

Rapid Chemical and Physical Processes in Solution

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**XDL 2011: Ultra-fast Science with “Tickle and Probe”
CHESS, Cornell, June 20-21, 2011**

Physical Science and Nanoengineering Problems

Confined liquids

liquids in nanoporous materials

crowded cellular environments

liquids in lithium batteries, fuel cells, and ultracapacitors

Solvation in biomolecular assemblies

functional sites for protein-protein, protein-nucleic acid binding

Binary, ternary, and more complex liquid systems

Ionic liquid polymer gel electrolytes

Biofuels

Devices: e.g., polymer-membrane support for enzymes in ionic liquids

Cellulase for breaking down cellulose to glucose

Carbonic anhydrase for capturing CO₂

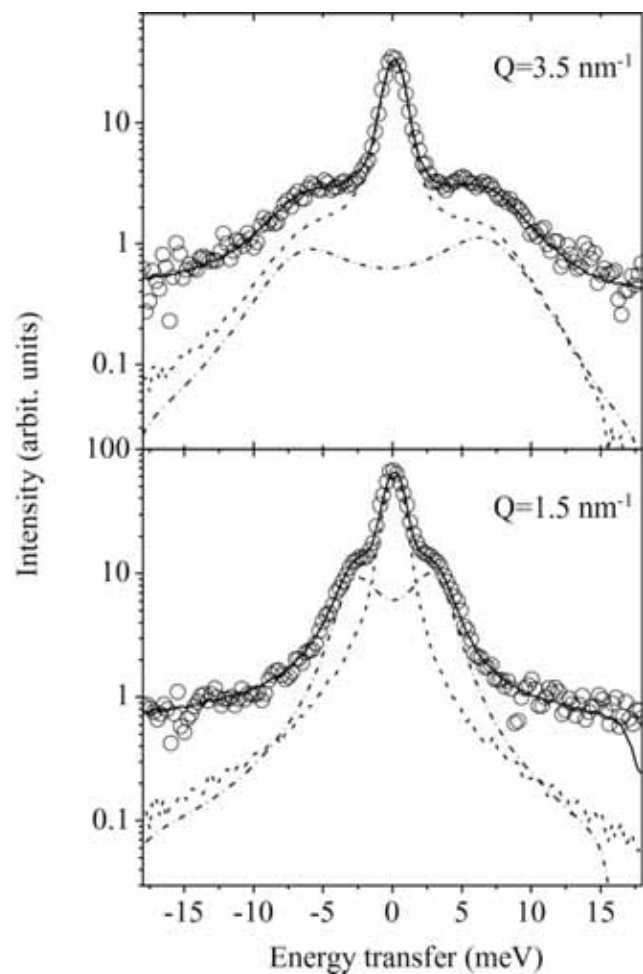
Need sensitivity for low-Z experiments- sometimes zero-metal environment, or no heavy atoms- just H, Li, B, N, C, O, F, P and S.

Simultaneous Observation of Structure and Dynamics

**Time-resolved x-ray spectroscopy (See L. Chen, et al.)
XAFS/EXAFS and XANES**

**Inelastic x-ray scattering (IXS)
(see also QENS and neutron spin-echo methods)**

Inelastic x-ray scattering from glycerol: P = 661 bar



Cunsulo, et al.,
J. Chem. Phys. 134, 184502 (2011)

Vibrational dynamics at 1.8 and 4.2 nm length scales.

Resonant inelastic x-ray scattering

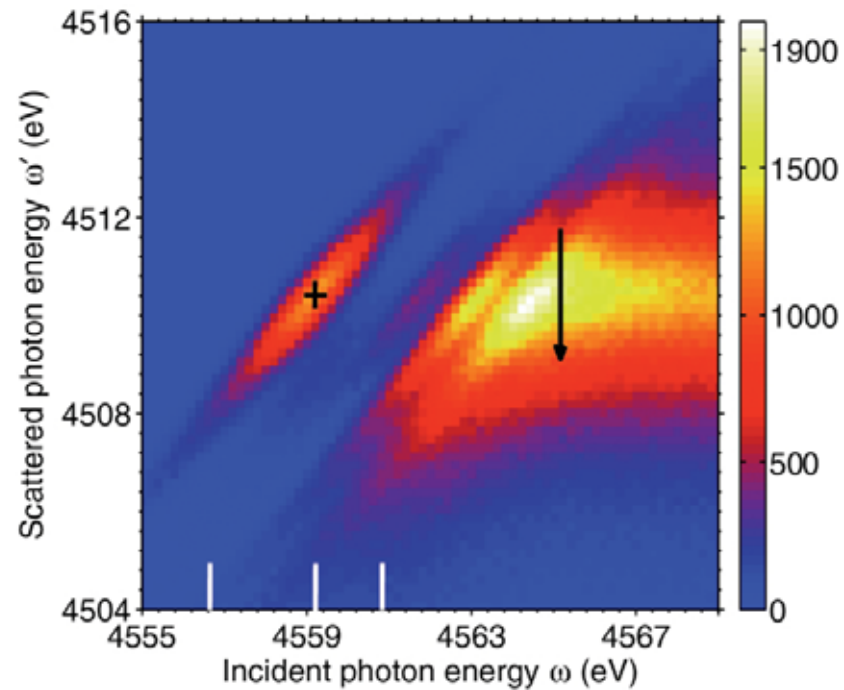


FIG. 1. Experimental RIXS spectra in CH3I recorded close to I L3-edge. The cross around the incident photon energy of 4559 eV shows the maximum of the L3–N4,5 emission line resulting from a resonant excitation $I 2p_{3/2} \rightarrow 15a_{12}$. The arrow around 4565 eV shows the onset of fluorescence corresponding to an approximate position of the CH3I ionization threshold.

Resonant inelastic x-ray scattering at the limit of subfemtosecond natural lifetime

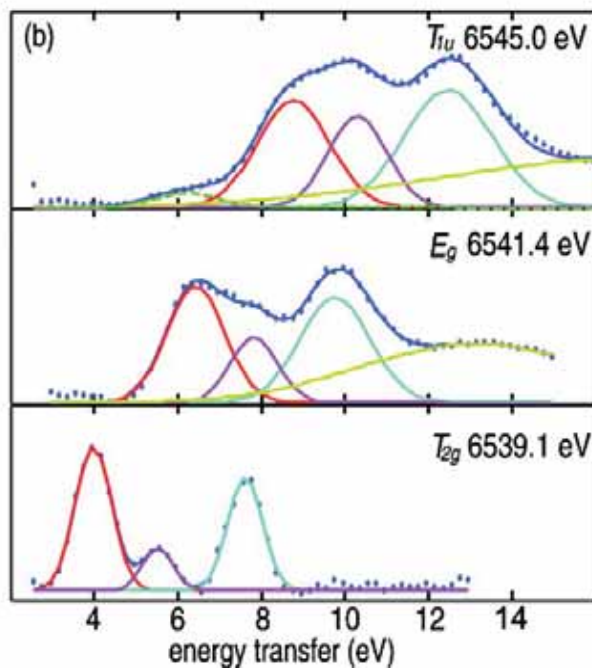
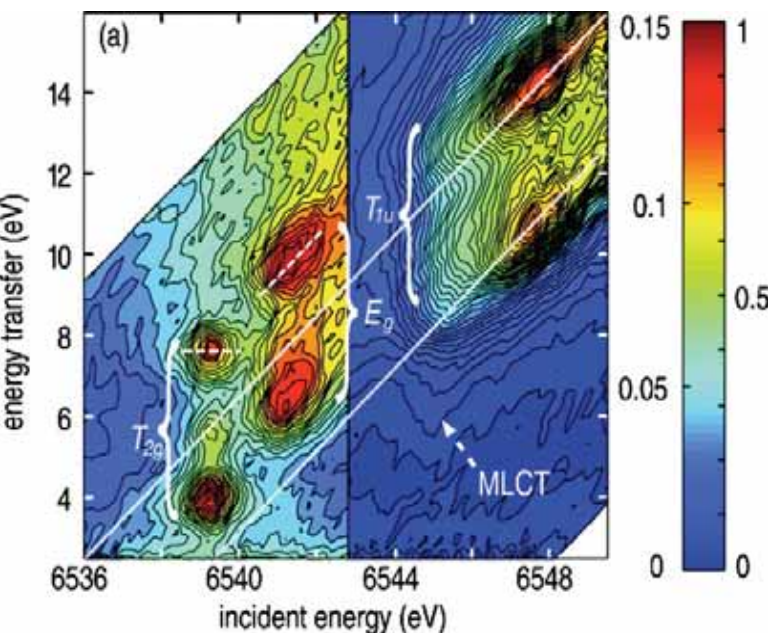
T. Marchenko, L. Journal, T. Marin, R. Guillemin, S. Carniato, M. Žitnik, M. Kavcic, K. Bucar, A. Mihelic, J. Hoszowska, W. Cao, and M. Simo, J. Chem. Phys. 134, 144308 (2011).

