LEAF ***BNL Laser-Electron Accelerator Facility***

Energy Applications of Ionic Liquids

James F. Wishart

Chemistry Department

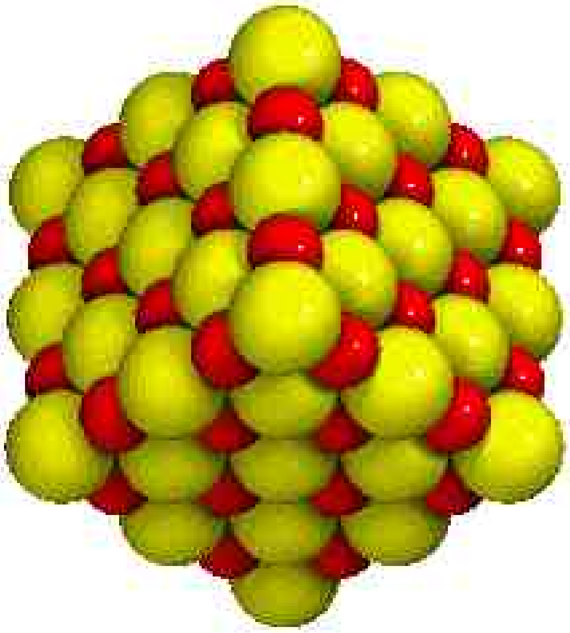
Brookhaven National Laboratory

U. S. Department of Energy
Basic Energy Sciences

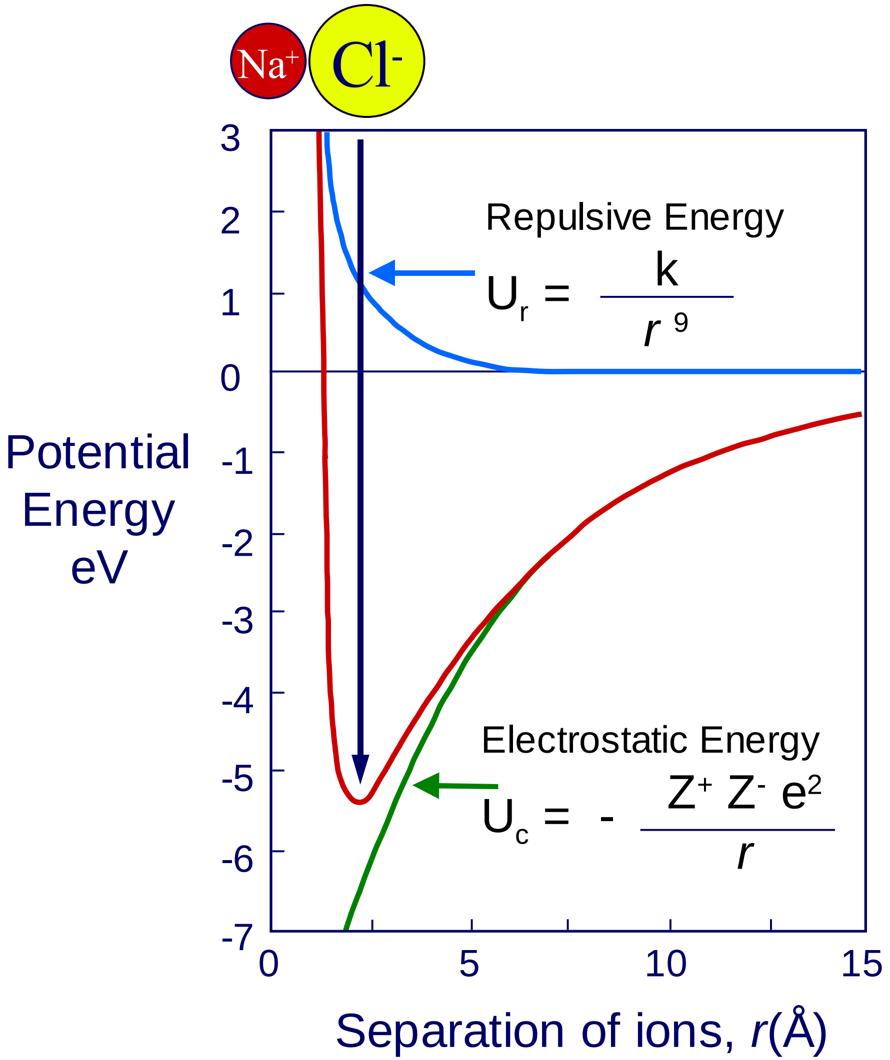
BROOKHAVEN
NATIONAL LABORATORY

Salts are held together by electrostatic forces

NaCl (melts at 801 ˚C)



Ionic lattice of Na^+ cations and Cl^- anions.



Ionic Liquids - Designing "Bad" Crystals

Pick ions to pack poorly.

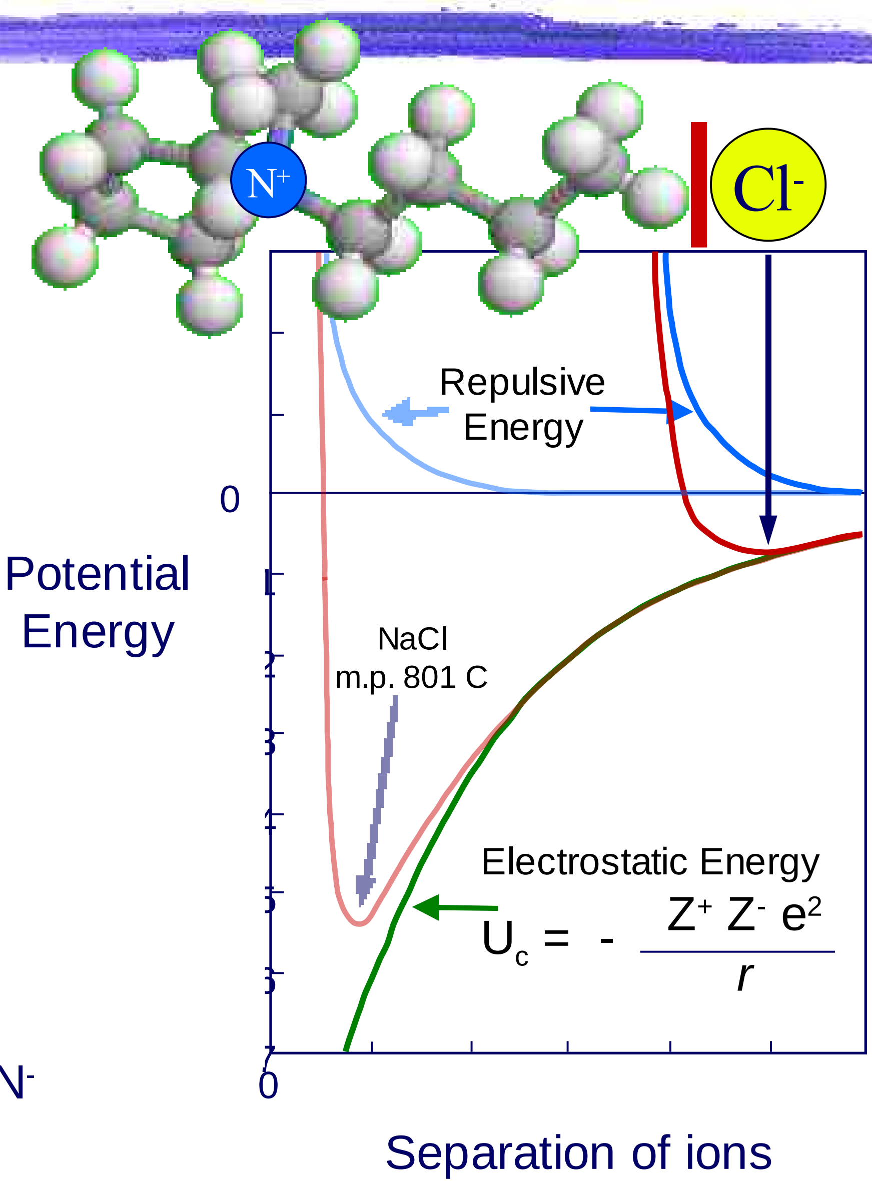
Disorder is our friend.

Size mismatch, bulky ions

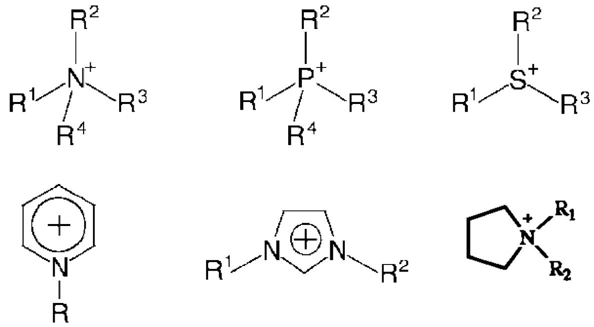
Low molecular symmetry

Rotational disorder ($R^1 \neq R^2$)

Mix-and-match as needed



Cations:



Anions:

BF_4^-, PF_6^-, NO_3^-, CF_3SO_3-, $(CF_3SO_2)_2N^-$

$CF_3CO_2^-$, $CH_3CO_2^-$, $CH_3SO_3^-$, $AlCl_4^-$

Ionic Liquids - Designing "Bad" Crystals

Pick ions to pack poorly.

Electrostatic attraction is still strong enough to make vapor pressure ~0.

If it can't evaporate, it can't burn.

Combine specific ions to give desired properties.

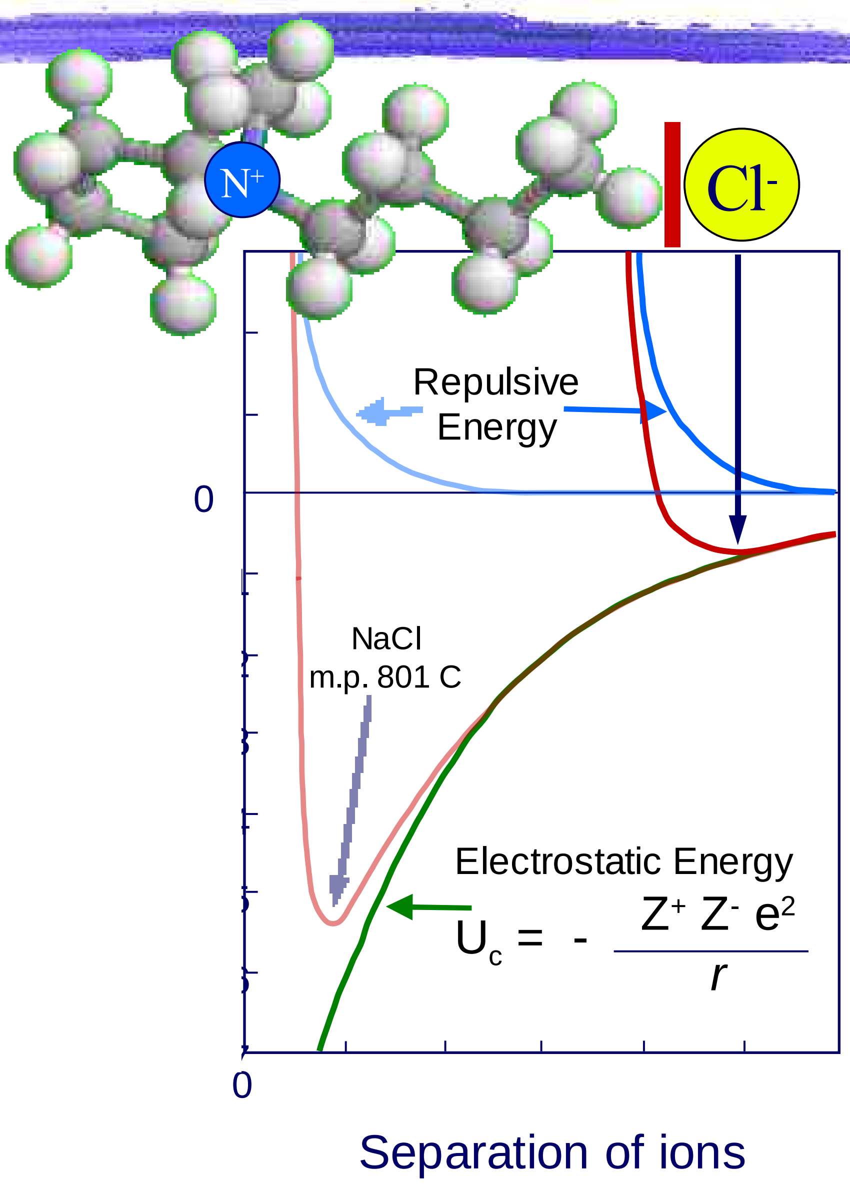
Control solubility of solids and liquids:

Phase separation (like oil and water).

Easy separation of products.

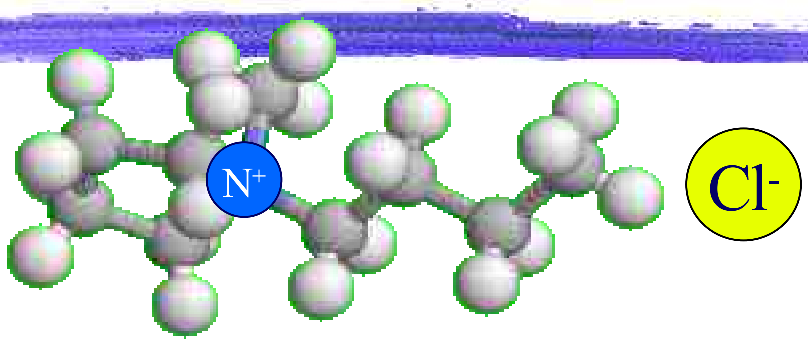
Make liquid easy to reuse/recycle.

- Inherently safer.
- More economical.
- Less environmentally burdensome.



Ionic Liquids - "Extreme Solvents"

Pick ions to pack poorly.



Electrostatic attraction is still strong enough to make vapor pressure ~0.

If it can't evaporate, it can't burn.

Combine specific ions to give desired properties.

Control solubility of solids and liquids:

Phase separation (like oil and water).

Easy separation of products.

Make liquid easy to reuse/recycle.

- Inherently safer.
- More economical.
- Less environmentally burdensome.

Ionic liquid properties lie at the edge of or beyond those of normal liquids.

Electrochemical range (≤ 6 V)
Liquidus range (≤ 250° C)
Vapor pressure (very low)
Viscosity (higher than normal)
Dissolve polar, non-polar, biopolymers
Intrinsically conductive

Ionic liquids provide a path to new science and technology.

Ionic Liquids are Finding Industrial Uses

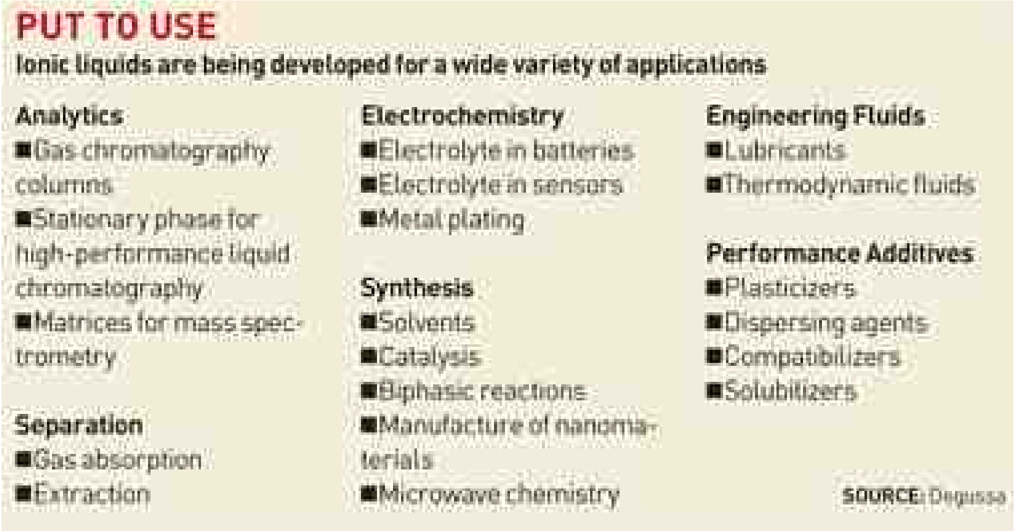
Photo: BASF

Cover Story

Chemical and Engineering News
April 24, 2006, pp. 15-21

Out Of The Ivory Tower

Ionic liquids are starting to leave academic labs and find their way into a wide variety of industrial applications



PUT TO USE

Ionic liquids are being developed for a wide variety of applications

Analytics
- Gas chromatography columns
- Stationary phase for high-performance liquid chromatography
- Matrices for mass spectrometry

Separation
- Gas absorption
- Extraction

Electrochemistry
- Electrolyte in batteries
- Electrolyte in sensors
- Metal plating

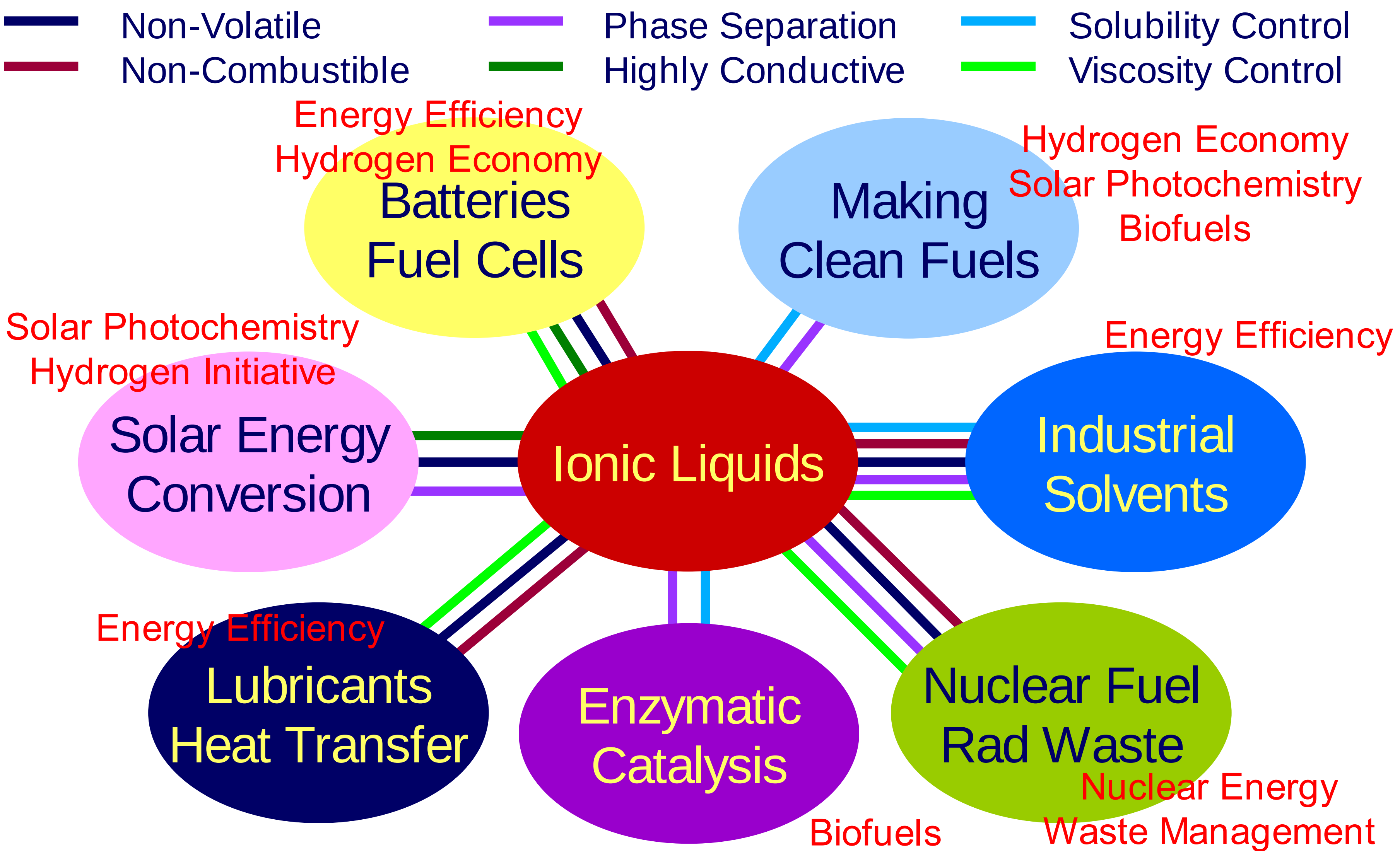
Synthesis
- Solvents
- Catalysis
- Biphasic reactions
- Manufacture of nanomaterials
- Microwave chemistry

