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Simulation of the polarization response of room-temperature ionic liquids

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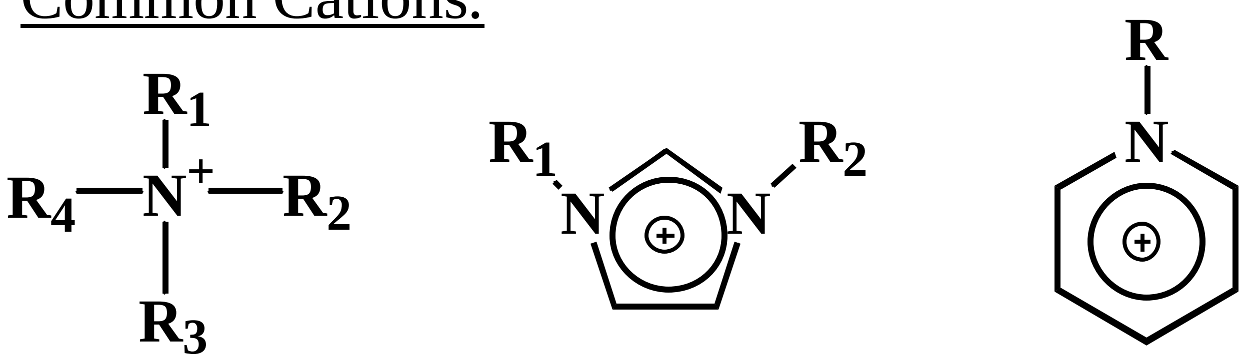
What are Room-Temperature Ionic Liquids?

- 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^- BF_4^- Cl^- 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

Synthesis:

- "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))

Separations and Analysis:

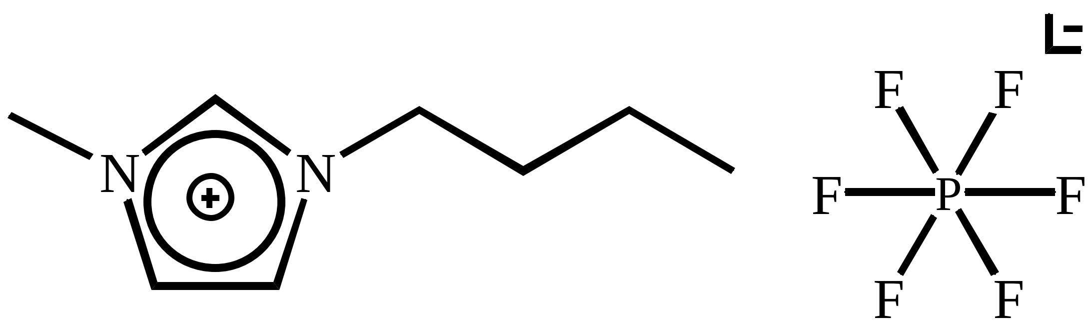
- Liquid-liquid extractions
  (simple, crown-ether, solvent-optimized)
- MALDI matrix for mass spectrometry
- Continuous loop bioreactor (membrane)

Electrochemistry:

- 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

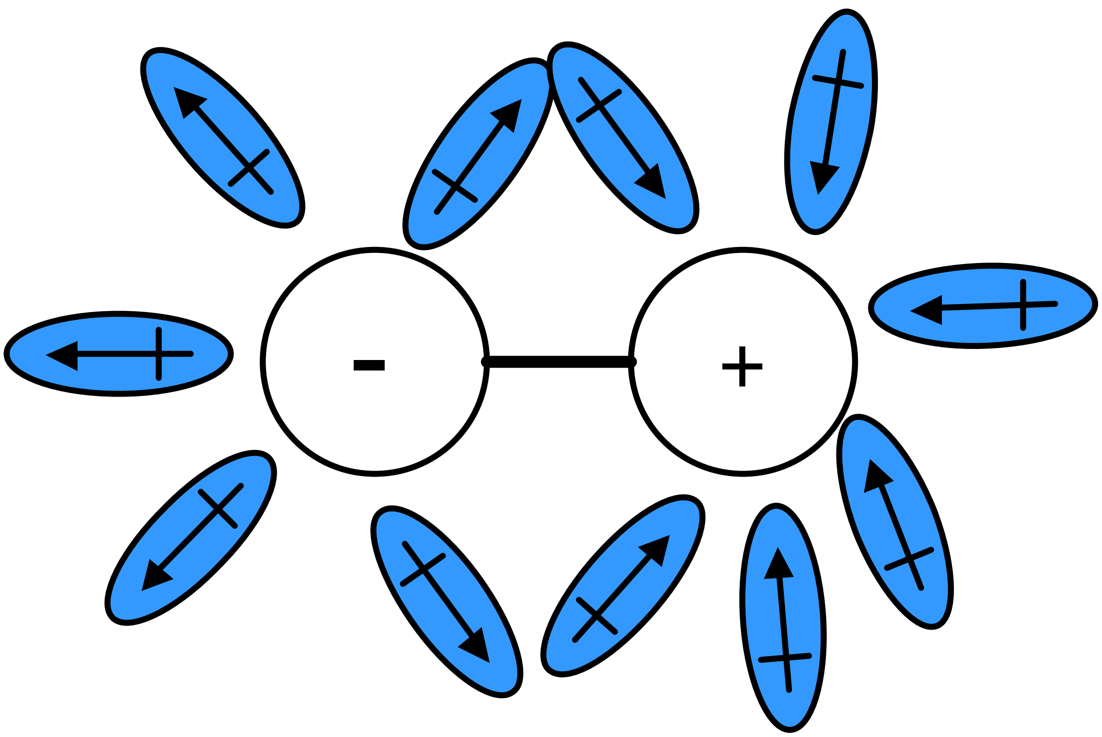
Identify which solute is most soluble in each solvent