Resonant inelastic x-ray scattering

J. Chem. Phys. **132**, 134502 (2010); doi:10.1063/1.3367958

Characterization of charge transfer excitations in hexacyanomanganate(III) with Mn K-edge resonant inelastic x-ray scattering

Drew A. Meyer, Xuena Zhang, Uwe Bergmann, and Kelly J. Gaffney

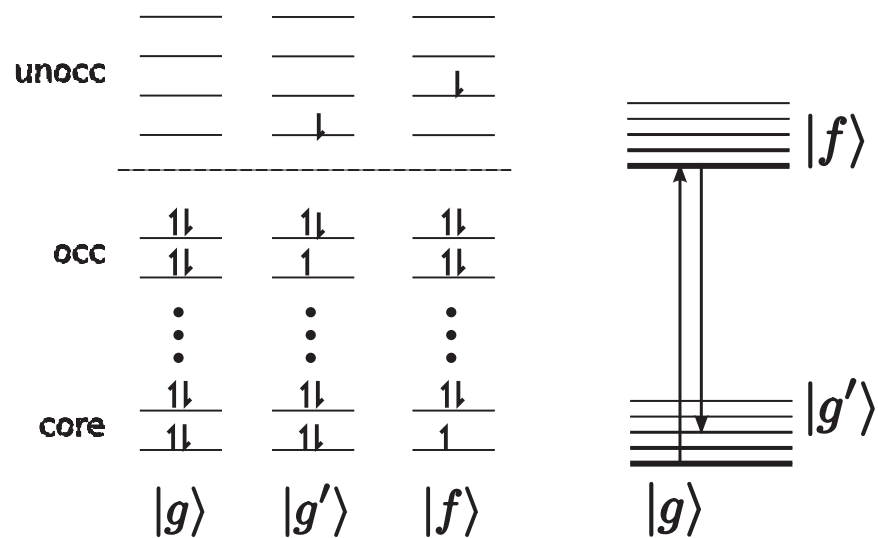


(a) RIXS spectra taken in the low energy transfer region. The energy transfer axis is simply the difference between the incident and emitted x-ray energies. The spectrum is split into two sections with different scalings to show features more clearly, with scaling for the left and the right panels respectively shown on the left and right sides of the color bar. Solid diagonal lines are drawn at constant emission energies corresponding to the fluorescence peaks in the NRXES. The labels T_{2g} , E_g , and T_{1u} refer to the intermediate states excited in the RIXS process. The brackets enclose the three T_{1u} final state holes generated in the RIXS process for each absorption resonance. The MLCT label refers to the T_{2g} final state hole generated in the RIXS process when resonantly exciting the unoccupied T_{1u} orbital. The labels in the contour plot can be related to the transitions presented in Fig. 6. (b) Resonant emission spectra extracted from the RIXS spectrum. Starting from the bottom, the incident energies are 6539.1, 6541.4, and 6545.0 eV.

“Simulation and visualization of attosecond stimulated x-ray Raman spectroscopy signals in trans-N-methylacetamide at the nitrogen and oxygen K-edges”,

Daniel Healion, Haitao Wang, and Shaul Mukamel

J. Chem. Phys. 134, 124101 (2011); doi:10.1063/1.3557057

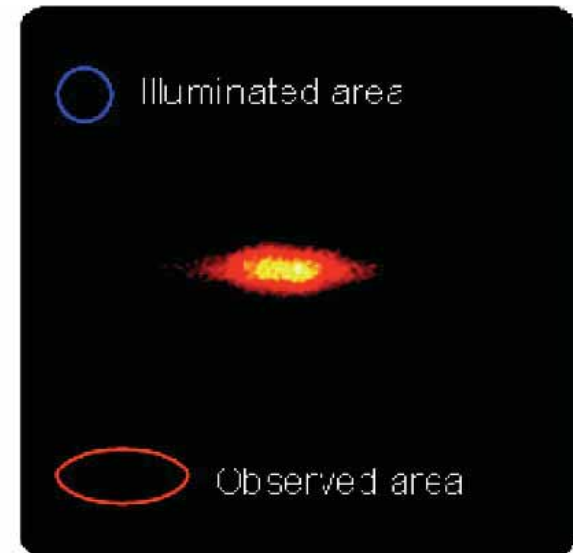
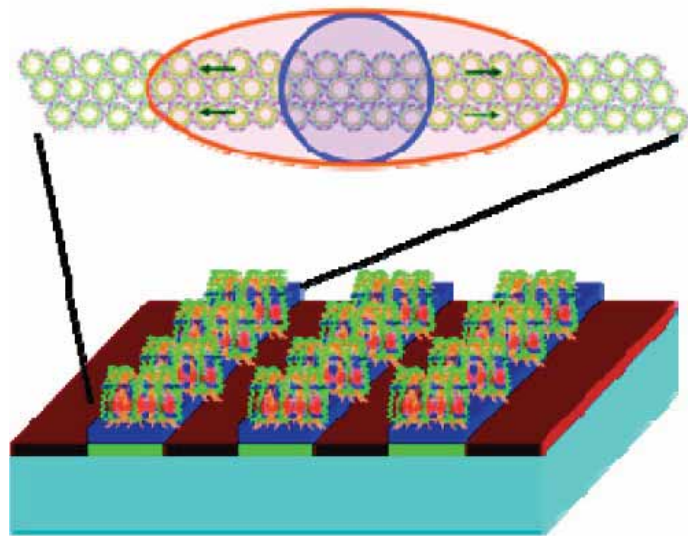


Long-range energy transfer following light-harvesting.

Linear array of LH2 arrays- $>1 \mu\text{m}$ coherent energy propagation.

LH2: Photosynthetic antenna protein- a ring of 18 B850 (bchl) molecules.

