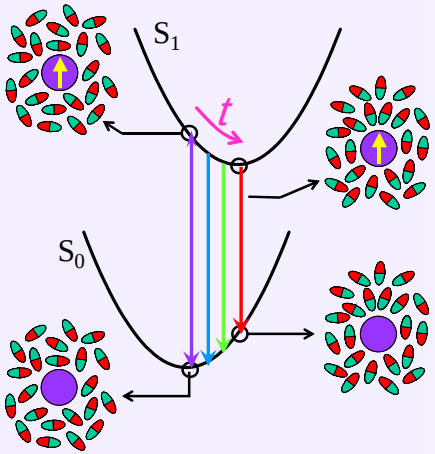
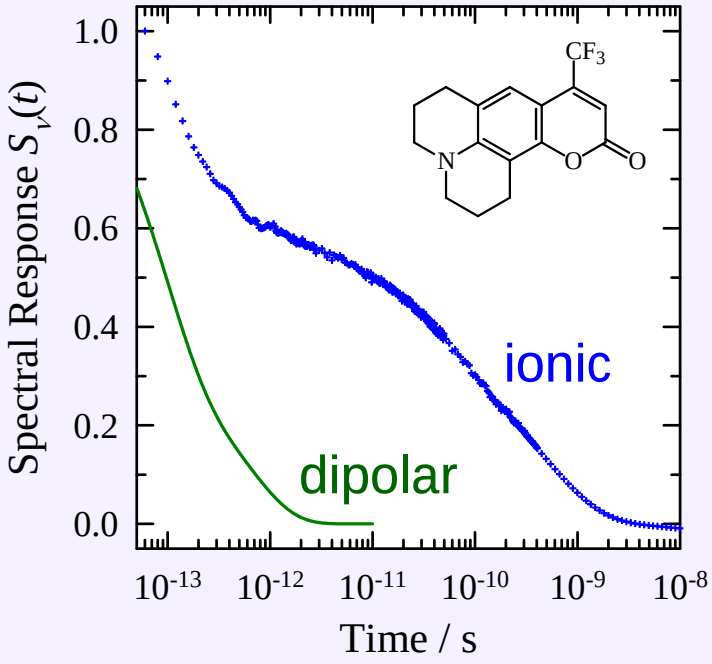
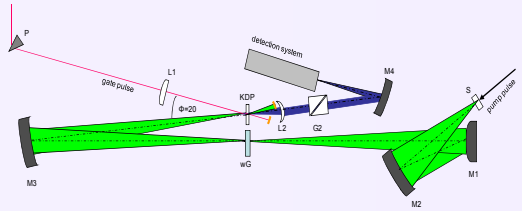
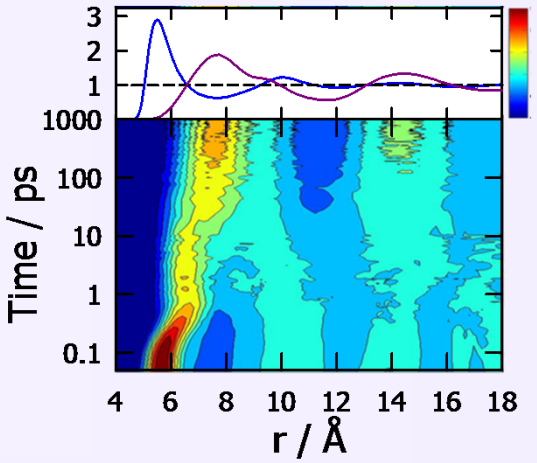
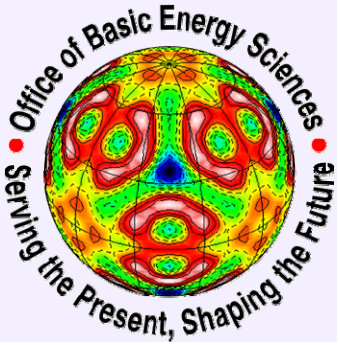
Dynamics of Polar Solvation (in Dipolar & Ionic Solvents)

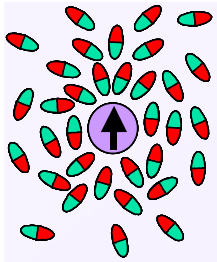






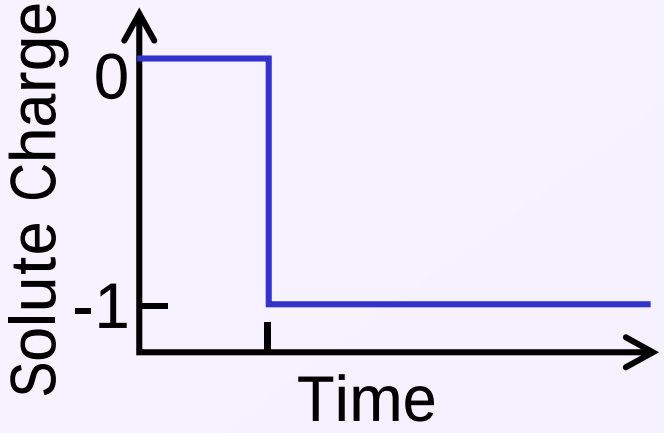




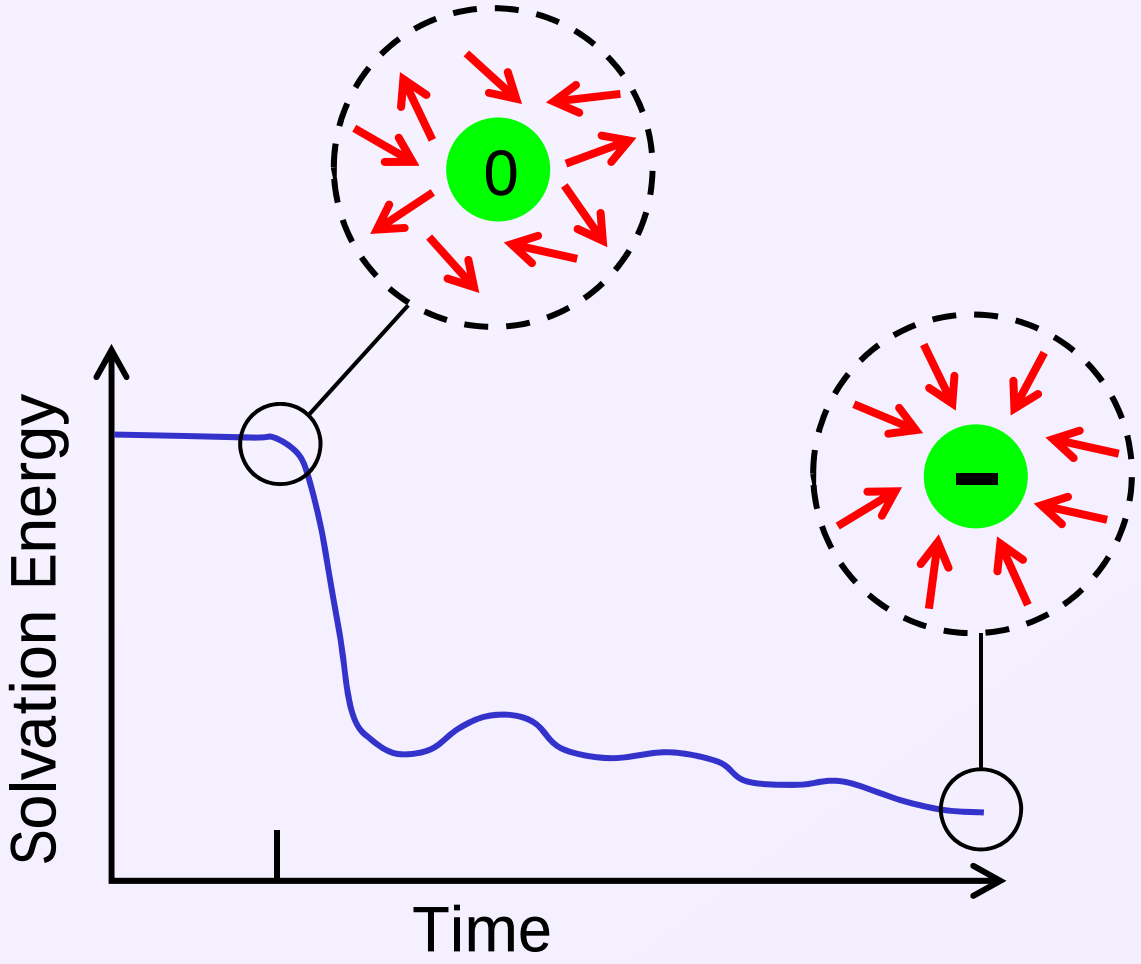


Solvation Dynamics?