Solute	Solvent
NaCl	Water
Phenol	1-propanol
Napthalene	Benzene
	BMIM[PF_6]

Mechanism of Solvation

Molecular Liquids:

- Specific interactions: Hydrogen-bonding
- Nonspecific interactions: Electrostatic effects

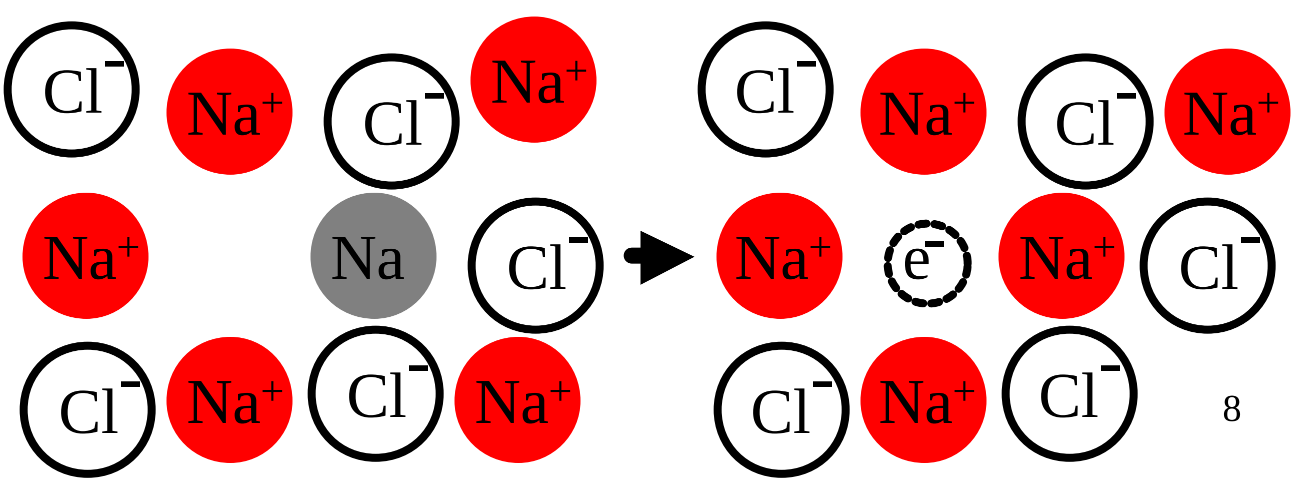


What can we say about RTILs?

