Znamenskiy V.S., Kobrak M.N.
Simulation of the polarization response of room-temperature ionic liquids
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What are Room-Temperature Ionic Liquids?

➢ Salts that are molten at room-temperature
➢ Recent interest spurred by the discovery
  of RTILs that are stable under ambient
  conditions

Common Cations:

Common Anions:

$$PF_6^- \qquad BF_4^- \qquad Cl^- \qquad NO_3^-$$
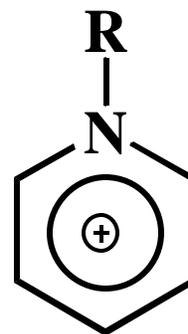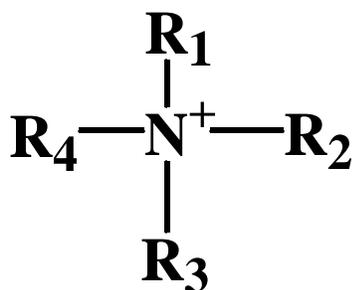
Properties of RTILs

Physical Properties:

➤ Nonvolatile

➤ Nonflammable

➤ Nontoxic(?)

➤ Wide Liquidus
   Temperature Range

} Good properties
for synthesis and
separations

➤ Conductive

➤ Wide Electrochemical
   Window

} Good properties for
electrochemistry

Solvation Properties:

➤ RTILs behave as moderately polar
   organic solvents

Applications of RTILs

<u>Synthesis:</u>
- ➢"Classic" organic chemistry
  Diels-Alder, Heck, Suzuki, *etc*.
- ➢Novel reactions
  (*e.g.* Synthesis of an extended coordination network, Jin *et al*. Chem. Comm. 2872 (2002))

<u>Separations and Analysis:</u>
- ➢Liquid-liquid extractions
  (simple, crown-ether, solvent-optimized)
- ➢MALDI matrix for mass spectrometry
- ➢Continuous loop bioreactor (membrane)

<u>Electrochemistry:</u>
- ➢Electroplating
- ➢Voltaic cells

Structural Features of RTILs

➢Most known species monovalent
➢Cation/anion sizes mismatched
➢Charge asymmetrically distributed in cation
➢Both ions highly polarizable
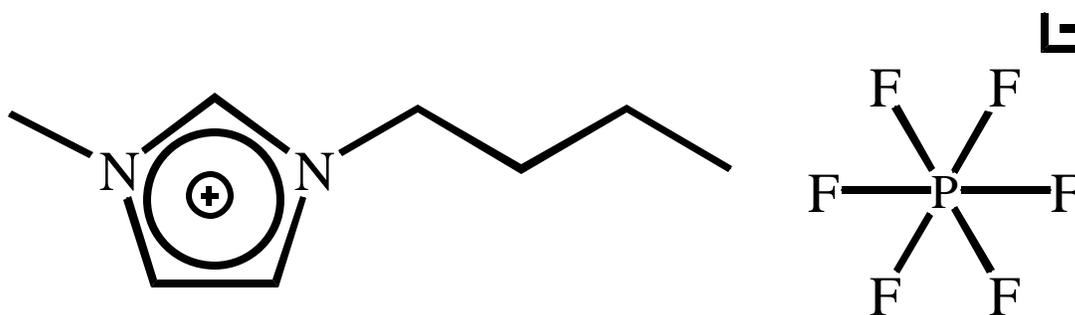
1-butyl-3-methylimidazolium
hexafluorophosphate (BMIM[PF_6])

Chemical Structure and Solvation

➢ Polarity of molecular solvents is connected to molecular structure by the dipole moment
➢ Polarity of ionic solvents is not understood

Match Game

Identify which solute is most soluble in each solvent

Solute	Solvent
NaCl	Water
Phenol	1-propanol
Napthalene	Benzene
	BMIM[PF$_6$]

Mechanism of Solvation

Molecular Liquids:

➢ <u>Specific interactions:</u> Hydrogen-bonding
➢ <u>Nonspecific interactions:</u> Electrostatic effects
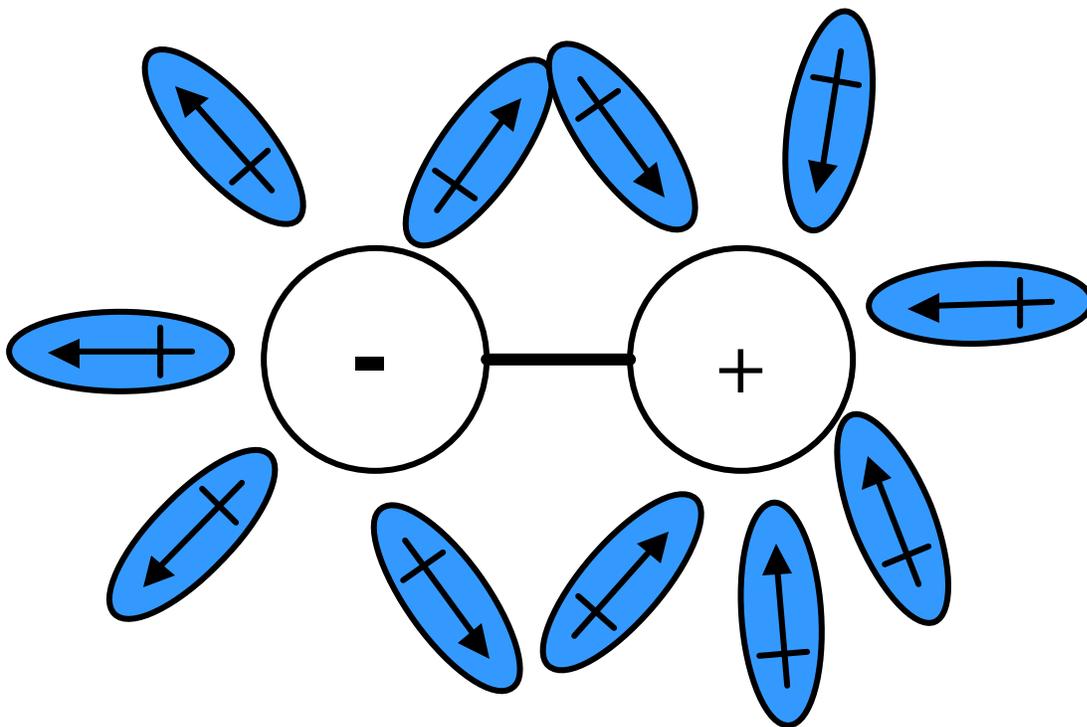
<u>What can we say about RTILs?</u>

The Chemical Environment of Fused Salts

➢ Most models based on a "solid lattice with holes" model

            Temkin model

            Quasi-lattice model

            Crystallite Model

            Hole Model

            Liquid Free-volume Model

            Significant structure Model

➢ Experimental NMR and optical measurements support this view

Spontaneous Ionization in a Metal-Fused Salt Solution

8
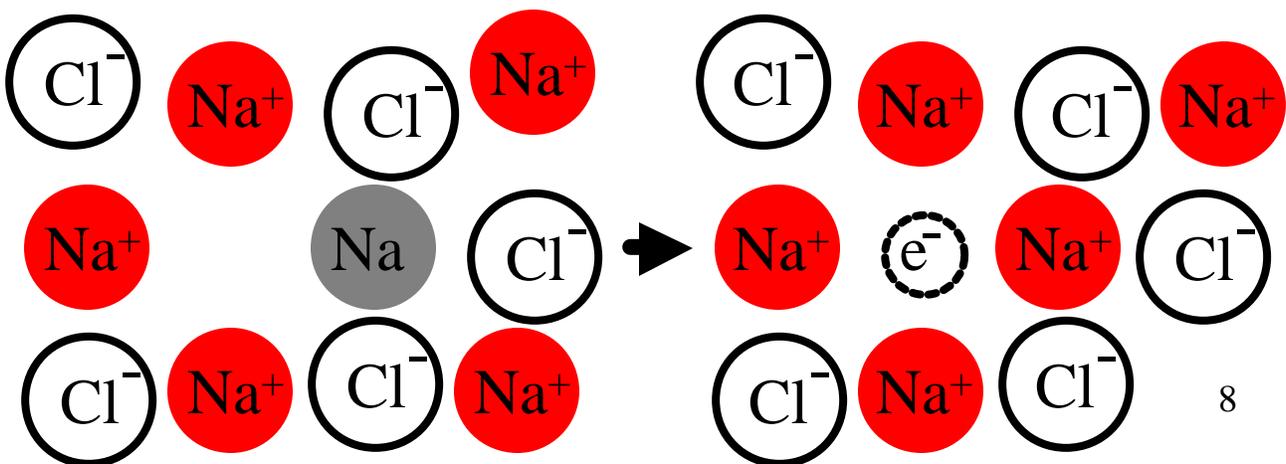
Stillinger Model

Stillinger *et al.* (JCP **32** 1837 (1960)):
Ion in a fused salt is surrounded by
alternating layers of positive and negative
charge
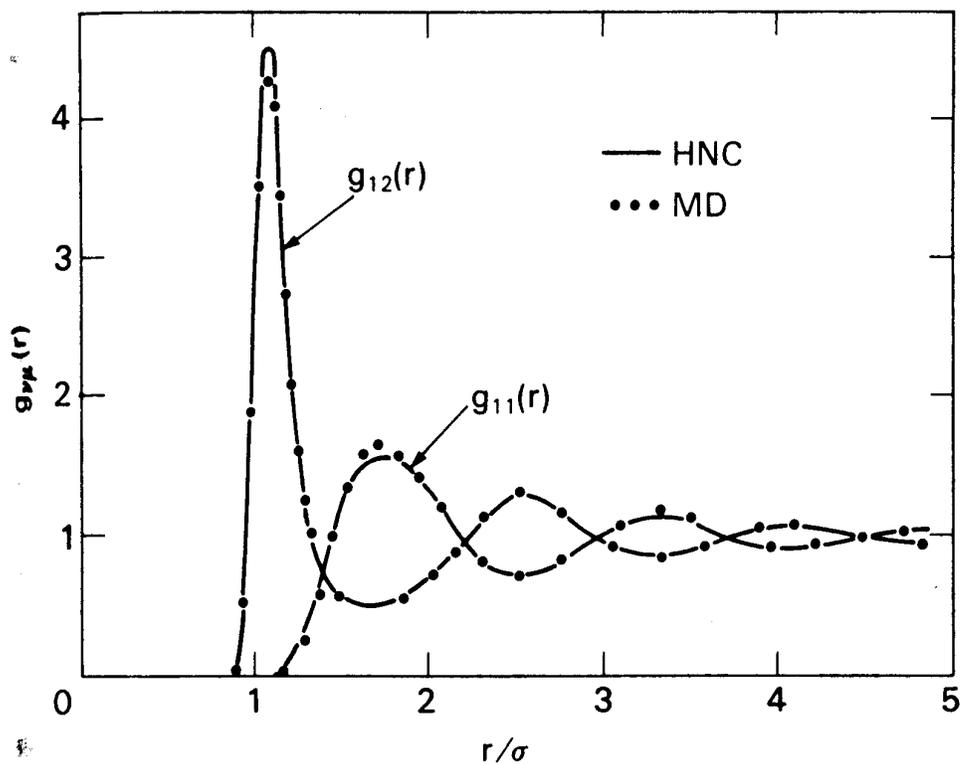
Cation-cation and cation-anion radial distribution functions for a model fused salt
(From "Theory of Simple Liquids,"
Hansen&McDonald, Academic Press,
London 1986)