M. Escalante; A. Lenferink; Y. Zhao; N. Tas; J. Huskens; C. N. Hunter; V. Subramaniam; C. Otto;
Nano Lett. 2010, 10, 1450-1457. DOI: 10.1021/nl1003569



LH2 complex:

18 BChl (B850 system)

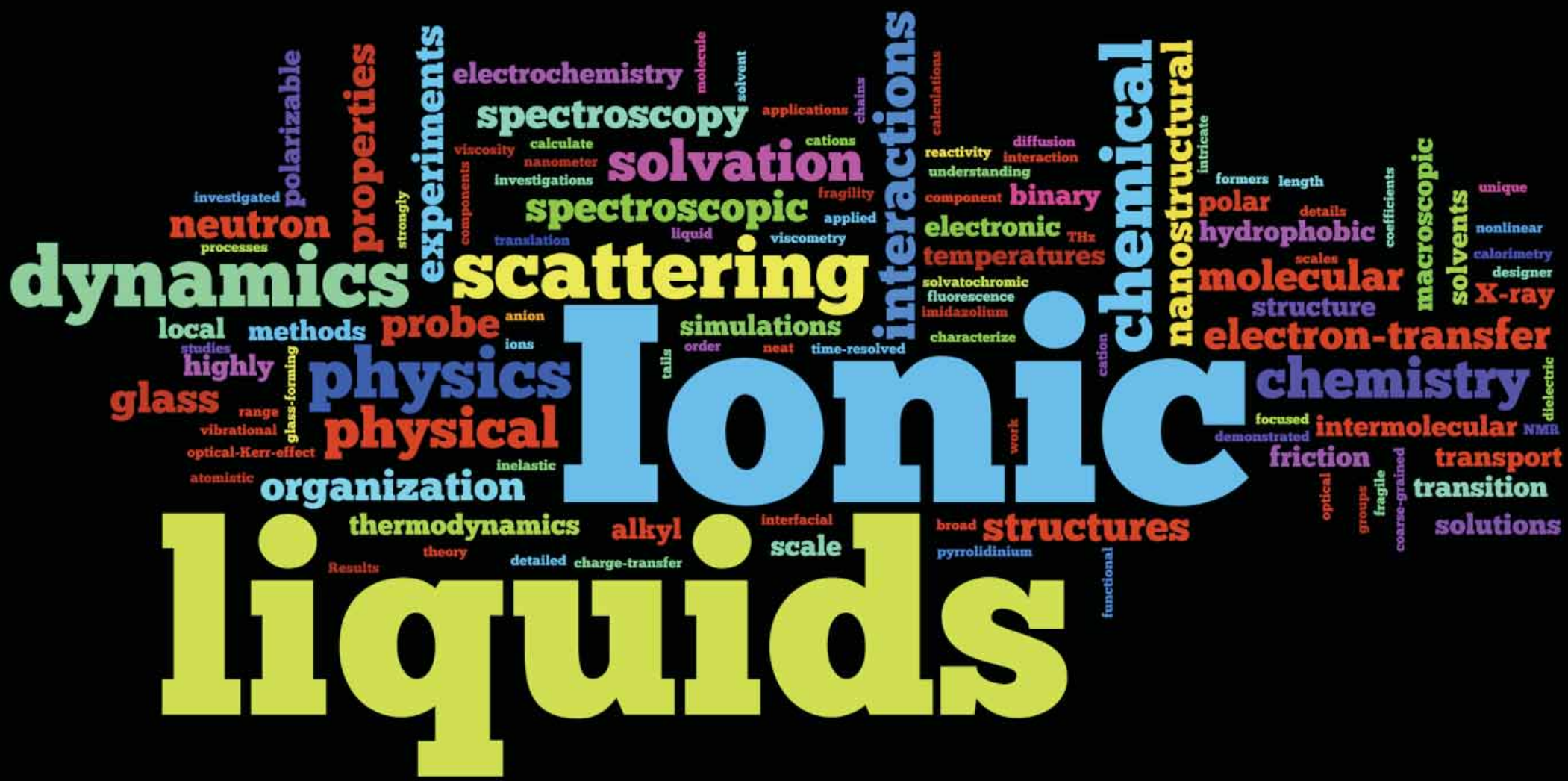
9 BChl (B800 system)

$h = 6.8 \text{ nm}$

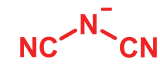
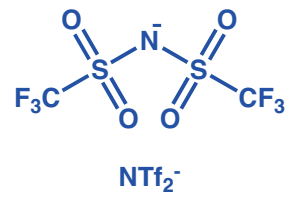
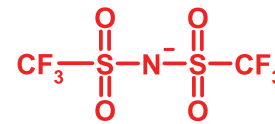
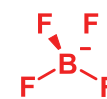
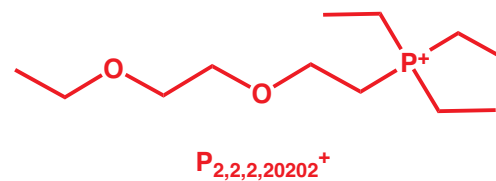
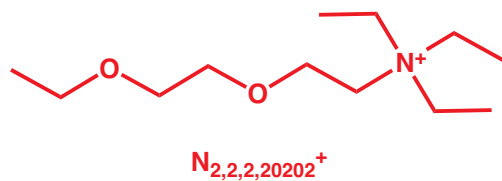
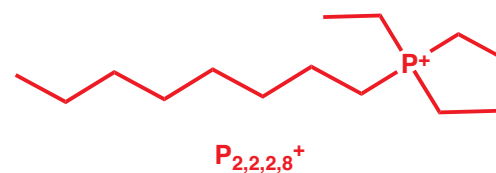
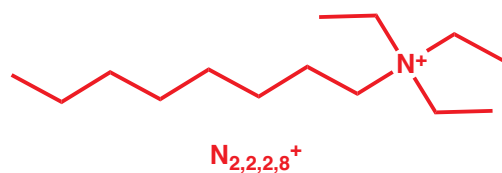
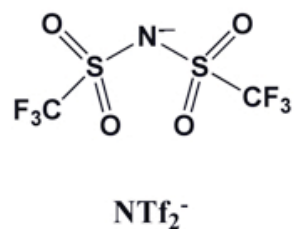
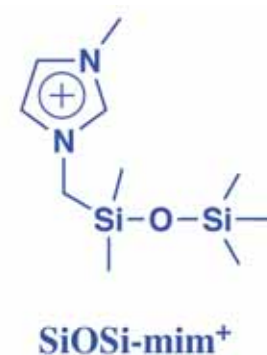
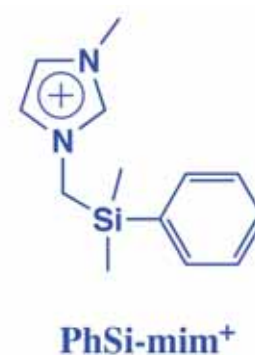
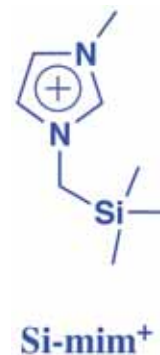
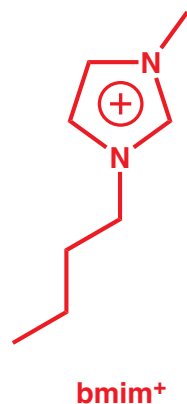
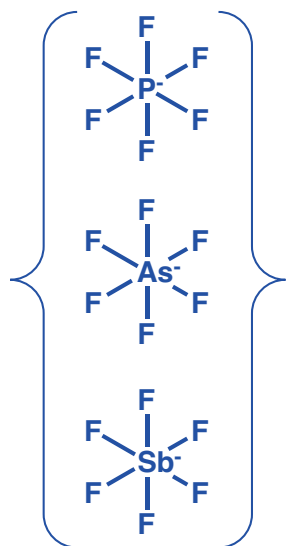
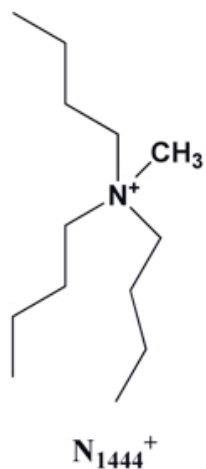
$d = 7 \text{ nm}$.

