

LEAF



Picosecond Radiolysis of Ionic Liquids

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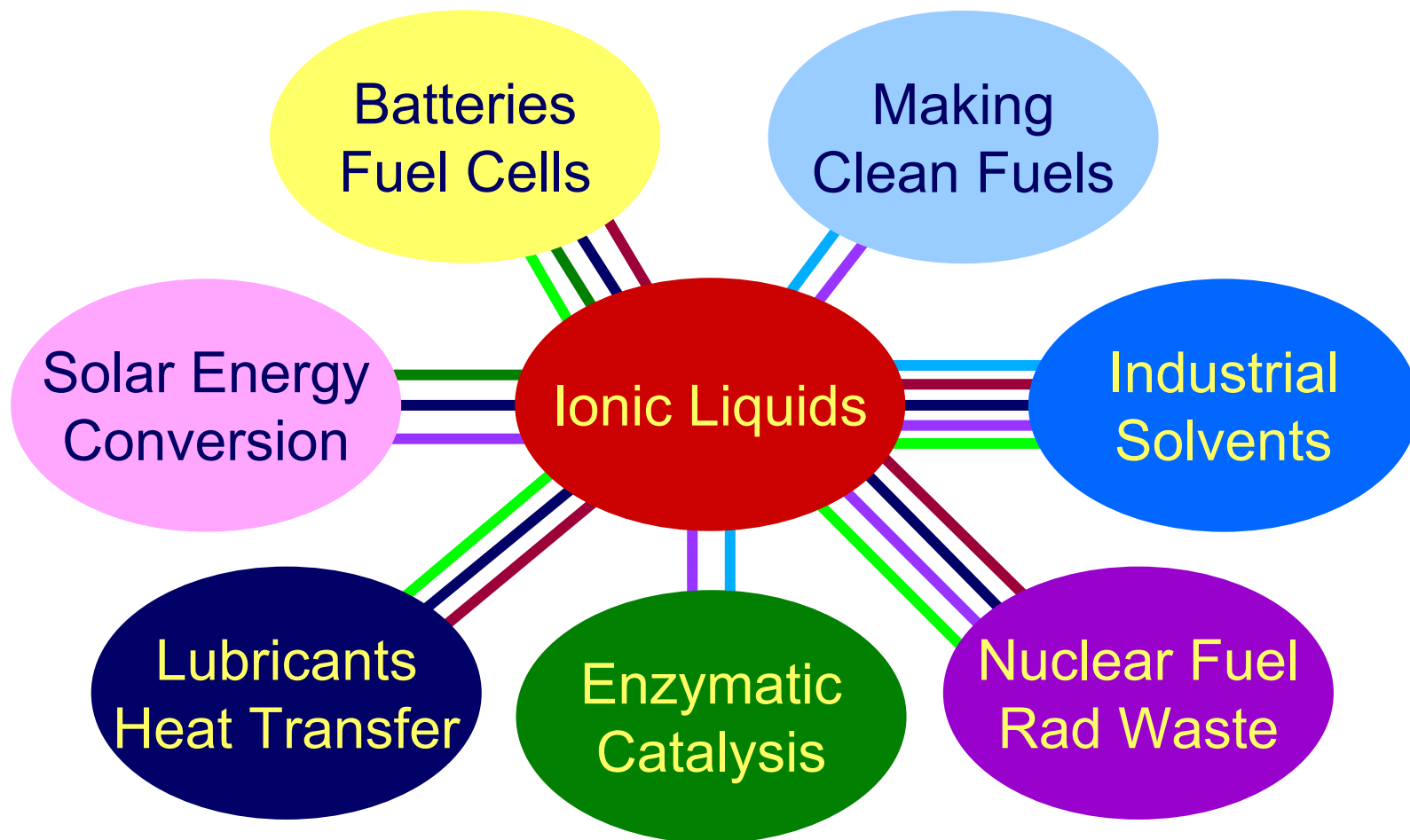
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Ionic Liquids

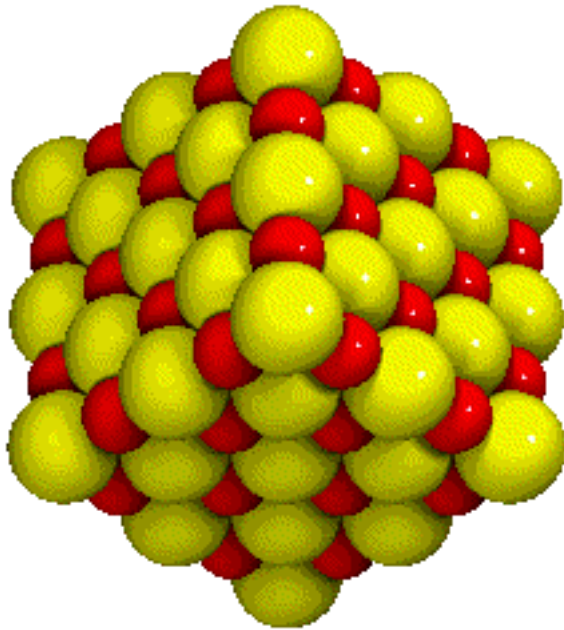
Designer Solvents for a Cleaner World

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

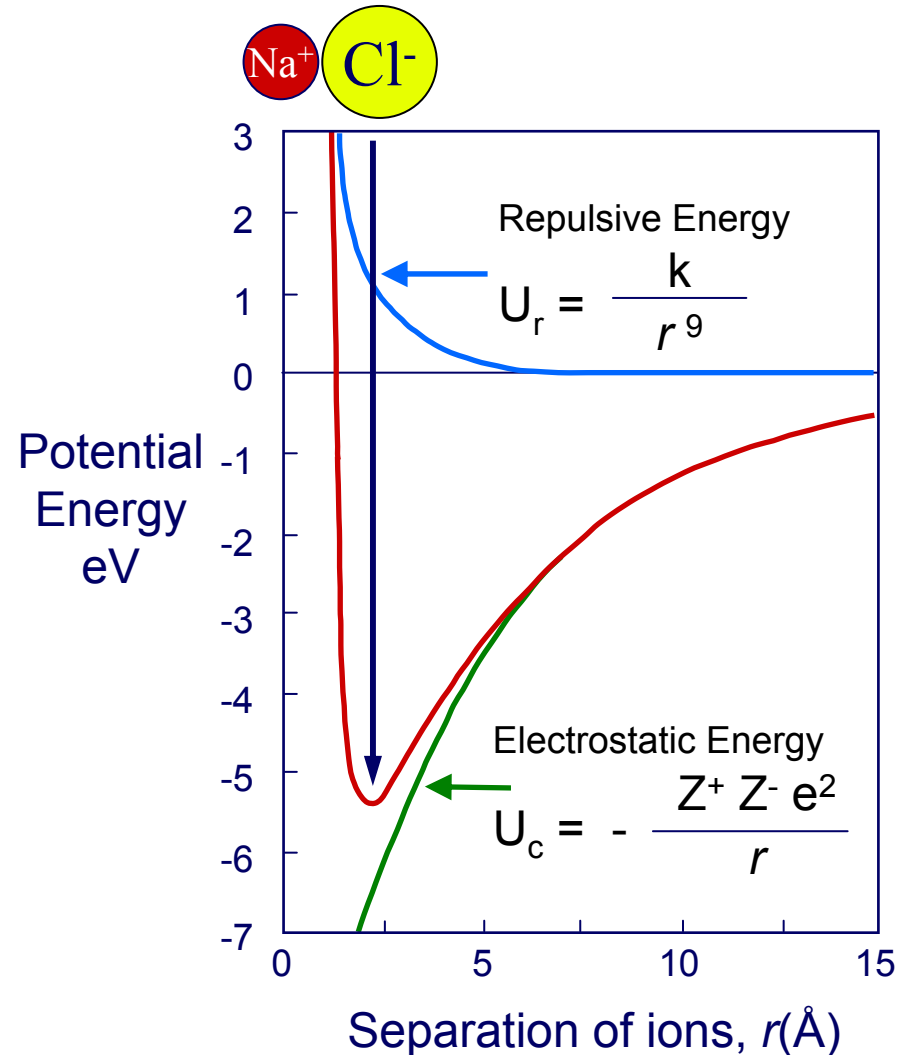


Salts are held together by Coulombic forces

NaCl (melts at 801 °C)



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



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.