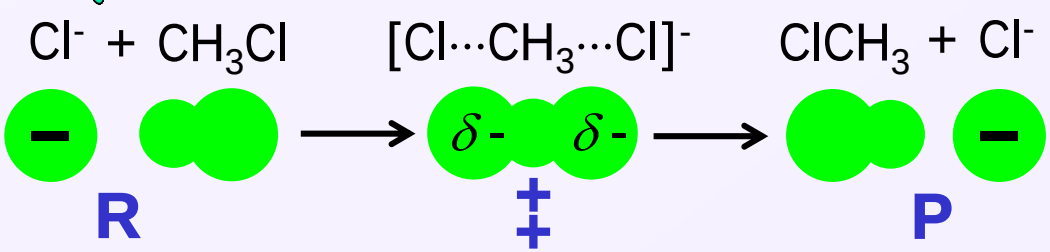
Solute Perturbation



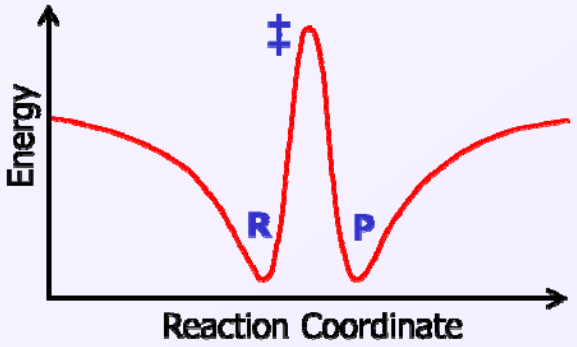
Solvation Response



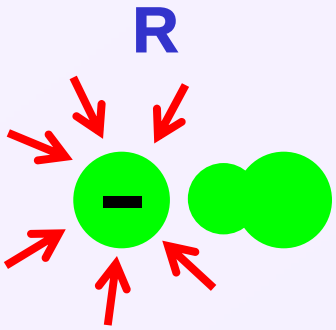
Why Study?

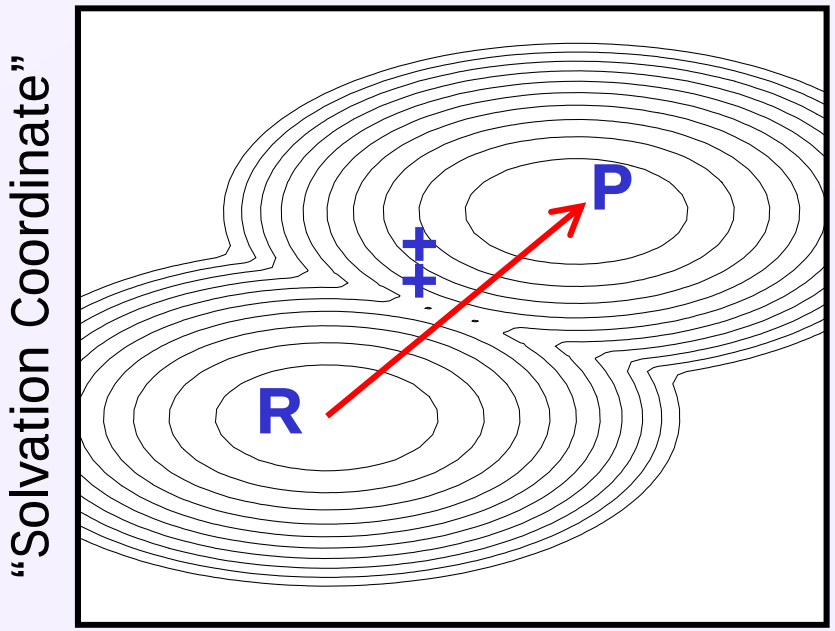


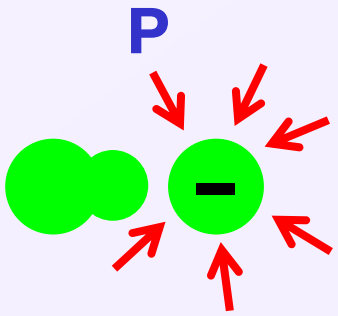
Gas Phase Rxn



Solution Phase Rxn



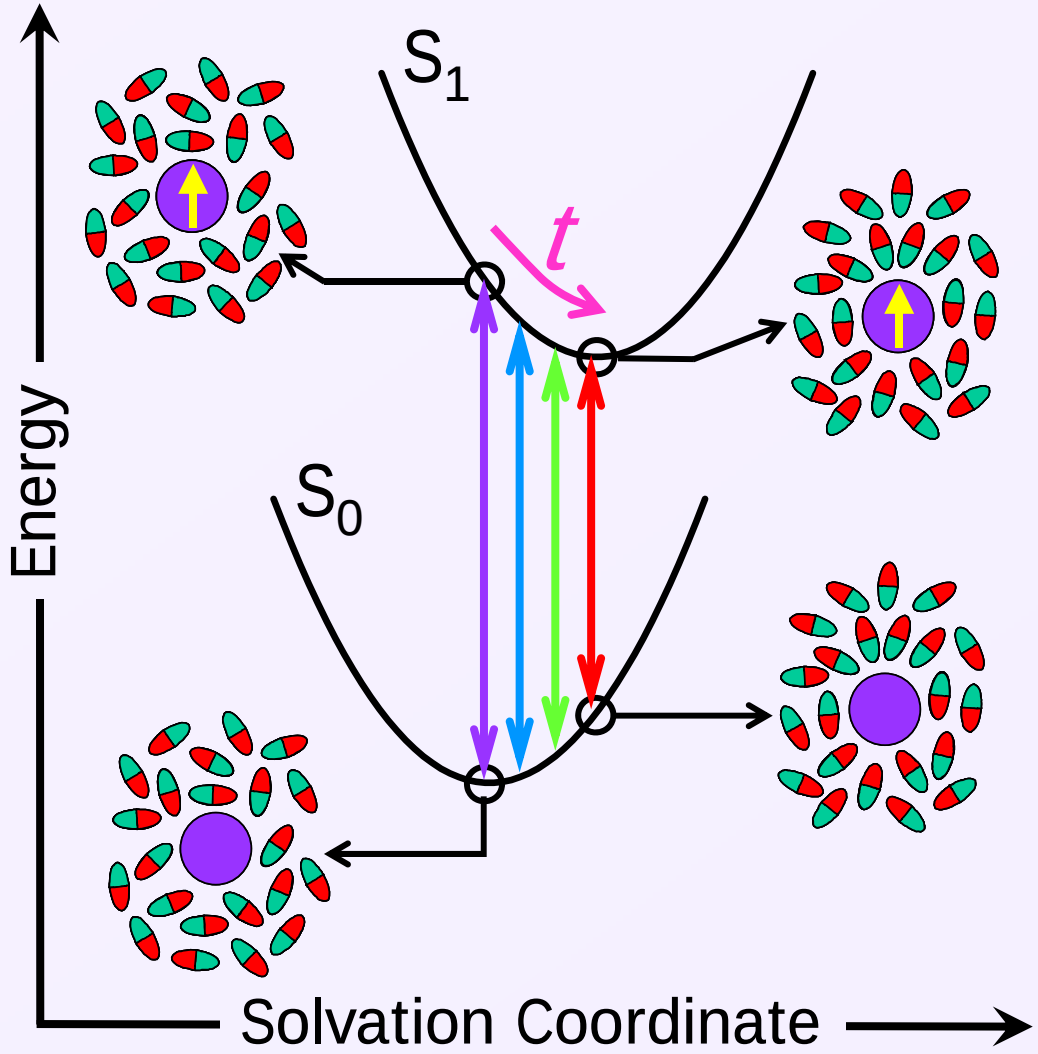


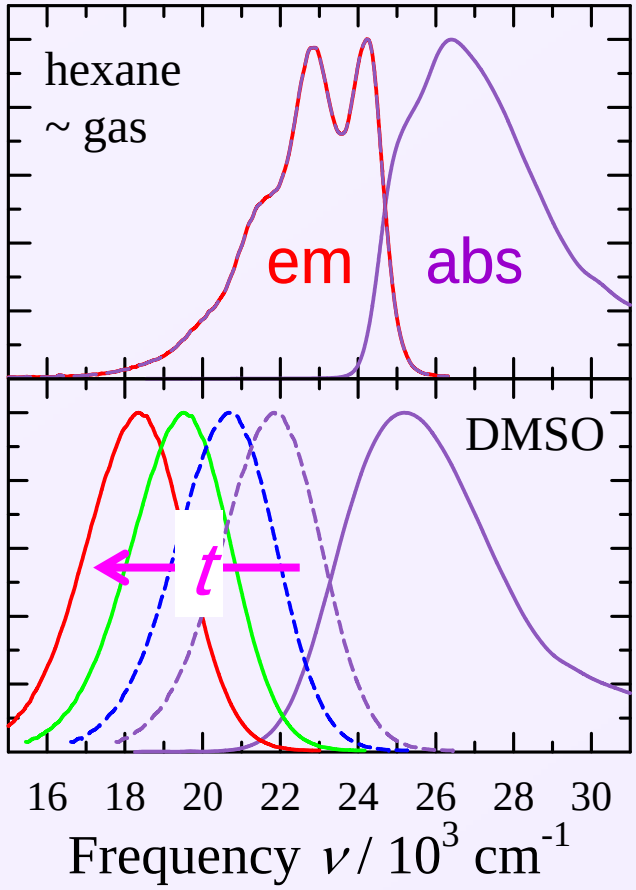


Gas-Phase Reaction Coordinate

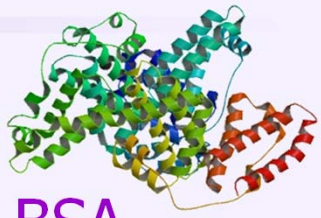
- Like it or not, solvent is part of the reaction coordinate!