Characterizing the Polarity of RTILs

➤Theoretical definition of polarity: None
➤Empirical scales for polarity:
    •Dielectric constant
    •Partitioning between bilayers
    •Solvatochromism of probe molecules

Partitioning of Solute Species

➢ Simple solubility experiments
➢ Reverse-phase chromatography
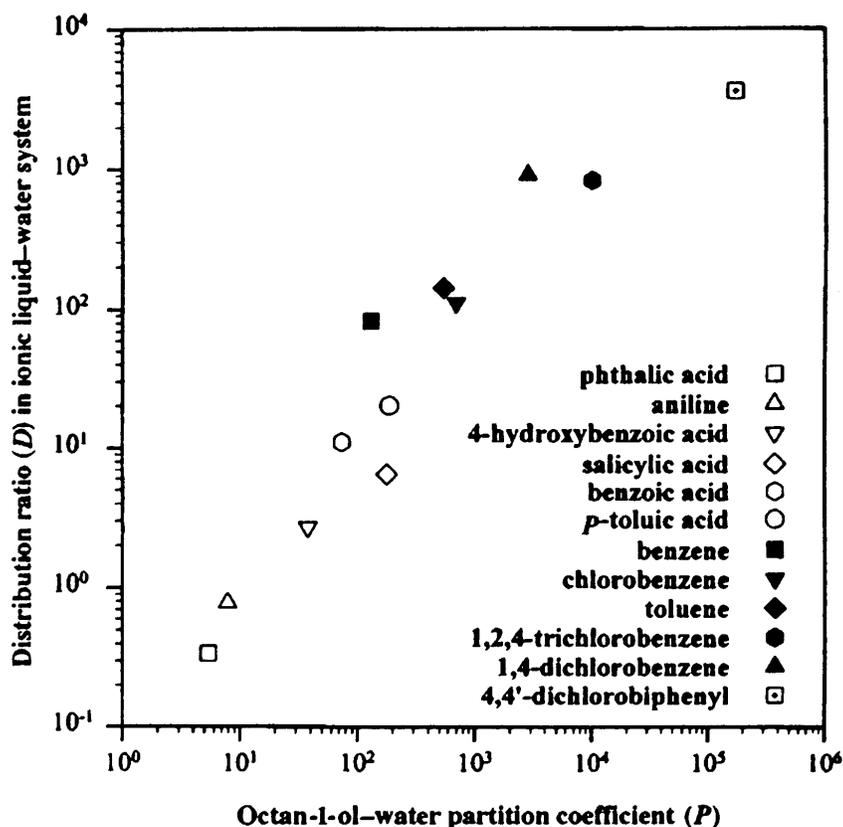
Comparison of partition coefficients for organic compounds in biphasic BMIM[PF$_6$]/H$_2$O and octan-1-ol/H$_2$O systems (from Huddleston *et al.* Chem. Comm. 1765 (1998)

11

Solvatochromism

➢ Based on the difference in dipole moment between chromophore electronic states
➢ Polarity scales and linear free energy relationships built on specific molecules

ΔE_V

ΔE_S
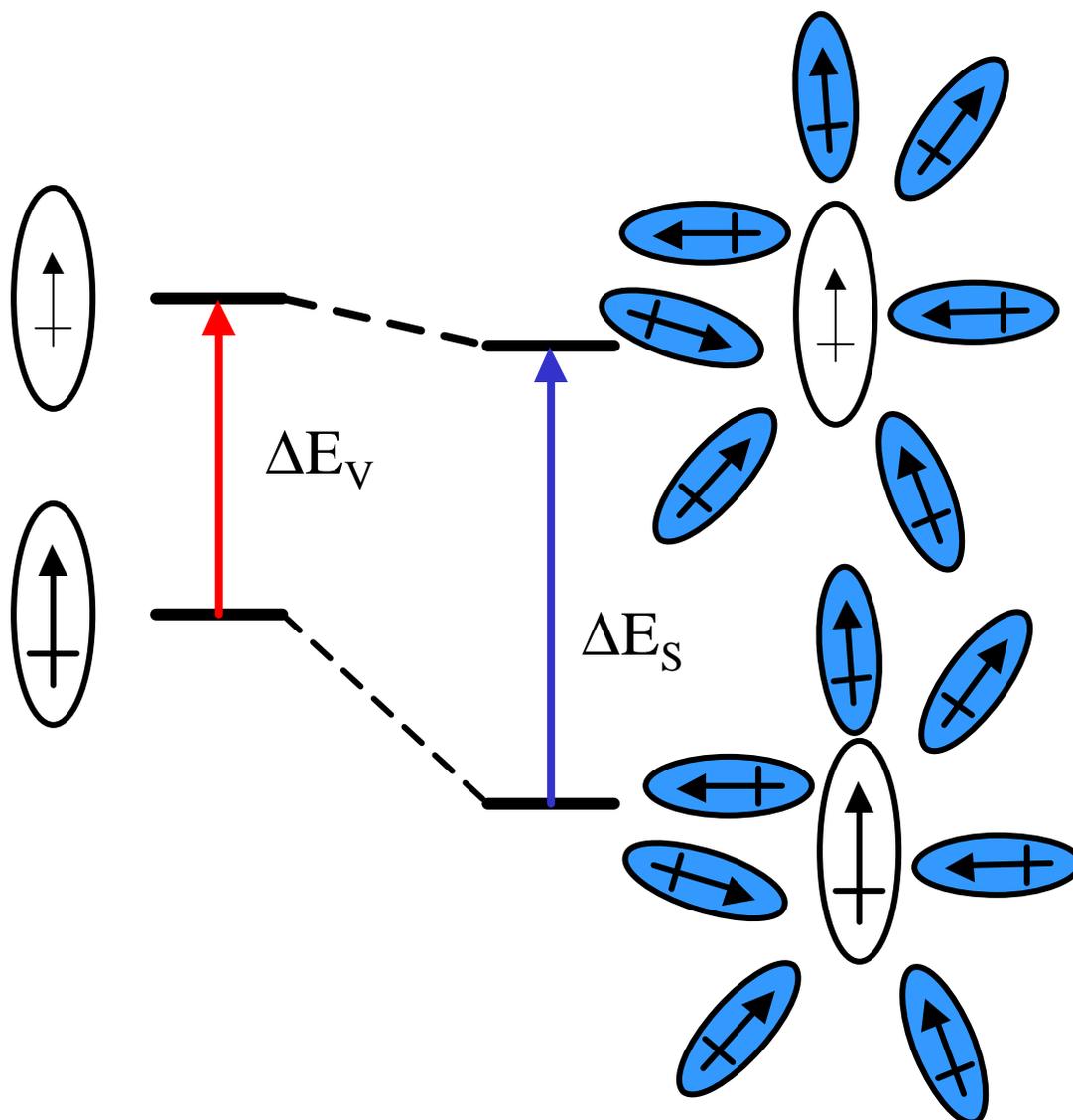
Solvent Polarity from Simulation

➢ Need to connect polarity to ionic behavior
➢ Must simulate an empirical measure of polarity

Simulate the solvatochromism of betaine-30 in BMIM[PF$_6$]

Ph

Ph   N$^+$ Ph

Ph   Ph

O$^-$
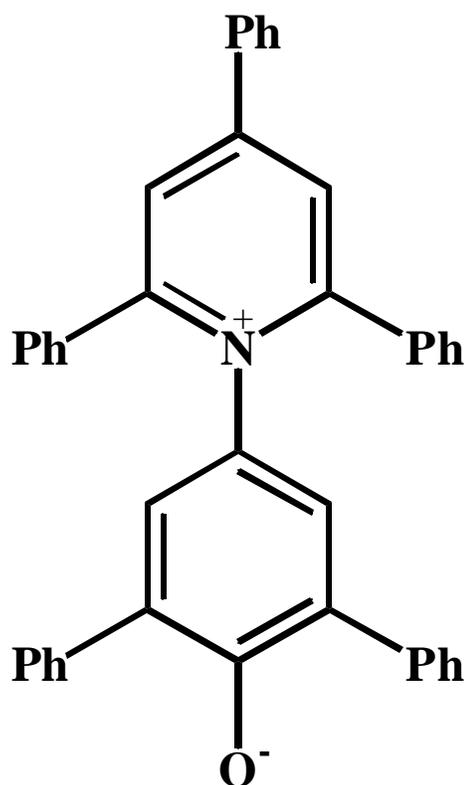
Solute and Solvent Structures
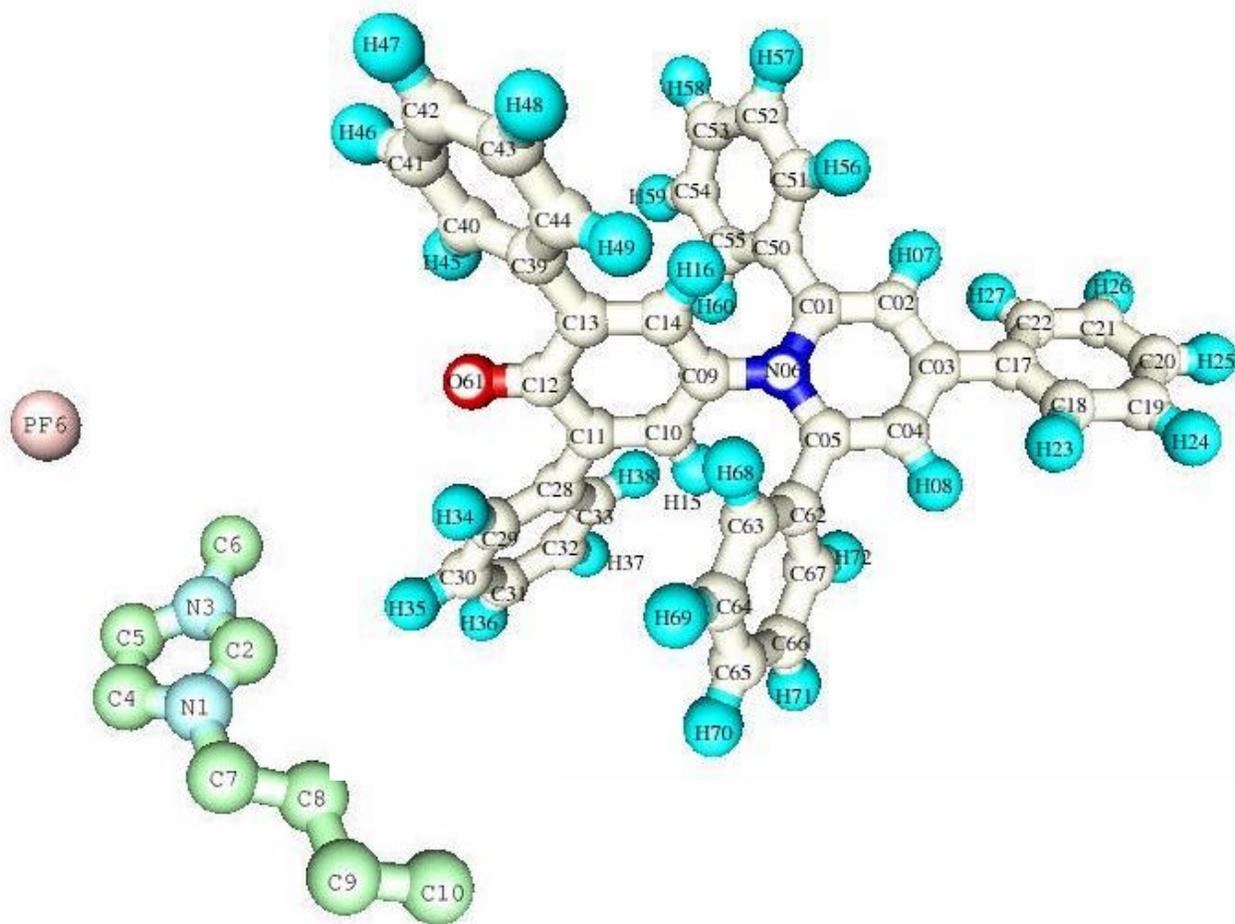
Simulation Details