Engineering Fluids
- Lubricants
- Thermodynamic fluids

Performance Additives
- Plasticizers
- Dispersing agents
- Compatibilizers
- Solubilizers

SOURCE: Degussa

Ionic Liquids and Energy
Designer Solvents for a Sustainable World



Non-Volatile
Non-Combustible
Phase Separation
Highly Conductive
Solubility Control
Viscosity Control

Energy Efficiency
Hydrogen Economy
Batteries
Fuel Cells

Making
Clean Fuels
Hydrogen Economy
Solar Photochemistry
Biofuels

Solar Photochemistry
Hydrogen Initiative
Solar Energy
Conversion

Ionic Liquids

Energy Efficiency
Industrial
Solvents

Energy Efficiency
Lubricants
Heat Transfer

Enzymatic
Catalysis
Biofuels

Nuclear Fuel
Rad Waste
Nuclear Energy
Waste Management

Wishart, Energy & Env. Sci. 10.1039/b906273d

Ionic liquids and energy production

- Solar Photoconversion
  - Photoelectrochemical cells (electrolytes and redox carriers)
- Solar Thermal Conversion
  - Heat transfer and storage fluids
- Biofuel production
  - Breakdown/dissolution of recalcitrant lignocellulosic feedstocks
- Fossil fuel desulfurization and extraction of aromatics
- Advanced nuclear fuel cycle
  - Separations by extraction and electrodeposition

Wishart, Energy & Env. Sci. 10.1039/b906273d

Ionic liquids and energy storage

Batteries

- Li Intercalation types.
- Li metal batteries – inertness is still a quest.

Supercapacitors

- Essential technology for buffering electrical loads in regenerative systems (hybrid vehicles, machinery).
- High stability and capacity are possible with ILs.

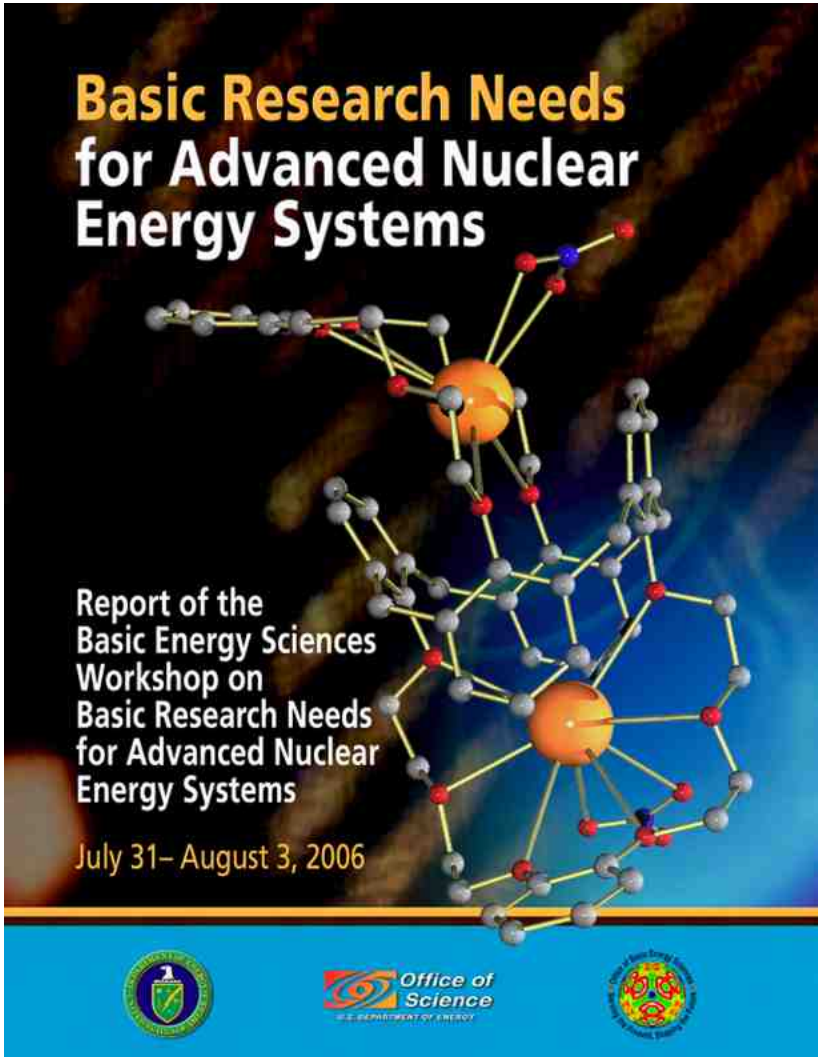
Wishart, Energy & Env. Sci. 10.1039/b906273d

Ionic liquids and efficient energy utilization

- Fuel cells
  - Protic ILs as proton carriers
- Gas separation (purification, H_2 production, carbon capture
  - Supported ionic liquid membranes
- Electroactive polymers and ILs
  - Electrochromic windows or displays
  - Electromechanical actuators/energy harvesters
  - Sensors
- Catalytic processes
  - Phase transfer catalysis (gas/liquid, liquid/liquid)

Wishart, Energy & Env. Sci. 10.1039/b906273d

DOE Workshop on Basic Research for ANES



Basic Research Needs for Advanced Nuclear Energy Systems

Report of the Basic Energy Sciences Workshop on Basic Research Needs for Advanced Nuclear Energy Systems

July 31– August 3, 2006

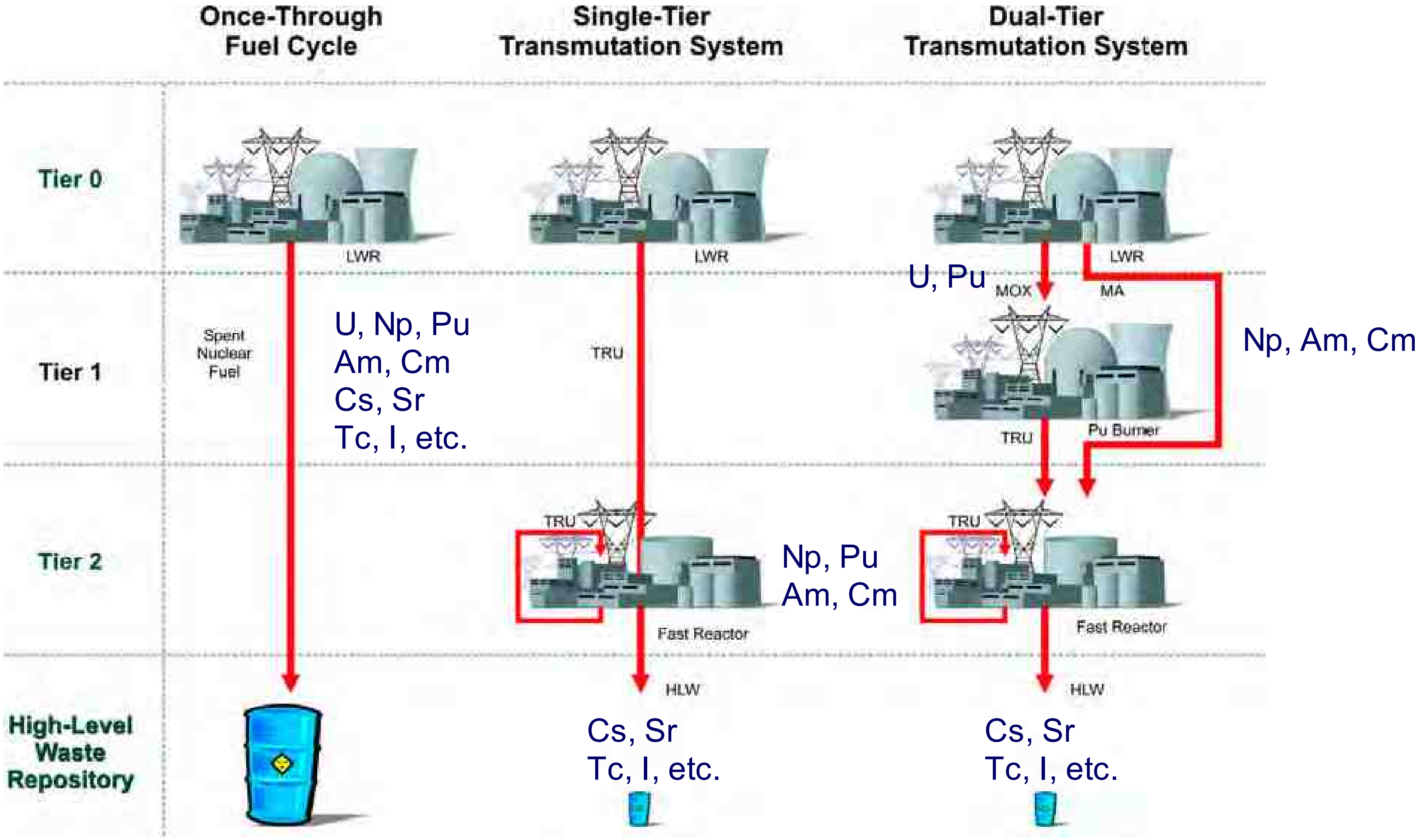
235 invited experts from:
- 31 universities
- 11 national laboratories
- 6 industries
- 3 government agencies
- 11 foreign countries

Panels:
- Materials under Extreme Conditions
- Chemistry under Extreme Conditions
- Separations Science
- Advanced Actinide Fuels
- Advanced Waste Forms
- Predictive Modeling and Simulation
- Cross-cutting themes

http://www.sc.doe.gov/bes/reports/list.html

Advanced Nuclear Energy Systems

Multi-tier reactor systems extract more energy and reduce the high-level waste burden.



U, Np, Pu
Am, Cm
Cs, Sr
Tc, I, etc.

Np, Am, Cm

Np, Pu
Am, Cm

Cs, Sr
Tc, I, etc.

Cs, Sr
Tc, I, etc.

Ionic Liquids and Nuclear Processing

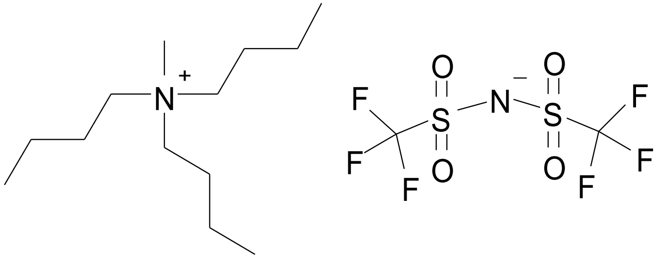
Ionic liquids could be used to process nuclear fuel, waste, and radiological contamination.

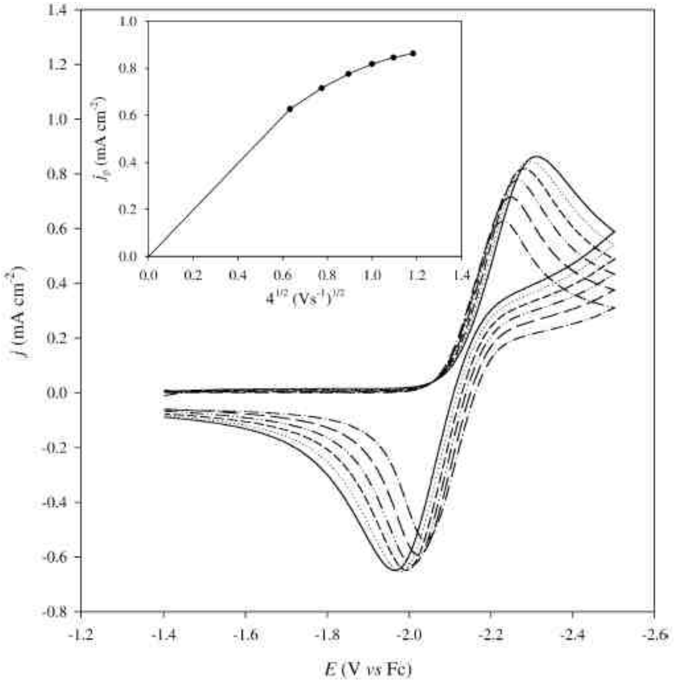
Beneficial features:

Solvent properties and substrate ligation can be controlled by design
Low volatility
Combustion resistance
High conductivity
Wide electrochemical windows.

“Electrodeposition of cesium at mercury electrodes in the tri-1-butyl-methyl-ammonium bis((trifluoromethyl)sulfonyl)imide RTIL”

P.-Y. Chen, C. L. Hussey, Electrochimica Acta *49*, 5125 (2004)

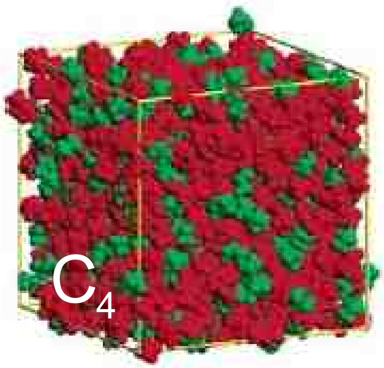




28 mM Cs^+ in $Bu_3MeN^+NTf_2^-$ at a HMDE as a function of scan rate.

Solvation and Separation Properties of ILs

Mixing oil (non-polar) and water (polar)



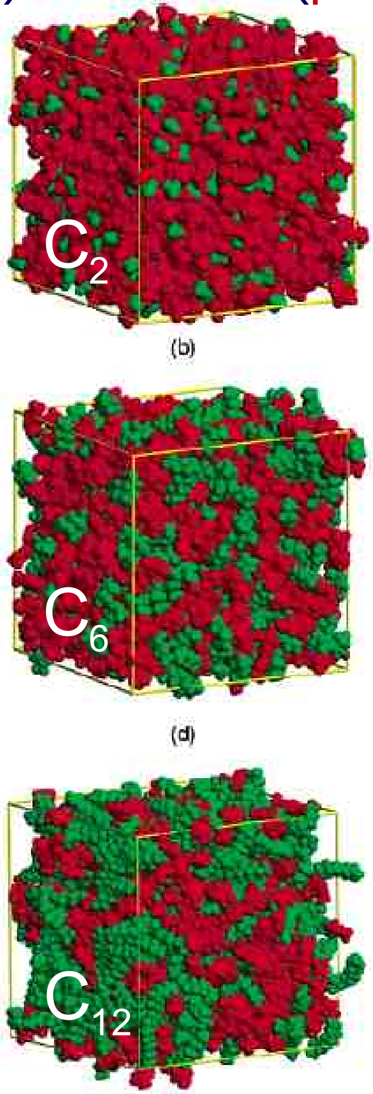


Figure 1: Nonaqueous solvents may derive many of their interesting properties from organization of the solvent molecules, as suggested by computational studies of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. Polar regions of the solvent are shown in red, while nonpolar regions are shown in green.

Changing anion changes selectivity

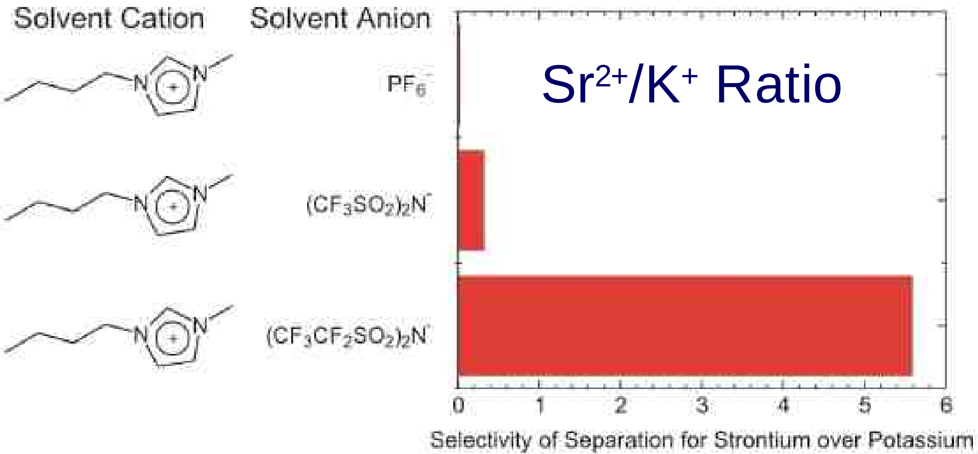


Figure 2: Designing a non-aqueous solvent for strontium separation. By changing the anion of the room-temperature ionic liquid used as the solvent, strontium extraction by a crown ether can be made almost 200 times more selective

Ionic Liquids for Reprocessing

Non-flammable, highly conductive and wide electrochemical windows

Actinides and Fission Products in ILs

Chemical speciation - structures and formulas

Oxidation and reduction chemistry - oxidation states

Solubilities of materials in ionic liquids

Extraction - separating one element from the others

Plating out by electrodeposition

Effects of radiation on ionic liquids?