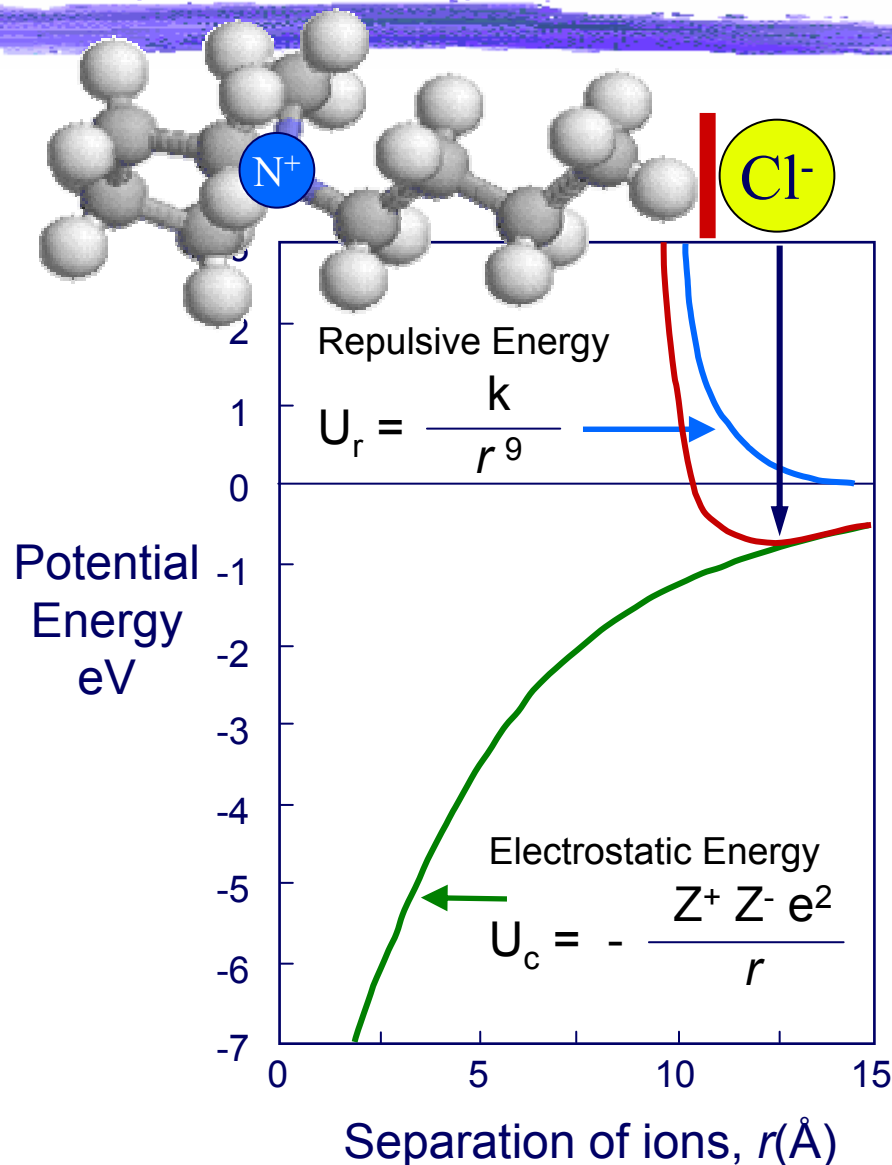
Control solubility of solids and liquids:

Phase separation (like oil and water).

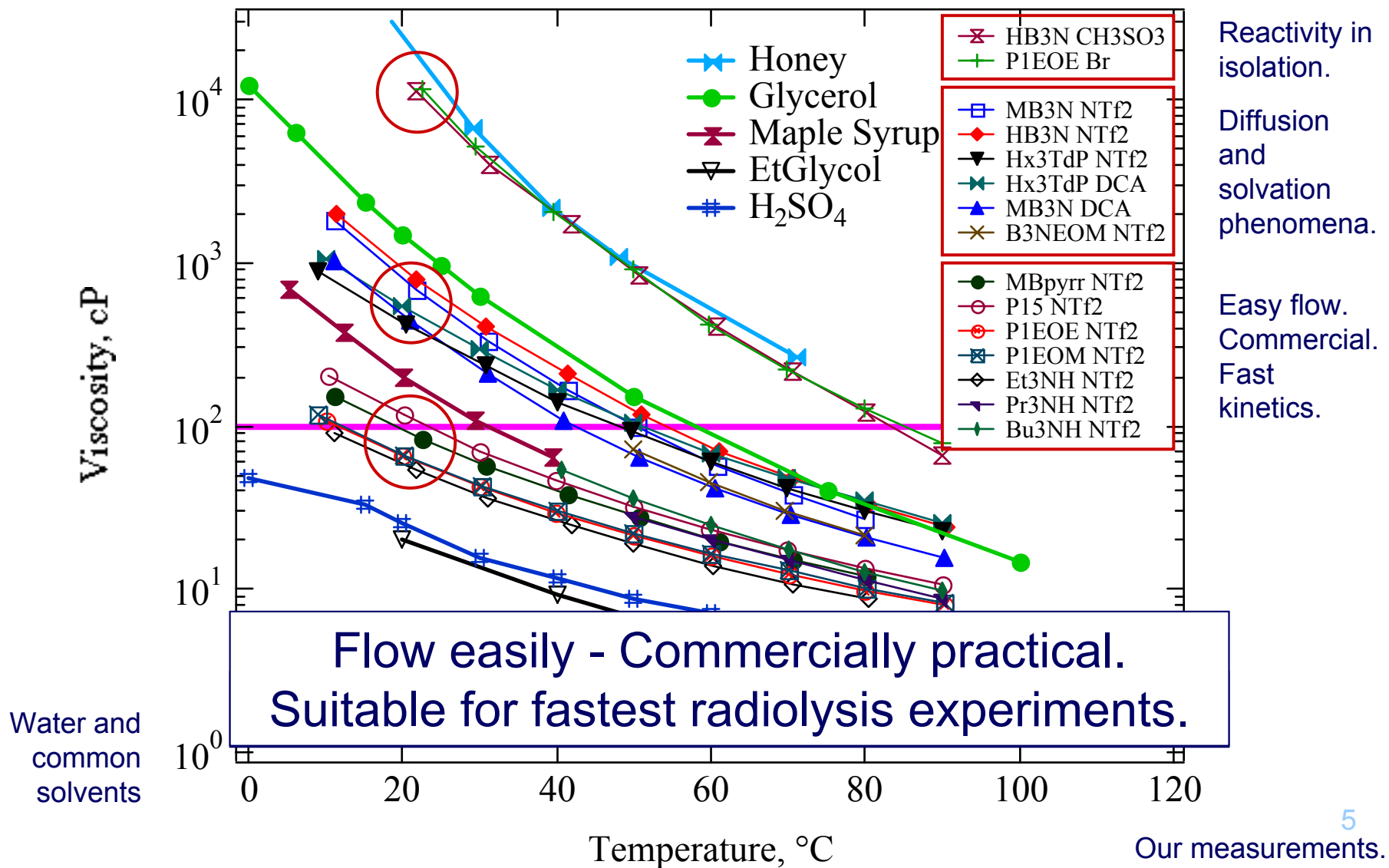
Easy separation of products.

Make liquid easy to reuse/recycle.