In *Rb. sphaeroides*, LH2 transfers energy to LH1,
then to Rxn. center. BChl = tetrapyrrole, Mg center.

Proposed experiment: map spatial charge migration and protein solvation using
x-ray probing following 800/850 nm photoexcitation. (Mg K-edge...)



What are Ionic Liquids? Some of our favorites...



Why Ionic Liquids Display Complex Structure and Dynamics

**Concentrated electrolytes
[C⁺/A⁻] ~ 3 Molar**

Hydrophobic

Polar and Polarizable

Binary Fluids

Highly structured

**Supercooled liquids &
fragile glass-formers**

ILs for solubilizing and processing biomass

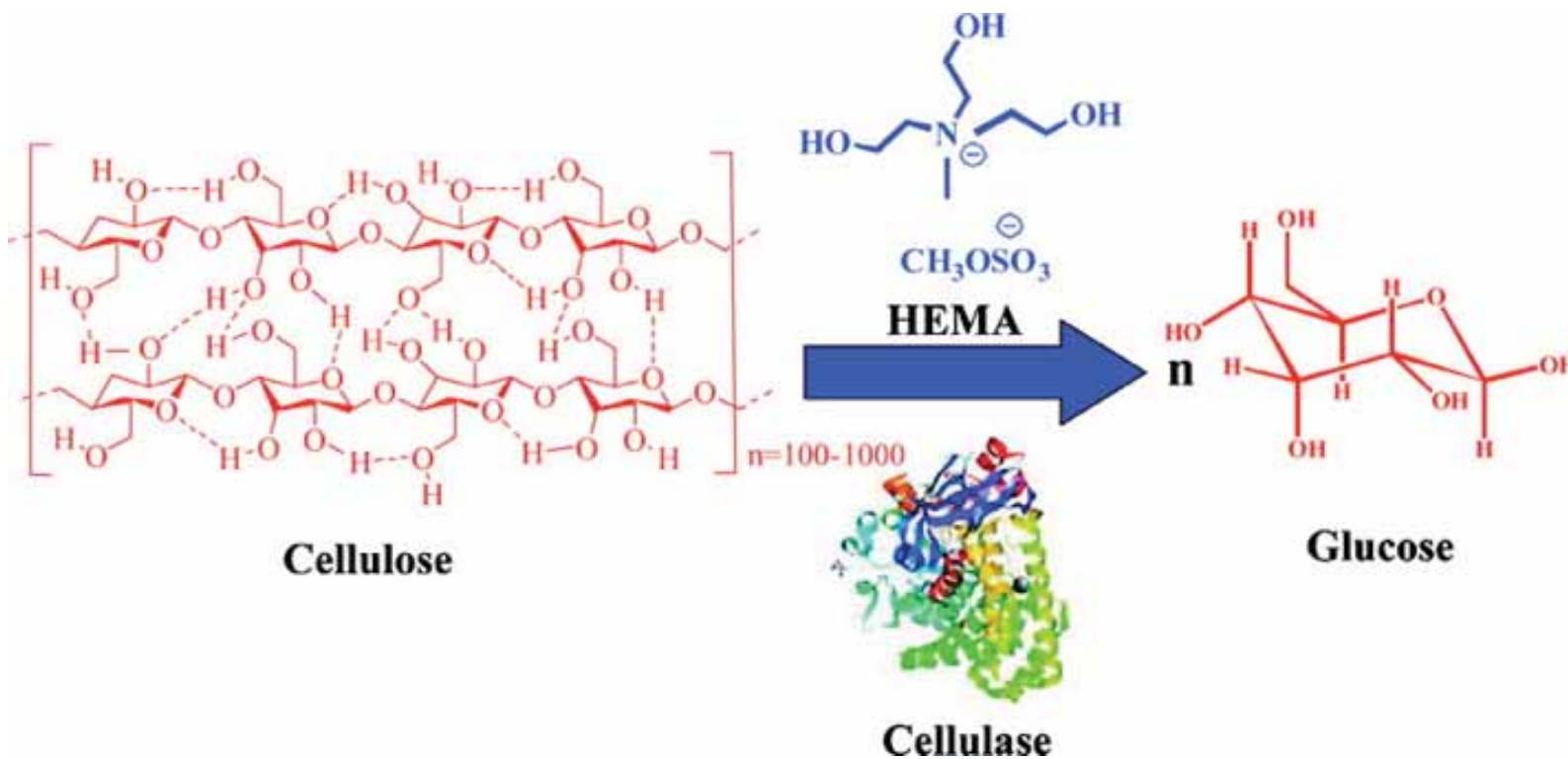
Dissolution of Cellulose with Ionic Liquids

Richard P. Swatloski, Scott K. Spear, John D. Holbrey, and Robin D. Rogers

J. Am. Chem. Soc., 2002, 124 (18), pp 4974–4975

DOI: 10.1021/ja025790m

(7 x 10¹¹ tons cellulose/year- most abundant organic molecule...)

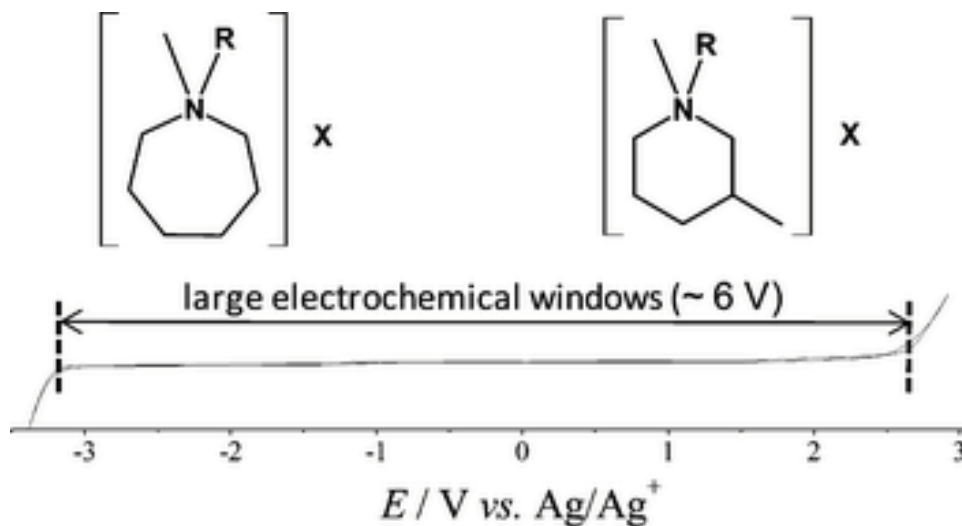


Enzyme-Catalyzed Hydrolysis of Cellulose in Ionic Liquids: A Green Approach Toward the Production of Biofuels

Sayantana Bose, Daniel W. Armstrong, and Jacob W. Petrich

J. Phys. Chem. B 2010, 114, 8221–8227, DOI: 10.1021/jp9120518

Why Are ILs so Important for Electron-Transfer?

