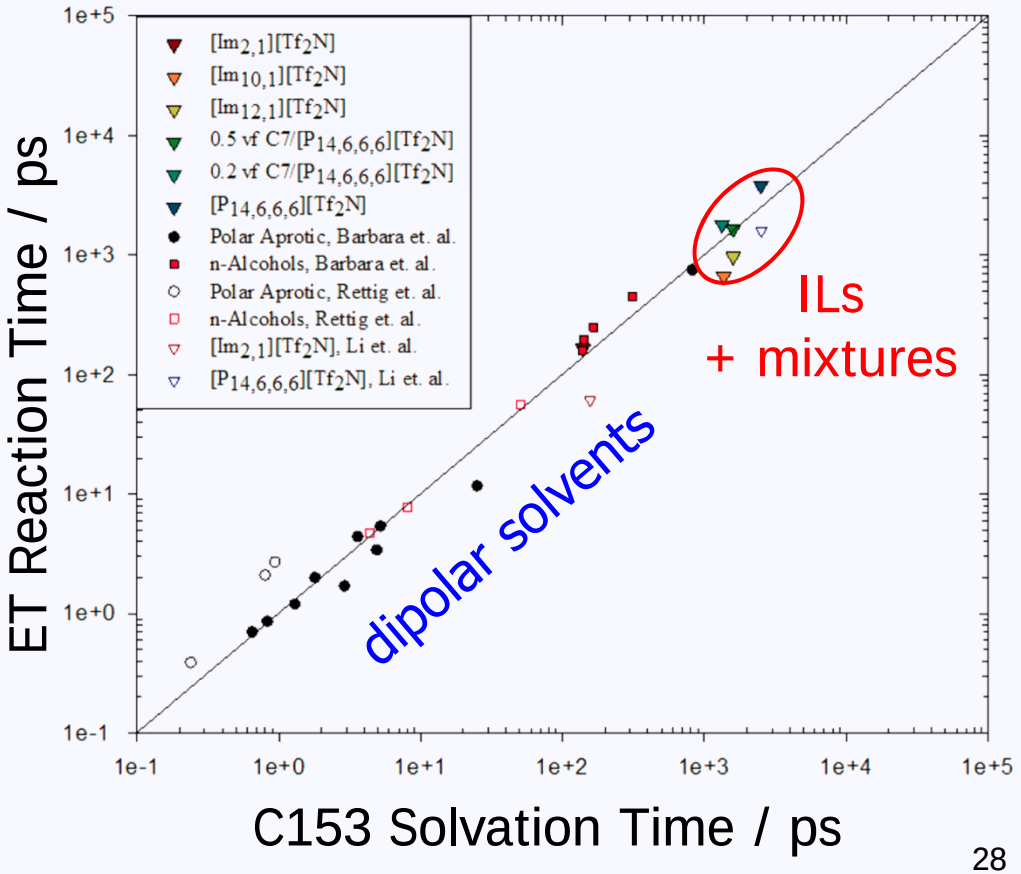
Bianthryl ET Reaction Times

TR Emission Spectra

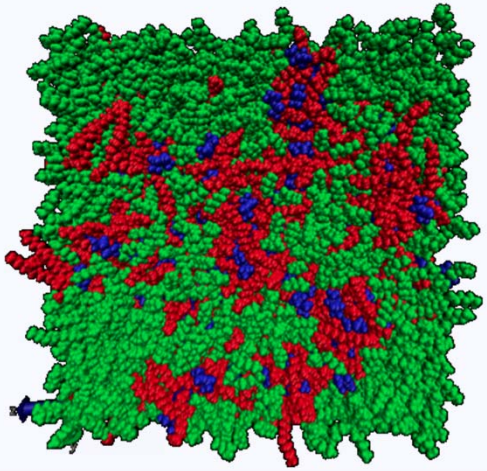




ET Reaction Times



$[P_{14,666}][Tf_2N]$ + n-C_6 x_{C6} =0.8



green=n-C_6
red=$P_{14,666}^+$
blue=Tf_2N^-

M. Liang,
preliminary results

Summary

Solute Translation & Rotation:

- D $\tilde{\propto}$ T/η as expected by hydrodynamic models, but Stokes-Einstein predictions can be wrong by factors of 100 or more (at room T)
- diffusion of small neutral versus charged solutes is markedly different
- rotations of small solutes can be far from hydrodynamic expectations

Solvation Dynamics:

- solvation is highly bimodal: ~1/3 sub-ps and 2/3 relax over 1 ps- 10 ns
- unlike dipolar solvents, translational solvent motions dominate
- S(t) and $\varepsilon(\omega)$ reflect the same underlying molecular dynamics but dielectric continuum predictions too fast by a factor >4
- solvation closely related to conductivity ($<\tau_{solv}>\propto 1/\sigma_0$)

Fast Reaction Kinetics:

- slow solvation/structural relaxation in ILs leads to heterogeneous reaction kinetics for fast reactions (τ<1 ns)
- origins of heterogeneity unclear (especially relevance of nanostructure)

Acknowledgements

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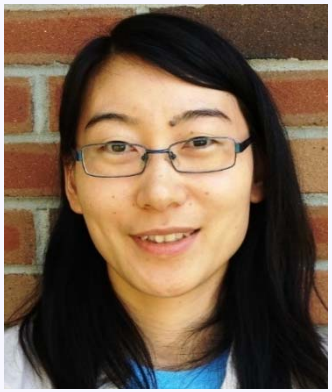

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