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



Viscosities of Some Ionic Liquids

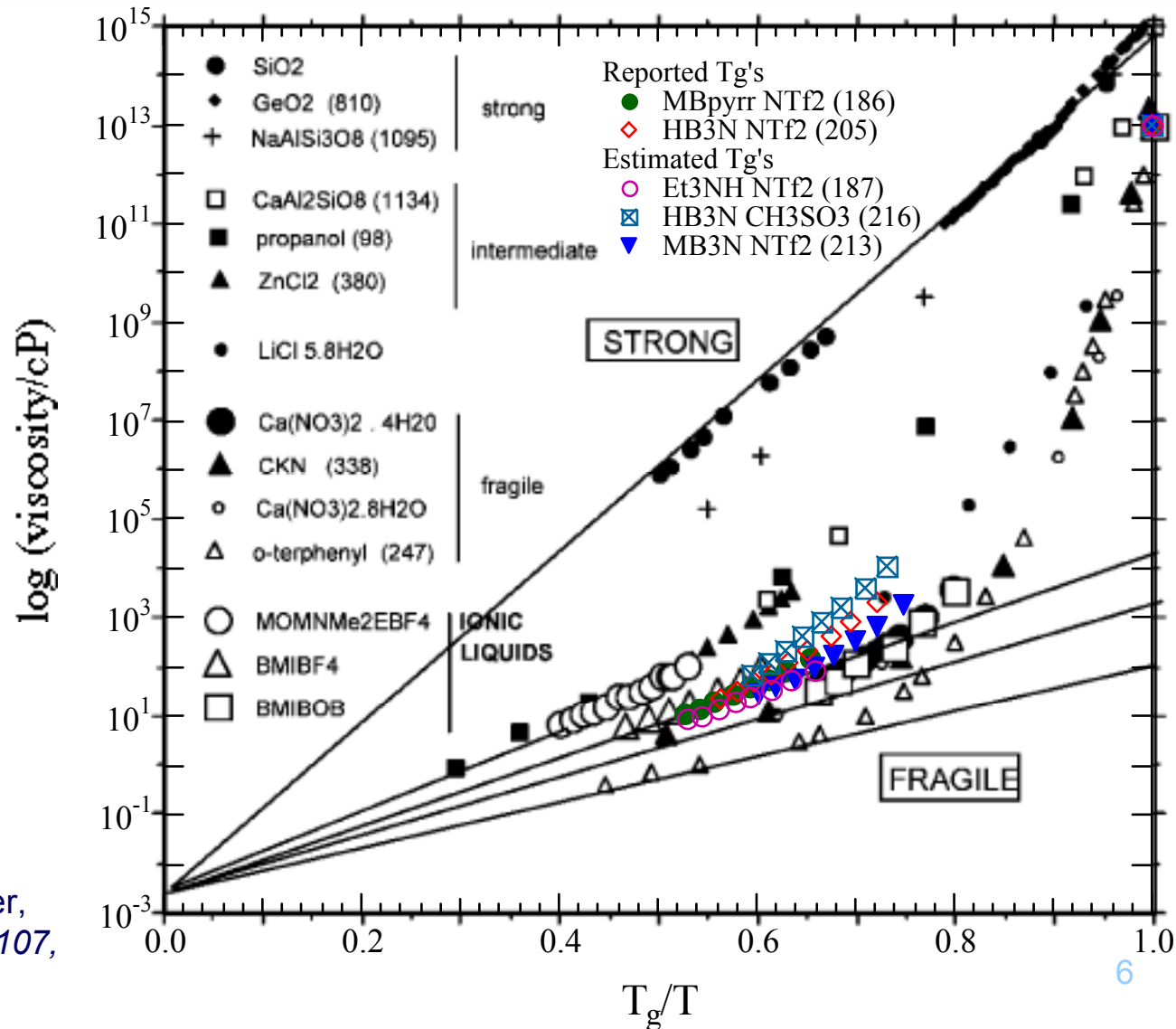


T_g -Normalized Arrhenius Plot

Many ionic liquids are “fragile” glass formers.

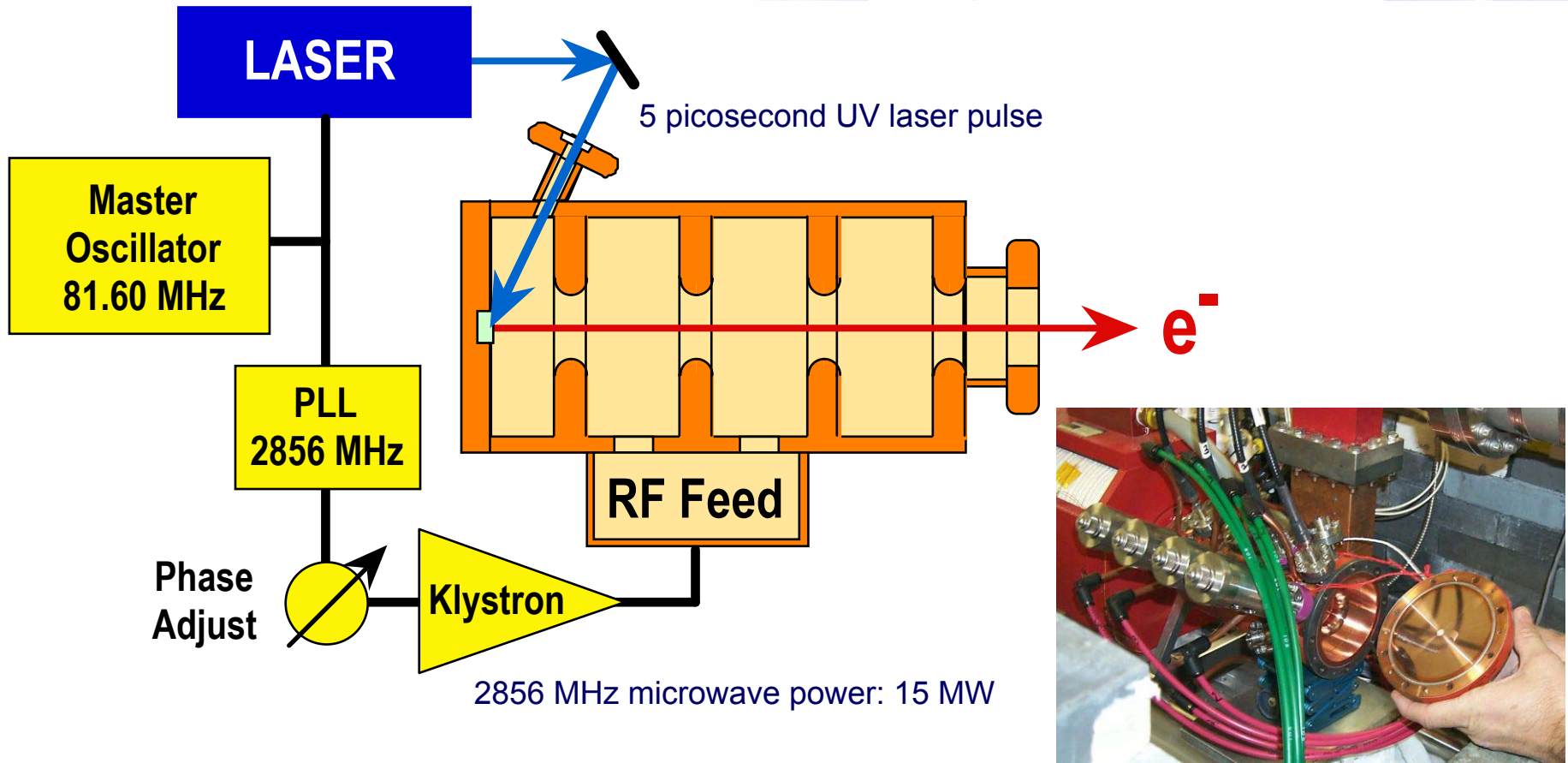
Rule of thumb:

$$T_m < 1.5 T_g$$



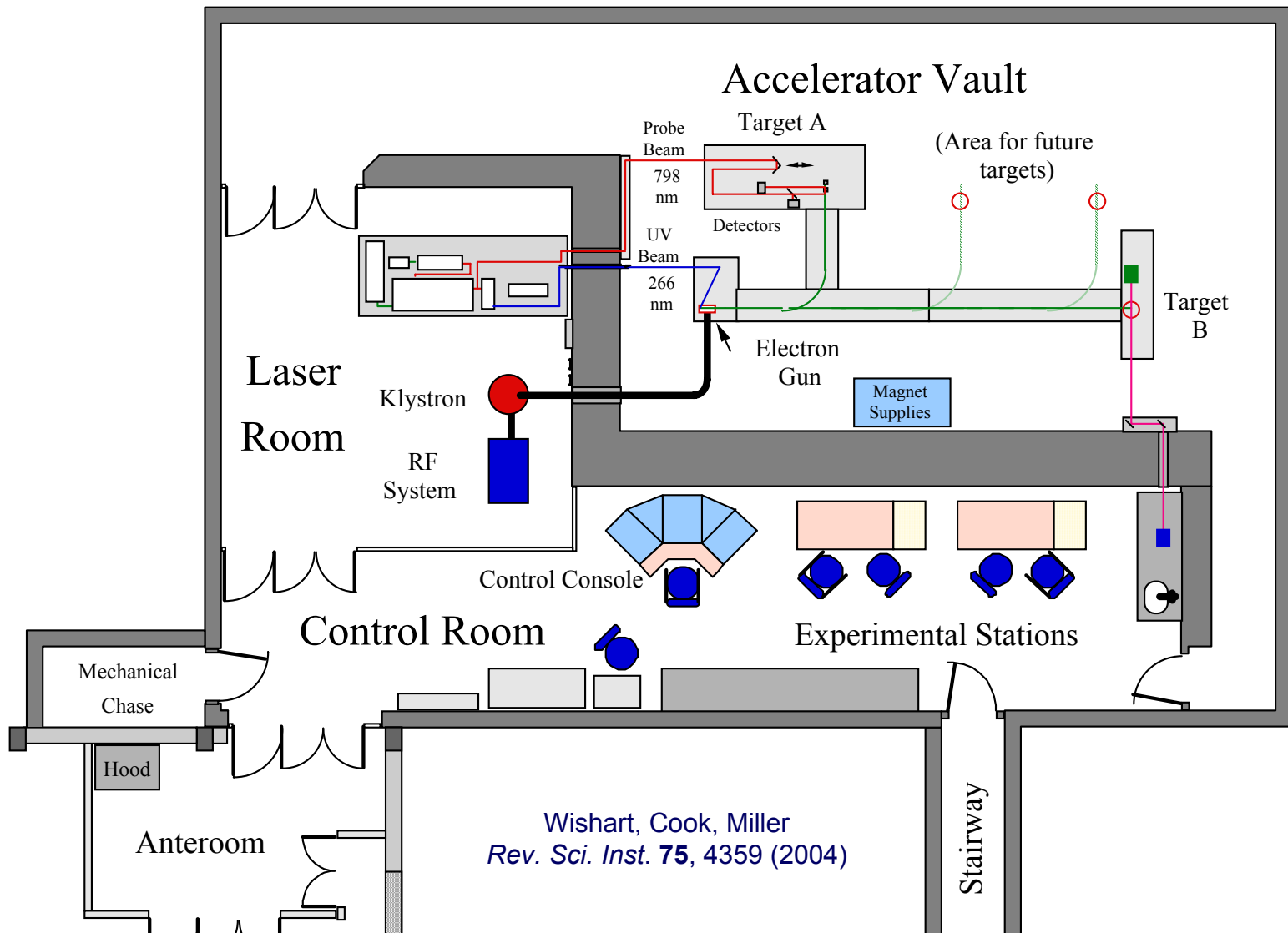
Black and white data: Xu, Cooper, Angell; *J. Phys. Chem. B*, **2003**, 107, p. 6174, fig. 6

Photocathode Electron Gun Accelerators: Laser-RF Synchronization at LEAF

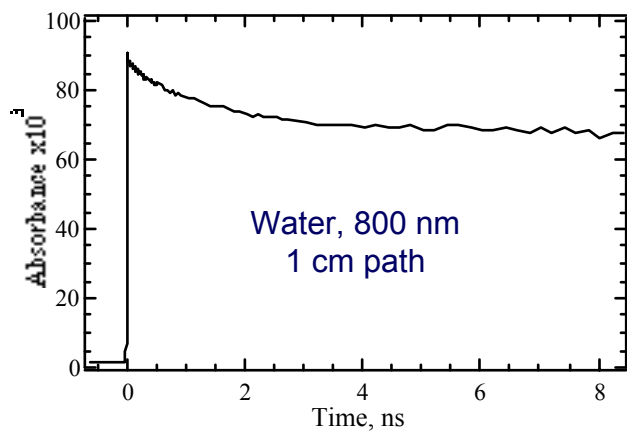
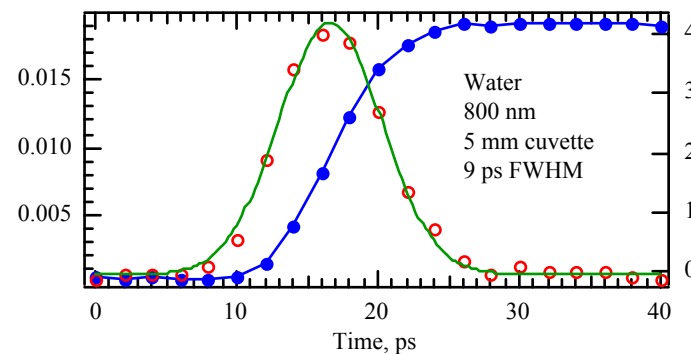
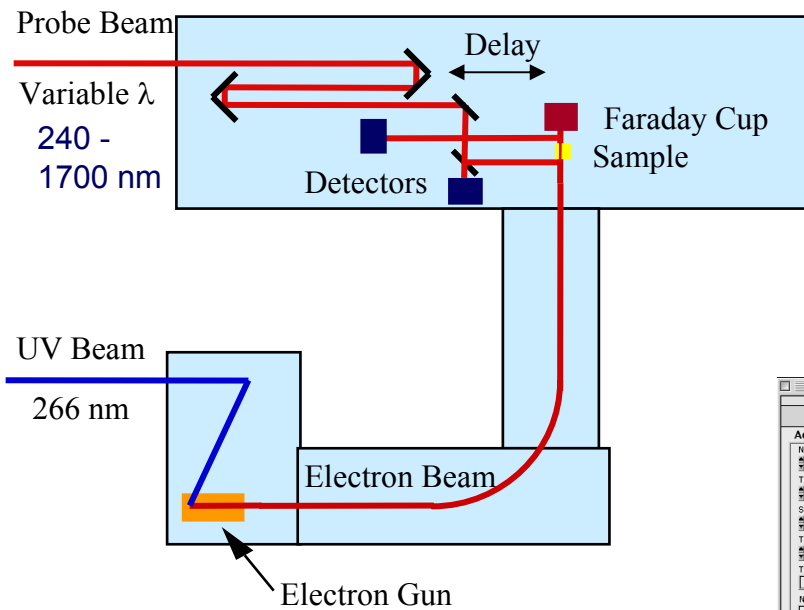


A picosecond-synchronized UV laser pulse generates photoelectrons, which are accelerated to 9 MeV by high fields (80 MV/m) in the **one-foot long** resonant-cavity structure.

LEAF Facility Layout



Pulse-Probe Experiment



Pulse-probe controller9

Acquisition parameters

Number of Shots per Point: 20
Time Interval per Point (ps): 200.0
Starting Delay Time (ns): -0.030
Total Time Window (ns): 9.800
Time Window Used (ns): 9.800
Number of Points: 50
Iteration: 136
Cumulative shots: 2720
Slope Trigger Rate (Hz): 10.0

Use Times from File: ON
New File
Save Timetable
Time Zero (ns): 1.520
Relative Times ON

I/O parameters

Root Data File Name: CD3CN
Data Folder Path: \\Macintosh HD\Users\jlm.041108\NIR
Next Data File is: CD3CN_16
File header/comment: CD3CN_sarated_still_settings 041110-a1_phase 16.3_8.75_MeV_3.1 nC
Vavelength, nm: 1400

Corrected Absorbance

Faraday Current

Abs STD: 0.002852
Base STD: 0.002631
Good points: 15
Stage position: 1458.00 [nm] 9.720 ns

Setup File Path: \\Macintosh HD:\Applications (Mac OS 9):\LabVIEW 6.1 user.lib:\ValueFromStopper:eng_14Nov97.asr

Why Study Ionic Liquid Radiolysis?

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

Solvent properties, non-volatility and combustion resistance make them a good candidate for chemical transformations of radionuclides.

British Nuclear Fuels, Ltd. - electron transfer reactions in ILs to recycle spent nuclear fuel. Several patents have been issued.

Calculations from Los Alamos indicate that the minimum critical concentration (above which a solution in a large container would go critical) for plutonium in representative tetrachloroaluminate and tetrafluoroborate ILs are 20 to 100 times greater, respectively, than in water.

Use of such ILs could dramatically decrease the risk of criticality accidents such as the one that occurred in 1999.

Why Study Ionic Liquid Radiolysis?



Ionic liquids provide a new environment to test theories of charge transfer and other reactions.