The Dynamic Stokes Shift

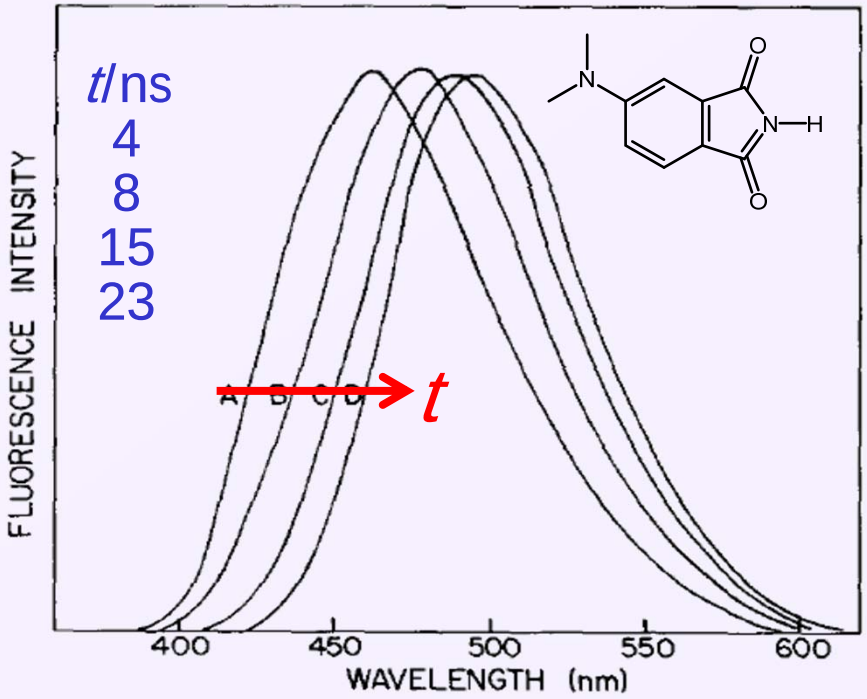




Pioneering Experiments

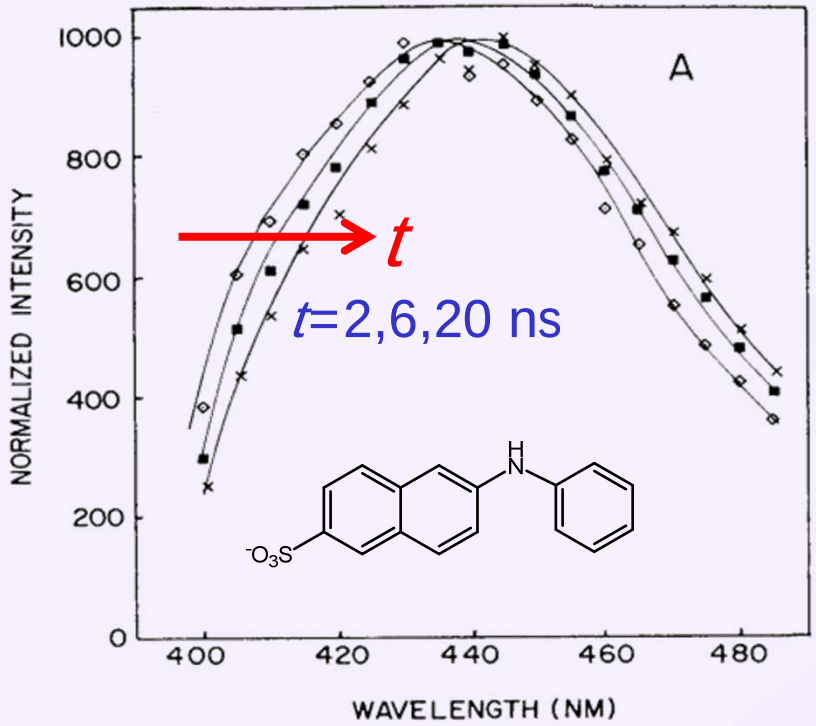


4-AP in 1-Propanol @ 203 K



Ware & Co: Chem. Phys. Lett. **2**, 356 (1968); J. Chem. Phys. **54**, 4729 (1971).

TNS Adsorbed to BSA



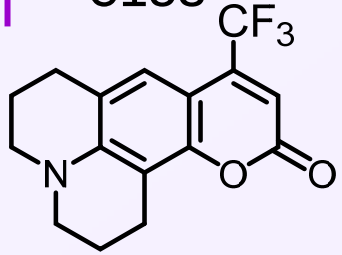
Brand & Gohlke, J. Biol. Chem. **246**, 2317 (1971).

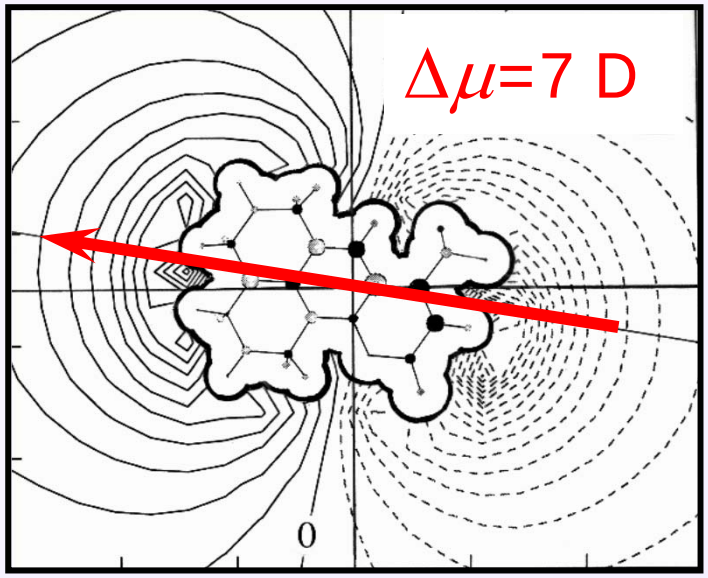
Dipolar Solvents (1995)

An Ideal Probe of Polar Solvation

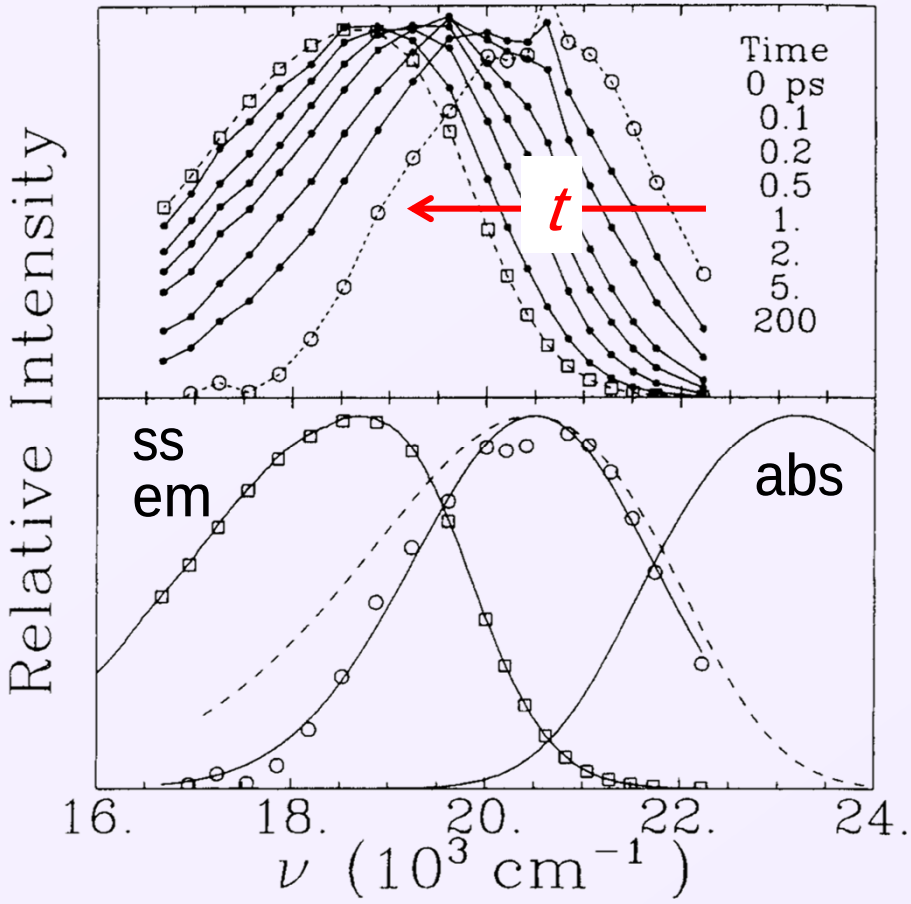
- simple S_1 state
- only non-specific solvation (Δ)