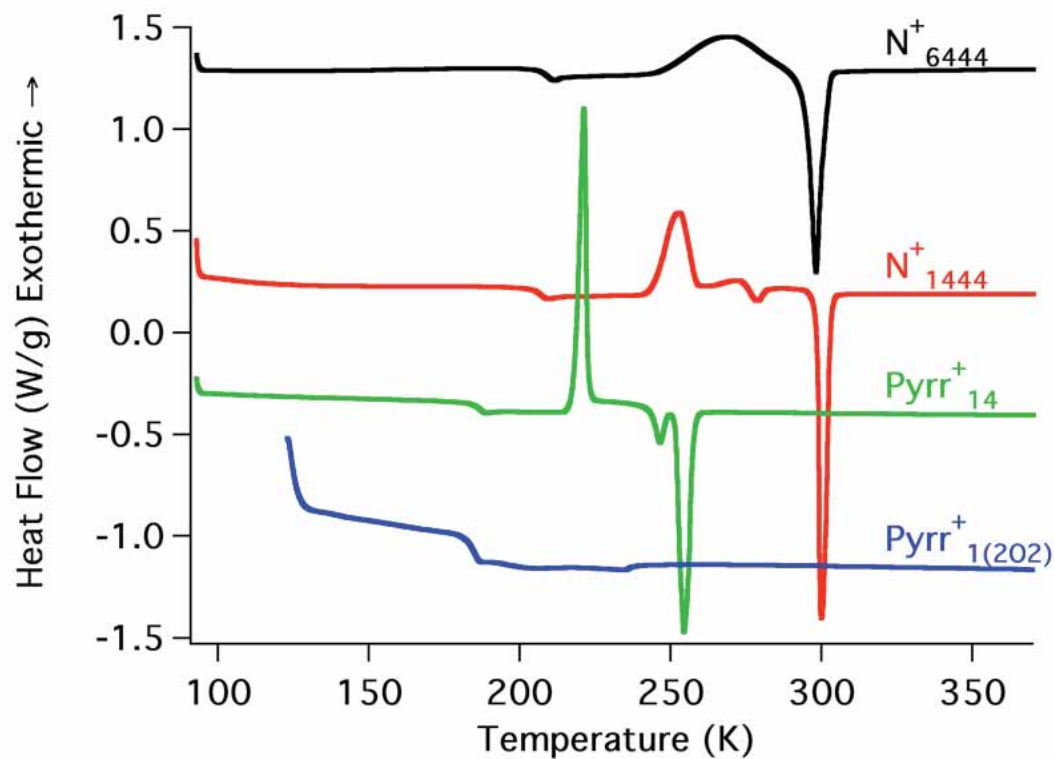
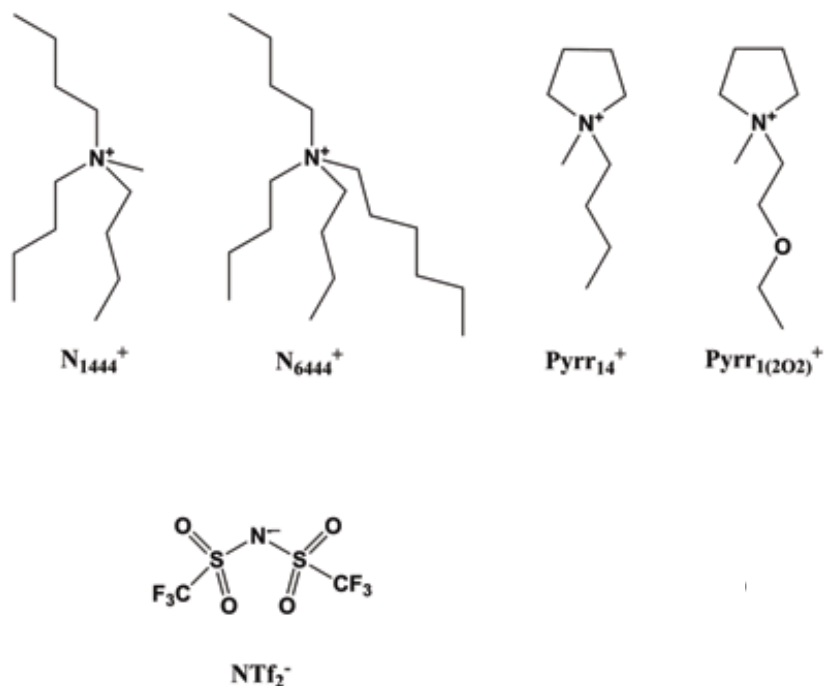


New ionic liquids from azepane and 3-methylpiperidine exhibiting wide electrochemical windows

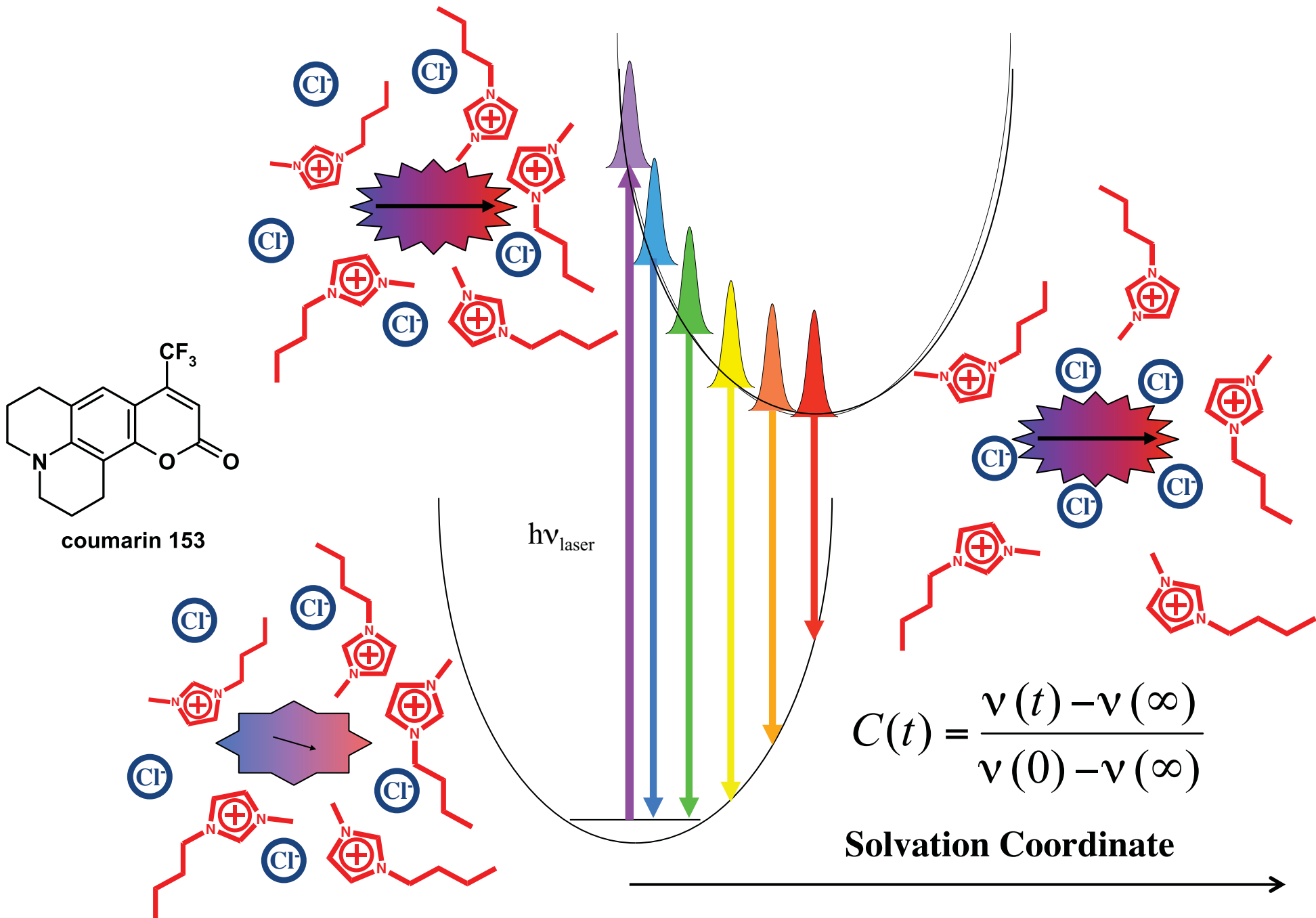
T. Belhocine, S. A. Forsyth, H. Q. N. Gunaratne, M. Nieuwenhuyzen, A. V. Puga, K. R. Seddon, G. Srinivasan and K. Whiston,