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

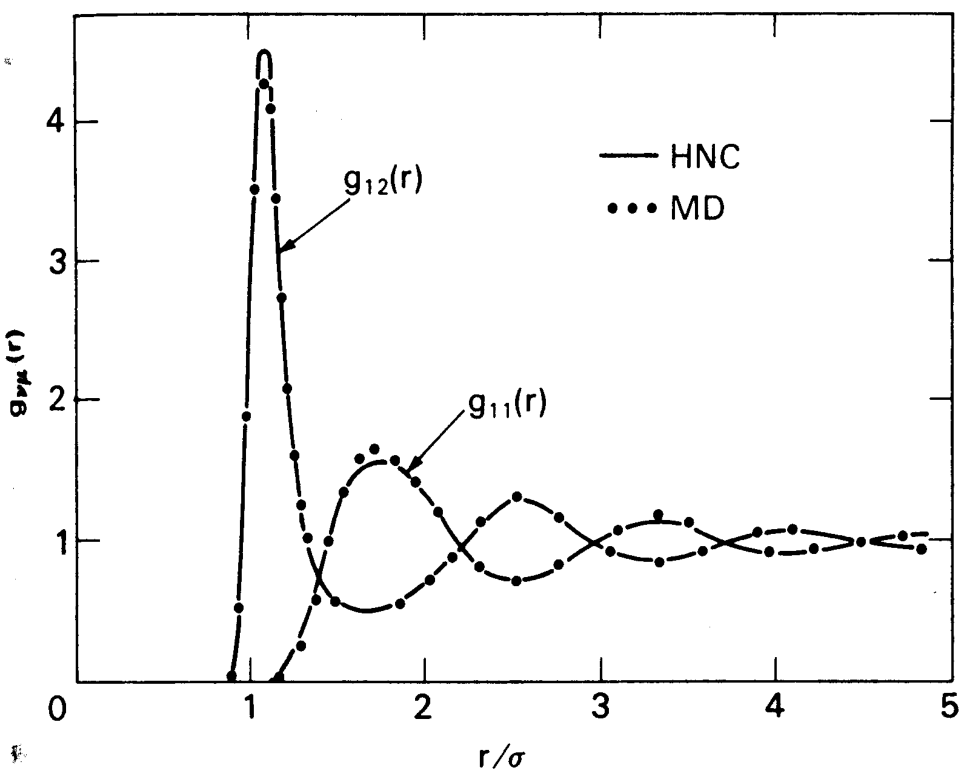
Spontaneous Ionization in a Metal-Fused Salt Solution



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

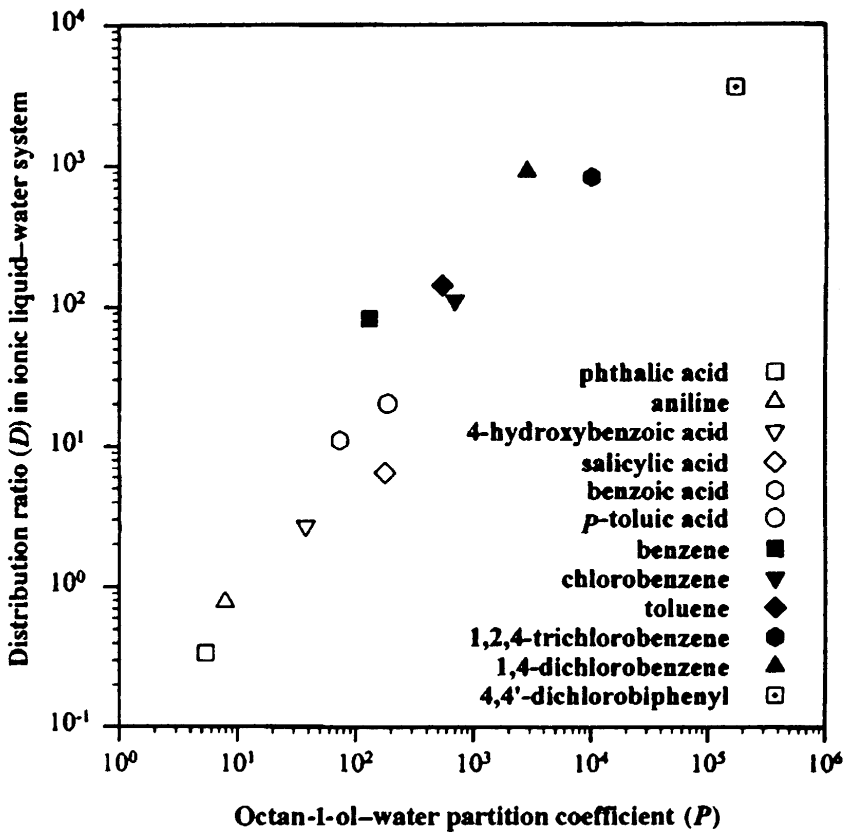
(From "Theory of Simple Liquids," Hansen&McDonald, Academic Press, London 1986)