- Force Field
    - RTIL f.f. by Shah *et al.*,
      Green Chem **4** 112 (2002)
    - Betaine-30 f.f. by Mente&Maroncelli,
      JPC-B **103** 7704 (1999)
    - Short-ranged forces: OPLS
    - Coulomb forces: Ewald summation
    - <u>United atom treatment of CH_n</u>
- 200 ion pairs/1 betaine-30
- ~700 ps equilibration time
- NPT ensemble

Calculation of the Absorption Spectrum

Vapor   **Solution**

$$V_{Ss}^{e}\{$$

$$\Delta E_v \qquad \Delta E_s$$
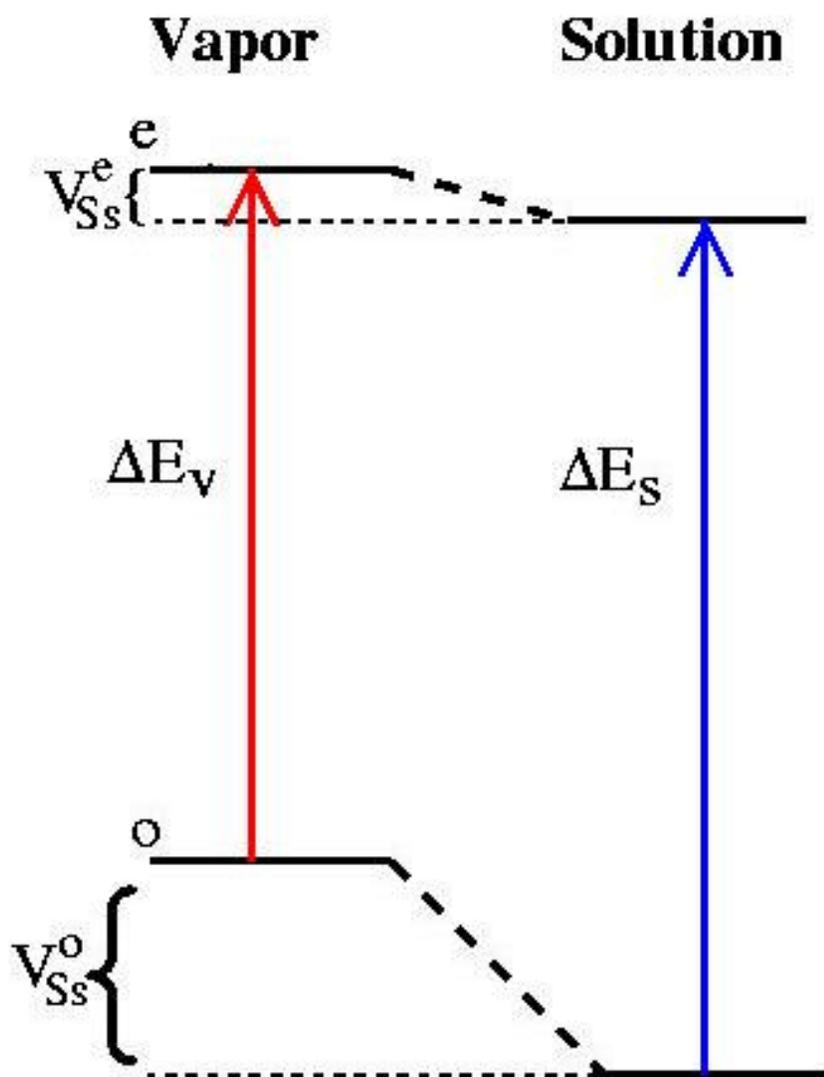
$$V_{Ss}^{o}\{$$

Difference in solute-solvent interaction energies for ground and excited states:

$$Z = \Delta E_s - \Delta E_v$$
$$= V_{Ss}^{e} - V_{Ss}^{o}$$

16

Time-Dependence of The Spectral Shift

Z vs. Time for Four Trajectories
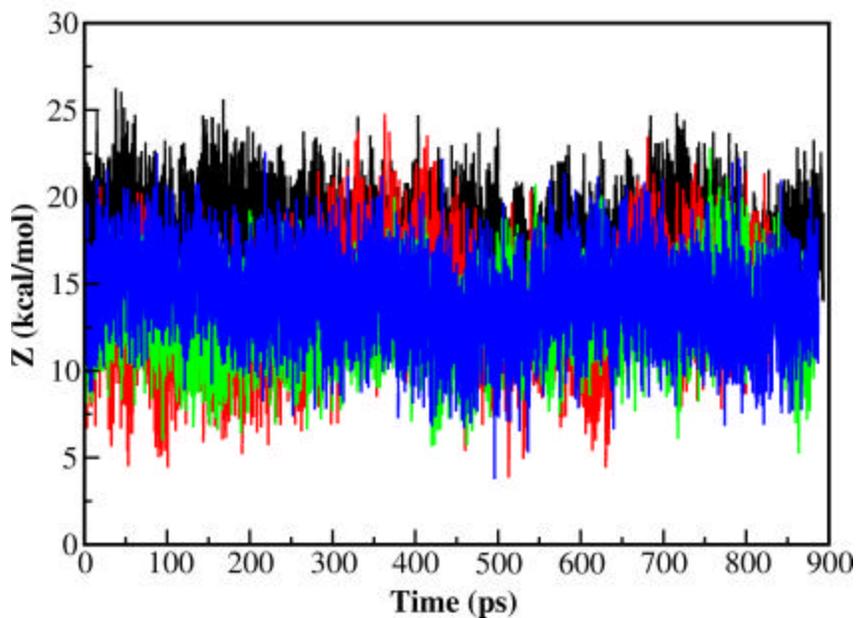
Z vs. Time for Four Trajectories
(Averaged Over 5 ps Intervals)