C153





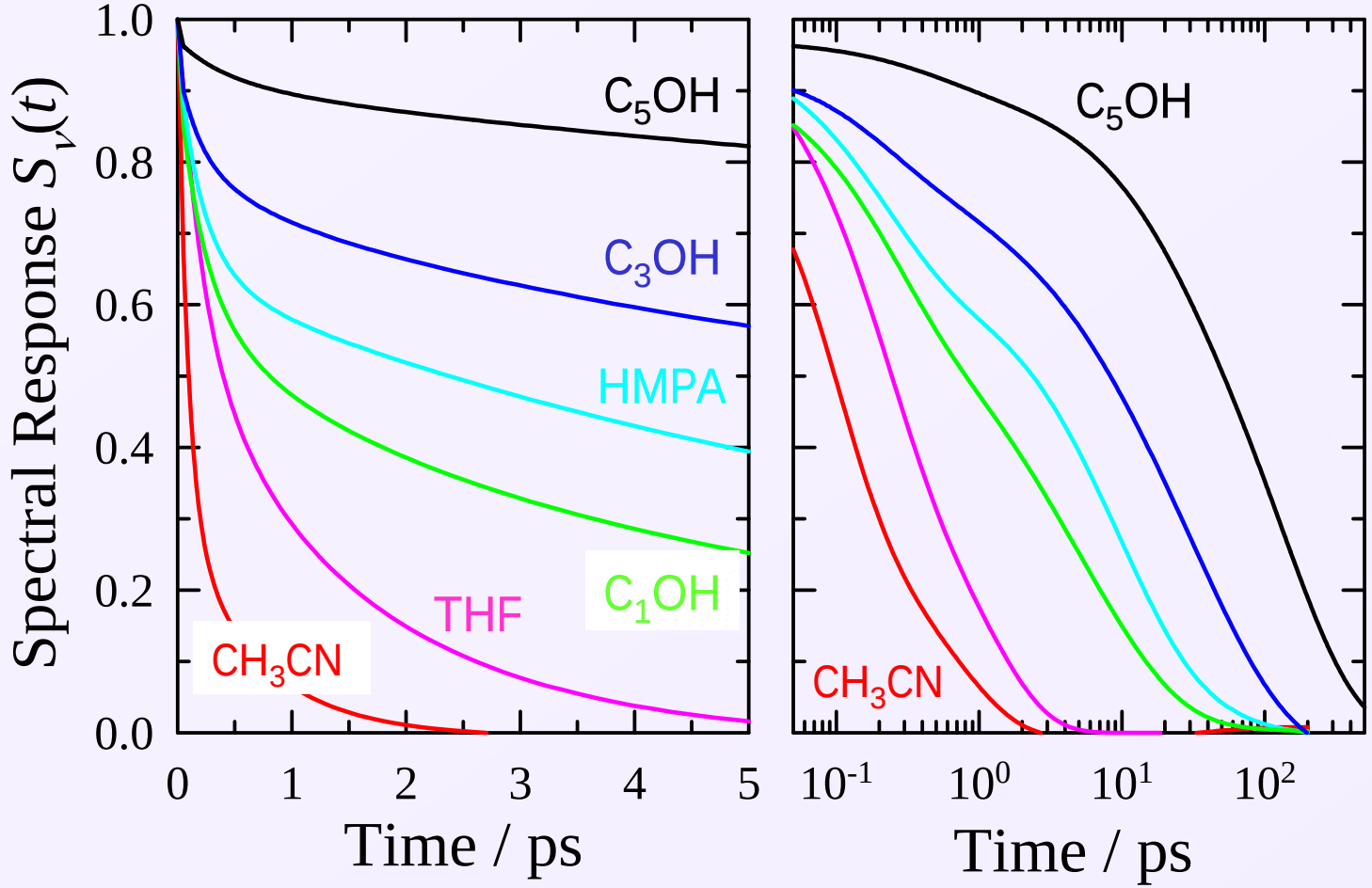
TR Emission: C153 in DMSO



The Solvation Response S(t)

$$S_\nu(t) \equiv \{\nu(t) - \nu_\infty\} / \{\nu_0 - \nu_\infty\}$$

Representative Response Fns. C153 298 K



Times

t_{1e}/ps

0.1

0.7

2

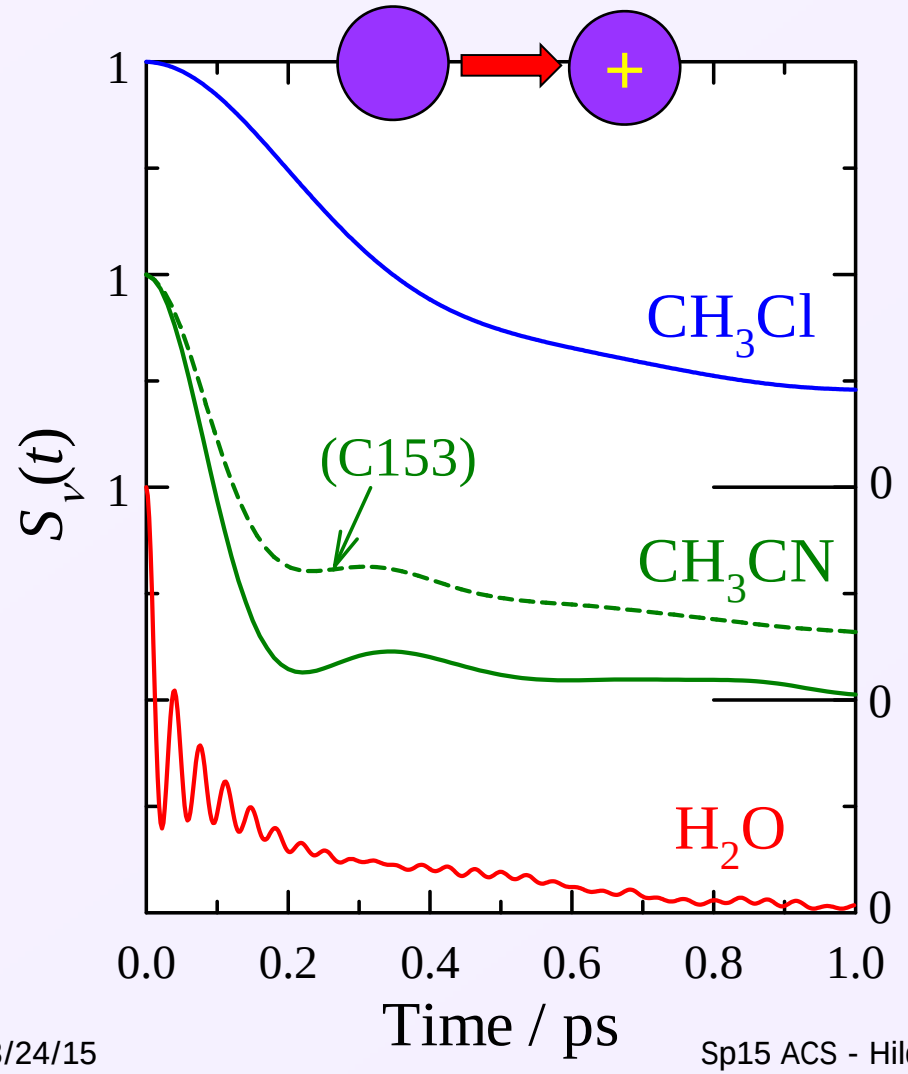
6

26

100

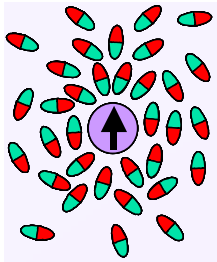
Molecular Dynamics Simulations

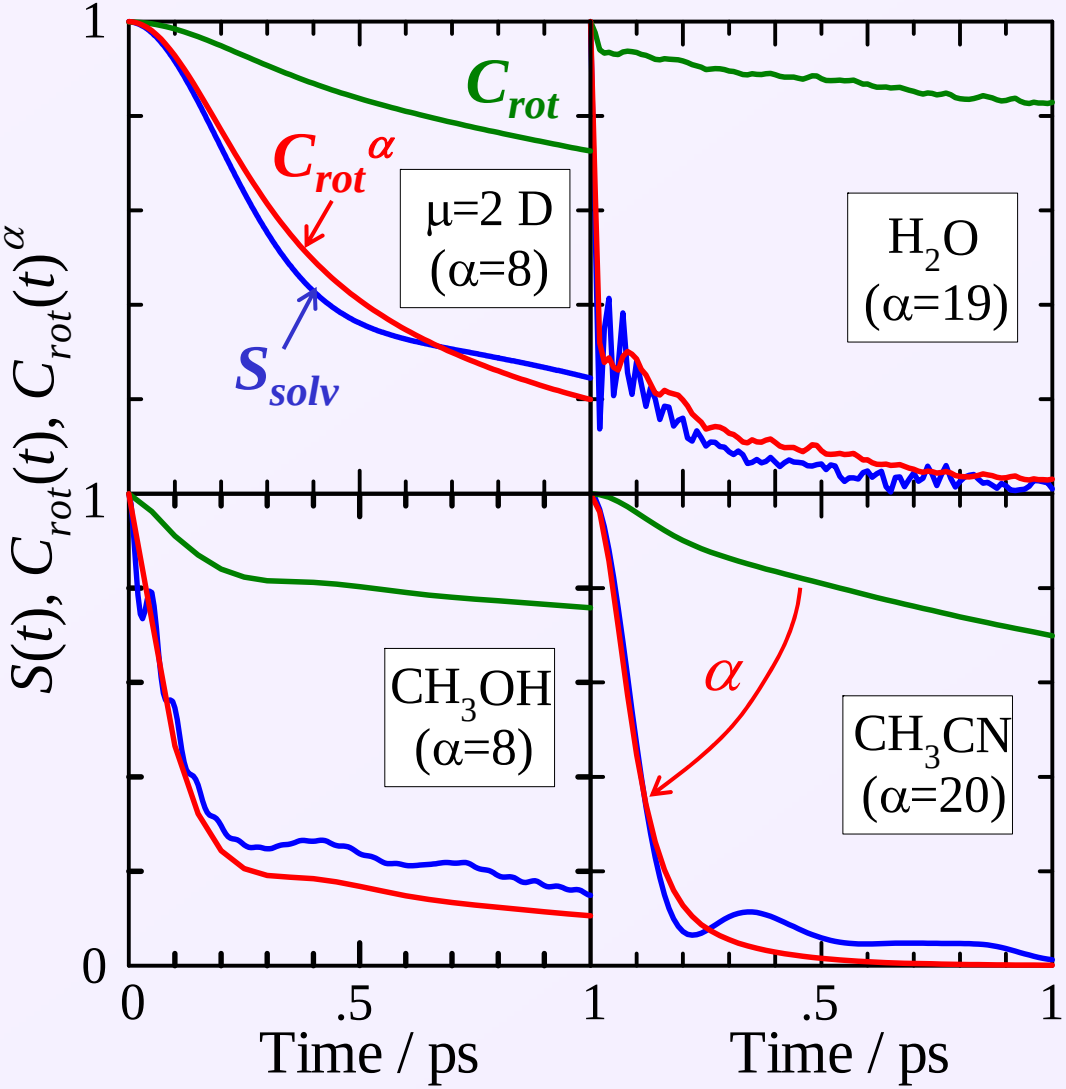
simulations provided many insights into solvation mechanism