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

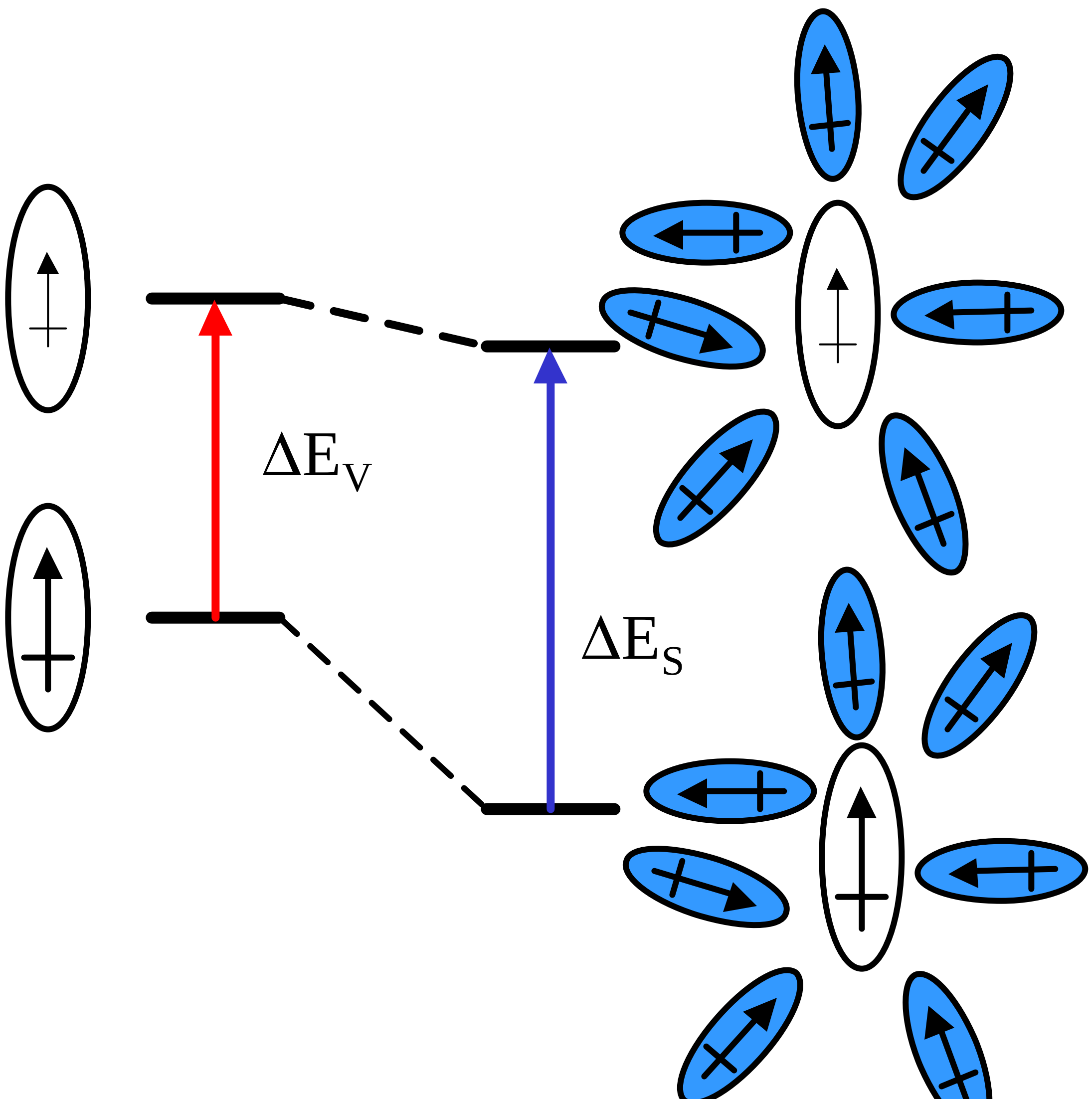


Comparison of partition coefficients for organic compounds in biphasic BMIM[PF_6]/H_2O and octan-1-ol/H_2O systems

(from Huddleston *et al.* Chem. Comm. 1765 (1998)

Solvatochromism

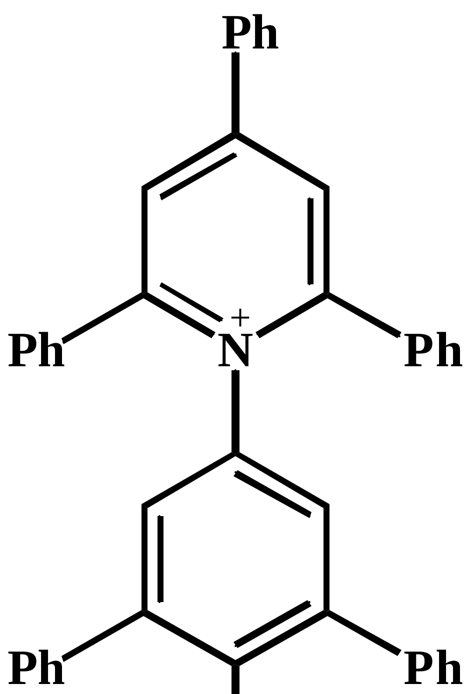
- Based on the difference in dipole moment between chromophore electronic states
- Polarity scales and linear free energy relationships built on specific molecules