Room-temperature ionic liquids: new solvents for *f*-element separations and associated solution chemistry

Ann E. Visser and Robin D. Rogers*

Journal of Solid State Chemistry 171 (2003) 109–113

J|A|C|S ARTICLES

Mechanisms of Metal Ion Transfer into Room-Temperature Ionic Liquids: The Role of Anion Exchange

Mark P. Jensen, John Neuefeind, James V. Beitz, S. Skanthakumar, and L. Soderholm

Uranyl Coordination Environment in Hydrophobic Ionic Liquids: An in Situ Investigation

(EXAFS)

Ann E. Visser,[†] Mark P. Jensen,[*,‡] Ivan Laszak,[‡] Kenneth L. Nash,[‡] Gregory R. Choppin,[§] and Robin D. Rogers[*,†]

Inorg. Chem. 2003, *42*, 2197

Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids[†‡]

Communication

Mark L. Dietz,* Julie A. Dzielawa, Ivan Laszak, Blake A. Young§ and Mark P. Jensen

Green Chemistry, 2003, *5*, 682

Synergistic effects in the facilitated transfer of metal ions into room-temperature ionic liquids[†‡]

Dominique C. Stepinski, Mark P. Jensen, Julie A. Dzielawa and Mark L. Dietz*

Green Chemistry, 2005, *7*, 151

Uranyl and Strontium Salt Solvation in Room-Temperature Ionic Liquids. A Molecular Dynamics Investigation

Alain Chaumont, Etienne Engler, and Georges Wipff

Inorg. Chem. 2003, *42*, 5348

Precipitation of a Dioxouranium(VI) Species from a Room Temperature Ionic Liquid Medium

Antonia E. Bradley,[†] Justine E. Hatter,[†] Mark Nieuwenhuyzen,[†] William R. Pitner,[*,†] Kenneth R. Seddon,[§] and Robert C. Thied[‖]

Inorg. Chem. 2002, *41*, 1692

PCCP

Formation of lanthanide phosphates in molten salts and evaluation for nuclear waste treatment

Vladimir A. Volkovich,[†a] Trevor R. Griffiths*[b] and Robert C. Thied[c]

Phys. Chem. Chem. Phys., 2003, *5*, 5053–5060

GC

An investigation of the radiochemical stability of ionic liquids

Donald Allen,[a] Graham Baston,[b] Antonia E. Bradley,[c] Tony Gorman,[a] Andy Haile,[d] Ian Hamblett,[e] Justine E. Hatter,[d] Matthew J. F. Healey,[c] Brian Hodgson,[a] Robert Lewin,[d] Kevin V. Lovell,[b] Bill Newton,[f] William R. Pitner,[c] David W. Rooney,[c] David Sanders,[c] Kenneth R. Seddon,*[c] Howard E. Sims[b] and Robert C. Thied[d]

Green Chemistry, 2002, 4, 152–158

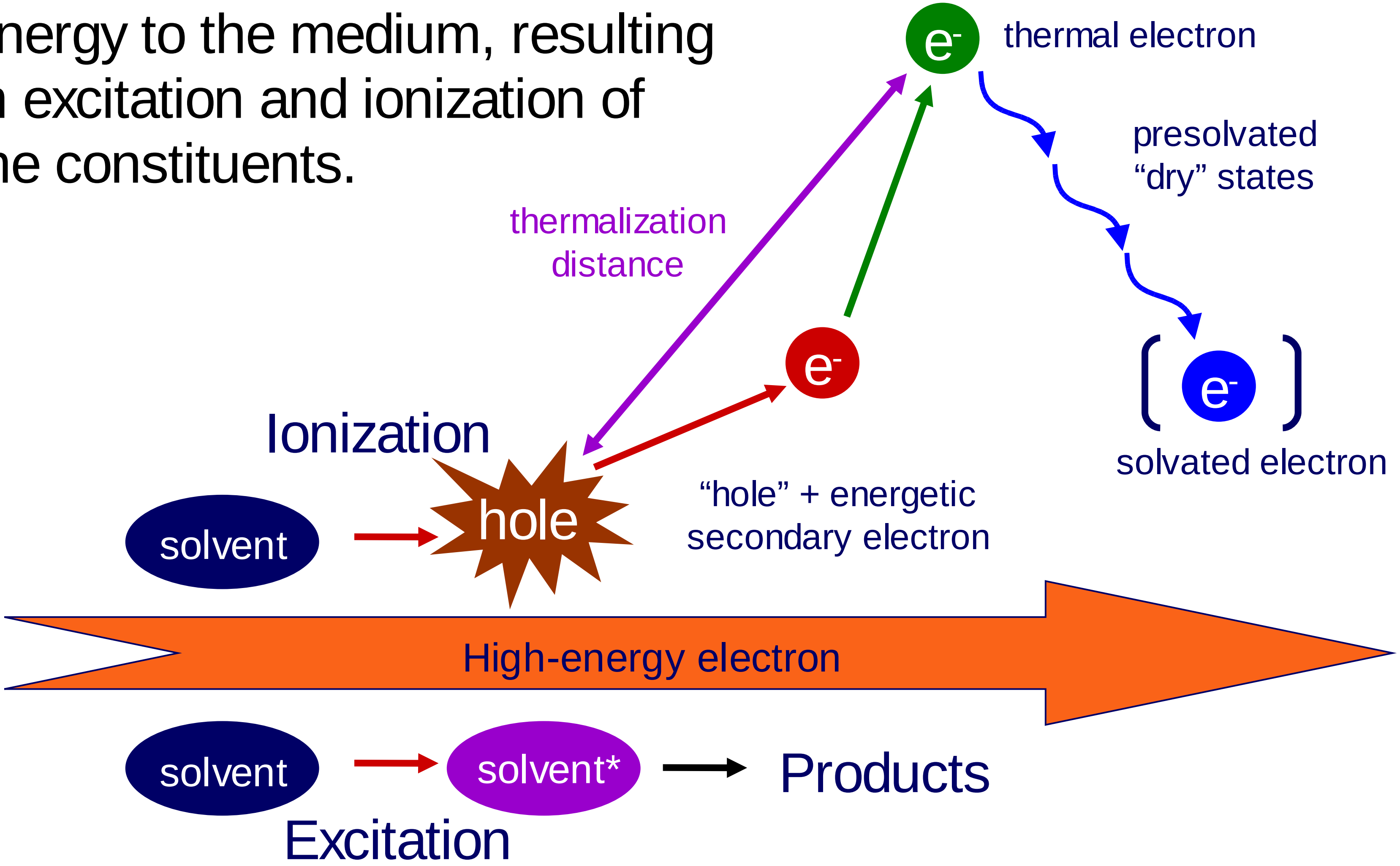
Electrodeposition of cesium at mercury electrodes in the tri-1-butylmethylammonium bis((trifluoromethyl)sulfonyl)imide room-temperature ionic liquid

Po-Yu Chen, Charles L. Hussey*[,1]

Electrochimica Acta 2004, *49*, 5125

Initial Events in Radiolysis

High-energy electrons transfer energy to the medium, resulting in excitation and ionization of the constituents.



e^- thermal electron

presolvated
“dry” states

thermalization
distance

e^-

e^-

solvated electron

Ionization

solvent

hole

“hole” + energetic
secondary electron

High-energy electron

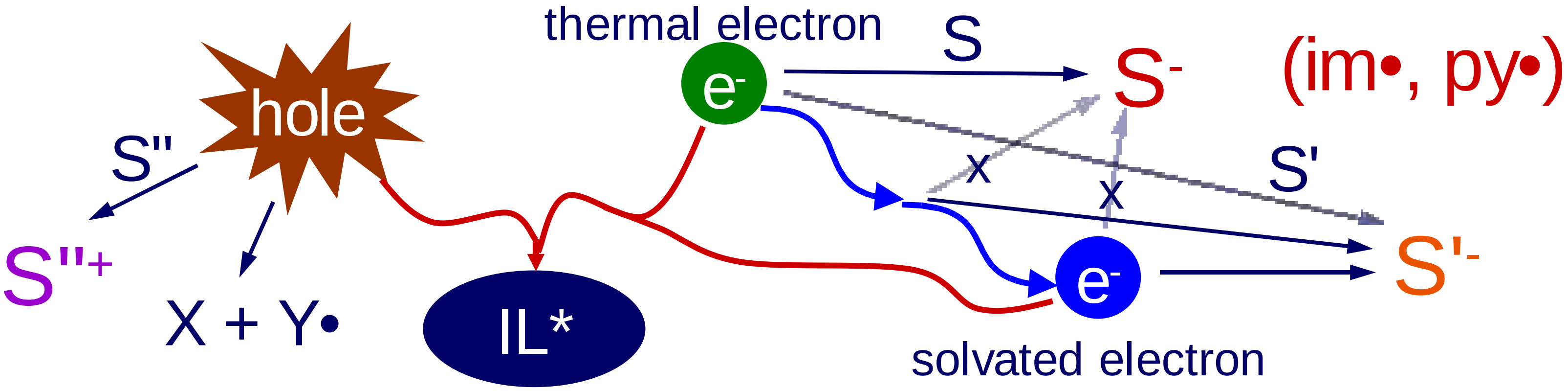
solvent

solvent*

Products

Excitation

Early Reactions in Radiolysis



thermal electron

e^-

S

S^-

(im•, py•)

hole

S''

S''^+

X + Y•

IL*

X

X

S'

e^-

S'^-

solvated electron

Early reactions define radiation damage pathways

Recombination of hole and electron

hole + e^- → IL or IL*

Dissociation (bond breakage)

hole → fragments (X + Y•)

Scavenging by solutes (or IL cations)

e^- + S or C^+ → S^- or C•

hole + S → $hole^-$ + S^+

We want to understand and control the reaction pathways to reduce net radiation damage and to control TRU and FP metal ion oxidation states for optimal separations.

Ionic Liquid Radiolysis

Ionic liquids will undergo radiolysis when used for nuclear processing.

What happens when ILs are irradiated?

- We must understand the primary radiation chemistry of ionic liquids.
- Effects of ionic liquid composition on:
  - The primary species produced by radiolysis (identity and yields).
    - Electron species, hole(s), reduced cations (Im•, Py•)
    - Spectroscopic and thermodynamic properties
  - Reactivity of primary species in neat solvent and with solutes.
  - Energetic transients: pre-solvated ("dry") electron reactivity and relaxation.

How can we use it?

Can the reactivity of primary species be exploited to achieve:

- Maximum radiation stability to prevent degradation and lowered efficiency

  or

- A high yield of specific products to assist the separations process?

Integrated research program on ionic liquids-based separations systems

Identify ionic liquid radiolysis products and understand how they interfere with separations. With that comprehension, create more stable ionic liquid sepatations systems. Control and direct the damage.

Radiation chemistry

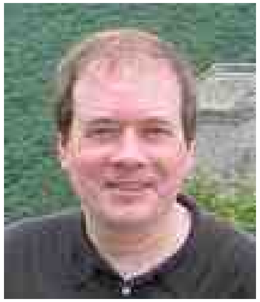
Jim Wishart
Brookhaven

Ilya Shkrob (and son)
Argonne

Supported by U.S. DOE

In cooperation with
CEA Saclay
(Baldacchino, Renault, Le Caër)
and CEA Marcoule (Moisy)

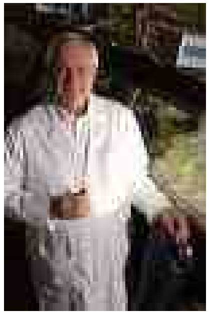
Separations chemistry



Mark Dietz
U. Wisconsin-Milwaukee

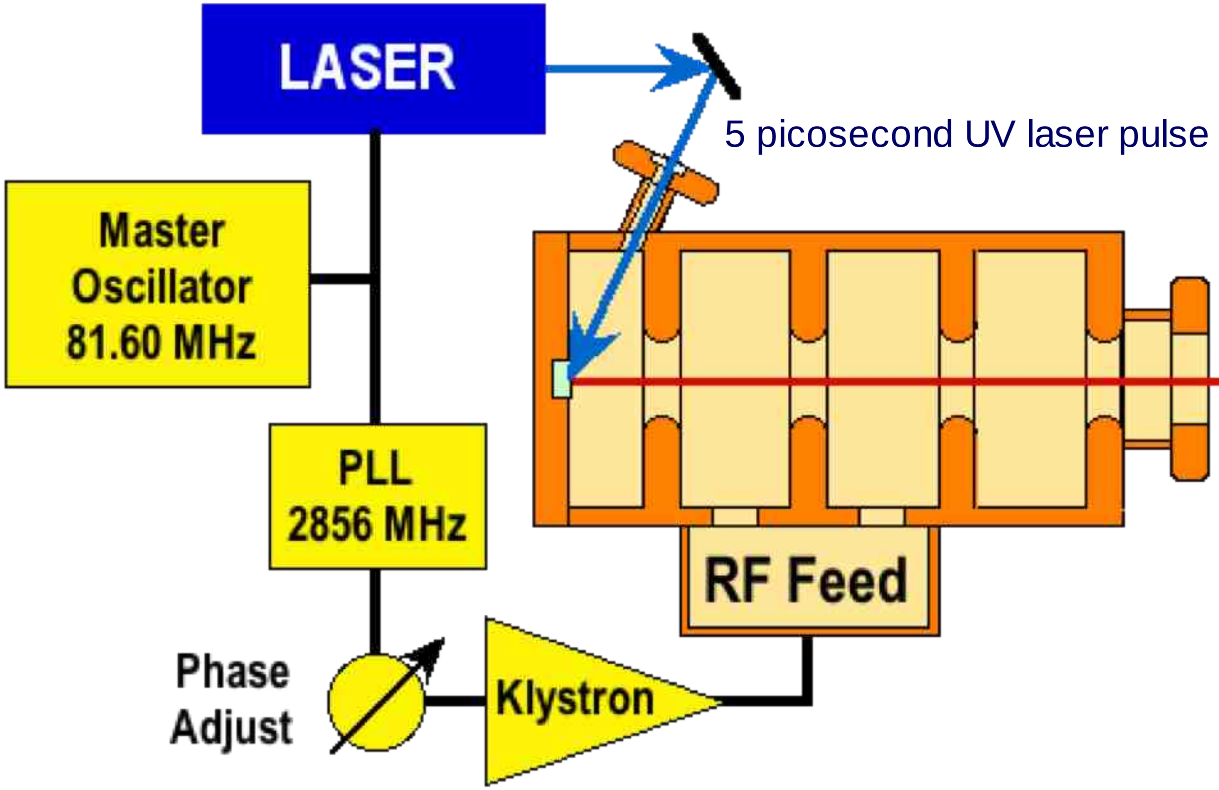
Sheng Dai
ORNL

Huimin Luo
ORNL



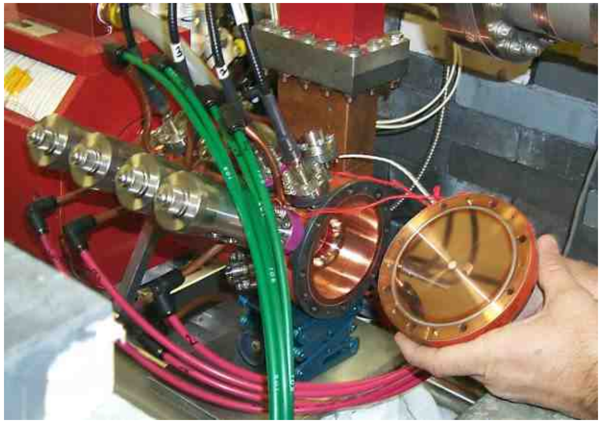
Chuck Hussey
U. Mississippi

Photocathode Electron Gun Accelerators: Laser-Microwave Synchronization at LEAF



5 picosecond UV laser pulse

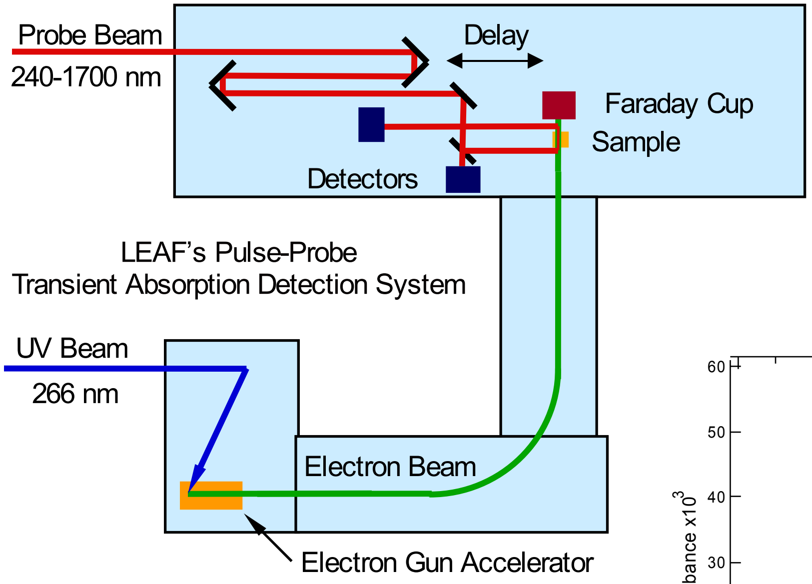
2856 MHz microwave power: 15 MW



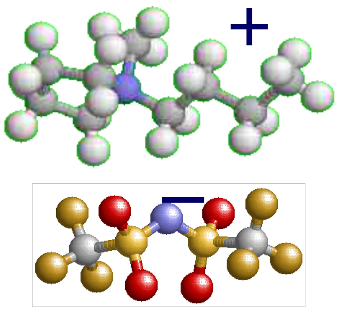
A picosecond-synchronized UV laser pulse generates photoelectrons, which are accelerated to 9 MeV by high fields (80 MV/m) in the **one-foot long** resonant-cavity structure.