Green Chem., 2011, 13, 59-63, DOI: 10.1039/C0GC00534G

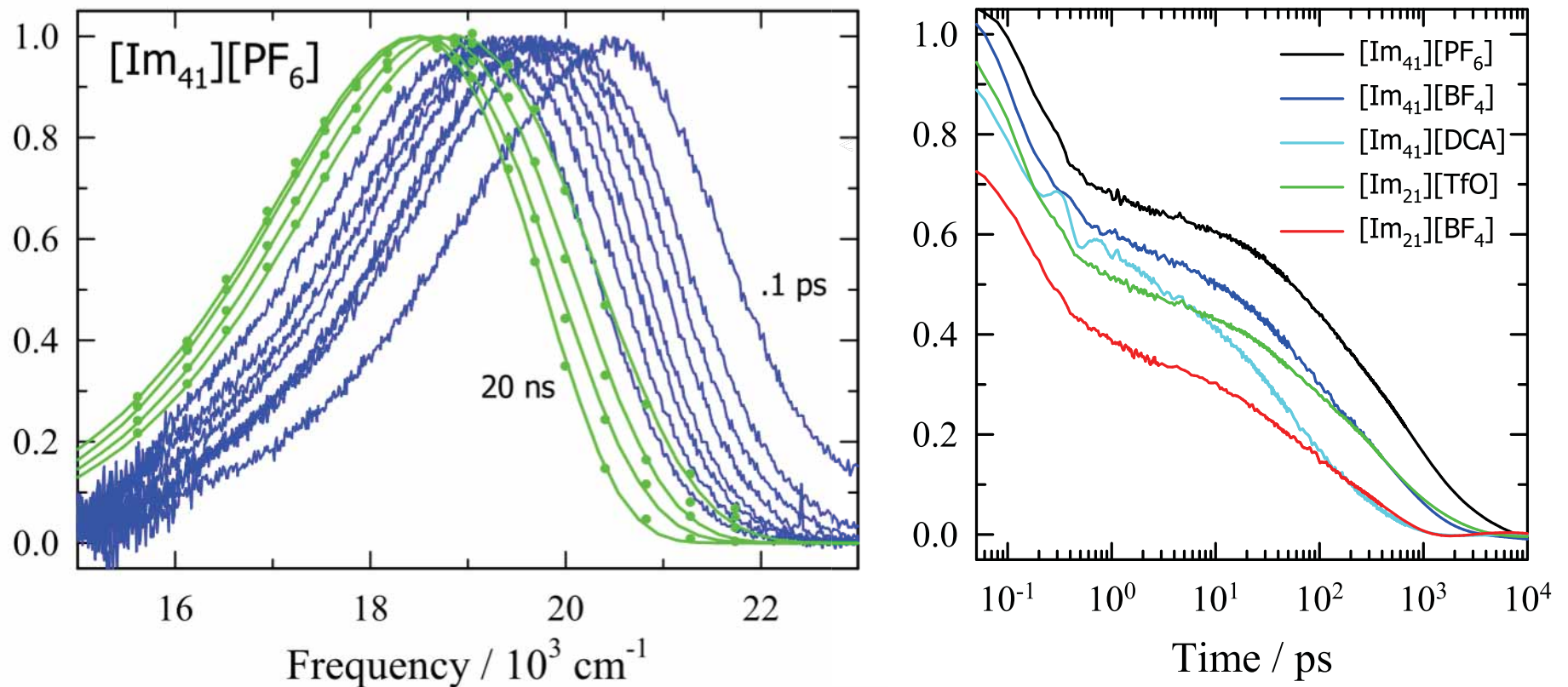
Ionic Liquids Have Complex Thermal Properties



Solvation in ionic liquids: Orientation *and* Translational



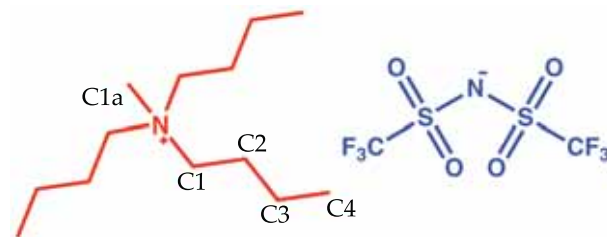
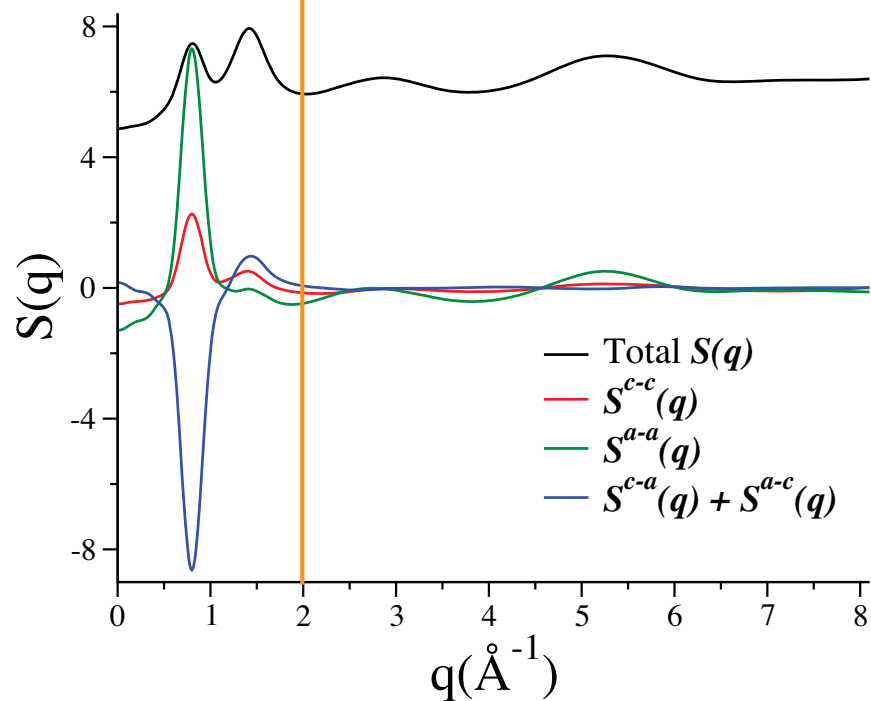
Solvent Reorganization Dynamics in Complex Fluids like Ionic Liquids span at least 4 decades in time.