17
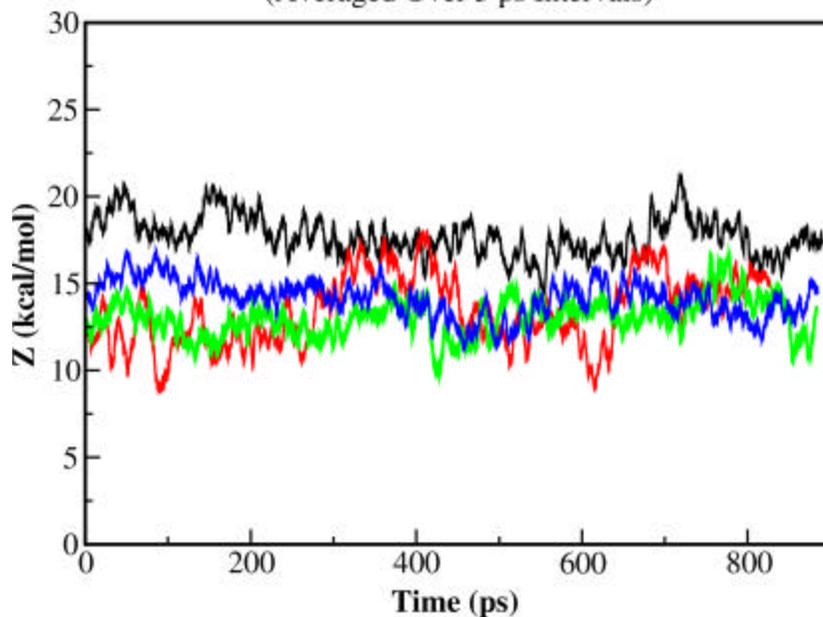
Time-Averaged Z-distribution

Distribution of Z for Betaine−30 in BMIM[PF$_6$]
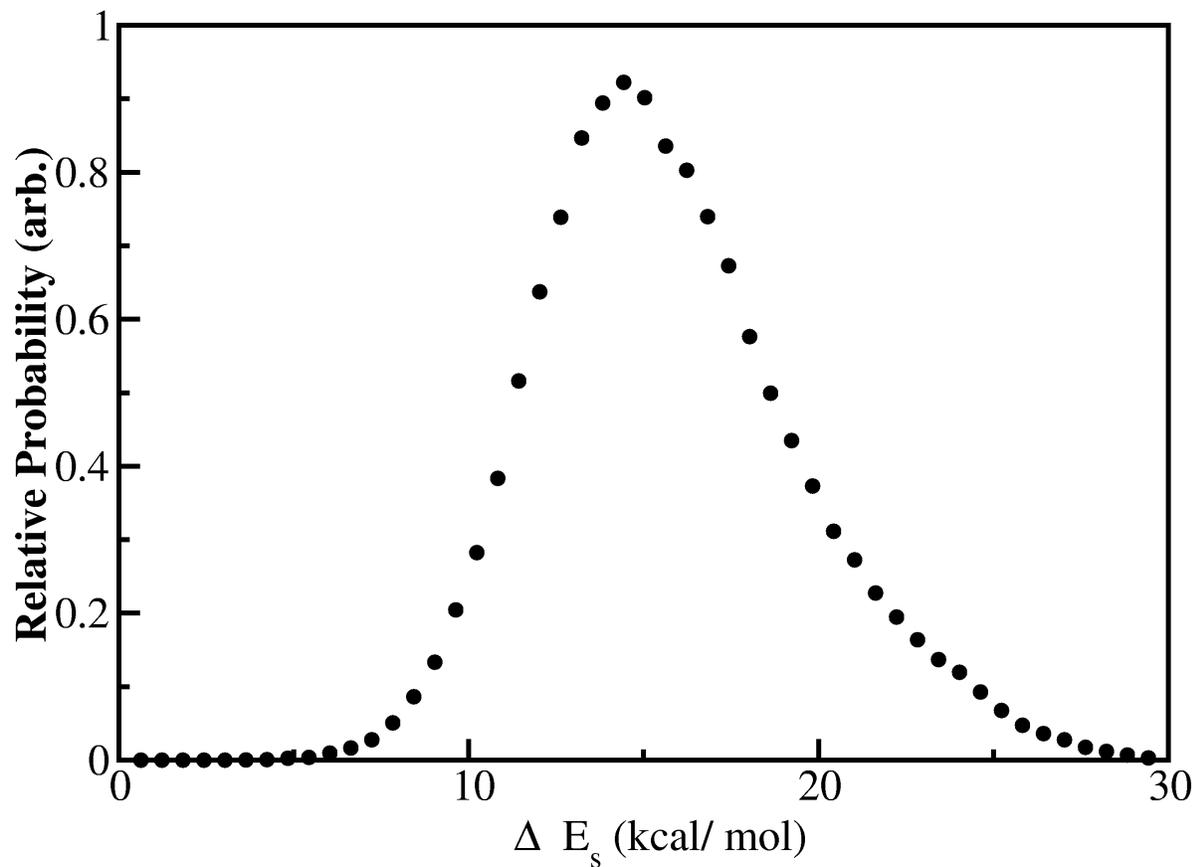
Calculated and Experimental Absorption Spectra

Absorption Spectrum of Betaine−30 in BMIM[PF$_6$]

Local Structure About Betaine-30 Oxygen Atom

O (Betaine–30) – [BMIM]
Radial Distribution Function

Local Structure About Betaine-30 Oxygen Atom
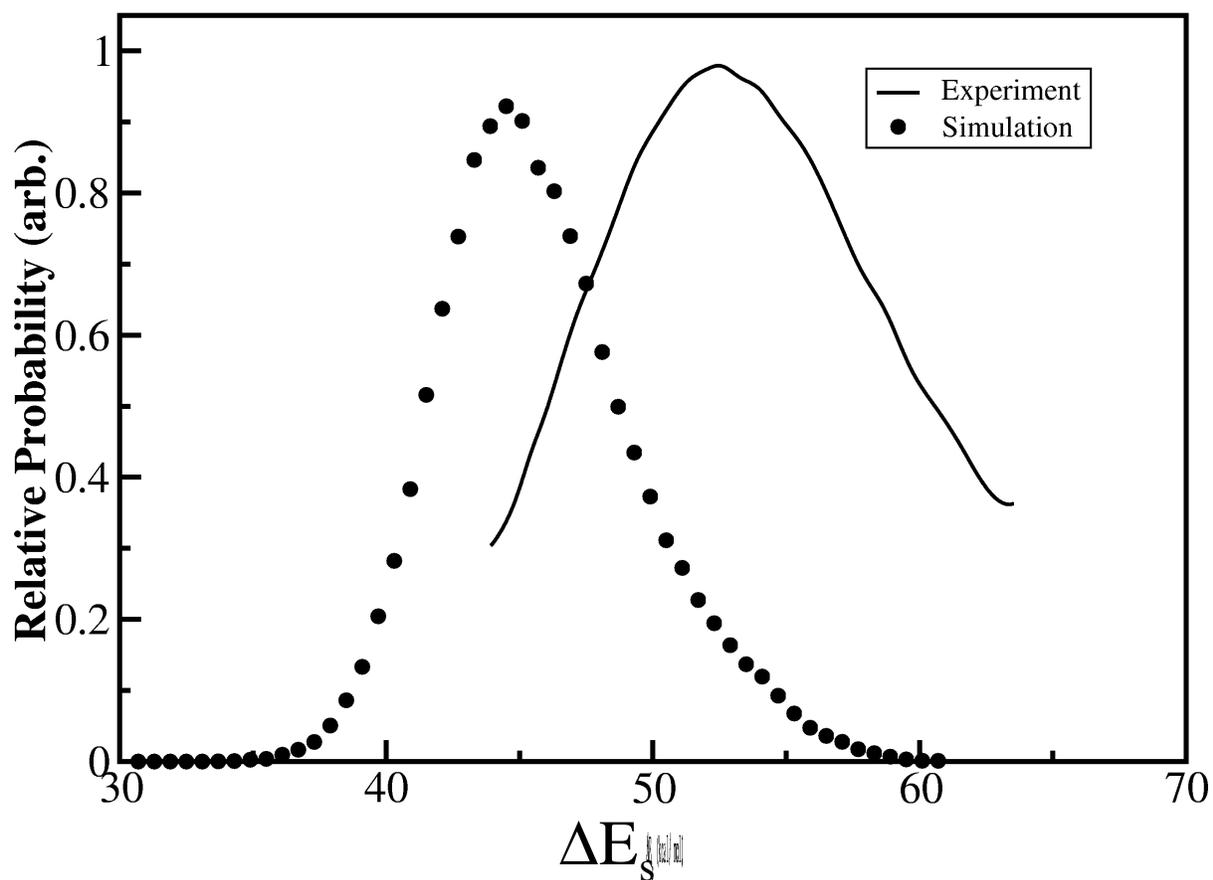
O (Betaine−30) − Ion
Radial Distribution Function
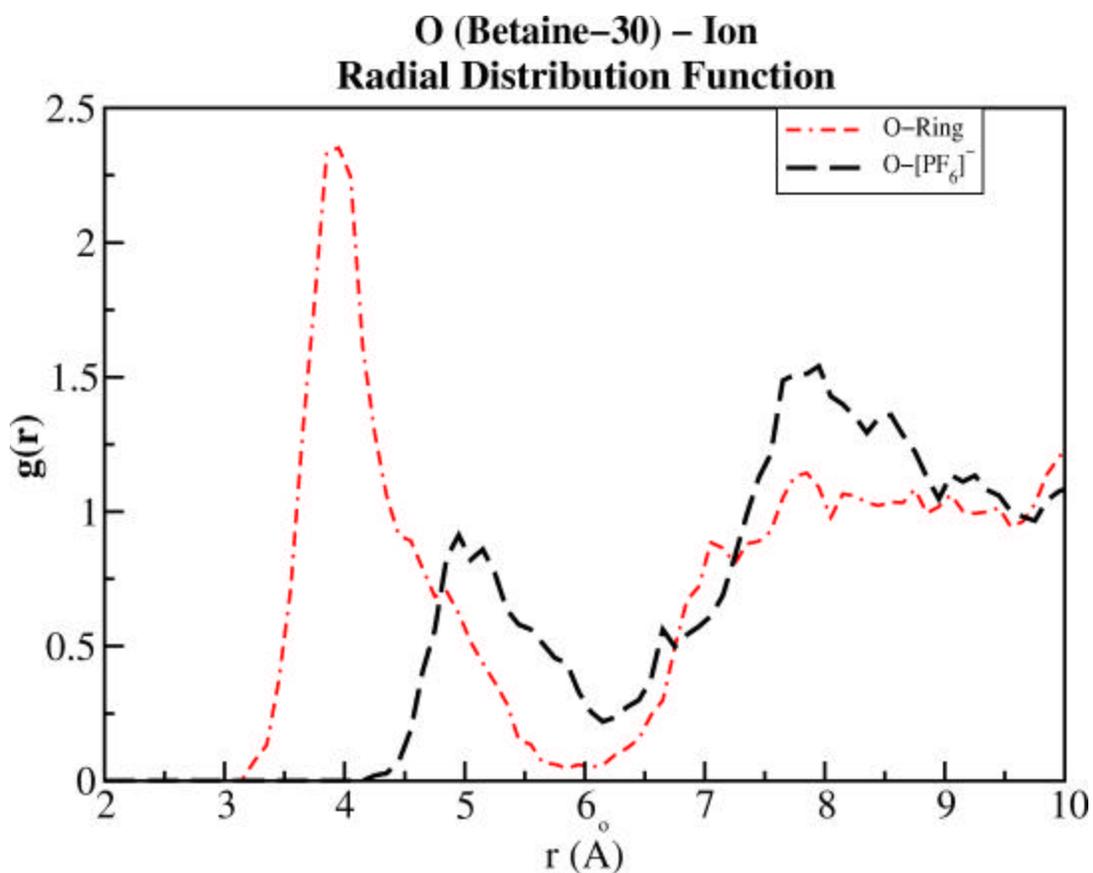
Z-Component of O-Solvent Interaction
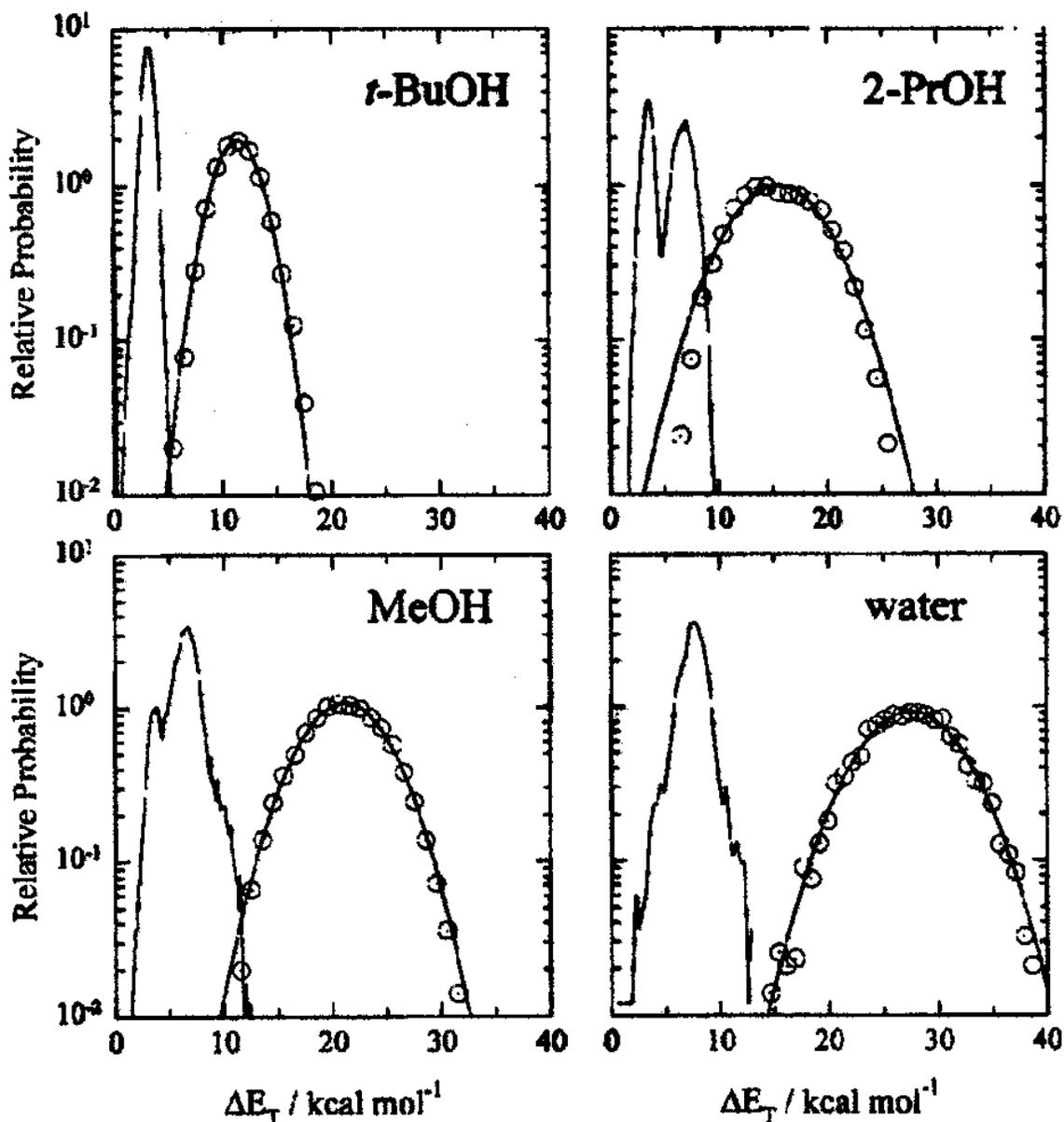
Mente and Maroncelli: Z-Contributions
from Specific Betaine O-Solvent Interactions