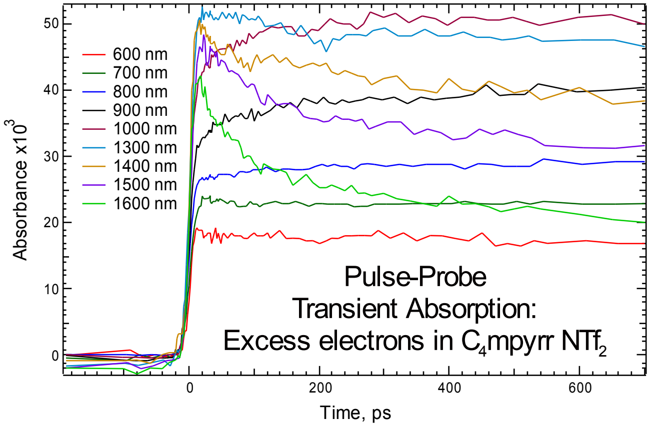
Wishart, Cook, Miller *Rev. Sci. Inst*. 75, 4359 (2004)

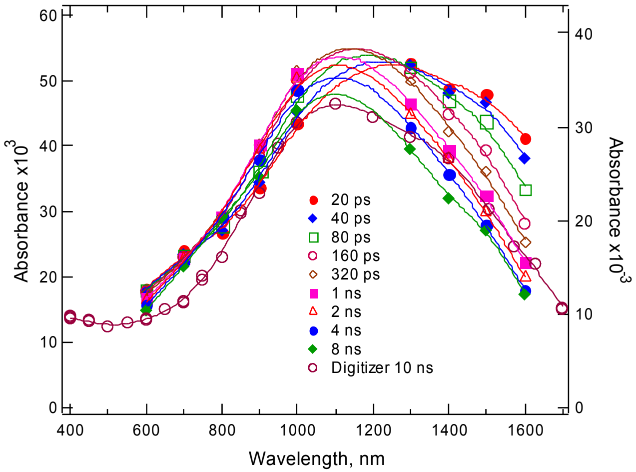
Slow electron solvation in ionic liquids observed by pulse-probe radiolysis at LEAF

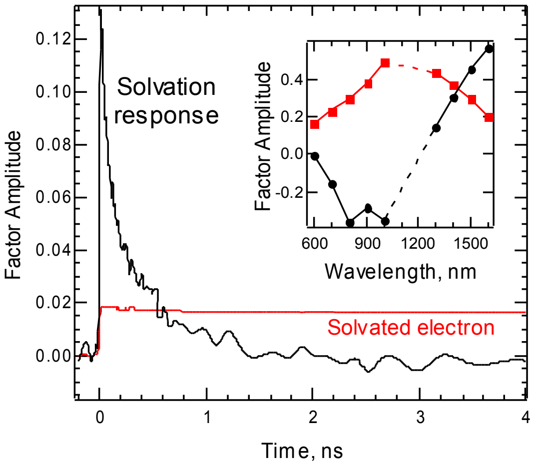


Ionic Liquid:
$C_4mpyrr^+ NTf_2^-$









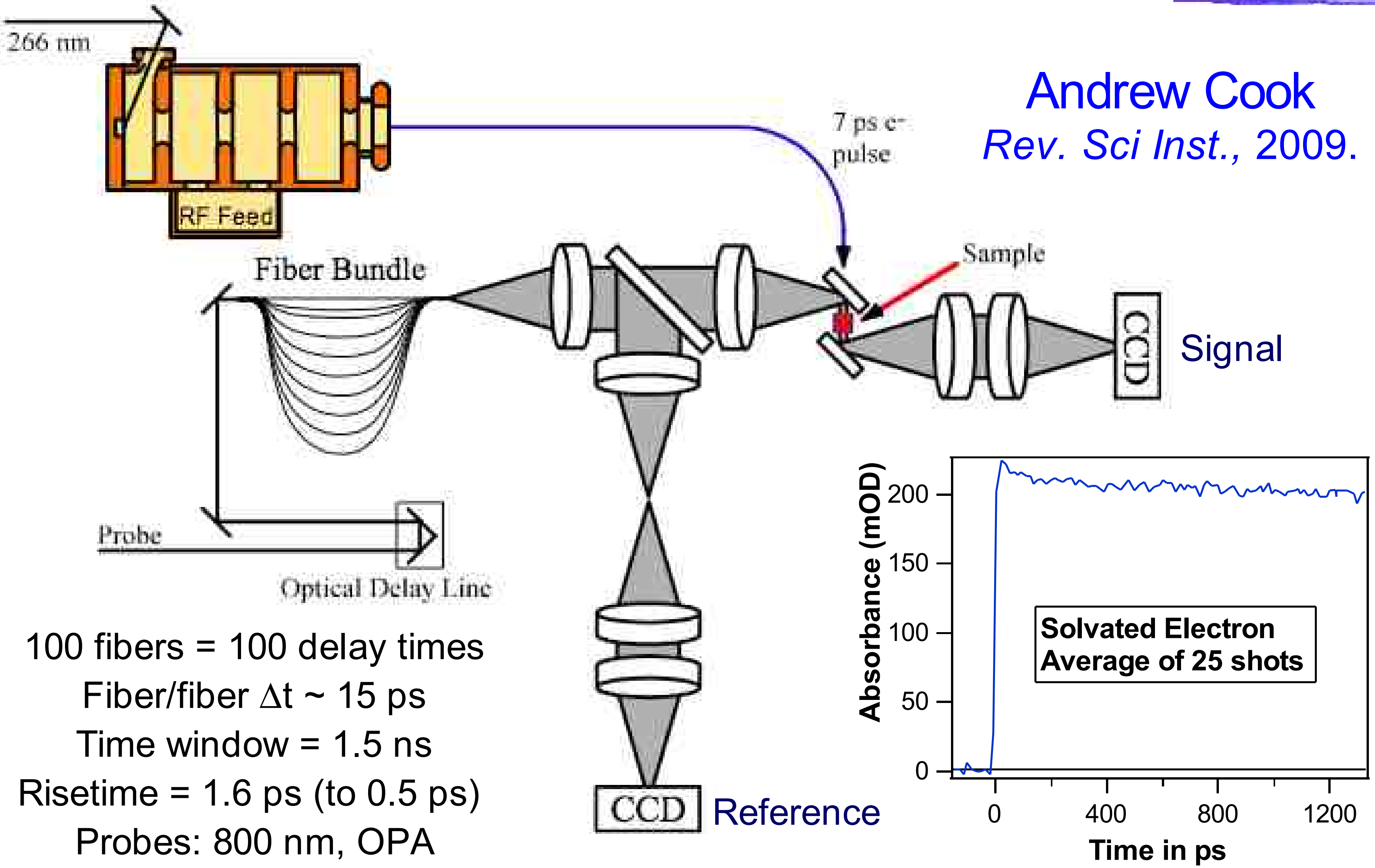
The average electron solvation time in $C_4mpyrr^+ NTf_2^-$ is 260 ps.

Solvation in ionic liquids operates by translation, not rotation.

Optical Fiber Single-Shot Detection (OFSS)

Andrew Cook

Rev. Sci Inst., 2009.



100 fibers = 100 delay times

Fiber/fiber Δt ~ 15 ps

Time window = 1.5 ns

Risetime = 1.6 ps (to 0.5 ps)

Probes: 800 nm, OPA

EPR studies of irradiated ionic liquid glasses

Done at ANL by Ilya Shkrob and Sergey Chemerisov.

EPR of matrix-isolated species :

Ionic liquid glasses and crystalline salts were treated at 77 K by:

Repetitive electron pulses:

(3 MeV VdG, average dose ~1.5 kGy)

Or repetitive KrF excimer laser pulses at 248 nm

Scanned with 9.44 GHz Bruker ESP300E with cryostat

Spectra taken at several temperatures upon warming.

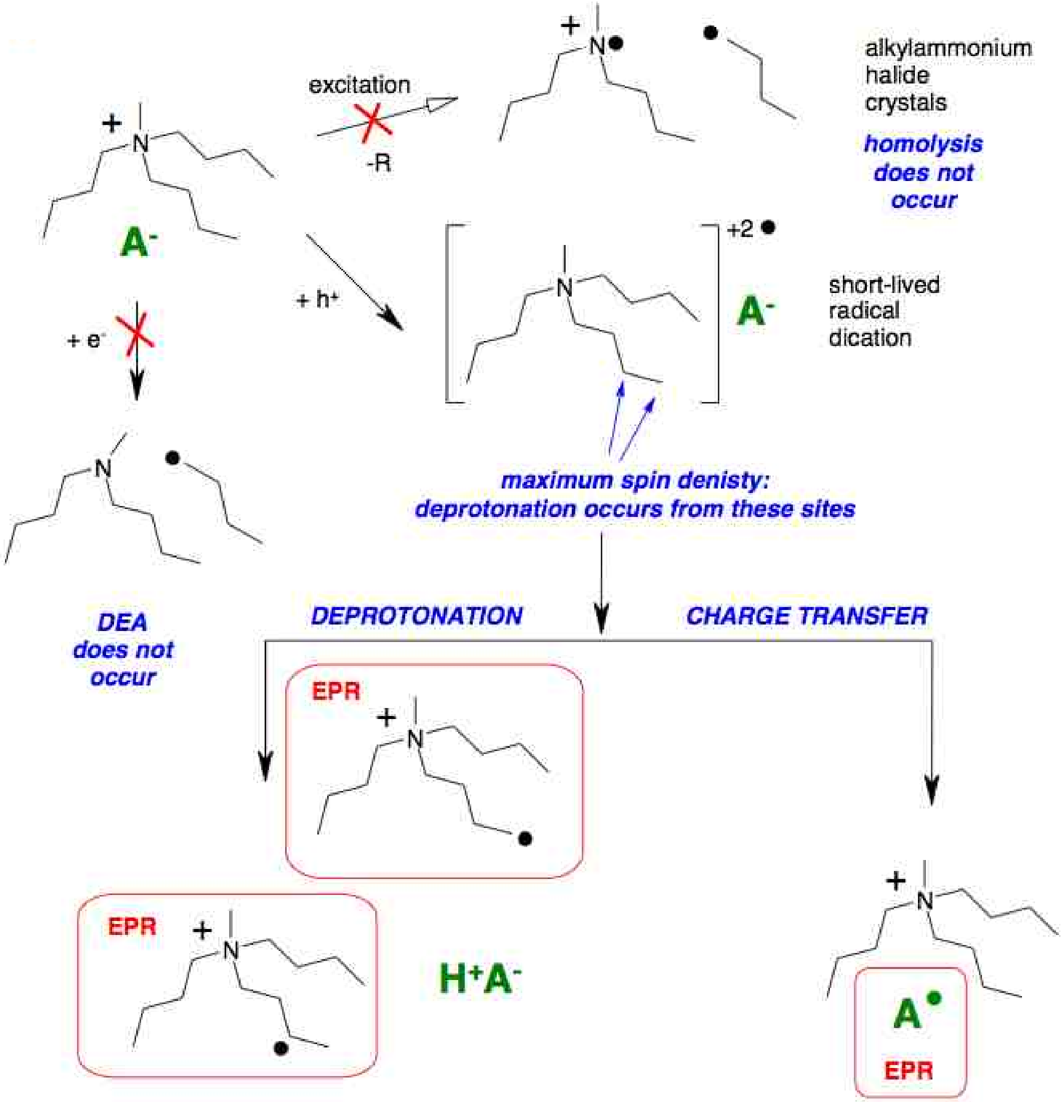
Many IL families have been studied (cations and anions).

Recently we have accumulated a large number of spectra of Ils with different anions and are now analyzing them.. Aromatic anions interest us..

New strategy : site specific deuteration of thecations to localize the damage sites. Underway – we are doing the syntheses

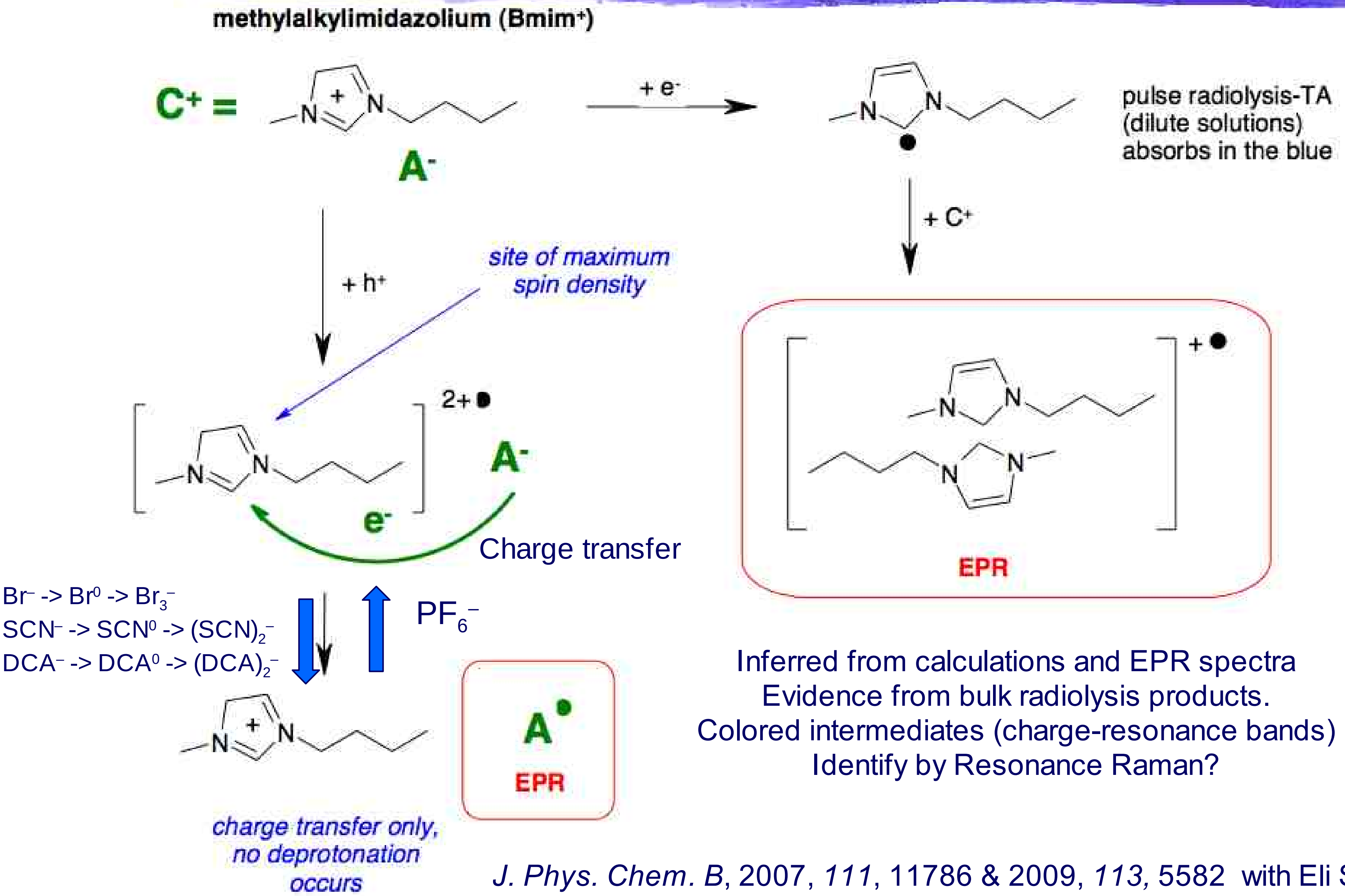
J. Phys. Chem. B, 2007, *111*, 11786 & 2009, *113,* 5582

Radiolysis of aliphatic cations



J. Phys. Chem. B,
2007, *111*, 11786
with Eli Shkrob

The radiolysis of imidazolium cations



pulse radiolysis-TA
(dilute solutions)
absorbs in the blue

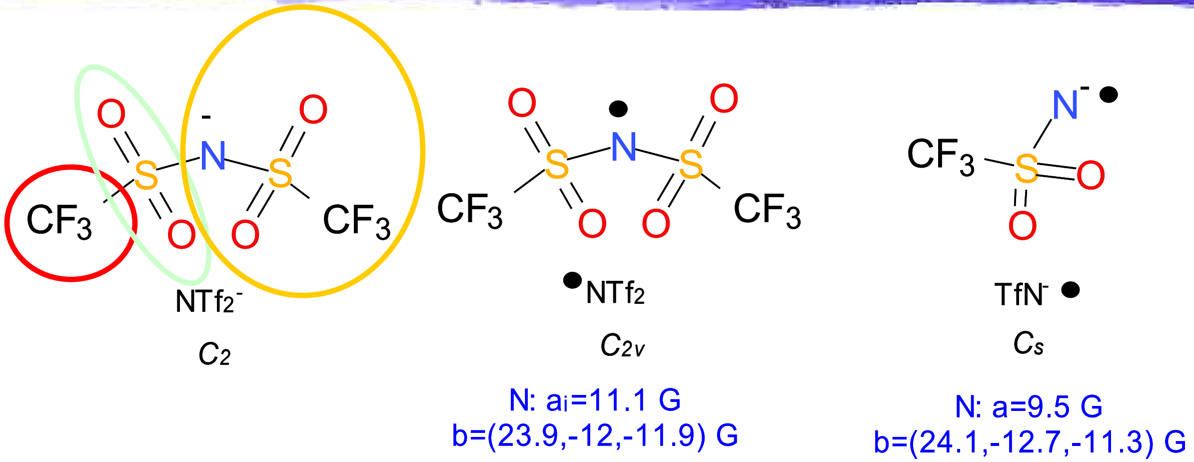
$Br^- \rightarrow Br^0 \rightarrow Br_3^-$
$SCN^- \rightarrow SCN^0 \rightarrow (SCN)_2^-$
$DCA^- \rightarrow DCA^0 \rightarrow (DCA)_2^-$

charge transfer only, no deprotonation occurs

Inferred from calculations and EPR spectra
Evidence from bulk radiolysis products.
Colored intermediates (charge-resonance bands)
Identify by Resonance Raman?

J. Phys. Chem. B, 2007, *111*, 11786 & 2009, *113*, 5582 with Eli Shkrob

Decomposition of NTf_2^- anion



- $^{\bullet}CF_3$ and $N^{\bullet}$ -centered (anion) radicals are observed by EPR
- $CF_3S^{\bullet}O_2$ radical is not observed (while $CF_3S^{\bullet}O_3$ was observed)
- DFT calculations indicate low barrier for $^{\bullet}CF_3$ + SO_2 dissociation (<0.3 V)
- There might be no barrier due to the hydration of the released SO_2 by clusters of water in the IL
- A product of $^{\bullet}CF_3$ and $TfN^{-\bullet}$ nitrene radical anion addition are observed by MS
- SO_3^{2-} is observed by product analysis (forms insoluble salts of Sr^{2+})

Eli Shkrob

Are Radiation-Durable IL-Based Extraction Systems Possible?

Ionic liquids are subject to radiation damage.

Bulk radiolysis studies: damage “accumulates slowly with dose.”

BNFL; CEA (G ~ 2-3/100eV for ion loss), Bartels G_{H_2} = 0.26 - 2.5

Separations bottom line: <u>durable performance of the system</u>.

PUREX: 30 wt% Tributylphosphate in hydrocarbon - dealkylation leads to dibutylphosphoric acid that *interferes with extraction*.

The hydrocarbon diluent directs reactivity to the extractant (DEA).

EPR measurements on radiolysis of $(MeO)_3PO$ and $(EtO)_3PO$ in ILs:

Radicals from phosphates ≤ 4% of radicals from ILs

KEY to durability: Protect extractant from damage and avoid degradation products that interfere with extraction (or electrodeposition).

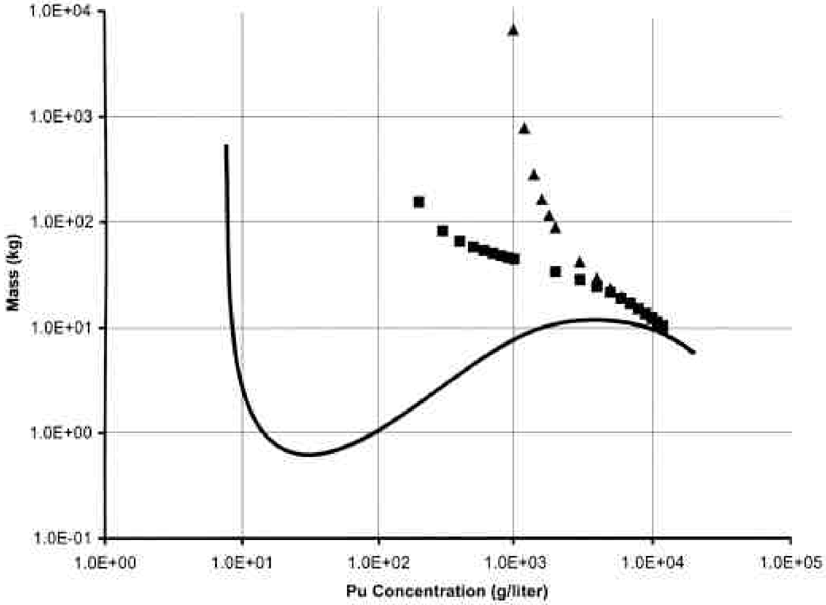
Direct the radiolysis into benign pathways.