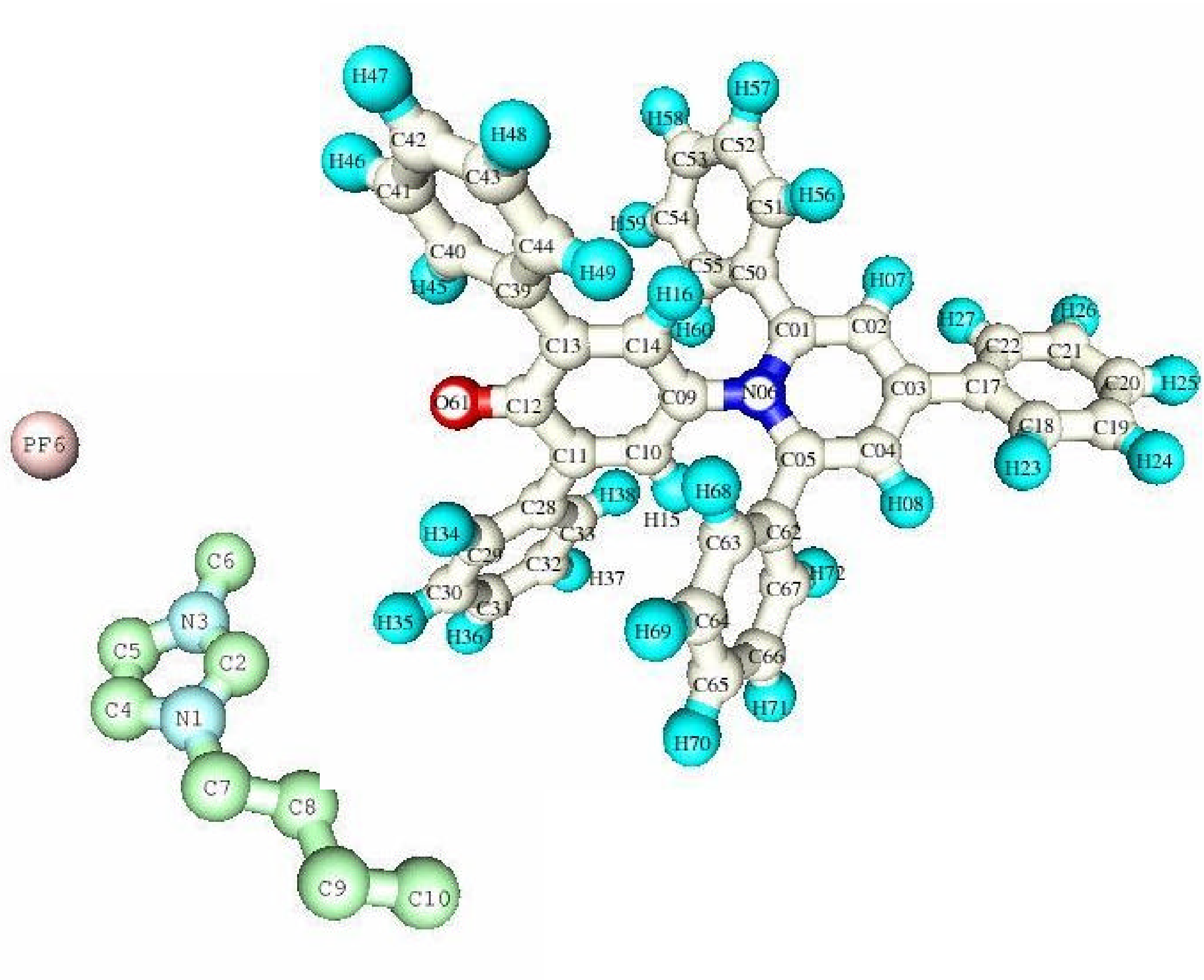
Solvent Polarity from Simulation

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

Simulate the solvatochromism of betaine-30 in BMIM[PF_6]