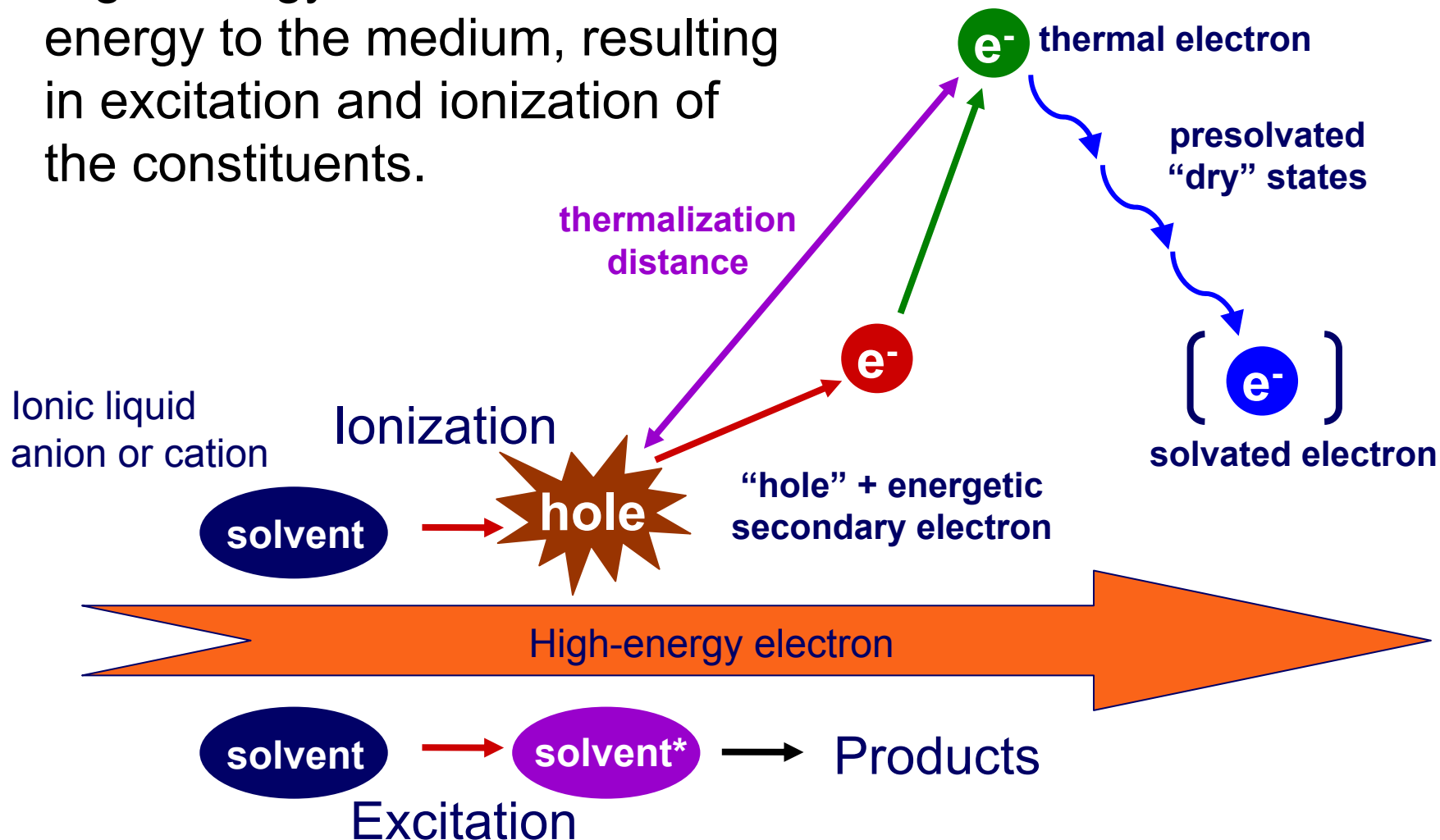
Characterization and reactivity of pre-solvated “dry” electron states.

Electron transfer: thermodynamics and reorganization energies as a function of distance in an ionic lattice environment, solvent dynamical control.

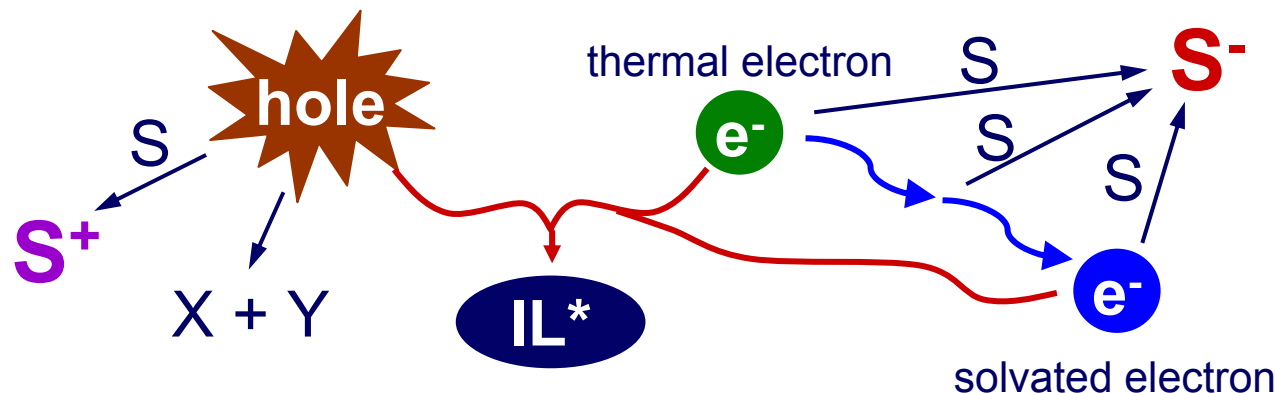
Radiolytic energy deposition in ionic lattices (liquid or solid): electron-hole distributions.

Initial Events in Radiolysis

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



Early Reactions in Radiolysis



Ionization branch:

Electron thermalization and solvation



Recombination of hole and electron



Dissociation (bond breakage)



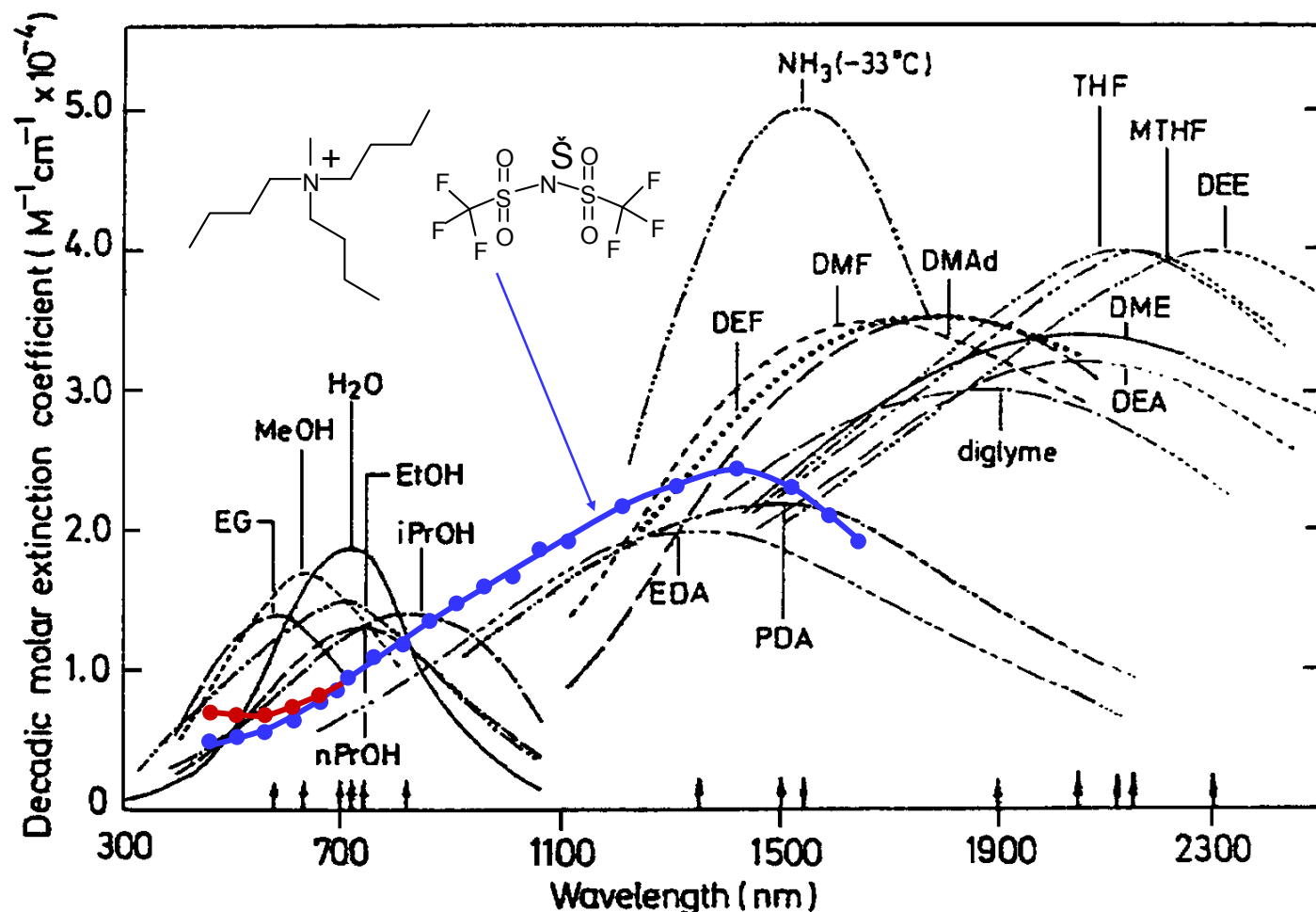
Scavenging by dissolved material



Radiation and laser techniques are complementary.