J. Phys. Chem. B, 2007, *111*, 11786

The Special Case for Borated Ionic Liquids

Processing fissile materials is very dangerous because of the risk of runaway chain reactions (“criticality accidents”).

Criticality calculations from LANL: water-reflected sphere of Pu solution.



nass versus concentration plots for Pu metal/solvent mixtures. 1.—Metal–water mix; 2. ■ Metal–$AlCl_3$ mix; 3. ▲

C.D. Harmon et al. / Radiation Physics and Chemistry 60 (2001) 157–159

“Criticality Safe” systems: It would be safer if criticality prevention was an inherent feature of the processing system instead of relying on administrative controls that are subject to human error.

^{10}B (20% abundance) has a very large thermal neutron cross section.

Use of borated ILs could dramatically lower the risk of criticality accidents.

1 kg Pu in 1 L butyl-methyl-imidazolium$^+$ BF_4^- (4 M)

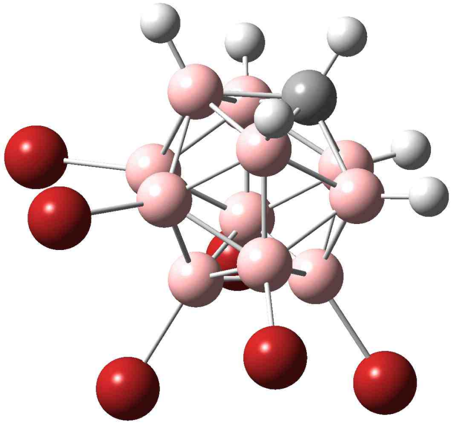
Some Boron-Containing Ionic Liquid Families

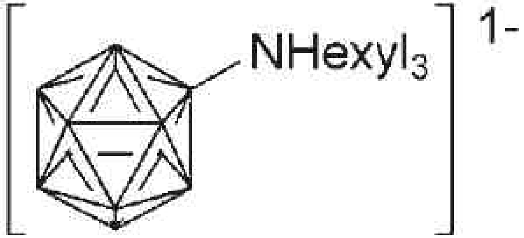
BF_4^- salts

$(C_nF_{2n+1})BF_3^-$ salts

$B(CN)_4^-$

(Car)boranes: $RC_{(0-2)}B_{(12-10)}H_{(11-5)}X_{(0-6)}^-$

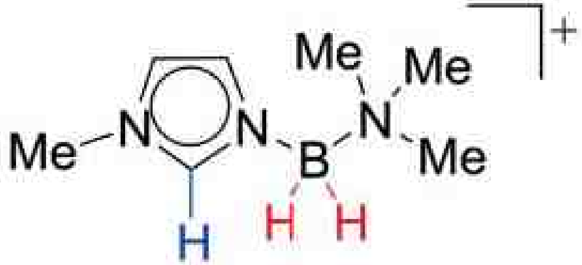




D. Gabel, U. Bremen

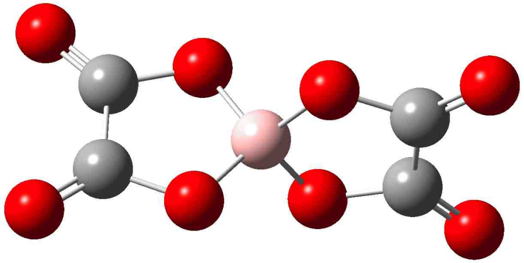
Chris Reed, U. C. Riverside, with John Holbrey
Chemically inert. X = H, Cl, Br
Loaded with thermal neutron scavengers.
Melting points 45° C and up.
Larsen, Holbrey, Tham, Reed *JACS* 122 (2000) 7264

Boronium cations



Fox, et al. (Davis, Rogers)
Chem. Comm. (2005) 3679

BOB: bis(oxalato)borate⁻



Reasonable fluid properties.
Commercially available.
Xu, Wang, Nieman, Angell
JPCB 107 (2003) 11749

Ionic Liquid Radiation Chemistry - Summary

Radiolysis products (= damage) accumulate more slowly in some ILs than in molecular solvents (or PUREX mixture), but other ILs are sensitive.

Some borated ions are reactive under radiation, but carborane and borane clusters are relatively inert and promising as additives to reduce criticality risk.

We are applying our knowledge of radiation chemistry to design radiation-resistant ILs that will be the basis for stable separation systems.

✓ Radiation effects in ILs are manageable and not a roadblock to reprocessing use.

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Profs. Sharon Lall-Ramnarine (QCC, CUNY) and Robert Engel (Queens Coll., CUNY)

Prof. Mark Kobrak (Brooklyn College, CUNY), Prof. Shawn Abernathy (Howard U.)

Ilya Shkrob, Sergey Chemerisov (ANL)

Andy Cook, John Miller, J.P. Kirby, Paul Poliakov, Sean McIlroy, Paiboon Sriarunothai

Summer Students (2003-2007, 2008):
Andre Grange, Kimberly Odynocki, Rabindra Ramkirath, Elina Trofimovsky, Neel Khanna, Alex Reben, Heidi Martinez, Vanessa Hernandez, Annu Itty Ipe, Heather Lee, Hughton Walker, Kathryn Sims, Kandis Stubblefield , Katherine Ureña, Steve Bagienski, Alejandra Castaño, Jinhee Gwon, Jasmine Hatcher, Jockquin Jones, Kijana Kerr, Charlene Lawson, Xing Li, Gina Zhou (PST)

U.S. Department of Energy, Basic Energy Sciences, Chemical Sciences Division

BNL Laboratory-Directed Research and Development (LDRD) Program

BNL Office of Educational Programs, BNL Diversity Office

New York Regional Alliance for Ionic Liquid Studies

Radiation Chemistry

Radiation Chemistry is the study of chemistry resulting from the interaction of ionizing radiation with matter.

Secondary electrons are expelled.
Radicals and ions are produced.
Bonds are broken.

Ionizing Radiations:

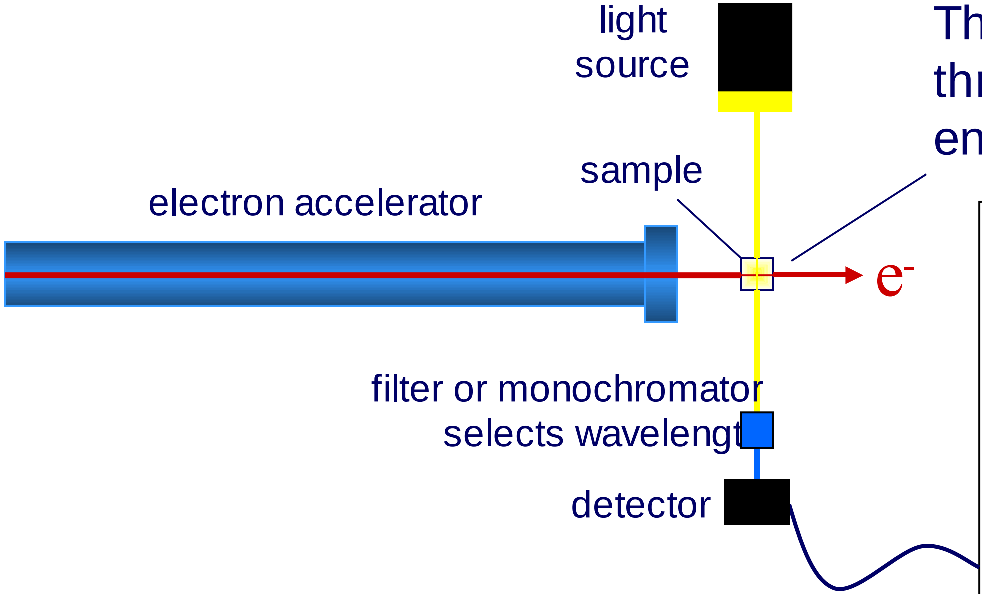
- X-rays
- Gamma rays
- Alpha particles (He^{2+})
- Beta particles (e^-)
- Protons (H^+)
- Nucleons (C^{6+}, O^{8+})
- Neutrons (n^0)

Features of Pulse Radiolysis:

- No back reaction ($A^* + B <=> A^+ + B^-$)
- Not limited by excited state lifetimes.
- Oxidation and reduction schemes are simple.
- Convenient dose measurement, shot-to-shot.
- No chromophore required - wider range of systems.

Pulse Radiolysis Kinetics Measurements

Pulse radiolysis is used to measure the speed of chemical reactions.



light source

sample

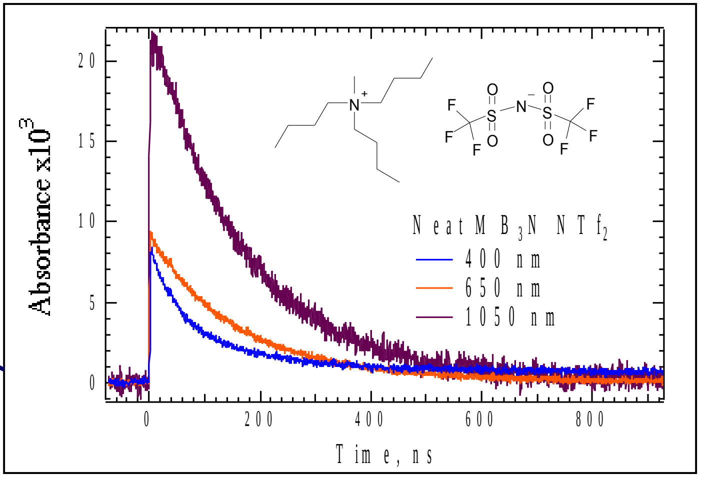
electron accelerator

e-

filter or monochromator selects wavelengt

detector

The electrons pass completely through the solution, depositing energy into the sample along the way.

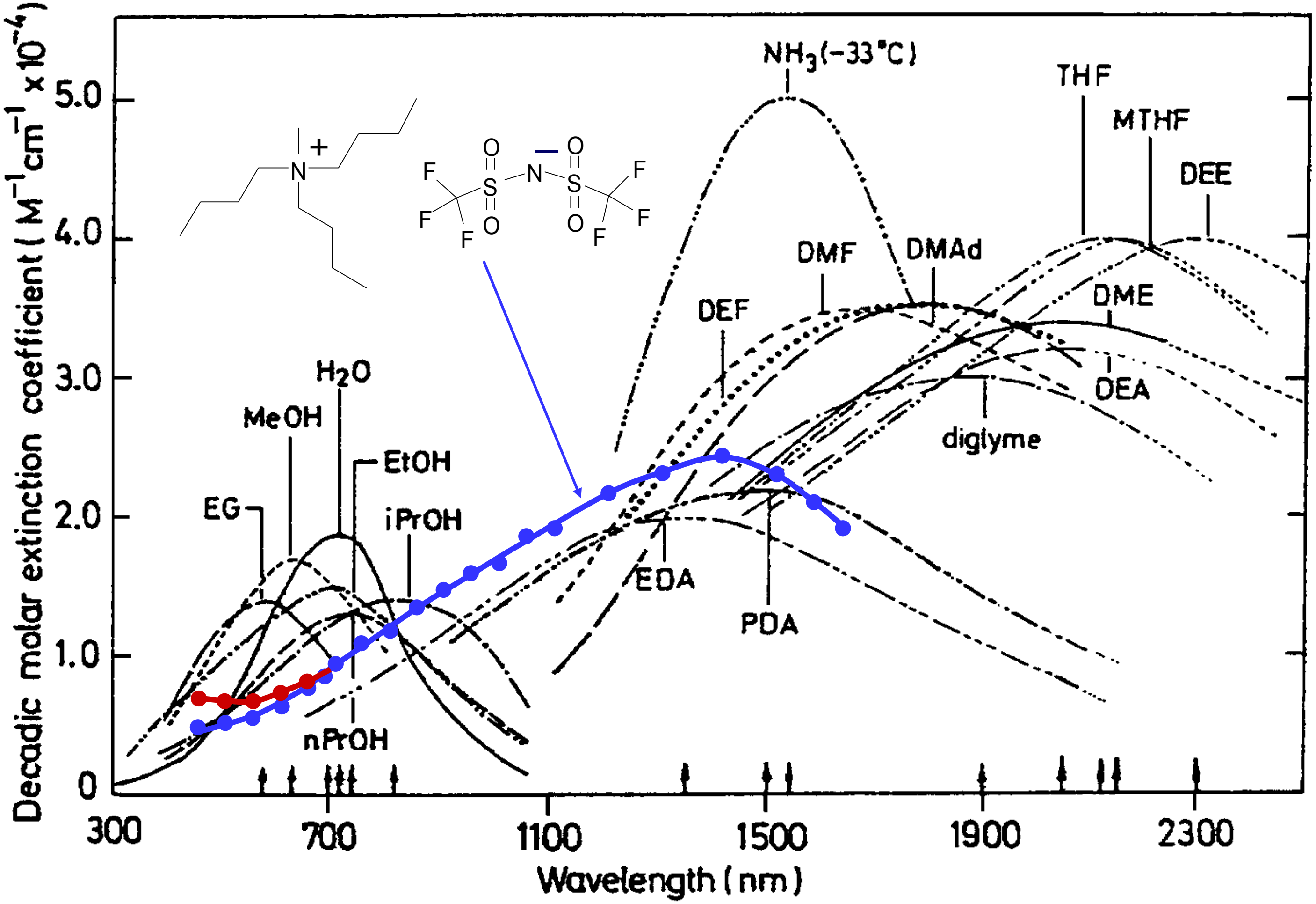


A short pulse of electrons initiates chemical reactions.

Detection using time-resolved (transient) absorption:

- Profile vs. time shows how the concentration of reactive species changes.
- Wavelength dependence (spectrum) identifies the species.

Solvated Electron in $MB_3N^+ NTf_2^-$



e$^-_{solv}$ decay: ≤ 400 ns

Hole(?) decay: 50 ns

ILs: 9 ≤ ε ≤ 15 by
Dielectric spect'ry
(Wakai, et al.)

IL polarities have also been ranked with solvatochromic dyes (e.g., betaine-30):

Alkylammoniums are similar to acetonitrile.

Imidazoliums appear more polar (due to H-bonding C-2 proton).

Dosimetry referenced to $(SCN)_2^-$ in water.

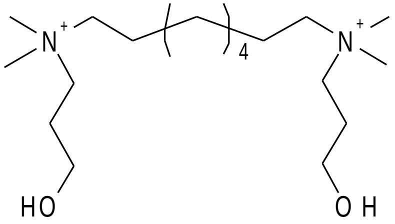
Z-Density corr: 1.16

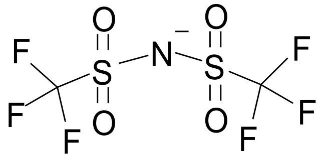
Electron yield: *G* = 0.7 per 100 eV absorbed.

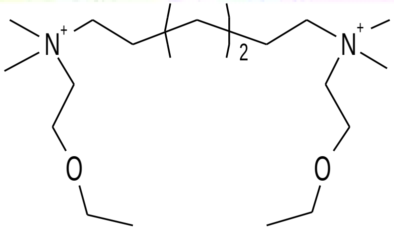
Wishart and Neta, *JPC B*, 107, 7261 (2003). Other spectra: Dorfman and Galvas (1975).

Electron solvation can be slow in ionic liquids

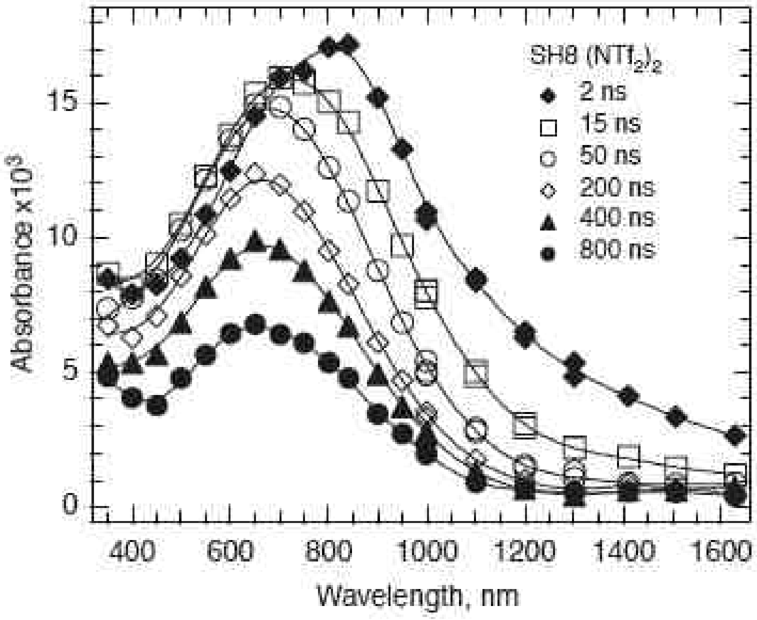
“SH8”

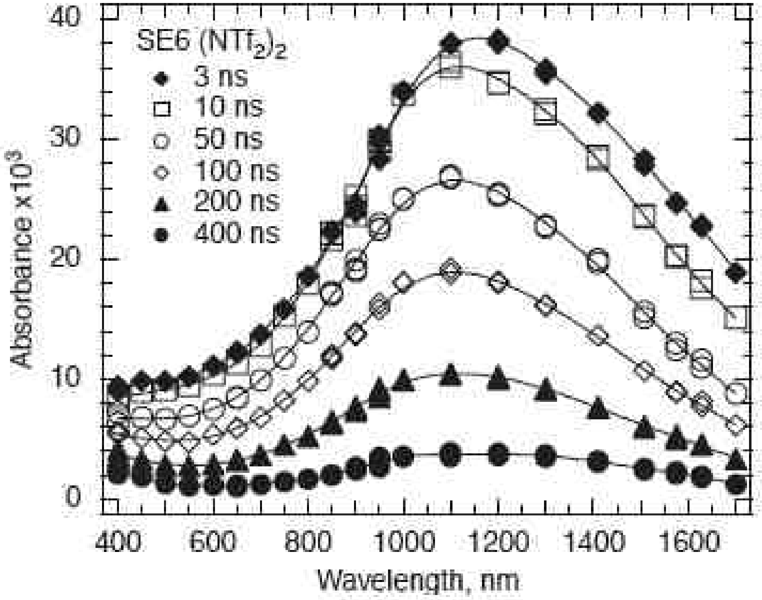






“SE6”



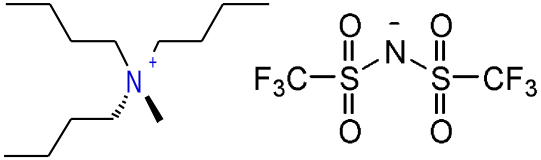


Solvent	Viscosity, cP	τsolv
SH8 (NTf$_2$)$_2$	4570	25 ns
1,2,6-(OH)$_3$hexane	2490	1 ns
MeOH, EtOH, EG	<1-20	<10 ps