Extremal Z-Component Spectra For Betaine-Solvent Interaction

Z−Contribution Spectra of Extremal $BMIM^+$ and PF_6^-
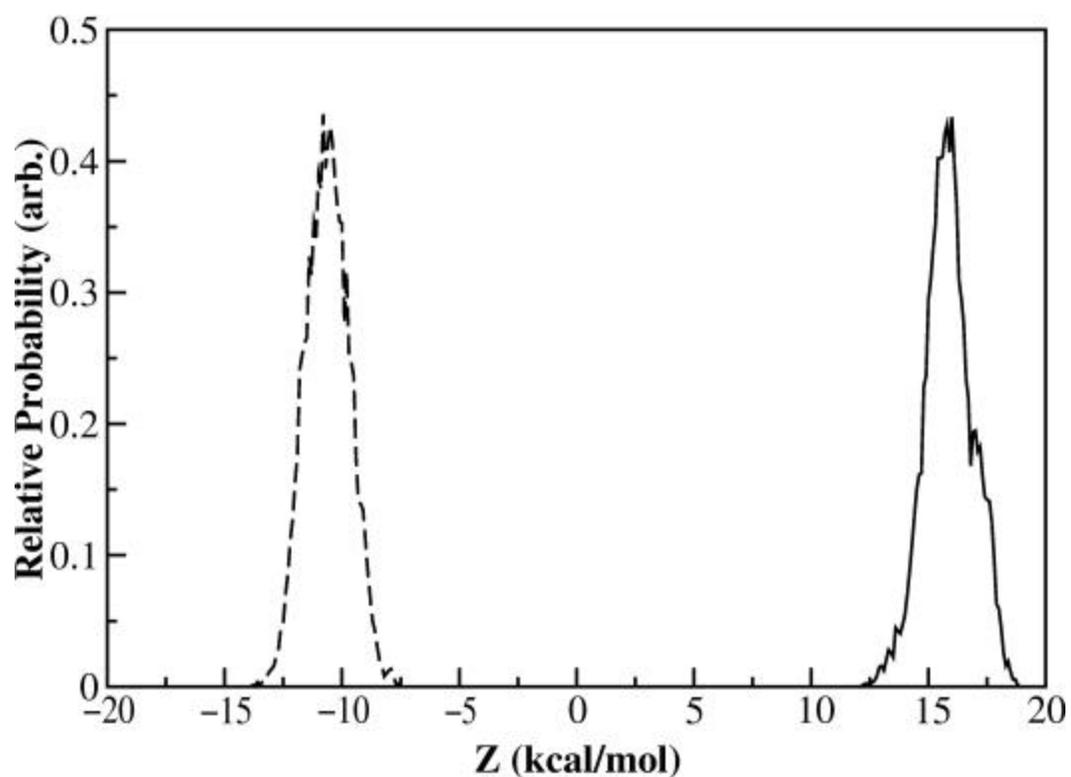
Sample Configuration of Largest Z-Contributors
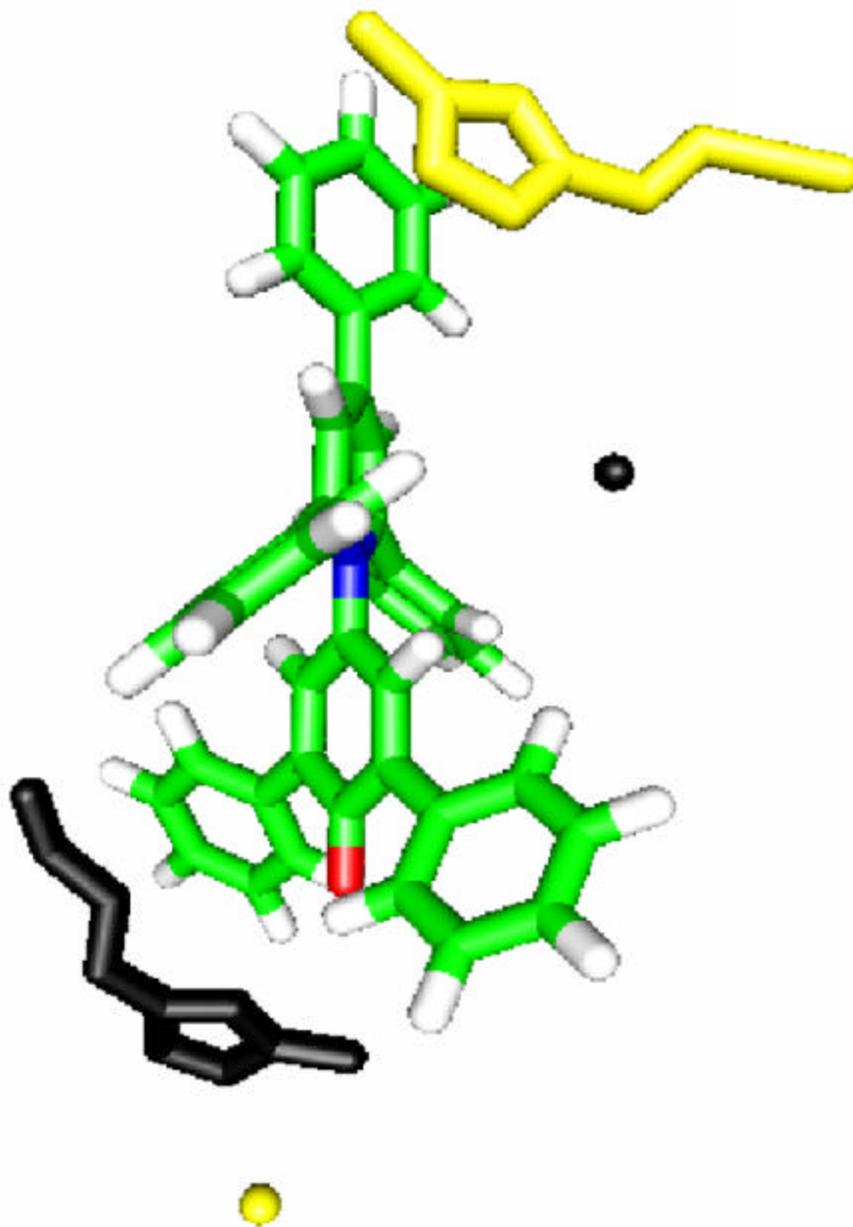
Z-Components of Extremal Betaine-Solvent Interactions