Radiolysis creates unique products that cannot be obtained via laser-induced photochemistry.

Solvated Electron in $MB_3N^+ NTf_2^-$



e^-_{sol} decay: ≤ 300 ns

Hole(?) decay: 50 ns

IL dielectric constants unknown.

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

Alkylammoniums are similar to acetonitrile.

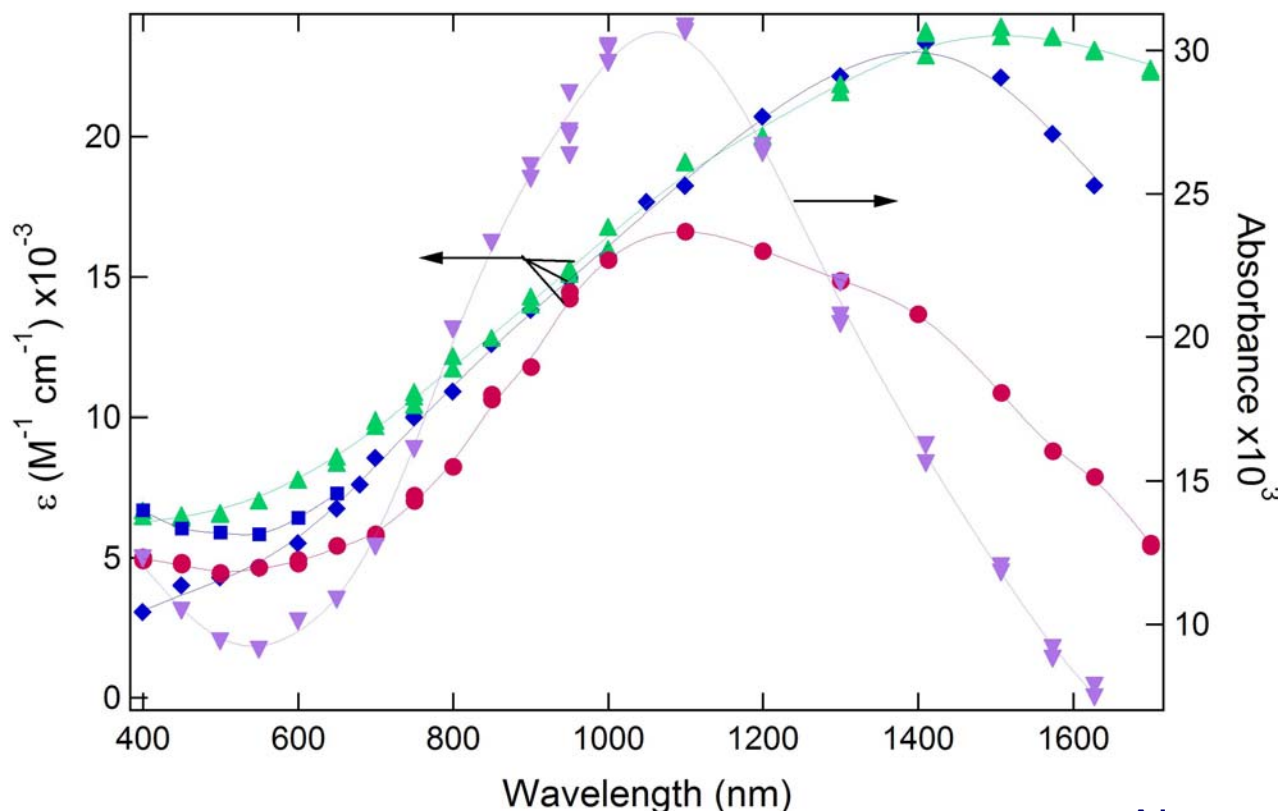
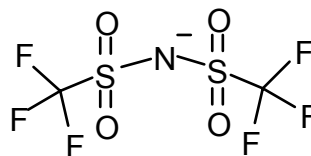
Imidazoliums appear more polar (due to H-bonding C-2 proton).

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

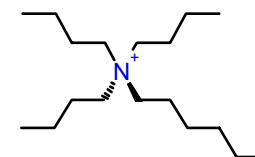
Wishart and Neta, *JPC B*, **107**, 7261 (2003). Other spectra: Dorfman and Galvas (1975).

Cation Effect on Solvated Electron Spectra

Constant anion (NTf_2^-):



Tetraalkyls



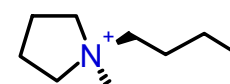
“NaCl”

CACA
ACAC
CACA

◆ $\text{MB}_3\text{N NTf}_2$

▲ $\text{HB}_3\text{N NTf}_2$

Pyrrolidiniums



layered

CCCC
AAAA
CCCC

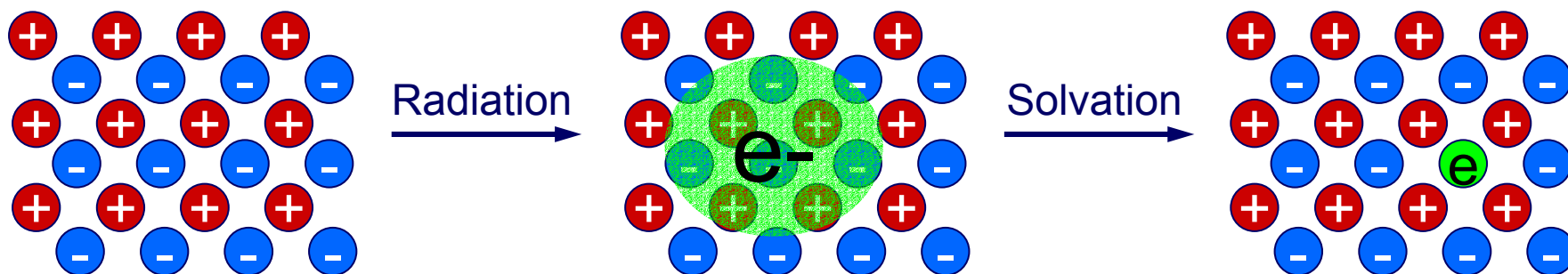
● MBpyrr NTf_2

▼ MEOM-pyrr NTf_2

Also applies for NCNCN^-

Observing slow solvation in ionic liquids

Pulse radiolysis: probe by absorption



Solvation of the electron in $\text{MB}_3\text{N NTf}_2$ is slow (~ 4 ns).

Ordinary liquids are on the order of picoseconds.

Can we observe solvated electron precursors in the near infrared?

Technical problem with digitizer experiments:

NIR diodes (InGaAs, Ge) have large secondary response at short times.