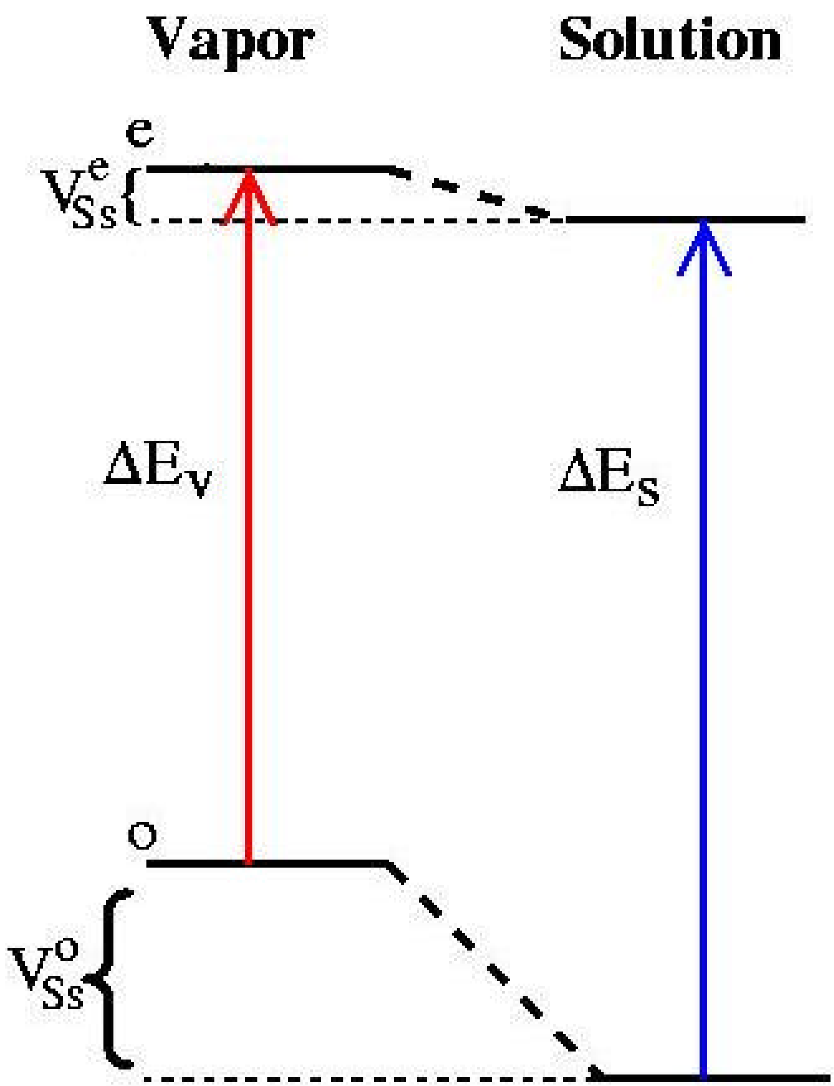
Solute and Solvent Structures



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
  - •United atom treatment of CH_n
- 200 ion pairs/1 betaine-30
- ~700 ps equilibration time
- NPT ensemble