Z-Contribution Spectra of Extremal Ions
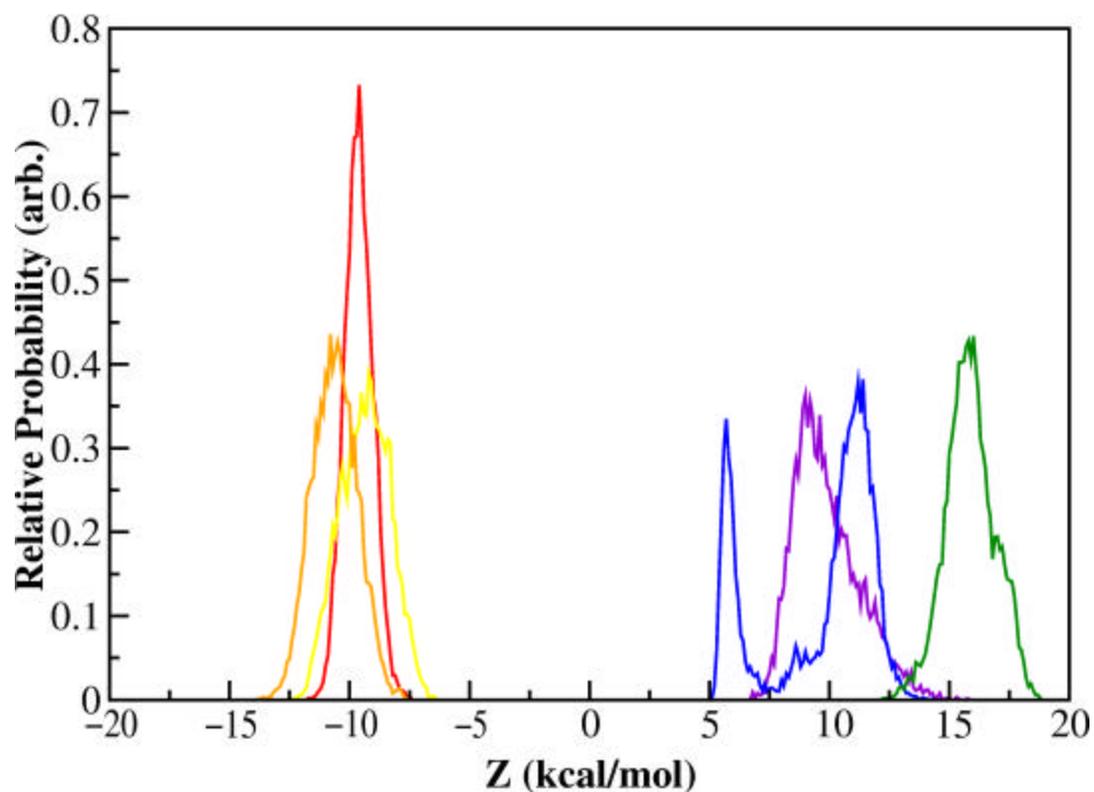
Spatial Distribution of Extremal Z-Contributors
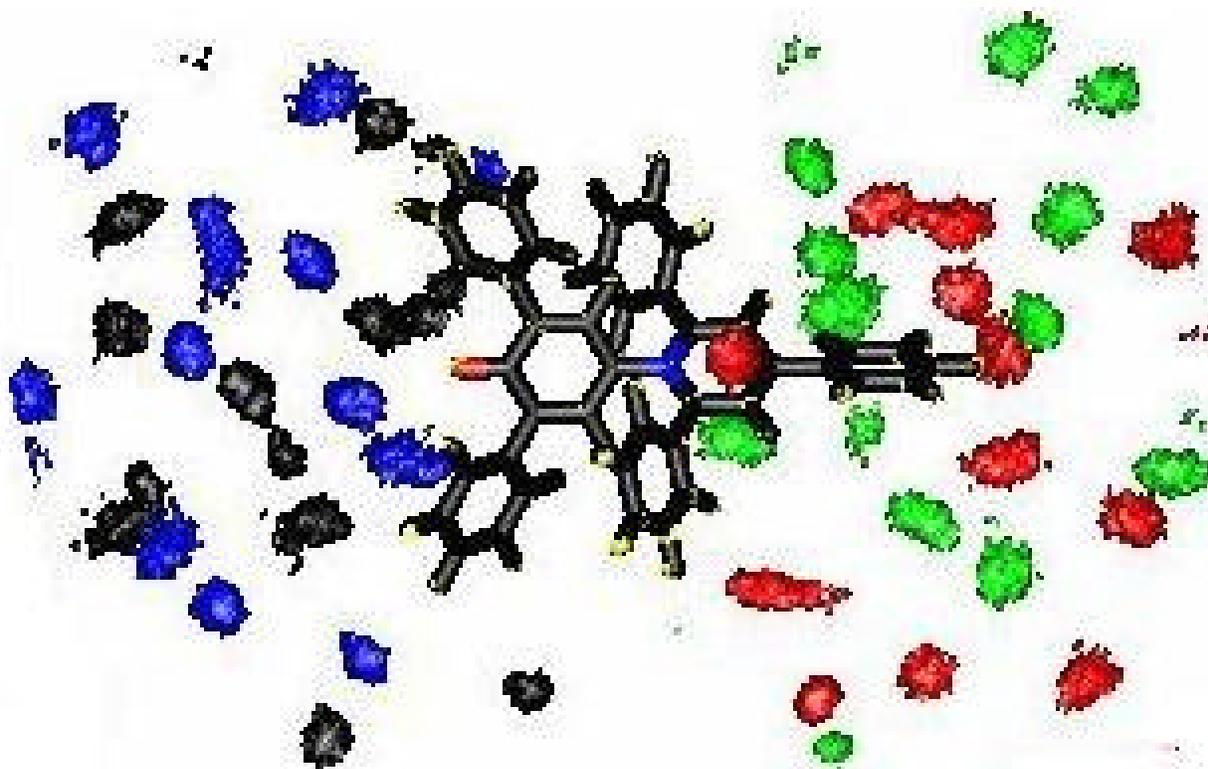
Contribution to Z as a Function of Solute-Solvent Distance

Average Magnitude of Z Contribution by Individual Ions as a Function of Solute−Solvent Distance

Contribution to Z as a Function of Solute-Solvent Distance
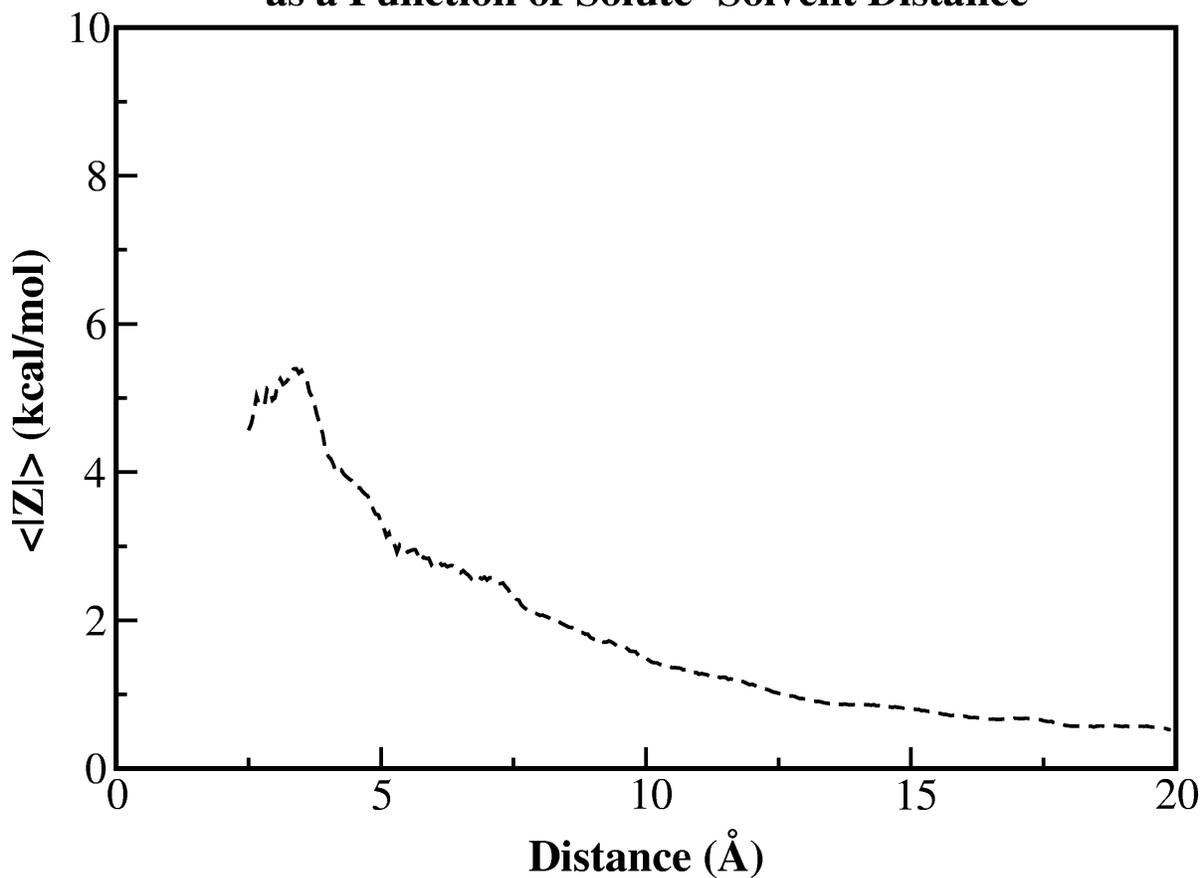
Contribution to Z as a Function of Solute−Solvent Distance
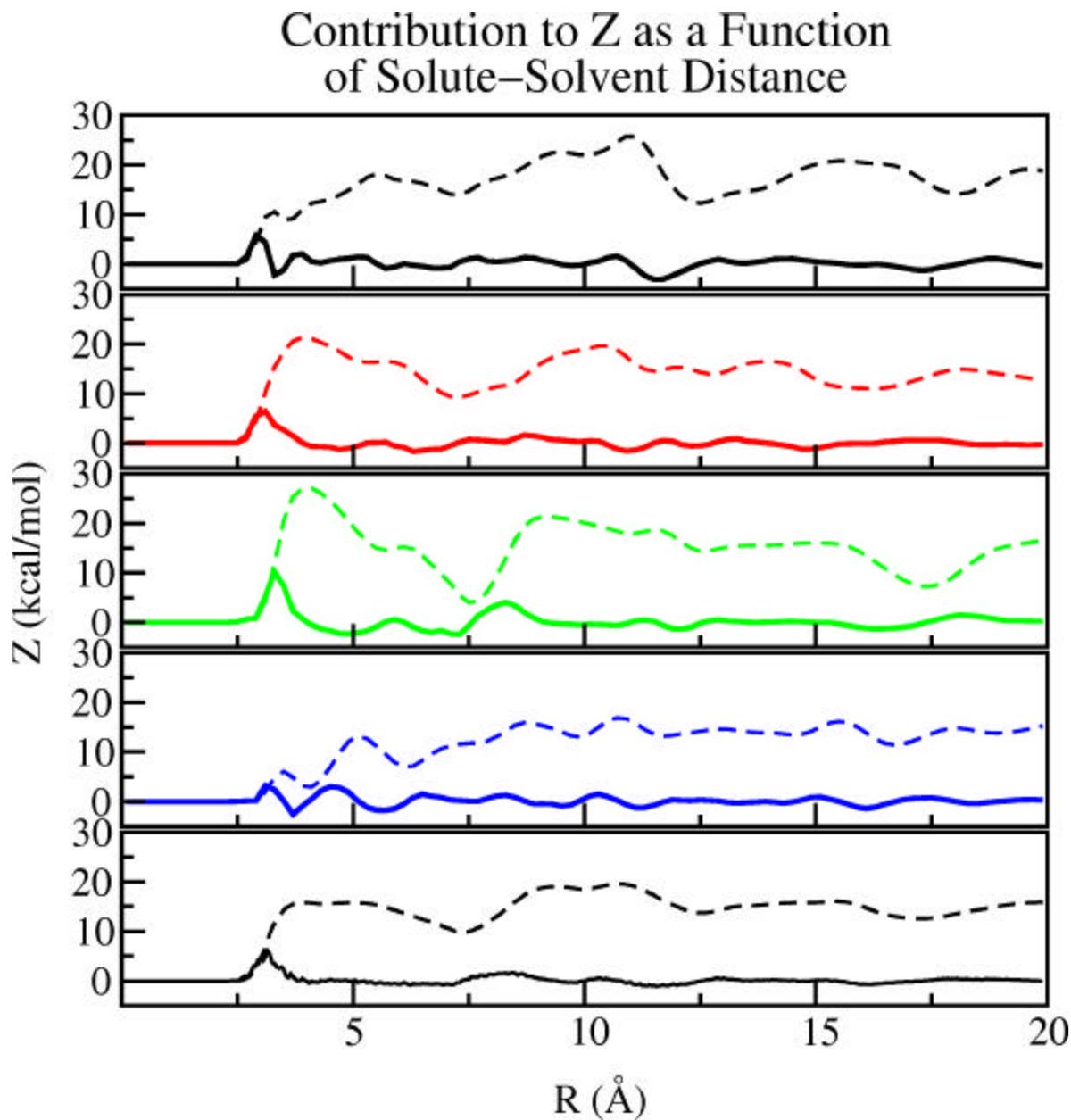
Nature of Polarity in RTILs

Hypothesis:

➢Large fraction of polarization due to reorganization of ions neighboring chromophore