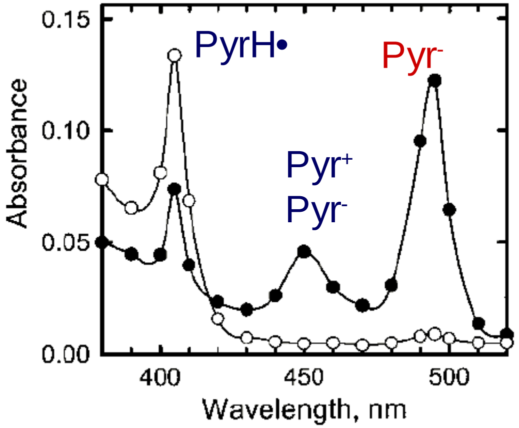
Viscosity 1120 cP at 20˚C

Collaboration with Engel group:
Wishart et al., *Radiat. Phys. Chem. 72*, 99 (2005)

Reaction of the electron with pyrene in MB_3N^+ NTf_2^-

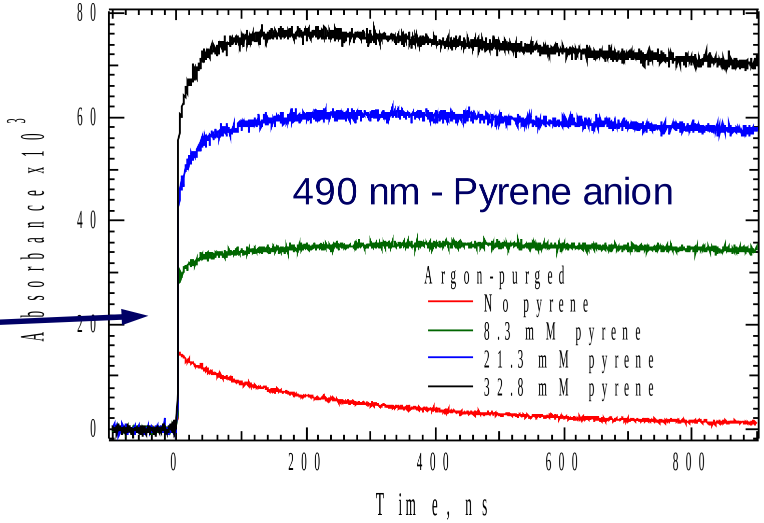


$e^- + \text{pyrene} \rightarrow \text{pyrene}^-$

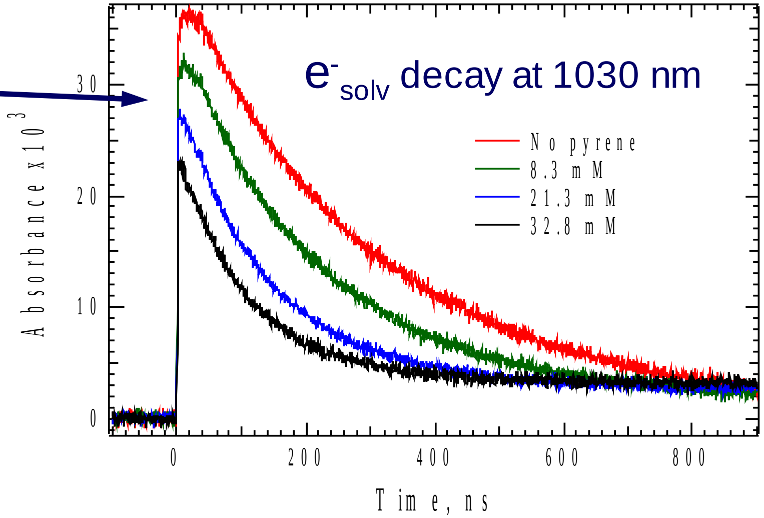


Solid circles: ~1 μs
Open circles: ~70 μs
18 mM pyrene.

Increasing Pyr$^-$ anion at “zero” time



Missing e^-_{solv} at “zero” time



Solvated electron capture is slow:

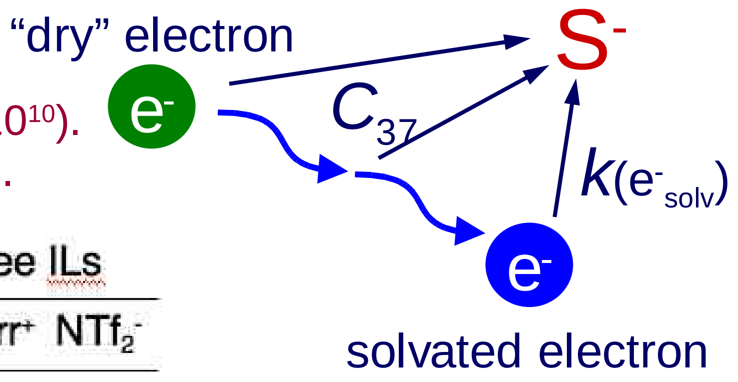
$$k(e^-_{solv}) = 1.7 \times 10^8\ M^{-1}\ s^{-1}$$

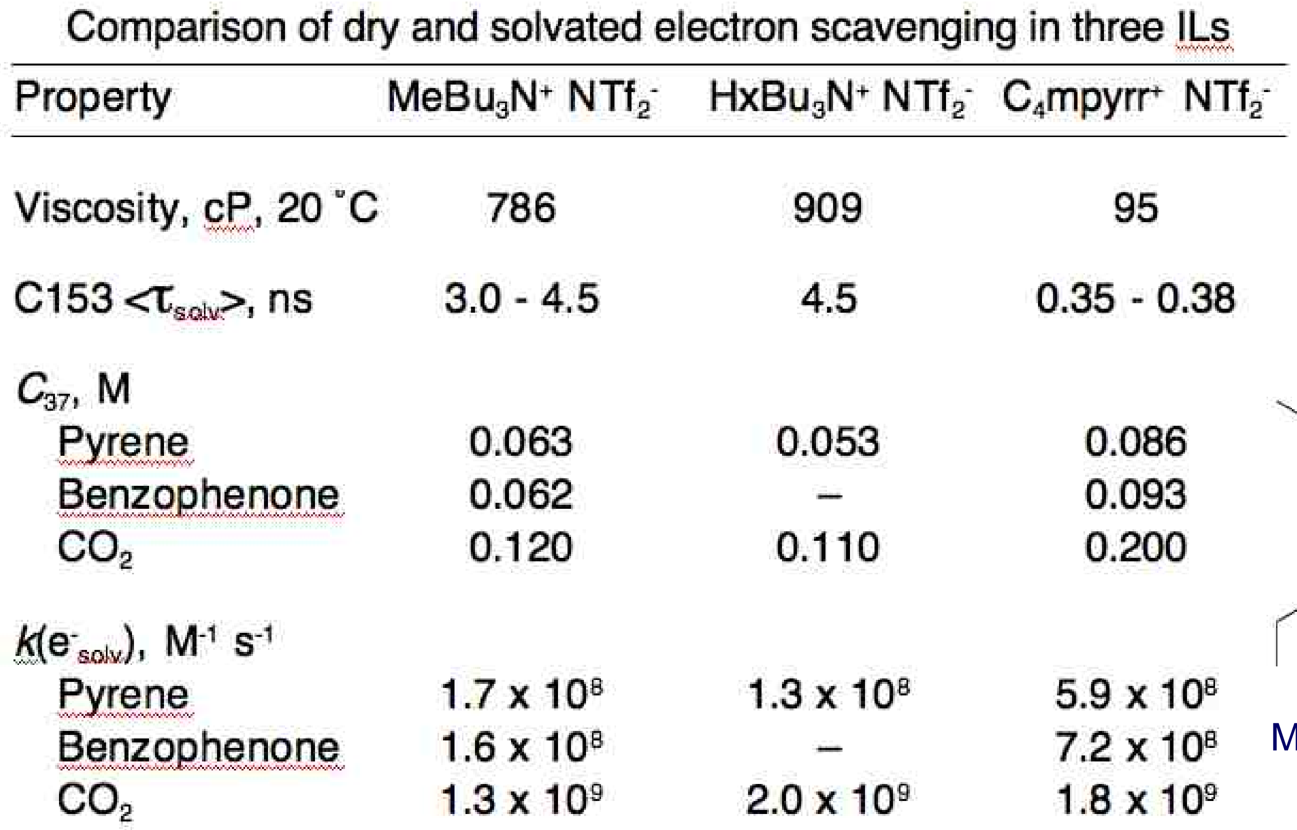
Pre-solvated electron capture is significant.

Wishart and Neta, *JPC B*, 107, 7261 (2003)

Electron reactivity vs. solvation

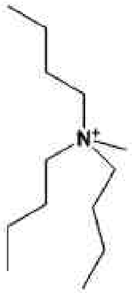
Solvated electron capture is slower than in normal liquids (~10^{10}).
Dry electron scavenging is remarkably efficient (high Q_{37}).



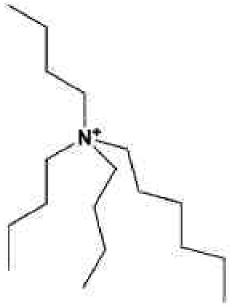

Comparison of dry and solvated electron scavenging in three ILs

Property	$MeBu_3N^+$ NTf_2^-	$HxBu_3N^+$ NTf_2^-	C_4mpyrr^+ NTf_2^-
Viscosity, cP, 20 °C	786	909	95
C153 <τ_{solv}>, ns	3.0 - 4.5	4.5	0.35 - 0.38
C_{37}, M			
Pyrene	0.063	0.053	0.086
Benzophenone	0.062	–	0.093
CO_2	0.120	0.110	0.200
$k(e^-_{solv})$, M^{-1} s^{-1}			
Pyrene	1.7×10^8	1.3×10^8	5.9×10^8
Benzophenone	1.6×10^8	–	7.2×10^8
CO_2	1.3×10^9	2.0×10^9	1.8×10^9

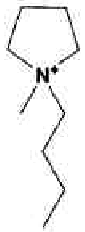
$$G_{[scav]}/G_0 = \exp(-[scav]/C_{37})$$



$MeBu_3N^+$



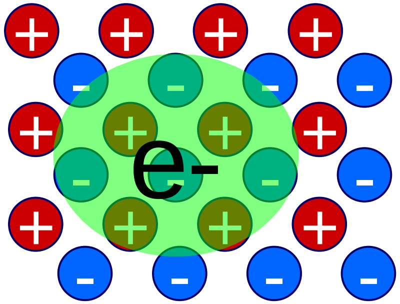
$HxBu_3N^+$



C_4mpyrr^+

Wishart and Neta, *JPC B*, 107, 7261 (2003) and recent work

Pre-solvated electron reactivity is important in ionic liquids



Pre-solvated electrons are mobile and reactive.

In most normal solvents, they only last picoseconds.

In some ionic liquids, they last 1000x longer.

In ionic liquids, solvation can be so slow that even low scavenger concentrations compete effectively.

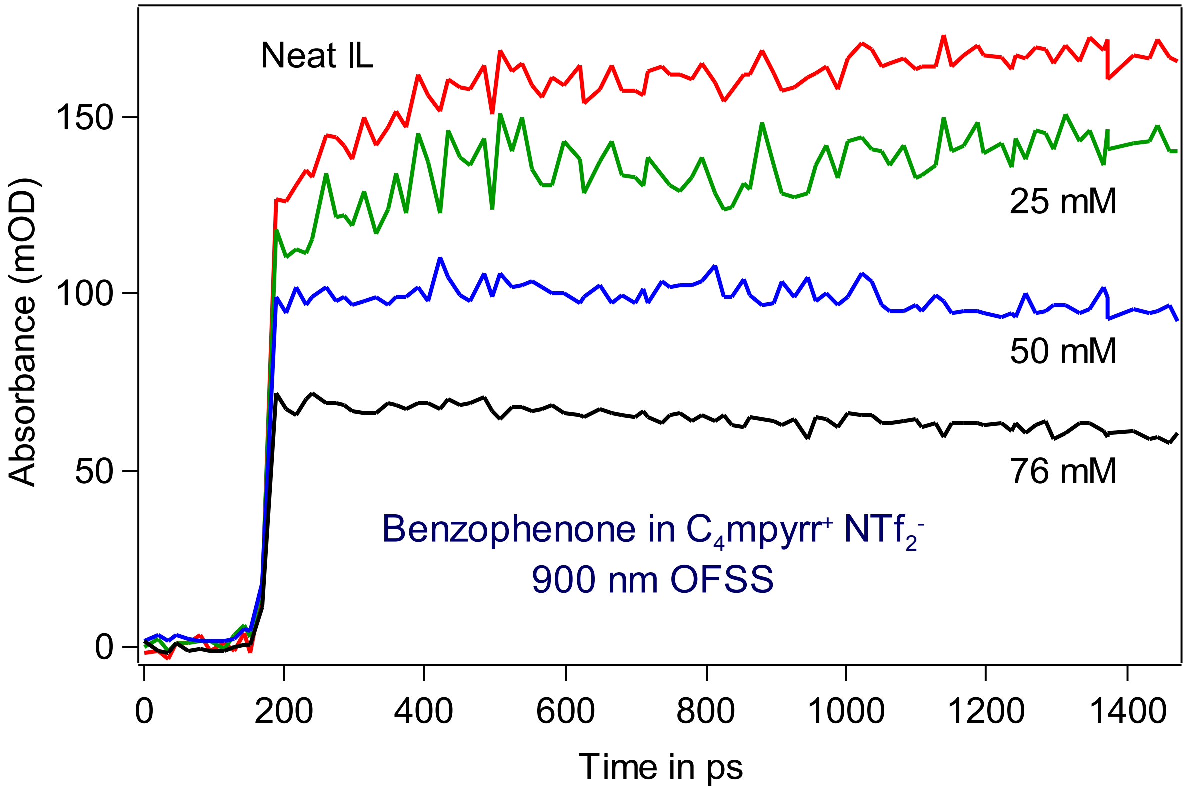
Implications:

- Concentrations of solutes that are too low to react with e^-_{solv} may still react with e^-_{pre}. Complication for reprocessing use?
- Energetic e^-_{pre} may react to form unique products unavailable from e^-_{solv}.
- Implies new strategies for stabilization.
- Easier to generate intermediates for chemical reactivity studies.
- Solvation studies over a range of ionic liquids are necessary.

OFSS observes pre-solvated electron scavenging

Preferential loss of the solvation process with increasing benzophenone quencher concentration.

Implies greater reactivity for the pre-solvated state.



Radiolysis yields of hydrogen gas

RTILs	**$G(H_2)$ (µmol/J)**
hmim Tf_2N	0.026
hDMAP Tf_2N	0.026
bmpyrr Tf_2N	0.065
Et_3NH Tf_2N	0.072
P_{88814} Tf_2N	0.25

Organics	$G(H_2)$ (µmol/J)
Benzene	0.004
Imidazole	0.003
Pyridine	0.003
n-Bu-benzene	0.026
Pyrrolidine	0.66
Me_3N	0.98

Tarábek, Bartels, *et al.*, *Radiat. Phys. Chem.* **78** (2009) 168

New scientific opportunities for pulse radiolysis

Radiation-induced chemistry at interfaces:

- Suspensions of colloids and solids in nuclear reprocessing
- Integrity/reactivity of fuel cladding

Charge-transfer processes in nanoscale materials, surfaces:

Radiolysis is an excellent method for inducing charge transfer.

- Photo/electrochemistry (e.g., Grätzel cells)
- Batteries
- Catalysis
- Polymer composites (including conducting polymers)
- Micelles

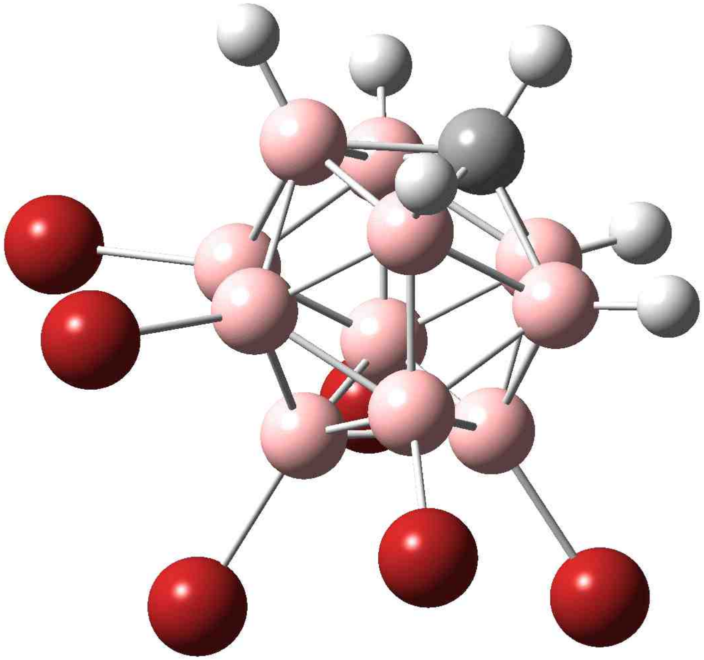
Radiolysis operates on the bulk material.

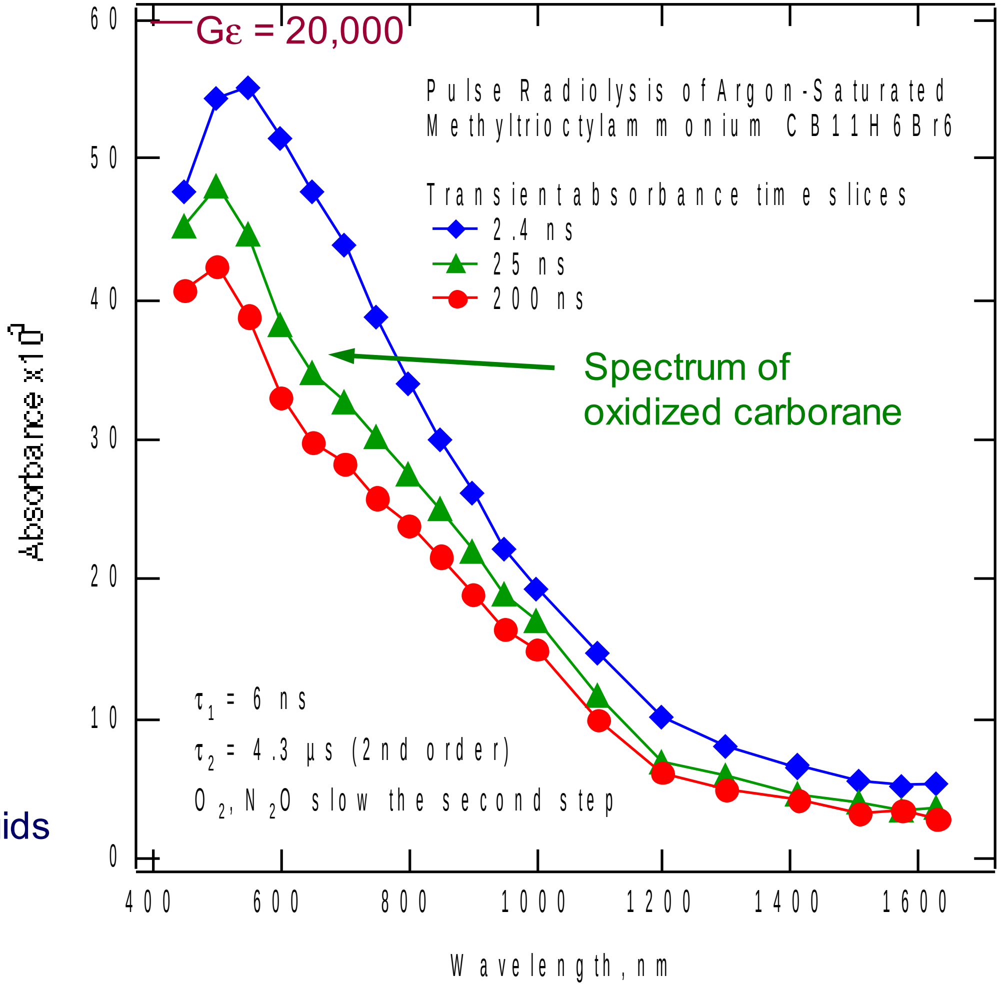
Interface-specific spectroscopic techniques are needed.