- prominent “inertial” or “Gaussian” decay
- response often linear
- mainly solvent rotational dynamics
- speed closely linked to solvent polarity

Solvation & Solvent Rotation





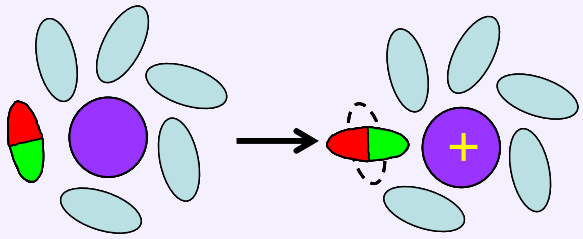
A Simple Conection

$$S_{solv}(t) \cong \{C_{rot}(t)\}^{\alpha}$$

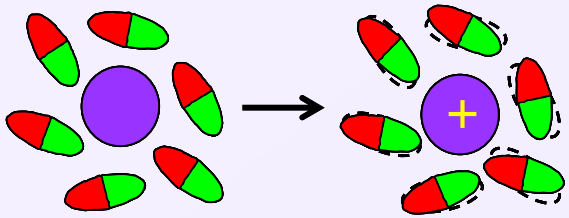
$$\alpha = \frac{4\pi\rho\mu^2}{3k_BT}(1-1/\varepsilon)^{-1}$$

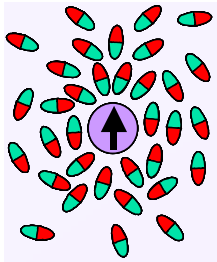
α = "cooperativity"

low polarity α=1



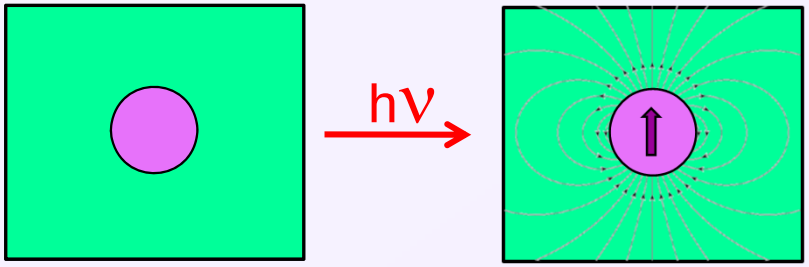
high polarity α>>1

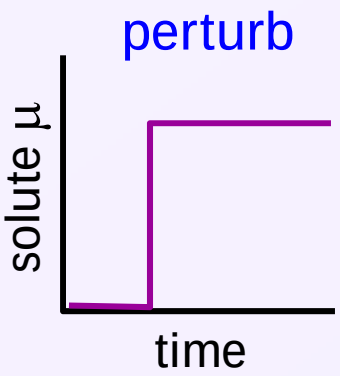


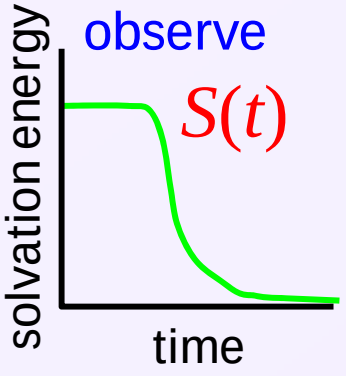


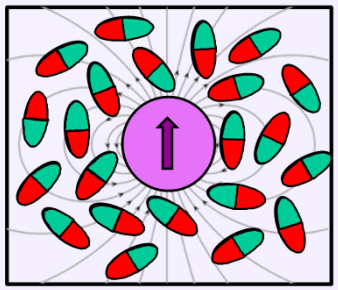
Solvation & Dielectric Dynamics

Solvation Dynamics

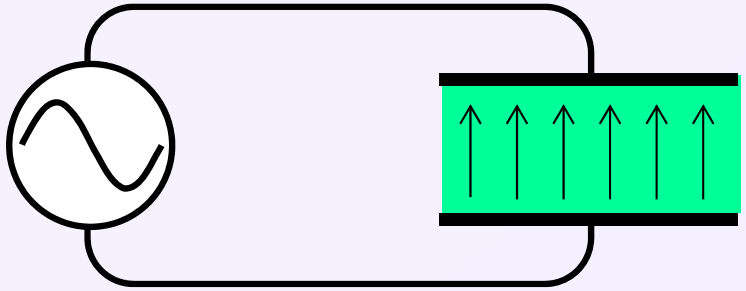


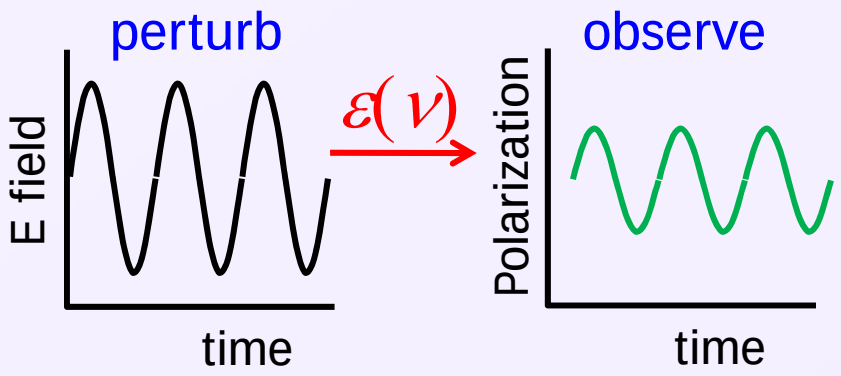


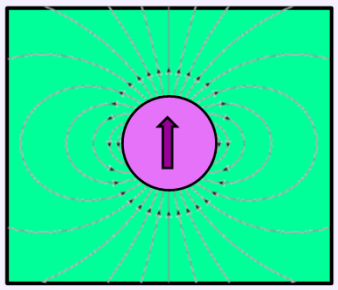




Dielectric Response

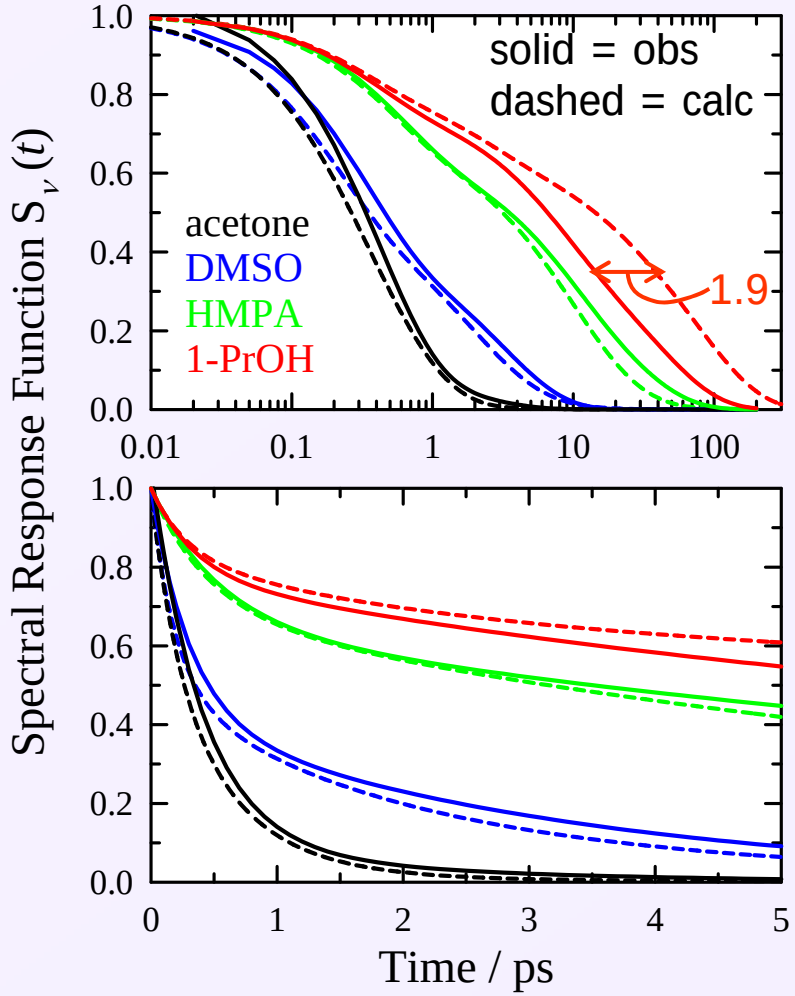




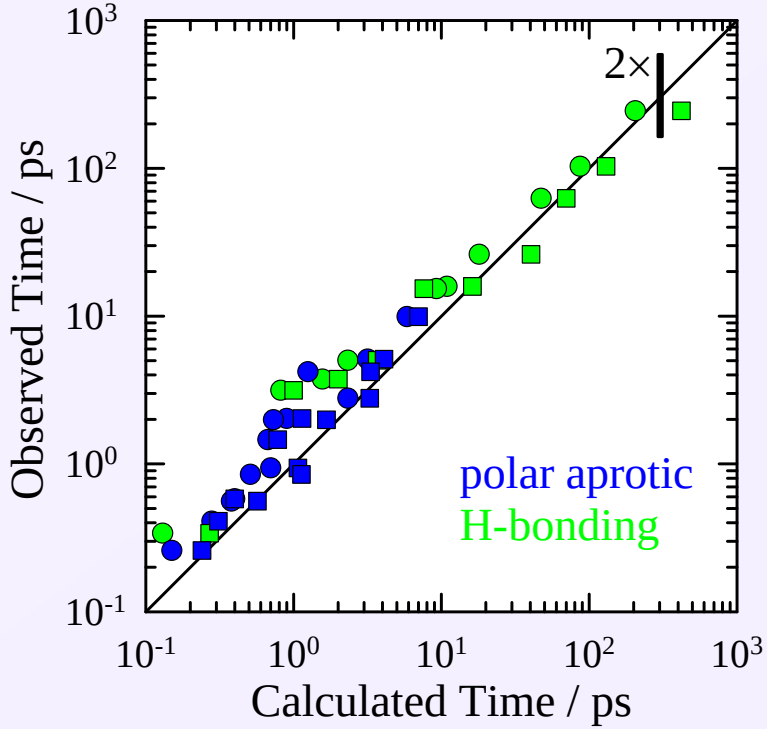


Dielectric Predictions

Spectral Response Fns.