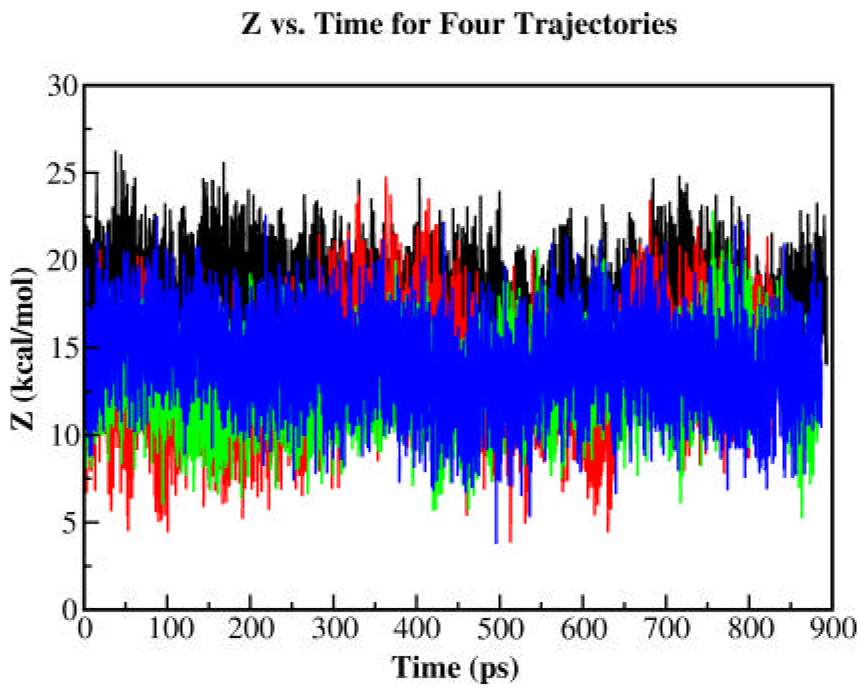
Calculation of the Absorption Spectrum

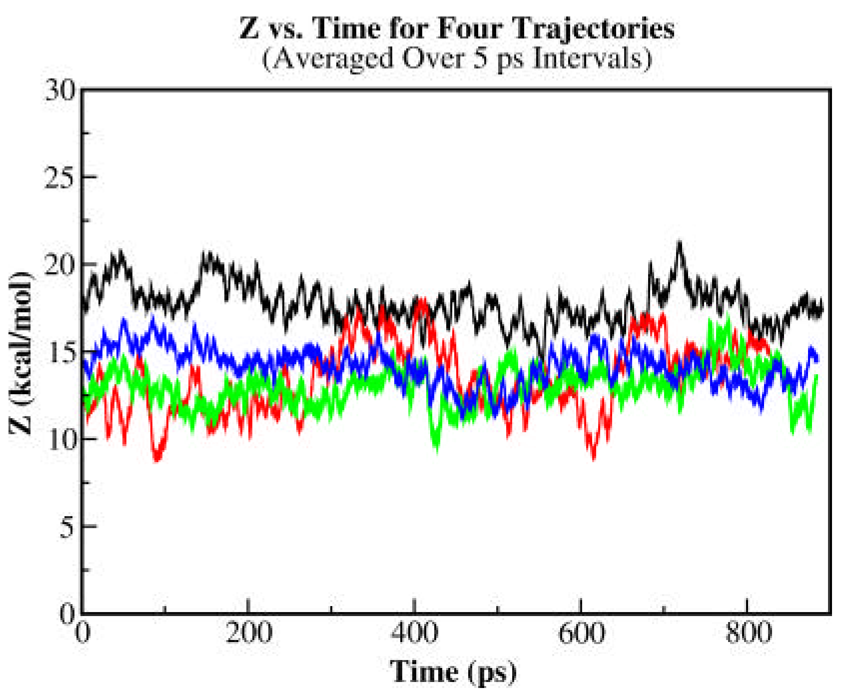


Difference in solute-solvent interaction energies for ground and excited states:

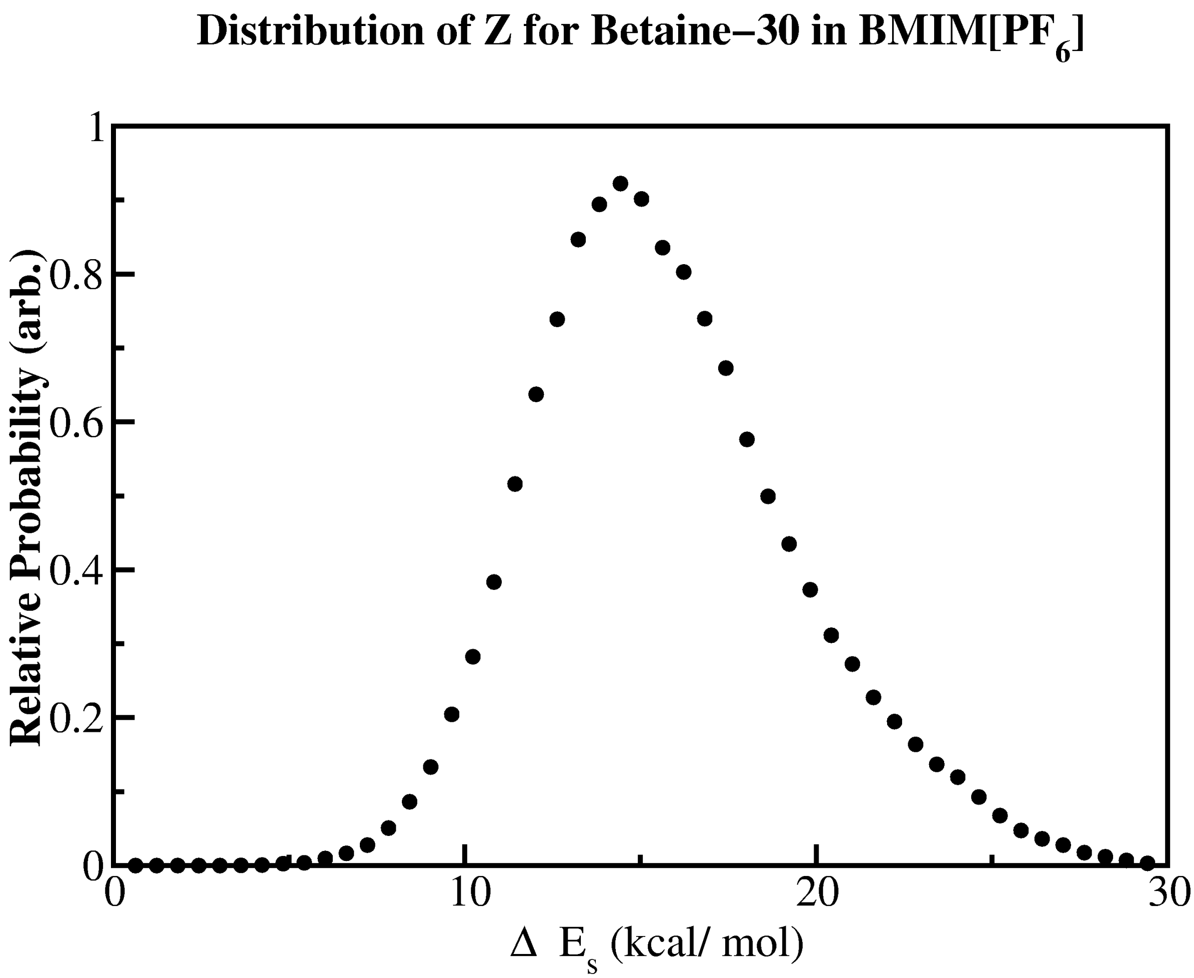
$$Z = \Delta E_s - \Delta E_v$$
$$= V_{Ss}^{e} - V_{Ss}^{o}$$