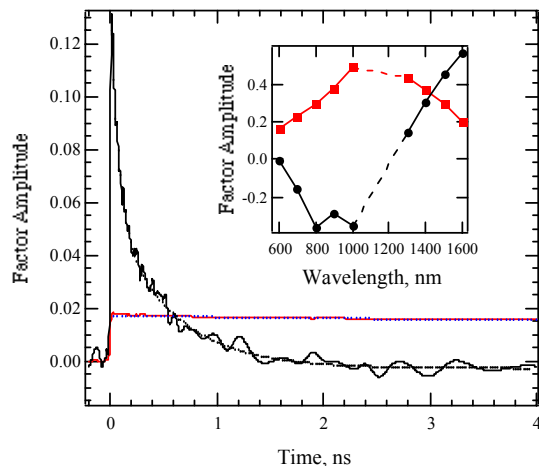
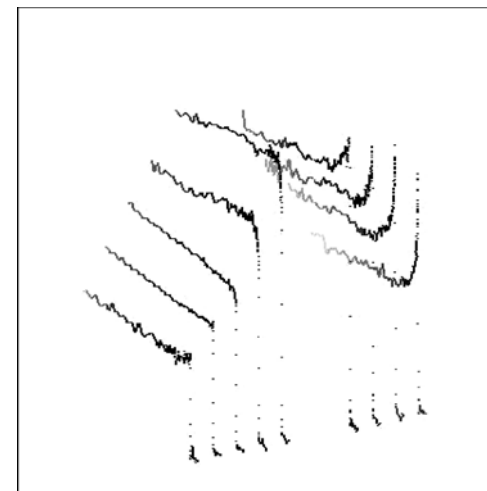
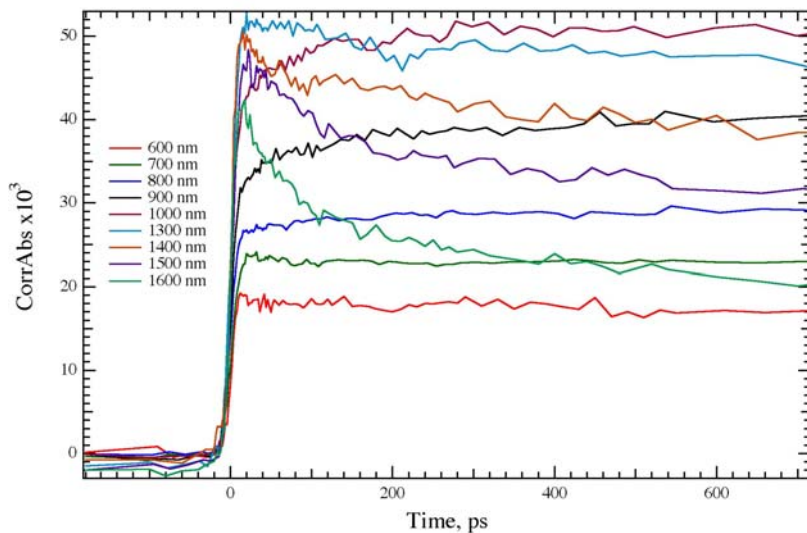
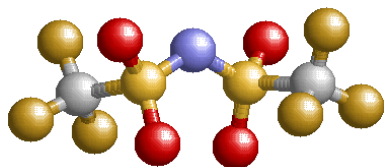
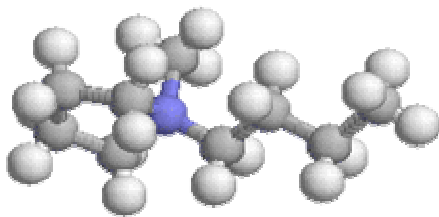
Solution: Pulse-probe transient absorption radiolysis

$\text{MB}_3\text{N NTf}_2$ is too viscous to flow (786 cP at RT).

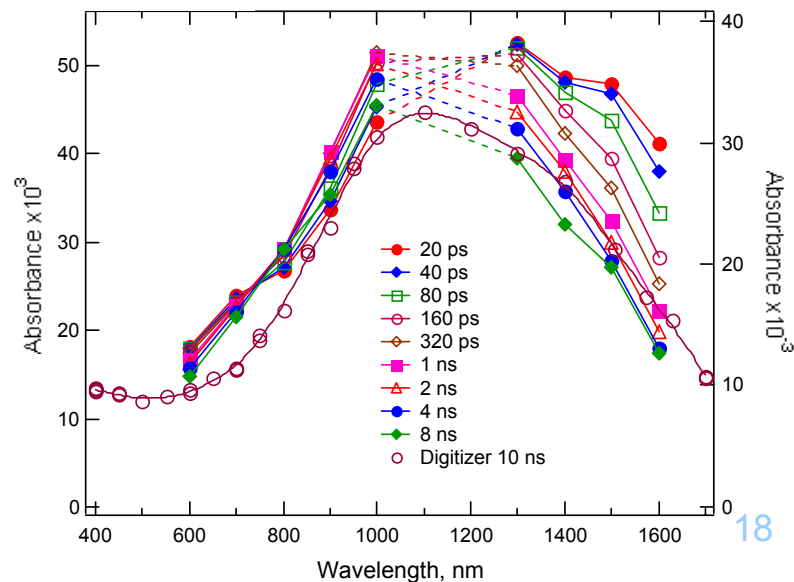
We will study low-viscosity pyrrolidinium ionic liquids.

Observing Electron Solvation in an Ionic Liquid by NIR Pulse-Probe

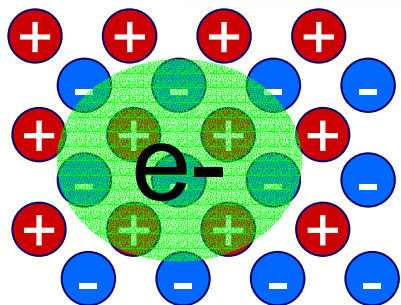
$P_{14}NTf_2$



$\tau \sim 260$ ps



Pre-solvated electron reactivity is important in ionic liquids



Pre-solvated electrons are energetic and reactive. In most normal solvents, they only last picoseconds. In some ionic liquids, they last 1000x longer.

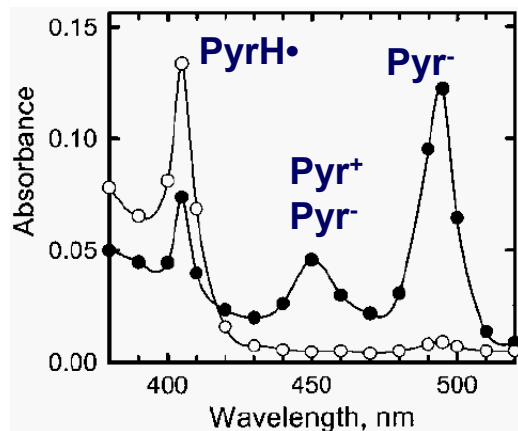
In ionic liquids, solvation can be so slow that even low scavenger concentrations compete effectively.

We have measured pre-solvated electron scavenging efficiencies well above those of normal liquids (5-10x).

Implications:

- Concentrations of solutes that are too low to react with e^-_{solv} may still react with e^-_{pre} . Complication for radiological use?
- Easier to generate intermediates for chemical reactivity studies.
- Solvation studies over a range of ionic liquids are necessary.

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



Spectra taken at $\sim 1 \mu\text{s}$ (solid circles) and $\sim 70 \mu\text{s}$ (open circles) after pulse, 18 mM pyrene.

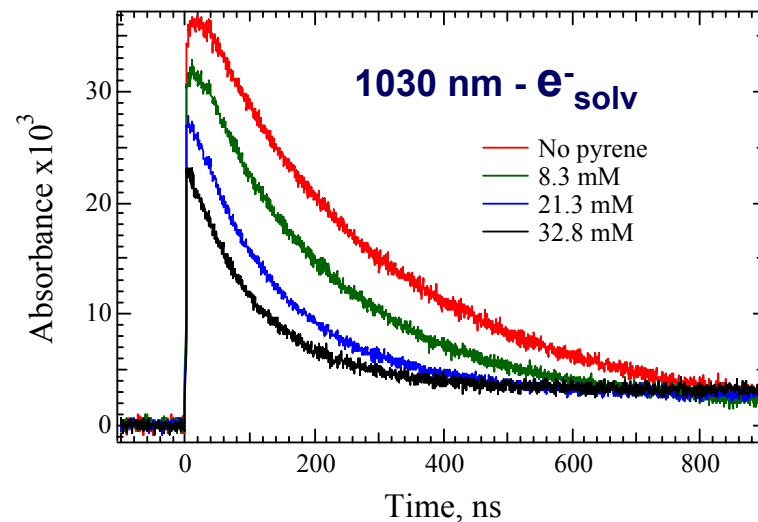
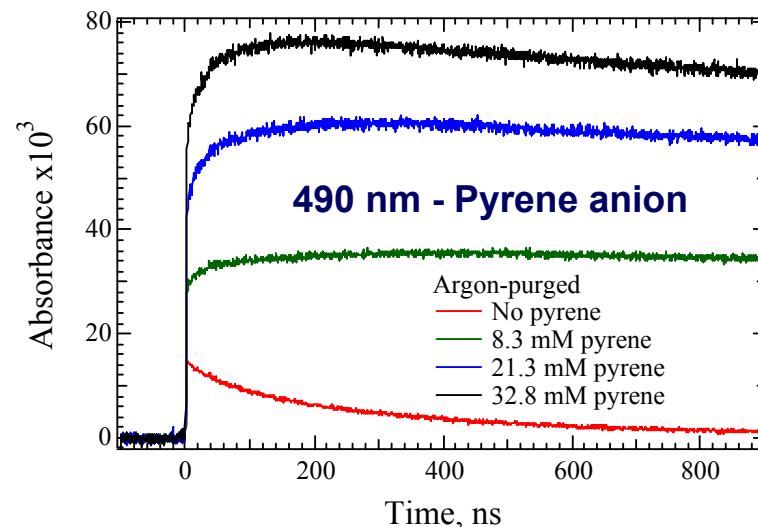
Pyrene anion peaks at 450 and 495 nm

Pyrene cation also at 450 nm

H-adduct at 405 nm.