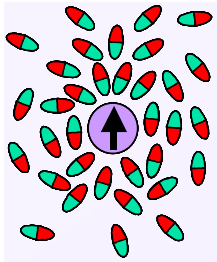


Response Times in 22 Solvents



- simple dielectric continuum predictions surprisingly accurate

Horng et al., *J. Phys. Chem.* 99, 17311 (1995).

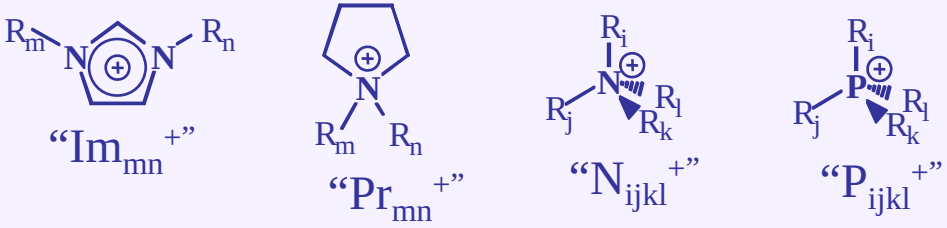


(Room T) Ionic Liquids

= molten salts liquid at (near) room temperature

Cation Families

imidazolium pyrrolidinium ammonium phosphonium

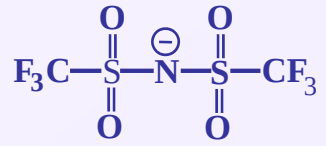


Common Anions

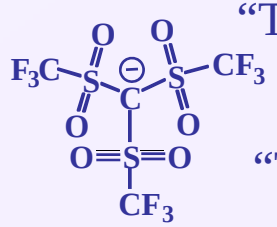
Cl^-, CH_3COO^-

NO_3^-, $CH_3SO_3^-$

BF_4^-, PF_6^-

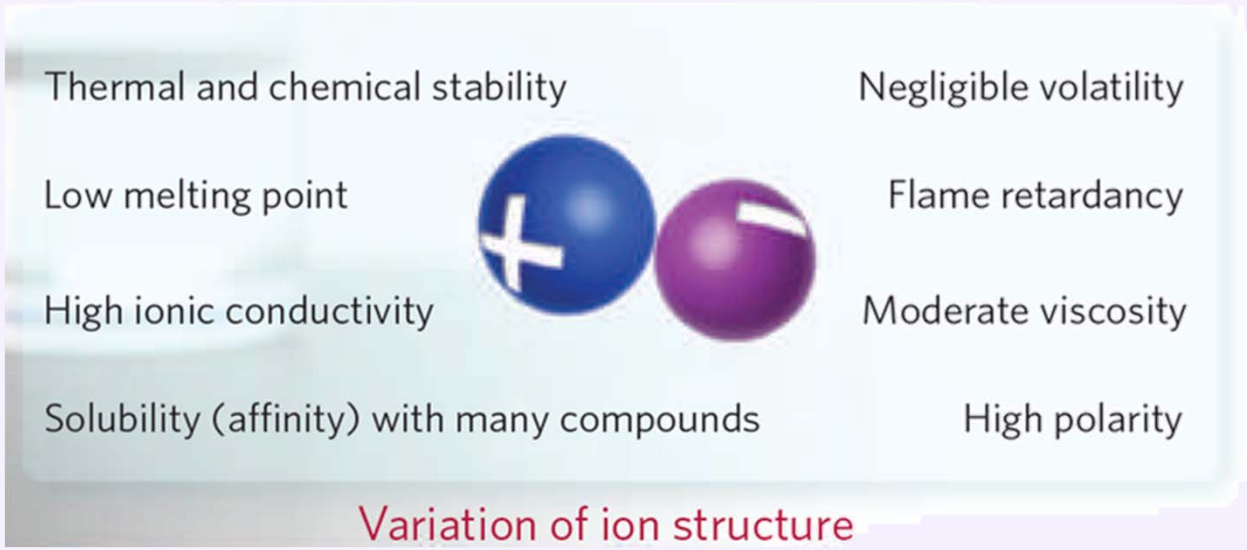


"Tf_2N^-"



"Tf_3C^-"

Properties

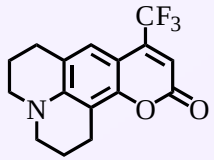


Applications

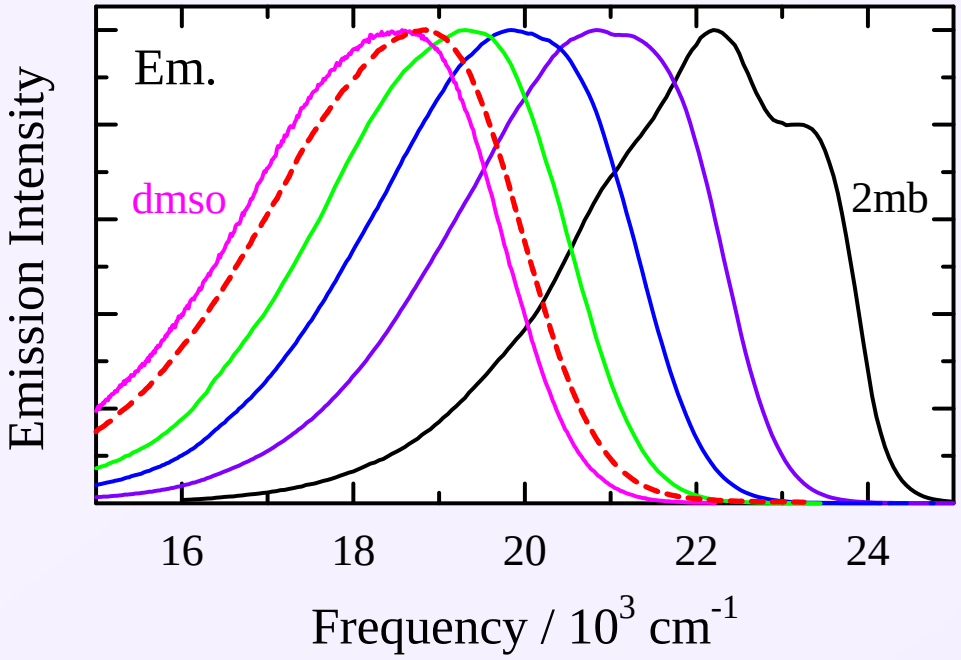
- ion conductive materials for electrochemical devices
- solvents for chemical reaction
- solvents for bioscience

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

Solvation Energies Unremarkable



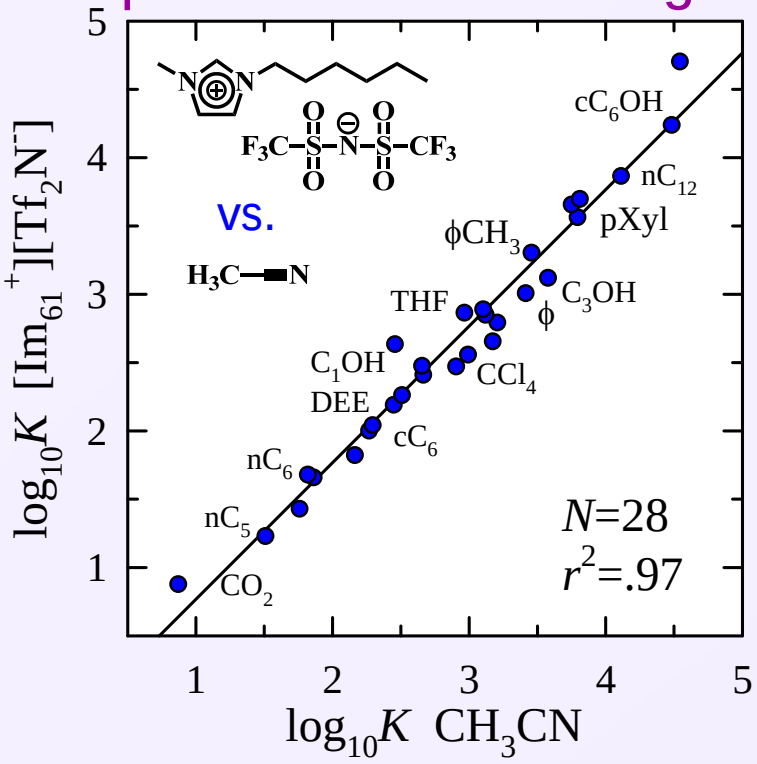
C153 Solvatochromism



- "polarity" comparable to DMSO, CH_3OH, CH_3CN
- solvation free energies can be remarkably similar to those of conventional solvents