➢Long-range contribution to polarization less significant
- •Individual interactions very strong
- •Collective solute-solvent interactions cancel out on average (statistical effect)

➢Concept of "solvation shell" applies to RTILs, but arises from different effects

Time-Resolved Fluorescence

➤ Fluorescence spectrum is difference between ground and excited state energies when solvent is equilibrated to the excited state configuration

➤ If system is excited by an ultrashort pulse, fluorescence spectrum changes in time until equilibrium is reached
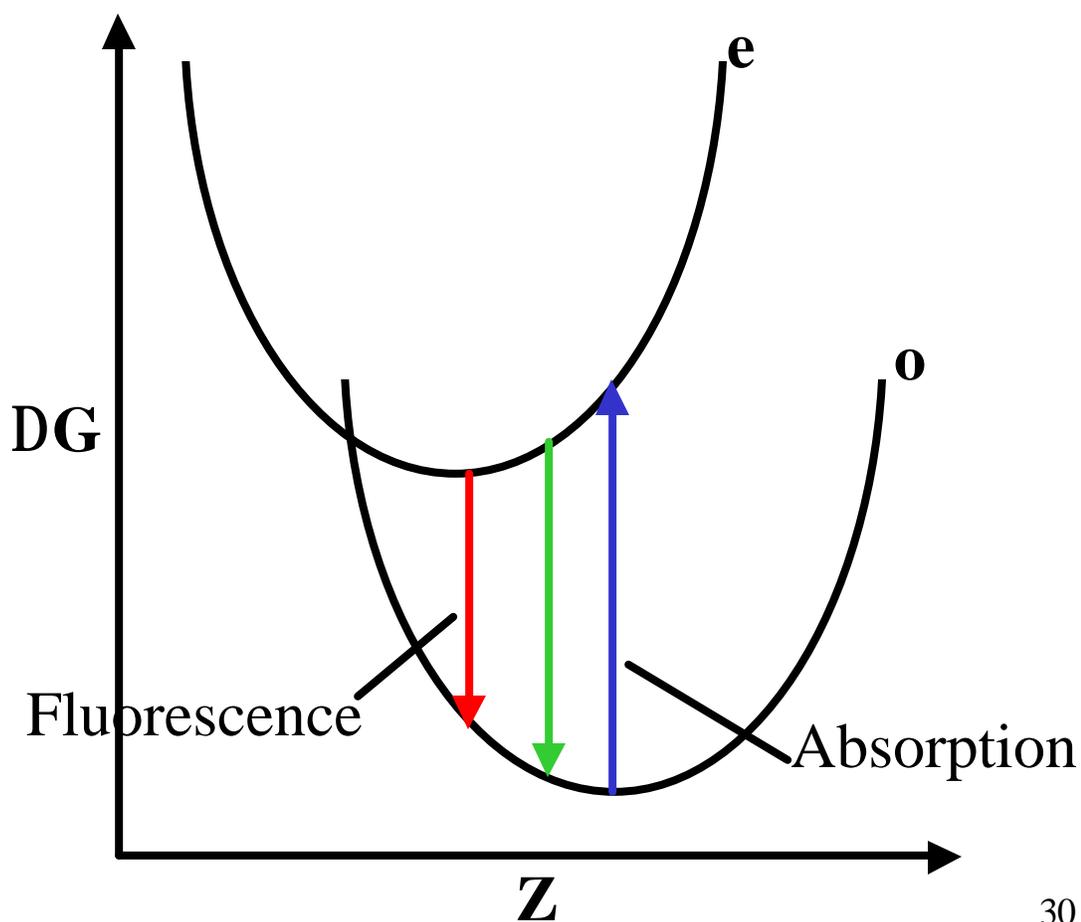
Time-Resolved Fluorescence in Molecular Liquids

➢Response occurs on two timescales

➢Timescales correspond roughly to rotational and translational motion of solvent
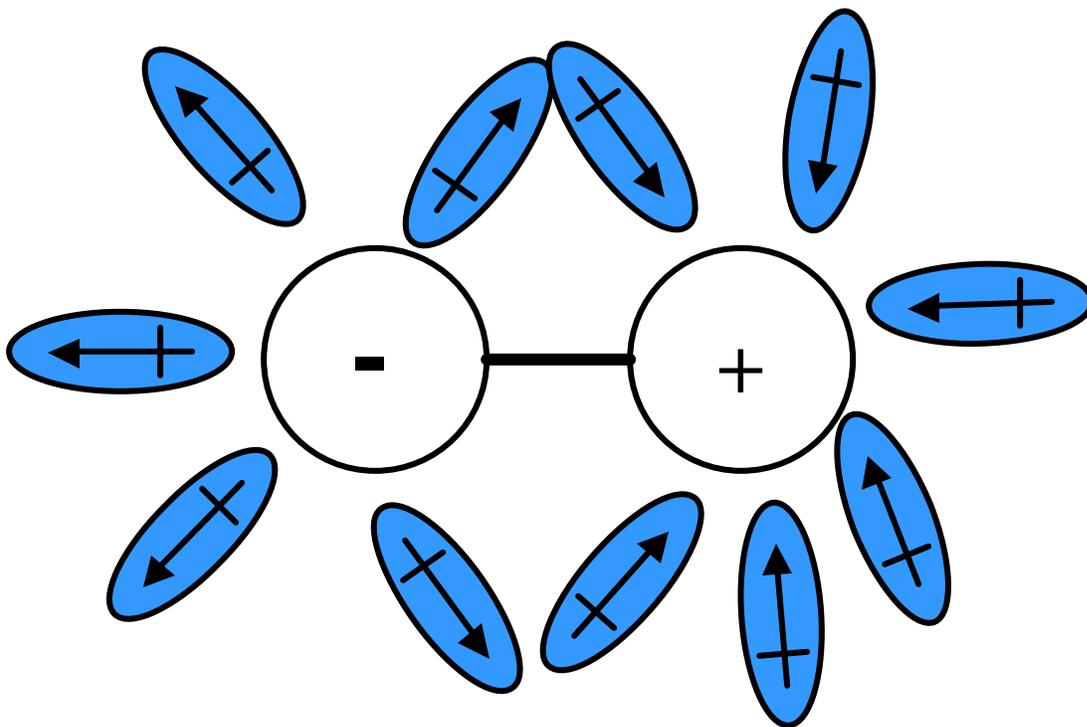
How does this work in Ionic Liquids?

Experimental Time-Resolved Fluorescence in Ionic Liquids

Results from Ingram *et al.* (Maroncelli group)

4-AP
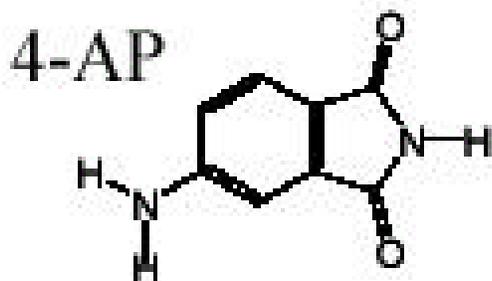
Studied t.r. fluorescence of 4-aminopthalimide in BMIM[PF$_6$]

0, 50, 100, 200 ps
.5, 1, 2, 5, 10 ns
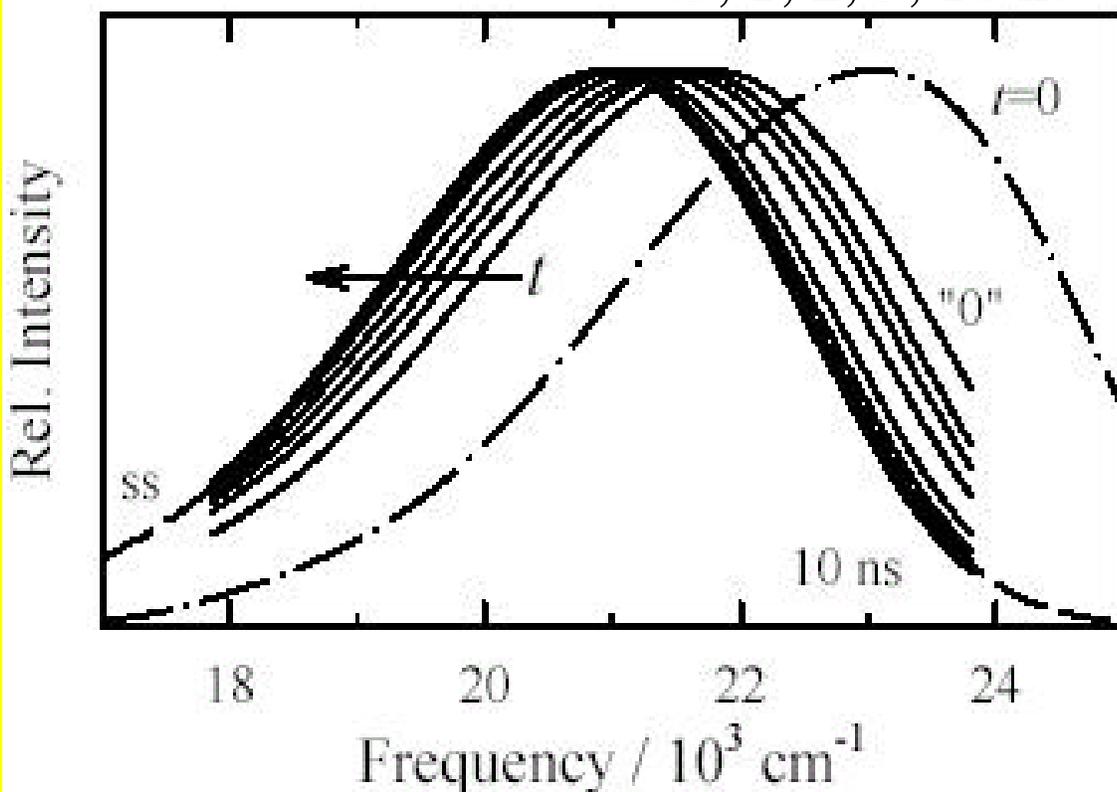
Experimental Observations

➢ Two timescales observed
➢ Widely separated (sub-picosecond vs. nanosecond)

Can get at solvent motion via simulation. (Caveat: Betaine-30 does not fluoresce)