Time-Dependence of The Spectral Shift



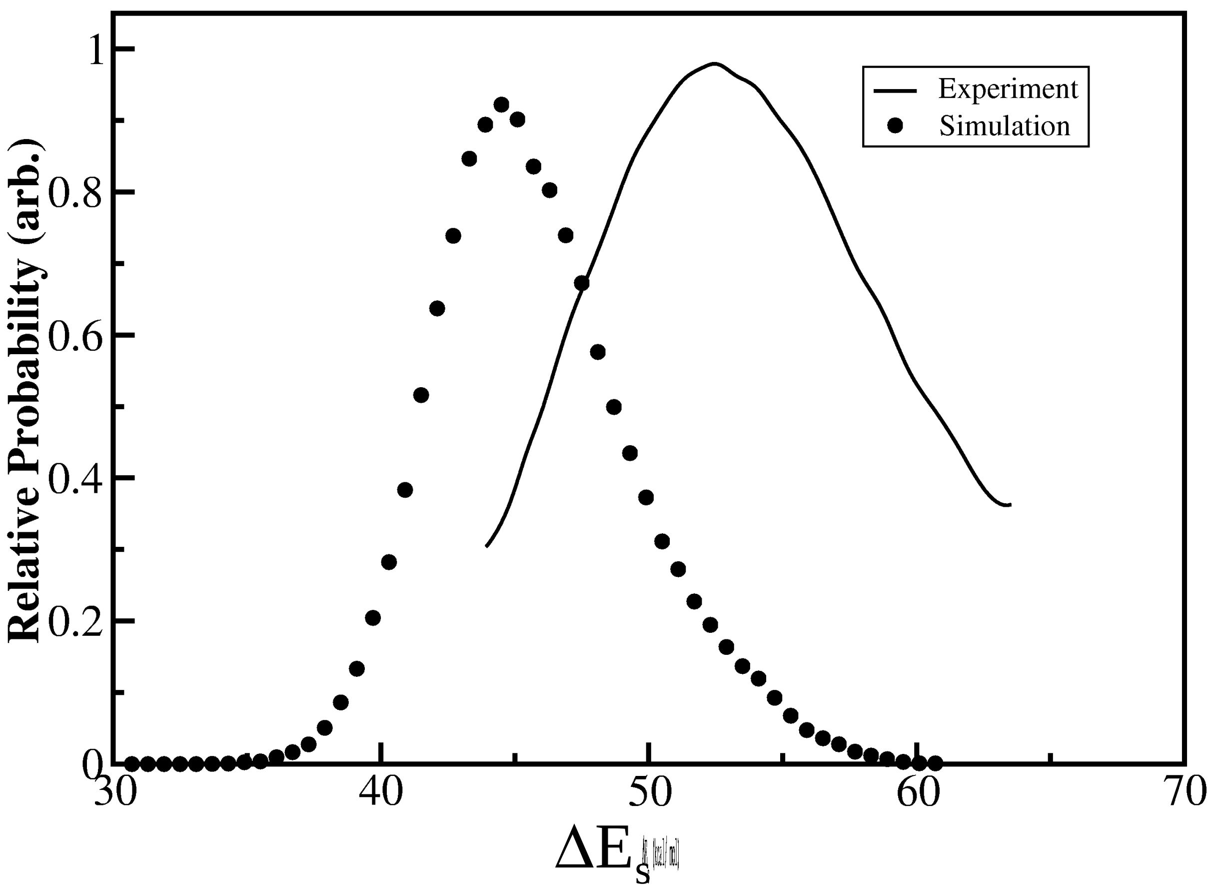


Time-Averaged Z-distribution



Calculated and Experimental Absorption Spectra

Absorption Spectrum of Betaine−30 in BMIM[PF_6]



Local Structure About Betaine-30 Oxygen Atom