- Anisotropy-dependent methods (SHG, SFG, etc.)
- Surface-enhanced effects
- Others?

Radiolysis of Carborane Salts (neat and in ILs)

Carborane: $CB_{11}H_6Br_6^-$



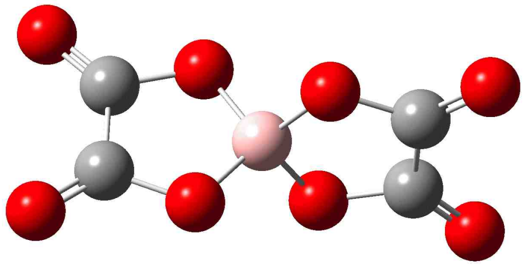


When carborane salts are dissolved in NTf_2^- liquids sharing the same saturated cation, the solvated electron is observed to react with the carborane anion (k = 3–7 x 10^8 dm^3 mol^{-1} s^{-1}), possibly producing bromide ion (H-atoms were not detected).

Wishart and Szreder, BNL, with C. Reed, U.C. Riverside

Radiolysis of BOB Ionic Liquids

Radiolysis of neat C_4mpyrr BOB shows no e^-_{solv} absorption transient.



In water:

- e^-_{aq} + oxalate^{2-} -> $k = 2.0 \times 10^7\ M^{-1}\ s^{-1}$
- e^-_{aq} + BOB$^-$ -> $k = 2.8 \times 10^7\ M^{-1}\ s^{-1}$

In C_4mpyrr$^+$ NTf_2^-:

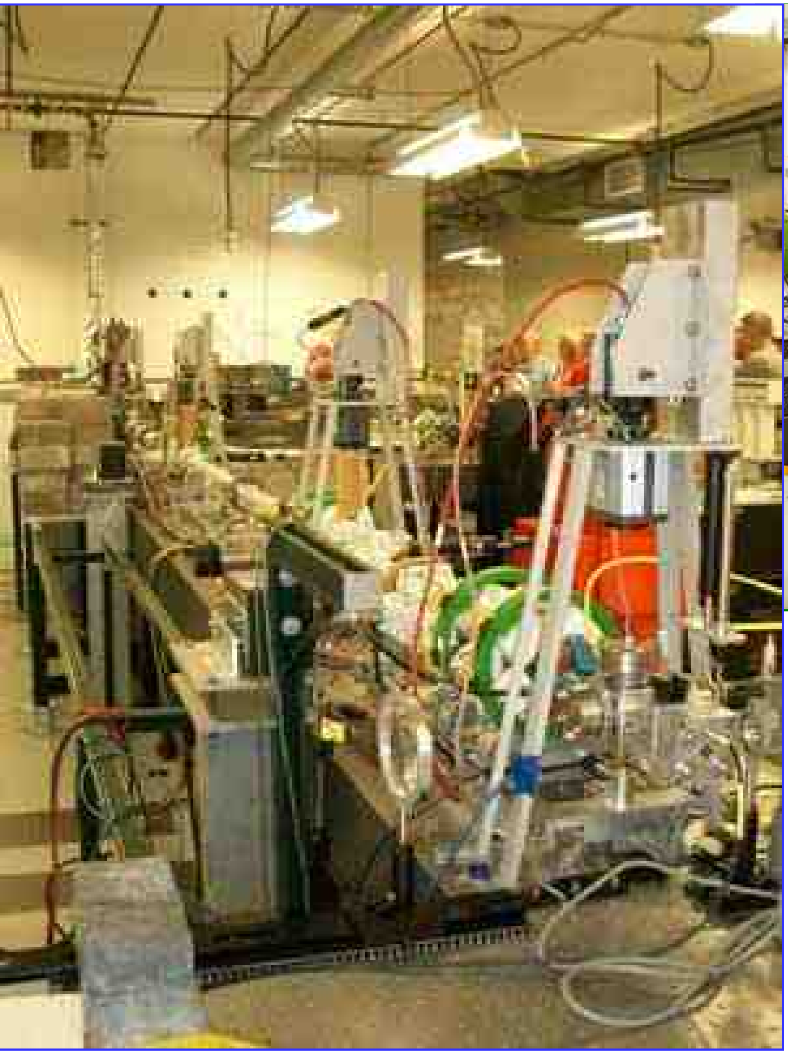
- e^-_{solv} + BOB$^-$ -> $k = 3.1 \times 10^8\ M^{-1}\ s^{-1}$
- e^-_{solv} + pyrene -> $k = 5.9 \times 10^8\ M^{-1}\ s^{-1}$

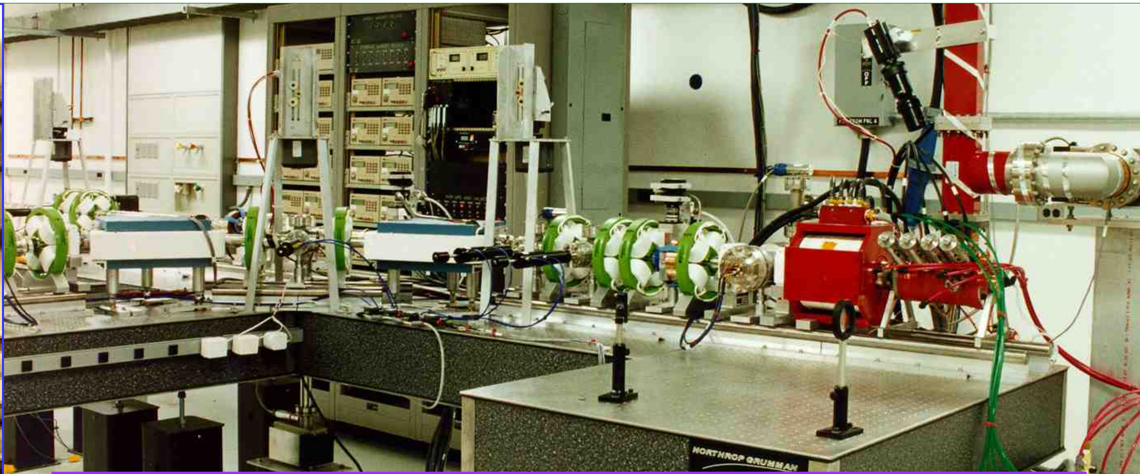
BOB reactivity with electrons is a problem for radiation stability.

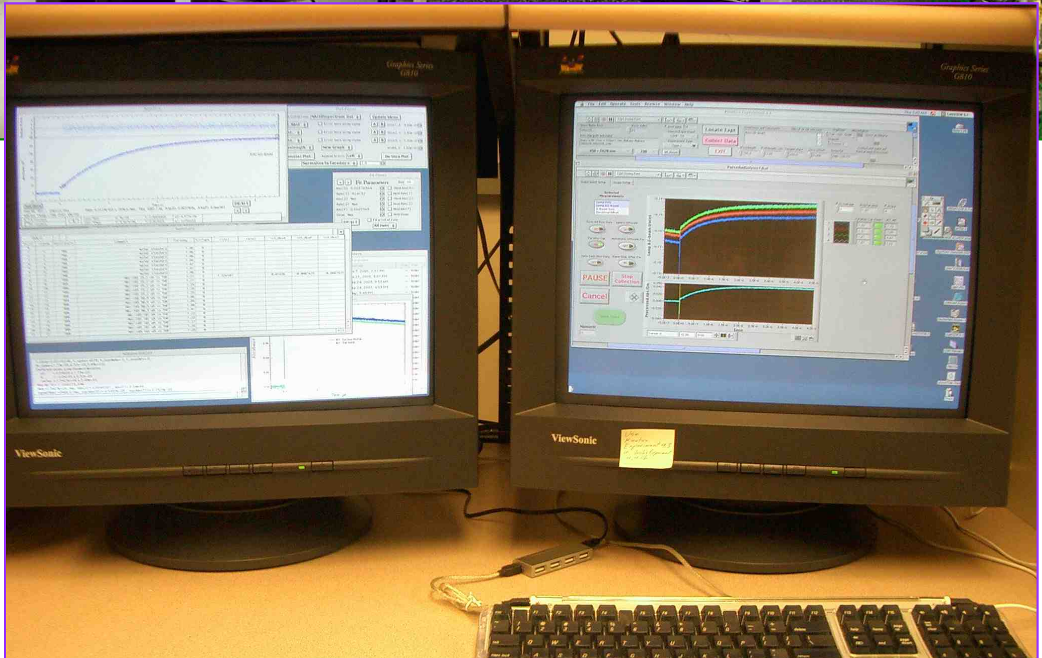
EPR results also indicate BOB$^-$ is radiolytically oxidized.

Radiation Physics and Chemistry, in

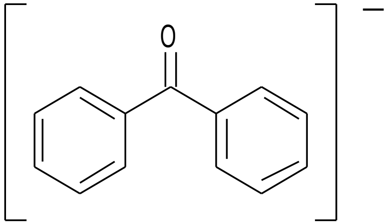
Laser-Electron Accelerator Facility

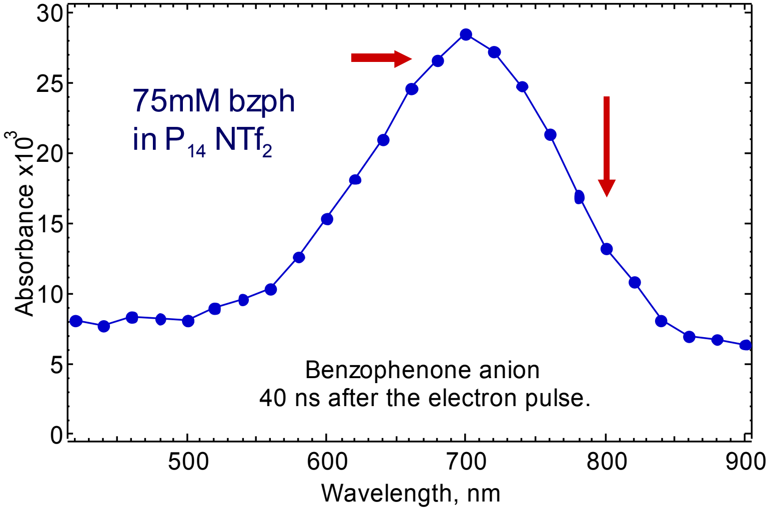


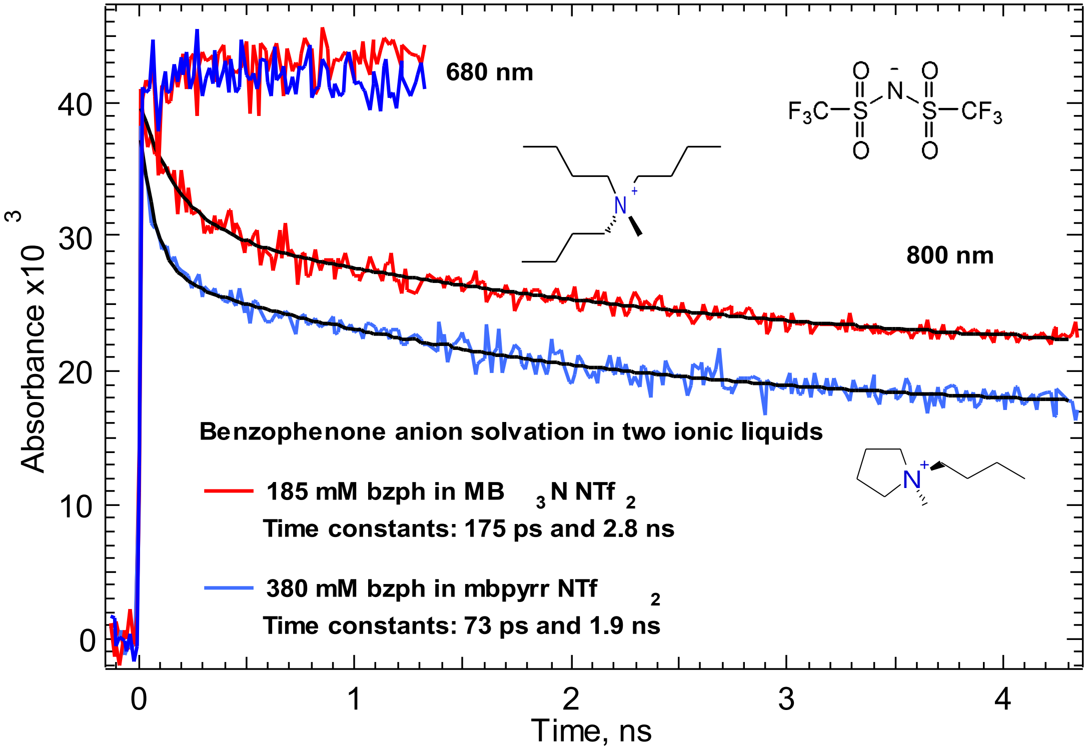




OFSS: Benzophenone anion solvation in ILs







Benzophenone anion solvation appears biphasic in these ILs:

MBpyrr NTf_2 (94 cP): 73 and 1900 ps.

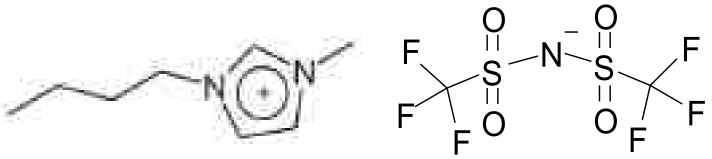
MB_3N NTf_2 (750 cP): 175 and 2800 ps.

Electrochemical Processing in Ionic Liquids

Spectroscopic and Electrochemical Studies of U(IV)–Hexachloro Complexes in Hydrophobic Room-Temperature Ionic Liquids [BuMeIm][Tf_2N] and [$MeBu_3N$][Tf_2N]

S. I. Nikitenko,[†] C. Cannes,[‡] C. Le Naour,[*,‡] P. Moisy,[§] and D. Trubert[‡]

Inorganic Chemistry, 44, 9497 (2005)



U(IV)–Hexachloro Complexes in Hydrophobic Ionic Liquids

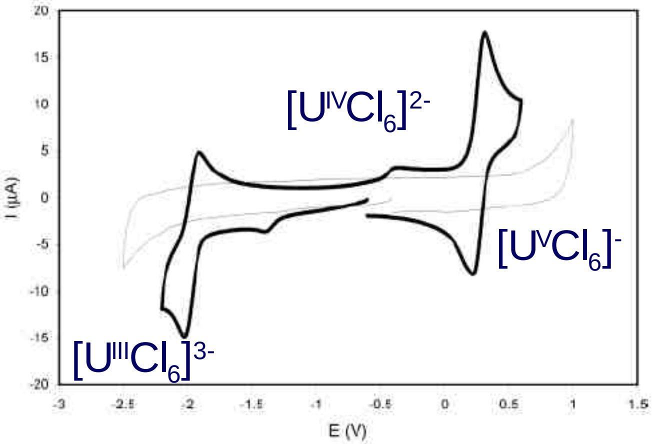
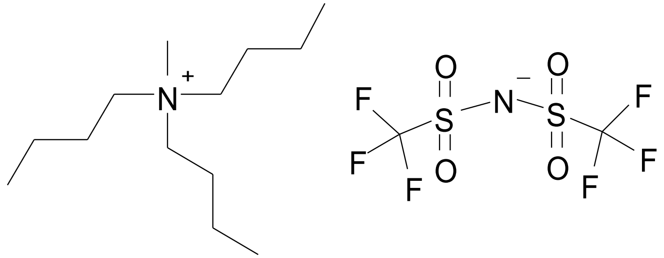
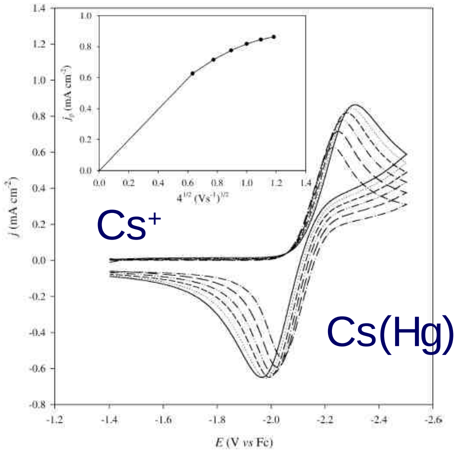


Figure 4. Cyclic voltammograms of [BuMeIm][Tf_2N] alone (grey line) and in the presence of 0.01 M $[BuMeIm]_2[UCl_6]$ (solid line). v = 100 mV

"Electrodeposition of cesium at mercury electrodes in the tri-1-butyl-methyl-ammonium bis((trifluoromethyl)sulfonyl)imide RTIL"

P.-Y. Chen, C. L. Hussey, Electrochimica Acta *49*, 5125 (2004)





28 mM Cs^+ in $Bu_3MeN^+NTf2^-$ at a HMDE as a function of scan rate.

Solvated Electrons in Ionic Liquids

Exist for microseconds in some ionic liquids.

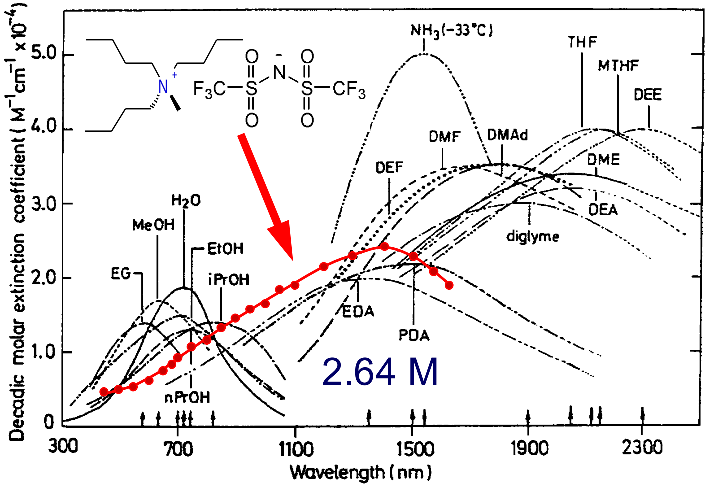
- Long enough to do chemistry.

Absorption spectrum tends to peak in near-infrared: 1000 - 1500 nm.