U_{EI} = solute-solvent interaction energy

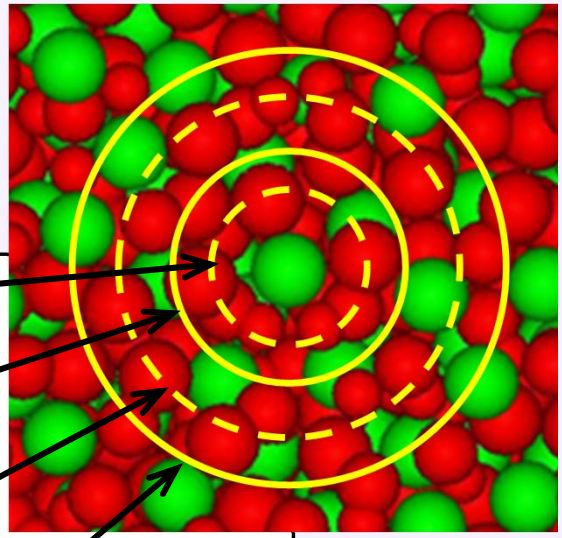
Experimental Free Energies

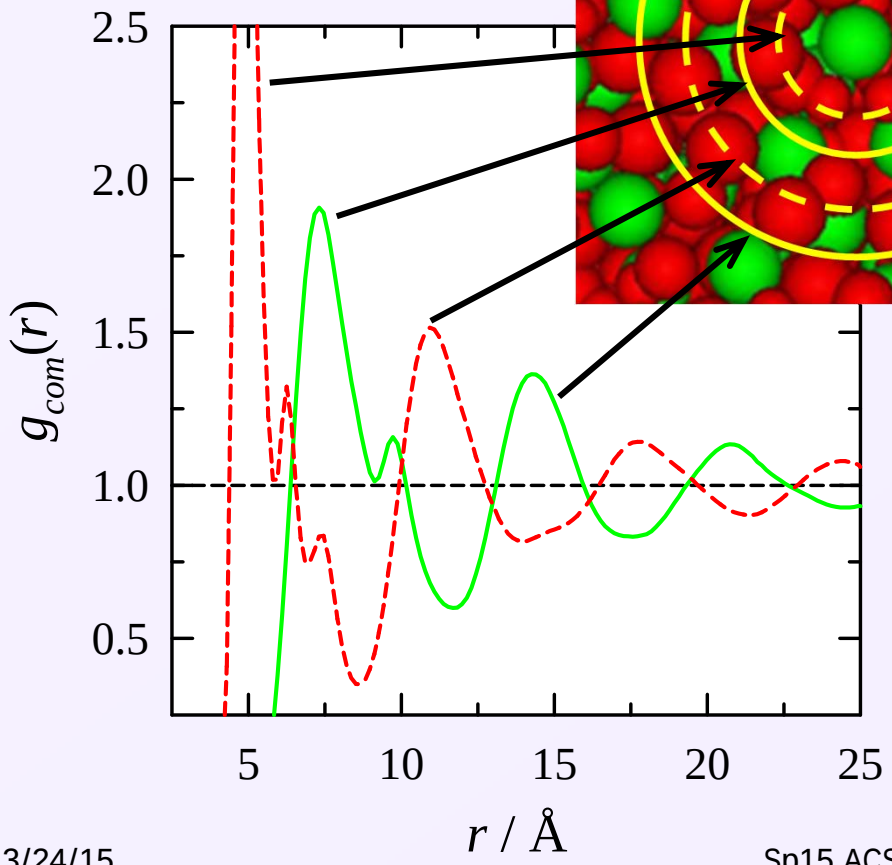


Abraham & Acree, *Green Chem.* **8,** 906 (2006).

Charge Structuring

RDF about a Central Anion



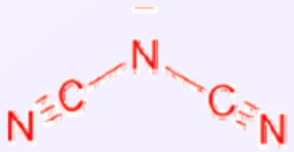


Effect of Charge

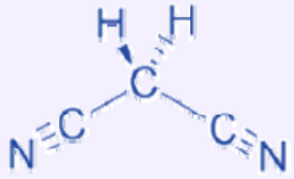
IL NM

MOEPy$^+$

MOEBz



DCA$^-$



DCM

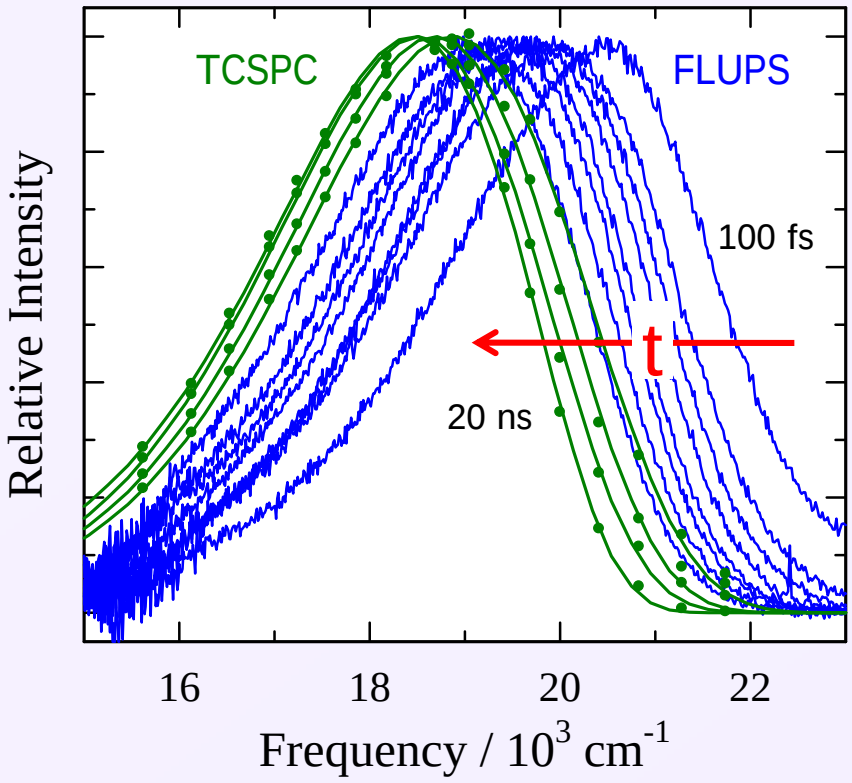
molar volume	↑	17%
fluidity 1/η	↑	29x

Shirota & Castner, *JPCA* **109**, 9388 (2005).

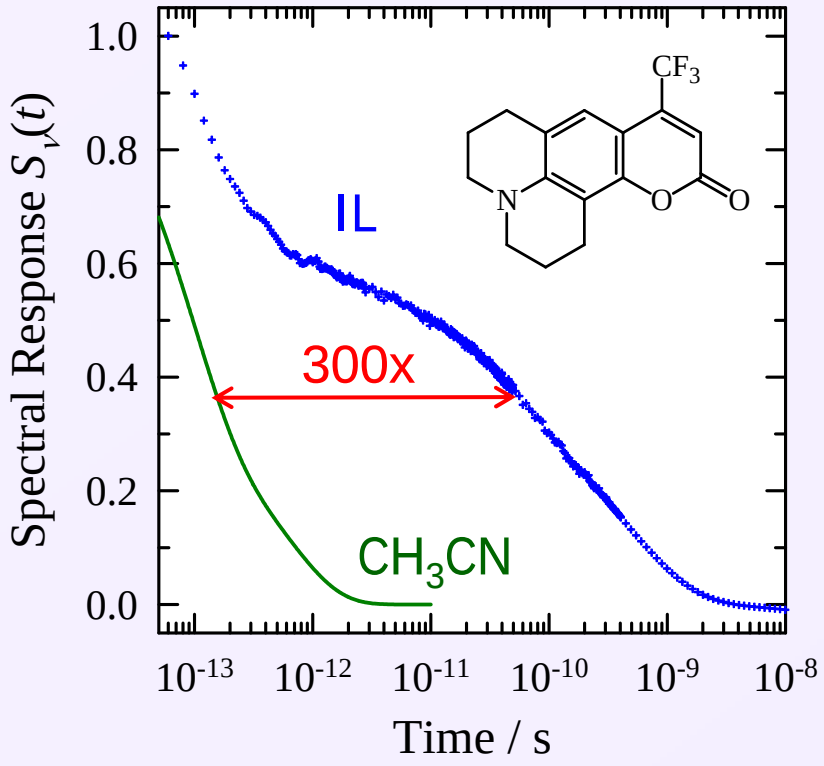
Solvation Dynamics

- experiments with Niko Ernsting capture the full response 80 fs – 40 ns

TR Emission of C153/[Im_{41}][PF_6]



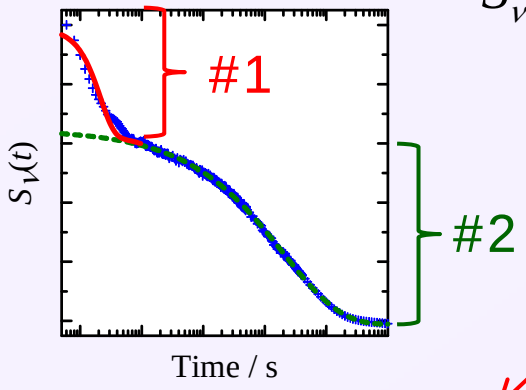
S(t) in CH_3CN & IL



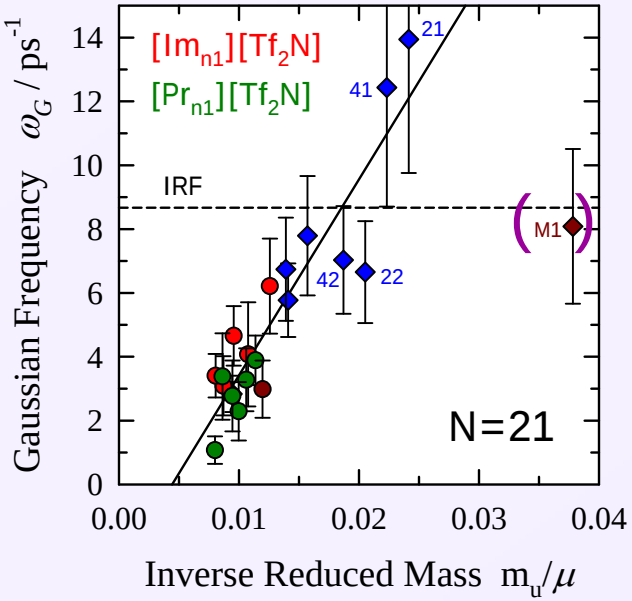
- ~100-fold slower than typical dipolar solvents
- strongly bimodal & broadly distributed in time