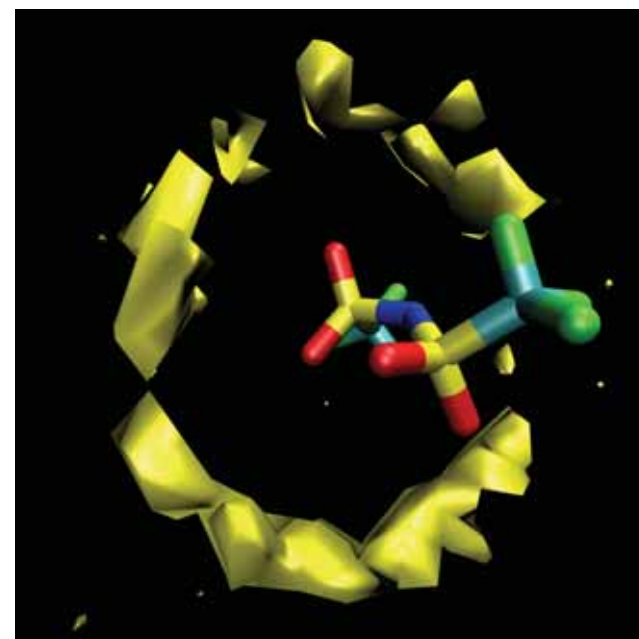
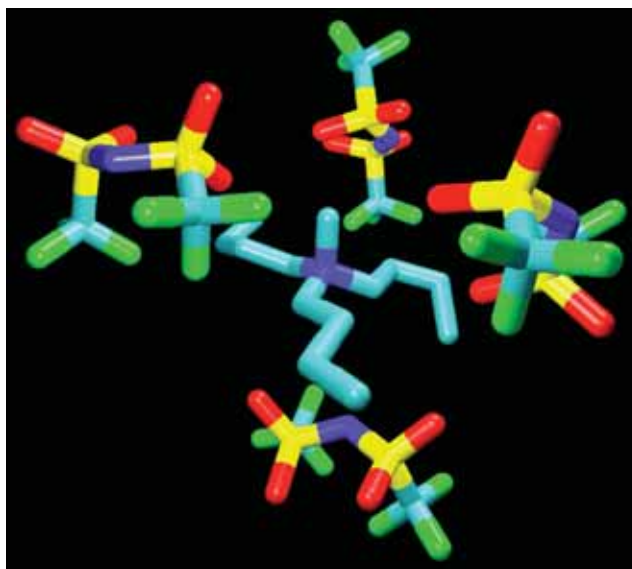
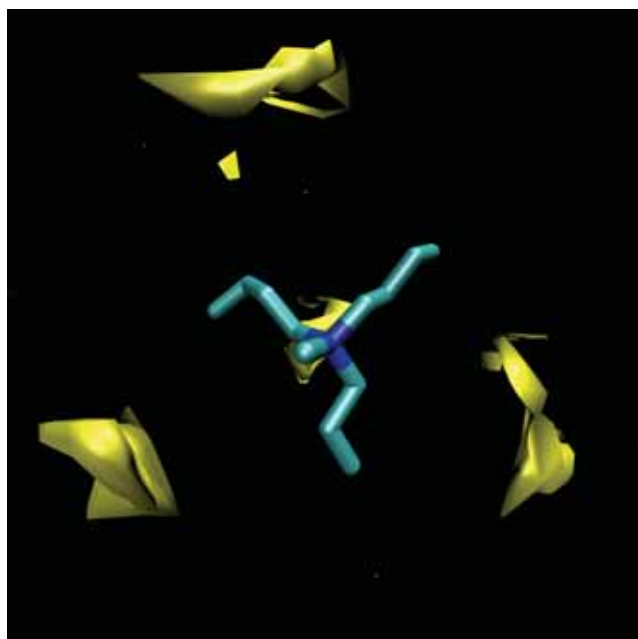
Measurements of the Complete Solvation Response of Coumarin 153 in Ionic Liquids...
Faraday Discussions 154, *in press* (2011)
Mark Maroncelli, Xin-Xing Zhang, Min Liang, Durba Roy and Nikolaus P. Ernsting

IL structure functions: x-ray and MD simulations

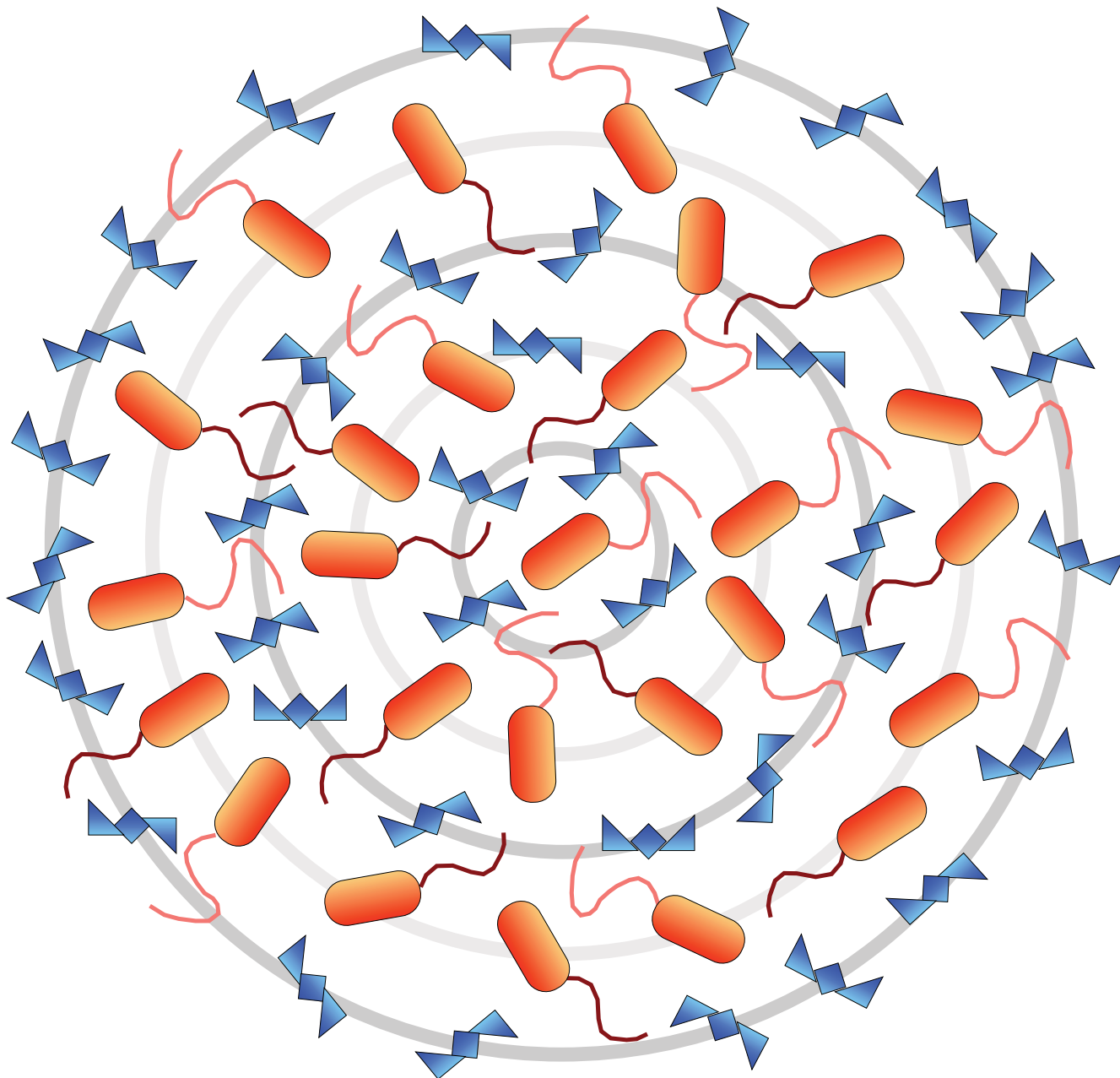
Inter-molecular ← Intra-molecular



Santos, Annapureddy, Murthy, Kashyap, Castner, and Margulis,
"Temperature-dependent structure of methyltributylammonium bis
(trifluoromethylsulfonyl)amide: x-ray scattering and simulations",
J. Chem. Phys., 134, 064501 (2011). doi: 10.1063/1.3526958