Time-Resolved Fluorescence Data

Fluorescence Response for Four Trajectories
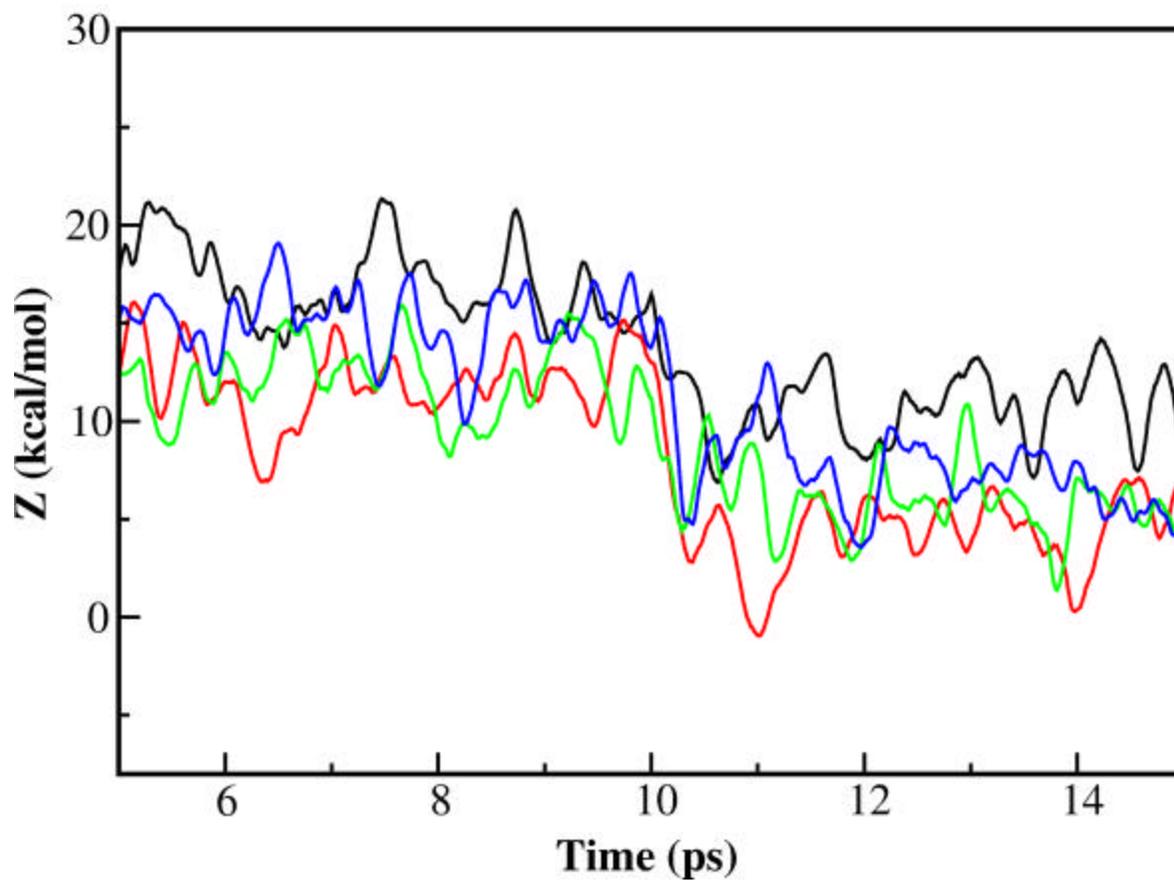
Time-Resolved Fluorescence Data

Fluorescence Response for Four Trajectories
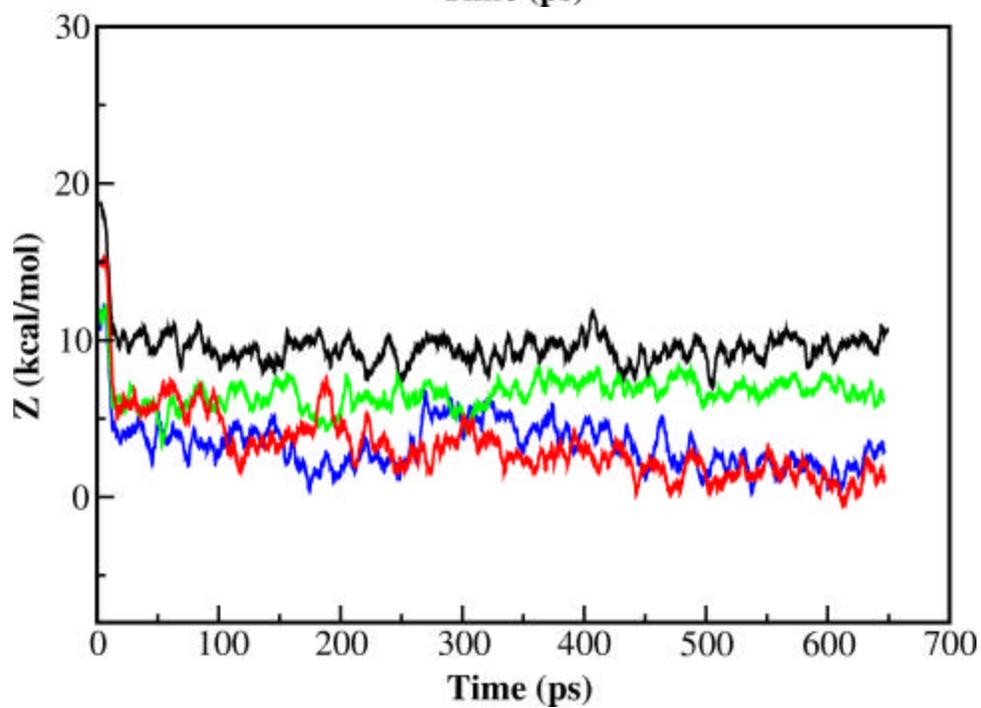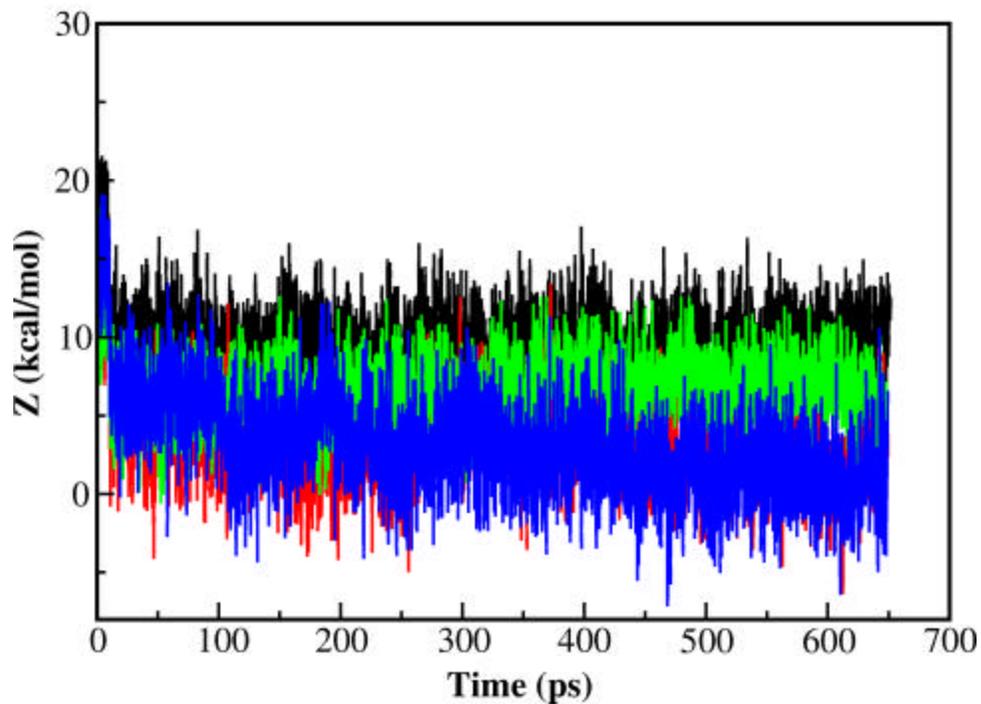
Calculated vs. Theoretical Decay Constants

Fit to Fluorescence Response
Experiment and Theory

Experimental Data from Ingram et al.
on 4−aminophthalimide (−50 kcal/mol)

Z (kcal/mol)

Time (ps)
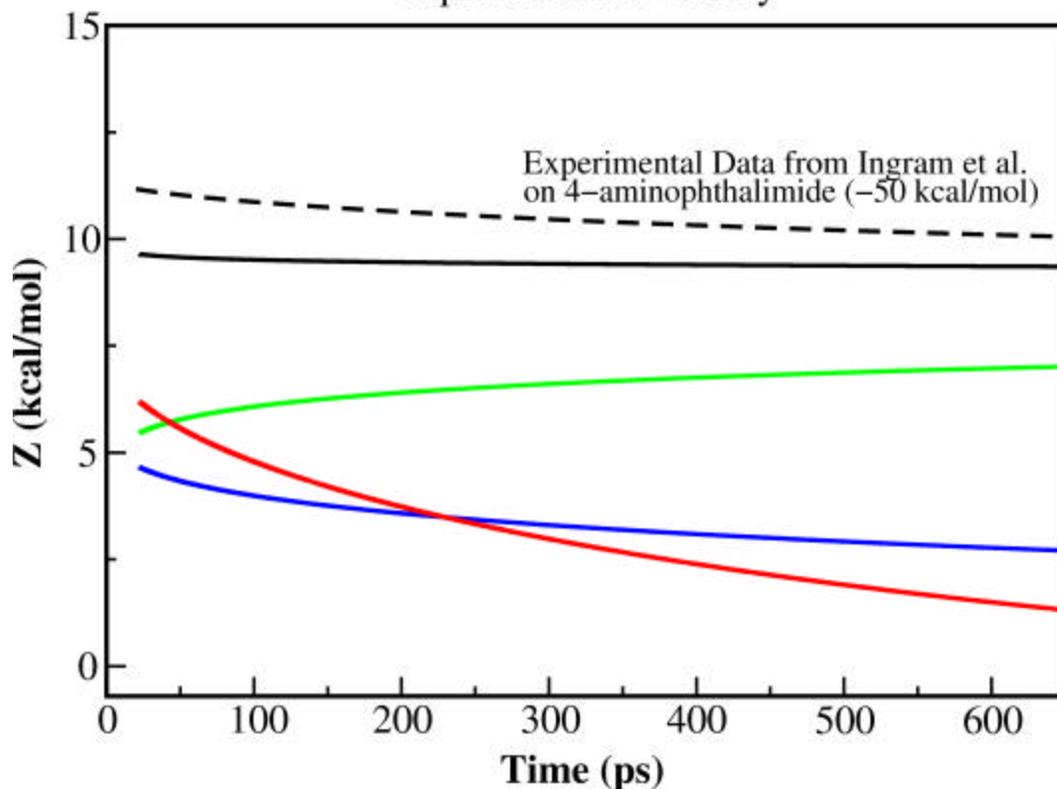
$$Z_{max}=Z_{inf} + A \exp[-(t/B)^c]$$

Nature of Time-Resolved Response

Hypothesis:

➢ Short-time response due to local motion of ions about chromophore

➢ Long-time response due to collective reorganization of solvent

- Involves relatively large distances
- Occurs slowly by weakly-biased random walk

Conclusions

➢ Solvation shell concept applies to RTILs, but arises from statistical cancellations at large distances

➢ Time-resolved fluorescence response consists of rapid response by inner shell, followed by slow diffusion of other ions (weakly driven by solute dipole)

Acknowledgements

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