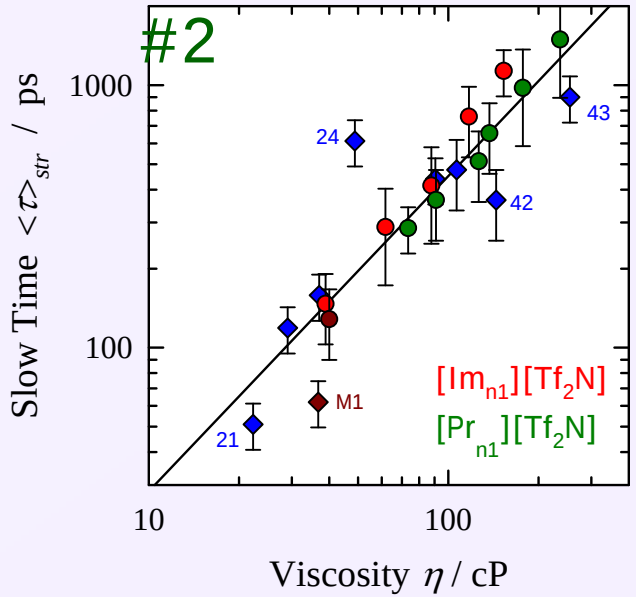
Experimental Survey of 21 ILs

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



#1





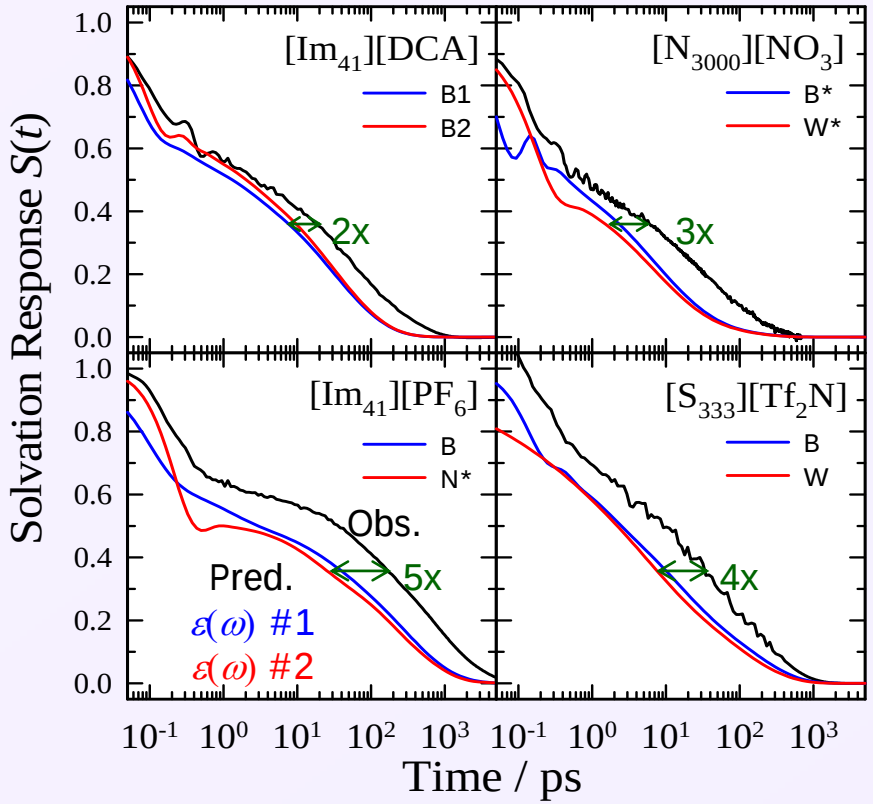
Mechanism (from MD Simulations):

- primarily ion translation
- #1: 30-40% inertial motion of 1st shell ions
- #2: overdamped, highly coupled ion motions
  $\Rightarrow$ subtle displacements of ions over <1σ

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

Relation to Dielectric Dynamics

Some S(t) Comparisons

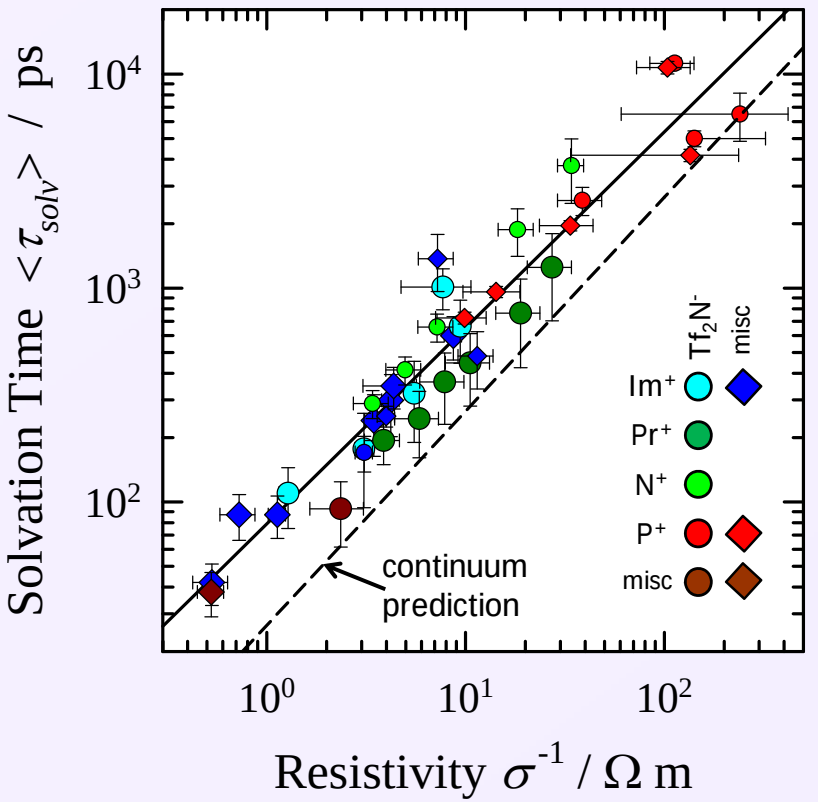


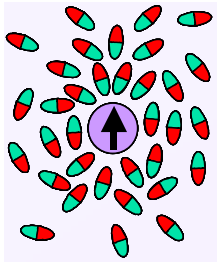
- dielectric continuum predictions qualitatively correct but too fast by factors of 3-4
- $\langle\tau_{solv}\rangle \propto 1/\sigma$

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

~const.

$\langle\tau_{solv}\rangle$ and Conductivity

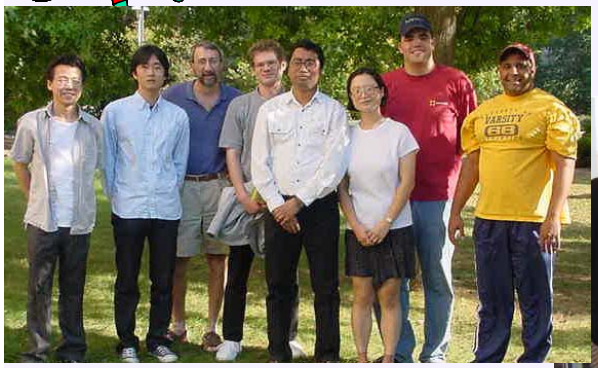


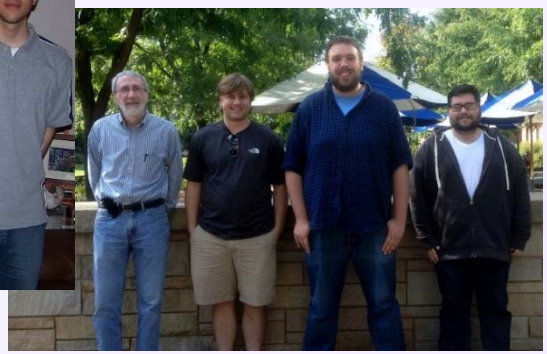


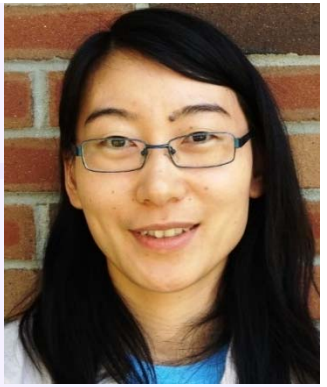
Summary

- solvation dynamics key component of solution-phase reactions
- dynamics in familiar dipolar solvents (reasonably) well understood
- dynamics in “neoteric” solvents like ionic liquids still being investigated
- dynamics in structured, mostly biological, also of current interest

Acknowledgements







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