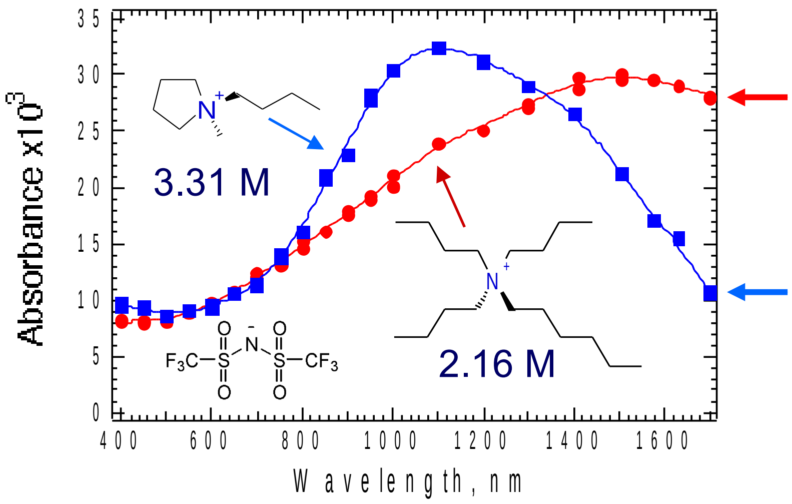
- Indicates that electrons are moderately trapped - less than in water.

Spectra are sensitive to cation structure, and possibly lattice environment.

- Hydroxyl-bearing cations show typical alcohol spectra.



First observation of the solvated electron in an ionic liquid.
Wishart and Neta, *JPC B*, 107, 7261 (2003).
Others: Dorfman and Galvas, 1975

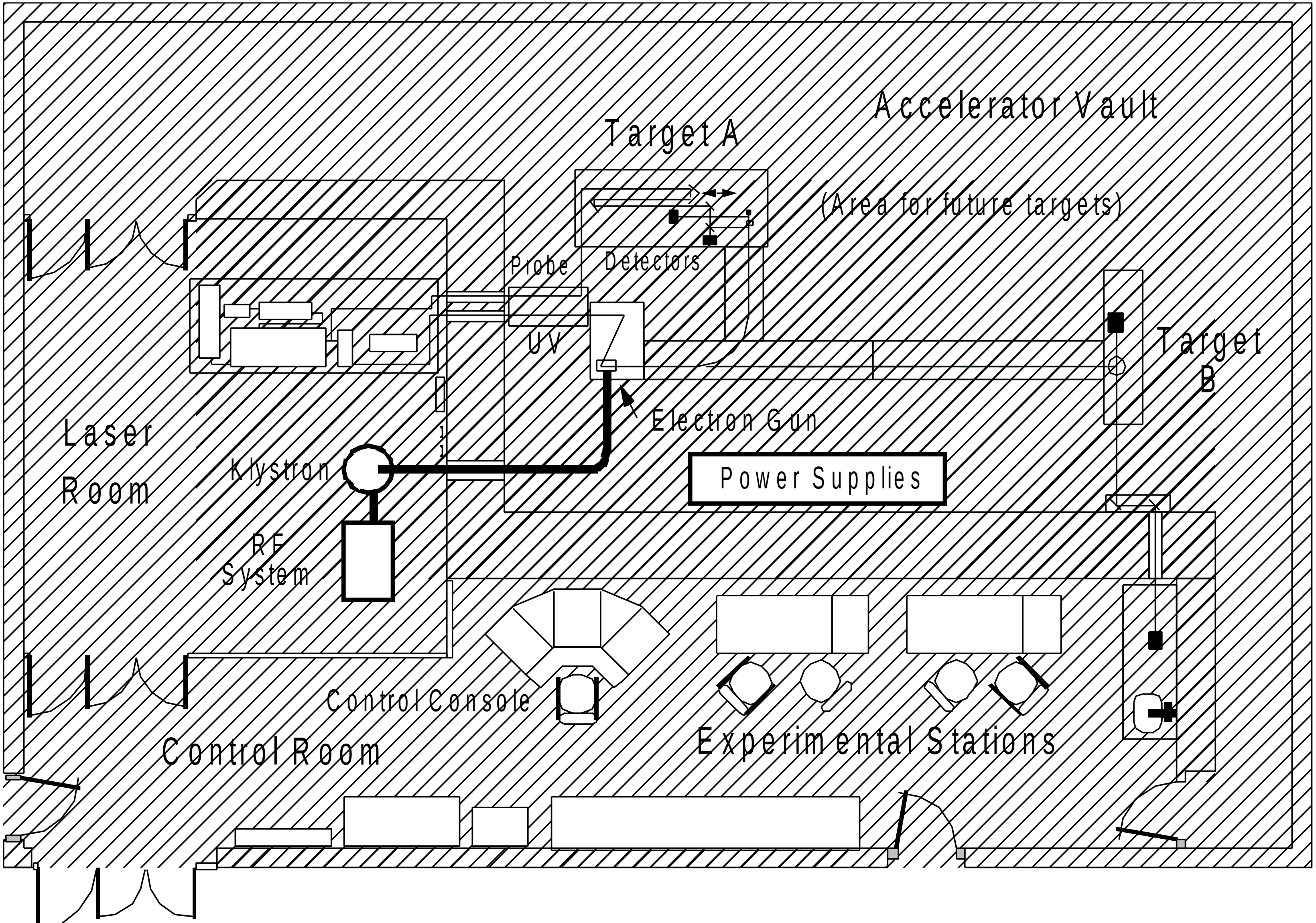


"NaCl"
CACA
ACAC
CACA

layered
CCCC
AAAA
CCCC

Spectra: Funston and Wishart, ACS Symp. Ser. 901
Lattice structures inferred from crystal structures of
Pr_4N NTf_2 Forsyth et al., Chem Mater. 2002
and C_4mpyrr NTf_2 Choudhury et al., JACS 2005

LEAF Facility Layout



Solvation Dynamics: Control of Electron Transport vs. Trapping

Watercross: open-water snowmobile racing

Dynamical Control of Charge Transport vs. Trapping

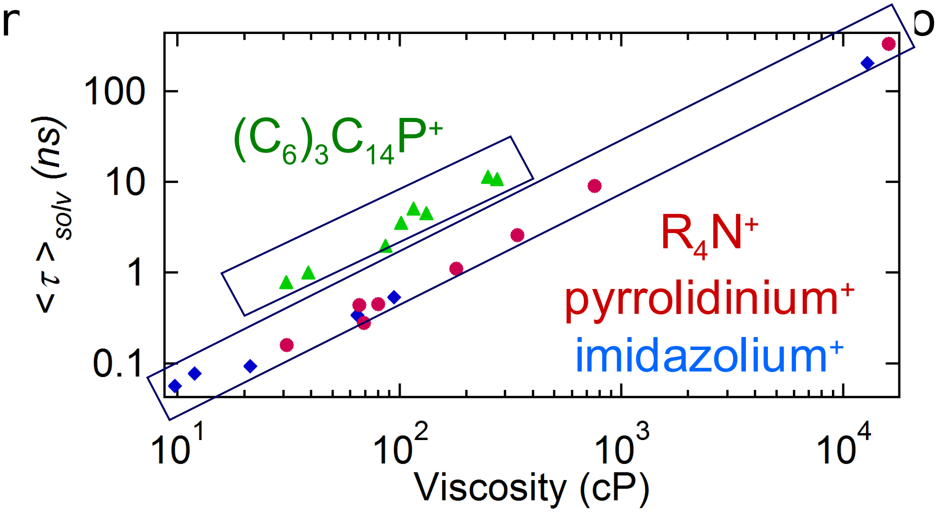
Watercross: as long as the snowmobiles move fast enough, they don't sink.

Electrons work the same way - if they move faster than the liquid can respond, they are very mobile.

We can now design ionic liquid systems to have solvation processes on selected timescales.

Control of energetics → product distributions

Cor … on



Blue and green points: M. Maroncelli

Tetrafluoroborate ILs: Radiation Chemistry

- Imidazolium and pyridinium BF_4 salts make low melting, low viscosity ILs.
  - Their radiation chemistry is focused on the formation and reactivity of im• and py• radicals. (Neta and coworkers)
  - No radiolysis product studies have been done.
- Saturated cations form higher-melting salts (C_3mpyrr BF_4: 64˚C, others higher).
- Reaction of e^-_{solv} with BF_4^- in ILs has not been studied, however:
  - e^-_{solv} does not react with BF_4^- in water ($k > 2 \times 10^5$ M^{-1} s^{-1})
- Unfortunately, BF_4^- is known to hydrolyze, just like PF_6^-, producing HF.
  - Solvated electrons in ILs react with acid, leading to degradation via H atom. (Grodkowski, Neta, Wishart *JPCA* 107, 9794 (2003)
  - CW radiolysis studies of PF_6^- salts show that they darken more than other ILs.
  - Therefore, BF_4^- salts may be susceptable to degradation in the same way.

Ionic Liquids in Photoelectrochemical Devices

Ionic liquids are finding roles in energy applications where charge transport processes predominate.

Photoelectrochemical cells convert solar energy to electricity using chemical reactions.

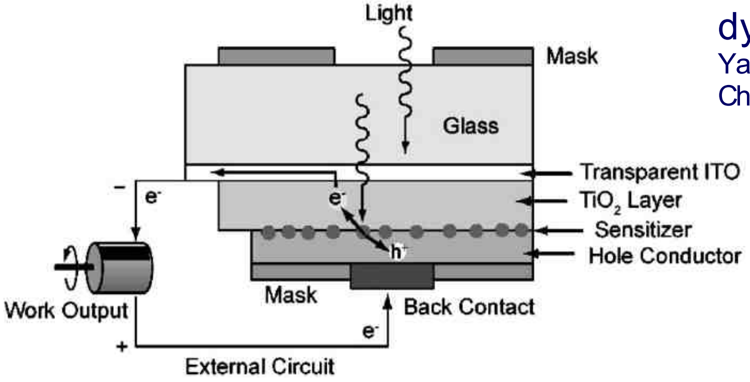
A Binary Ionic Liquid Electrolyte to Achieve ≥7% Power Conversion Efficiencies in Dye-Sensitized Solar Cells

Chem. Mater. (2004)

Peng Wang, Shaik M. Zakeeruddin,* Robin Humphry-Baker, and Michael Grätzel*

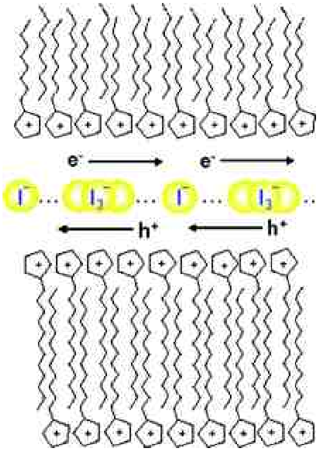
1-propyl-3-methylimidazolium iodide
1-ethyl-3-methylimidazolium thiocyanate

R. Sastrawan et al.
Solar Energy Materials & Solar Cells (2006)



B. Li et al.
Solar Energy Materials & Solar Cells (2006)

Ionic liquid crystal as a hole transport layer of dye-sensitized solar cells
Yamanaka et al.
Chem Comm, 2005, 740



Ionic Liquids and Nuclear Processing

Ionic liquids could be used to process nuclear fuel, waste, and radiological contamination.

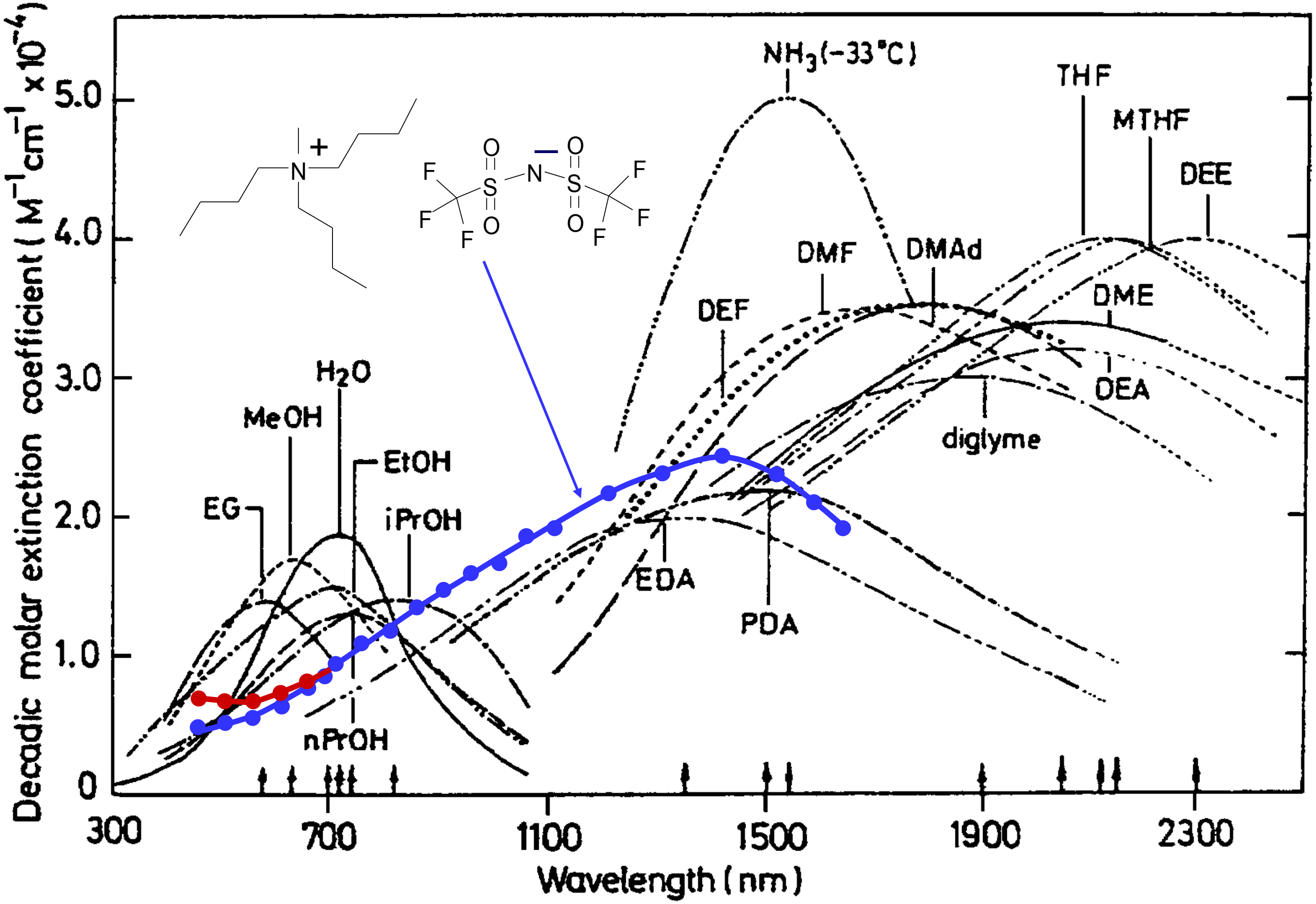
Beneficial features:

- Solvent properties and substrate ligation can be controlled by design
- Low volatility
- Combustion resistance
- High conductivity
- Wide electrochemical windows.

Interested organizations:

- U. S. Dept. of Energy (Separations and Heavy Element Chemistry Programs)
- British Nuclear Fuels, Ltd. and associated companies
- French Atomic Energy Commission
- China, Japan, Russia, India

Solvated Electron in $MB_3N^+ NTf_2^-$



Electron yield: *G* = 0.7 per 100 eV absorbed.

Wishart and Neta, *JPC B*, 107, 7261 (2003). Other spectra: Dorfman and Galvas (1975).

e^-_{solv} decay: ≤ 400 ns

Hole(?) decay: 50 ns

ILs: 9 ≤ ε ≤ 15 by Dielectric spect'ry (Wakai, et al.)

IL polarities have also been ranked with solvatochromic dyes (e.g., betaine-30):

Alkylammoniums are similar to acetonitrile.

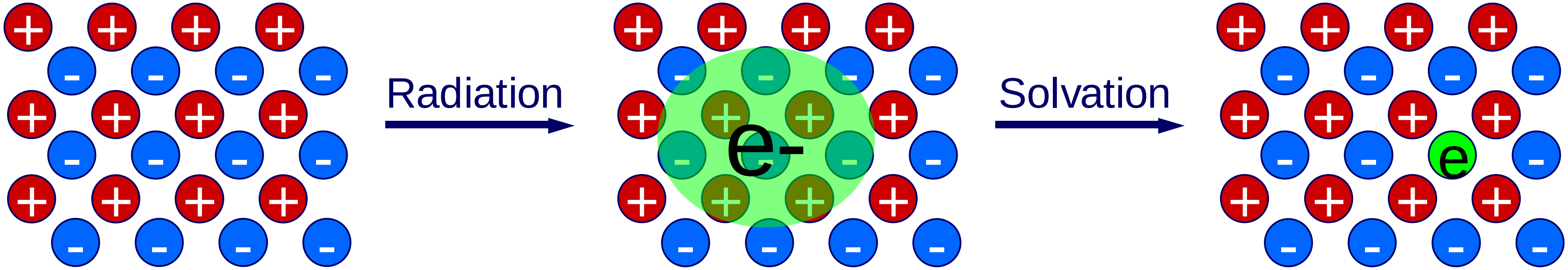
Imidazoliums appear more polar (due to H-bonding C-2 proton).

Dosimetry referenced to $(SCN)_2^-$ in water.

Z-Density corr: 1.16

Slow solvation in ionic liquids

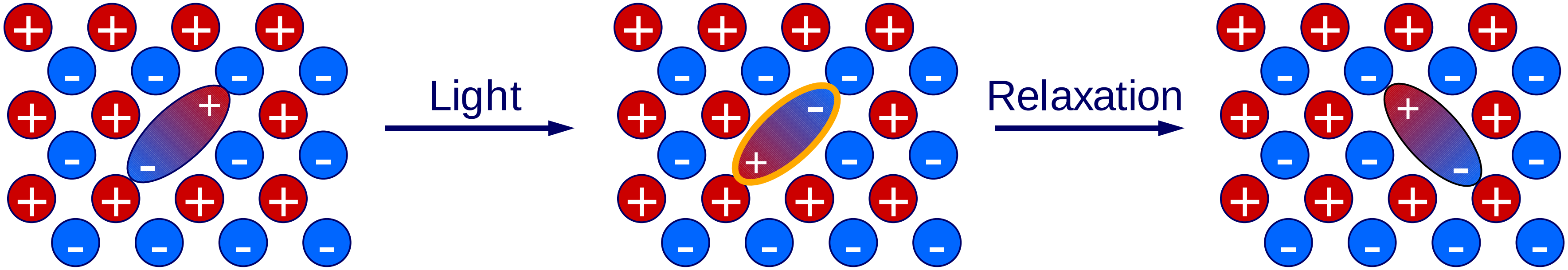
Pulse radiolysis: probe by absorption



Solvation of the electron in MB$_3$N NTf$_2$ is slow (~ 4 ns) but hard to observe.

Ordinary liquids take about one picosecond.

Laser photolysis: probe by fluorescence



Laser photolysis measurements: 4 ns relaxation in MB$_3$N NTf$_2$, C$_4$mpyrr NTf$_2$: 220 ps