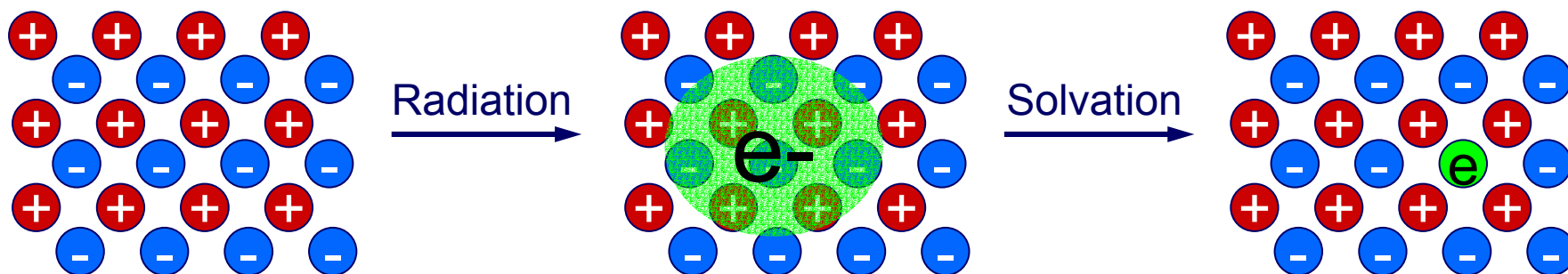
$$k = (1.72 \pm 0.02) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

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



Observing slow solvation in ionic liquids

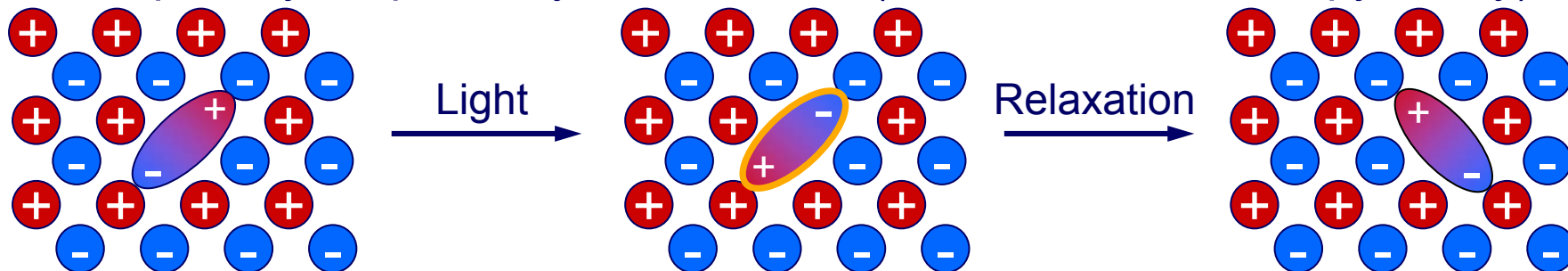
Pulse radiolysis: probe by absorption



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

Ordinary liquids take about one picosecond.

Laser photolysis: probe by fluorescence (Stokes shift, anisotropy decay)



Coumarin 153: $\text{MB}_3\text{N NTf}_2$ $\langle \tau_{\text{Stokes}} \rangle = 4.5$ ns (Maroncelli), $\text{P}_{14} \text{NTf}_2$: $\langle \tau \rangle = 220$ ps

Detailed studies of micro vs. macro viscosity with E. Castner (Rutgers).

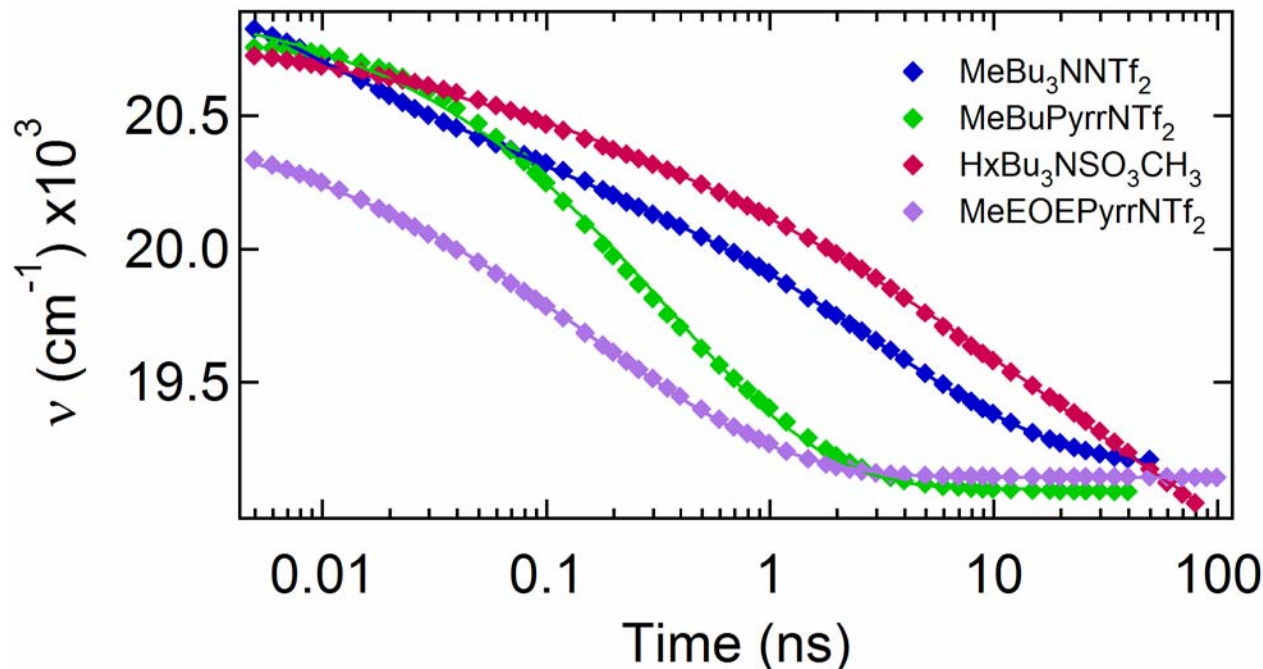
Theory (molecular dynamics simulations) with M. Kobrak (CUNY Brooklyn)

Time Dependent Fluorescent Stokes Shift

- Resolve most of the Stokes Shift
- Complex, non-arrhenius broad distributions, β 0.2 – 0.6
- Consistent with viscosity, anisotropy measurements

$$\nu(\infty) + \Delta\nu \exp[-(t/\tau_0)^\beta]$$

$$\langle \tau \rangle_{\text{solv}} = (1/\Delta\nu) \int_0^\infty [\nu(t) - \nu(\infty)] dt = \tau_0/\beta\Gamma(\beta^{-1}) \quad 0 < \beta \leq 1$$



Diffusion is not simple in ionic liquids

Poor packing in ionic liquids creates voids.

The voids should depend on the structure of the ionic liquid.

Small, uncharged molecules could move faster through the voids than the solvent itself can move.

Evidence:

- Rates for reaction of e_{solv}^- with O_2 and CO_2 are the same for $\text{P}_{14}\text{NTf}_2$ and HB_3NNTf_2 but the viscosities differ by 10x.

For diffusion-controlled reactions in normal liquids: **Rate \propto 1/viscosity**

- Neutral $\text{H}\cdot$ atoms react 10x faster than solvated electrons in ionic liquids. In normal liquids, the ratio is reversed.
- Diffusion rate of O_2 is 30x higher than that of O_2^- in HE_3NNTf_2 (220 cP). In emim NTf_2 (32 cP) the factor is less than 3. (Buzzeo et al. JPC 2003)

Applications:

Controlled reactivity based on diffusion control.

Reduction-oxidation modulation of transport phenomena.

Summary



- Solvated electron is an observable product of ionic liquid radiolysis
Absorption maxima 1000 – 1600 nm (alcohols 700 nm)
- Electron solvation is relatively slow compared to molecular solvents
Blue-shift of absorption due to relaxation (100 ps - 50 ns)
- Dry electron capture by aromatic acceptors can be significant.
- Solvation dynamics studies will provide important data for understanding pre-solvated electron reactivity.
- Reaction rates of solvated electrons with added solutes are also slow compared to those of molecular solvents (diffusion controlled).
- Reaction rates do not correlate with viscosity.

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