Charge-Ordering and Intermediate Range Order in Ionic Liquids



Intermediate Range Order: First Sharp Diffraction Peaks (FSDPs) in IL x-ray and neutron structure functions

FSDPs appear at q values of:

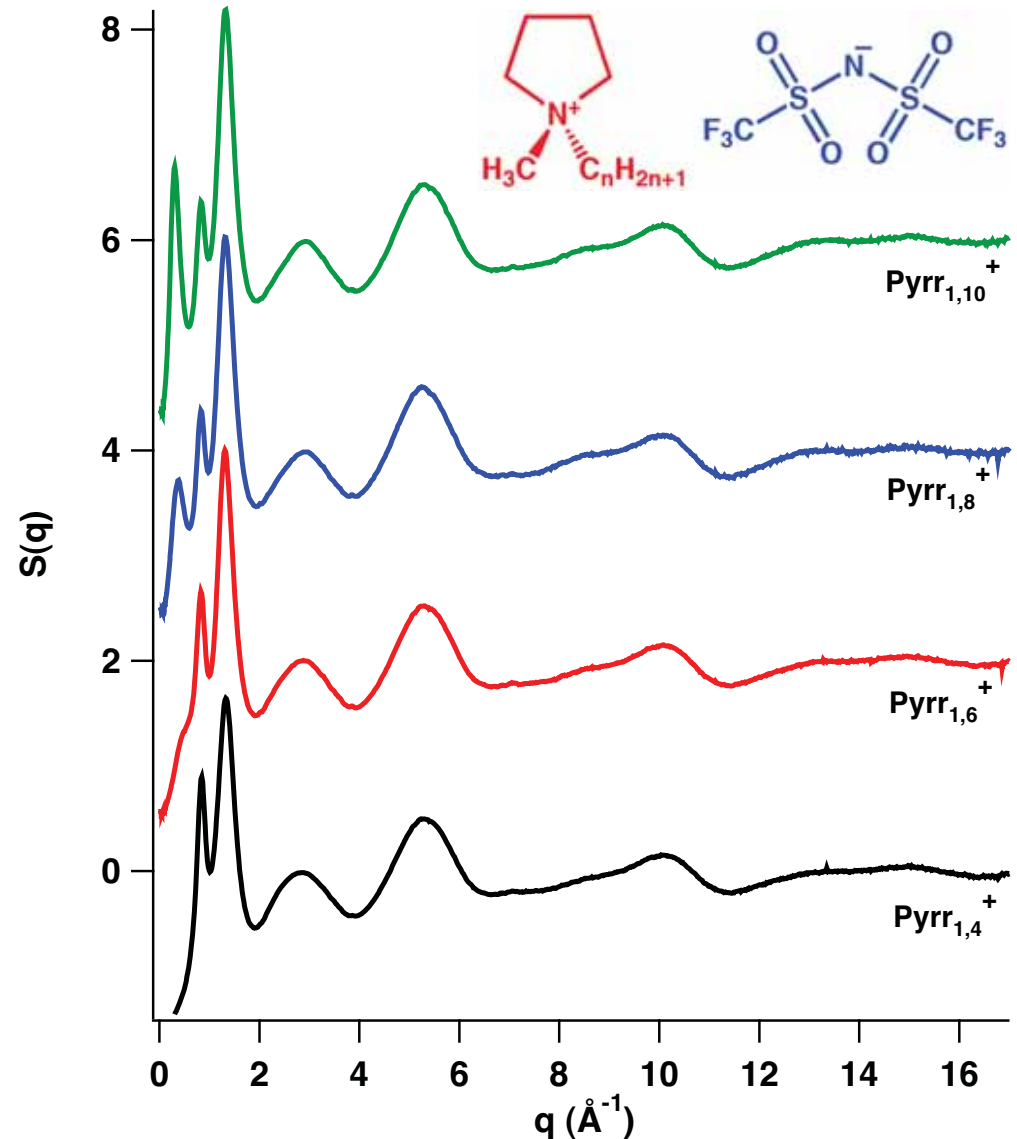
0.30 \AA^{-1} ($n = 10$)

0.38 \AA^{-1} ($n = 8$)

0.53 \AA^{-1} ($n = 6$)

The FSDP position correlates with increasing cation sizes.

Santos, Murthy, Baker, Castner, "X-ray scattering from ionic liquids with pyrrolidinium cations",
J. Chem. Phys., 134, 121101 (2011), doi: 10.1063/1.3569131.



Recurring questions about ionic liquids

Does the dynamic heterogeneity observed for ionic liquids derive from an inhomogeneous distribution of chemical environments, or intrinsic non-exponential responses for all environments?

How do the intrinsic structural and dynamical features of ionic liquids present obstacles or advantages to chemistry?

How can we best apply ionic liquids to chemistry for sustainable energy?

Design challenges for next-generation time-resolved x-ray sources

**Need sensitivity for low-Z experiments- sometimes zero-metal sample
other samples with no heavy atoms- just H, Li, B, N, C, O, F, P and S.**

Range of time-scales often requires lower pulse repetition rates.

Photo-excited triplet generation: ms to sec. recovery times

Photo-bleaching (e.g., quantum dots: 1 to 100 sec.)

Sample replacement- max. kHz repetition rates.

Laser/x-ray synchronization for photochemistry

1 ps straightforward; 100, 10, 1 fs more challenging

Summary

For two homologous series of ILs, the absence of a First Sharp Diffraction Peak at low values of Q in the liquid structure function S(q) correlates with low viscosities and hence faster diffusion-controlled reaction rates.

Measured self-diffusion rates for an electron-donating ionic liquid are 2.5 times slower than for the homologous neutral donor in a typical IL.

Rates for a photo-induced electron-transfer reaction are at the diffusion-controlled limit in CH₃CN solvent, while they are 40-50 times faster than this limit in the Pyrr₁₄⁺ / NTf₂⁻ IL.

This results from the fact that time-dependent reaction rates persist until at least 5-10 ns in ILs, or two orders of magnitude longer than for low-viscosity neutral solvents.

Despite high viscosities, bimolecular charge-transfer reaction rates are only 6-7 times less than for low- viscosity CH₃CN.

Special thanks to...

Outstanding beamline scientists:

**Dr. Chris Benmore and Dr. Yang Ren,
APS 11-ID-C (115 keV WAXS)**

**Dr. Steve Weigand and Dr. Denis Keane
APS 5-ID-D (DND-CAT, SAXS-WAXS @
9 and 17 keV)**

Dr. Lin Yang (BNL X9A, SAXS)

Who did the experiments and analysis?



Heather Lee
Rutgers Univ.



Dr. Cherry Santos
Rutgers Univ.



Matthew Sasso
Rutgers Univ.

@ beamline 5 ID-D
Advanced Photon Source, anl.gov

EWC



Tania Fadeeva
Rutgers Univ.



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NJ Center for Biomaterials



Dr. Jim Wishart
Brookhaven Nat'l Lab.



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