Measurements of the complete solvation response of coumarin 153 in ionic liquids and the accuracy of simple dielectric continuum predictions

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Introduction – Ionic liquids

Liquids consisting of only cations and anions

	Melting point/°C
$[C_4mim][PF_6]$	10
$[C_4mim][BF_4]$	-81
$[C_8mim][BF_4]$	-60
$[C_2mim][Tf_2N]$	4

Properties of ionic liquids:

- Low- melting, broad liquid range
- They are neither volatile nor combustible
- Negligible vapor pressure, High solubility for many chemicals

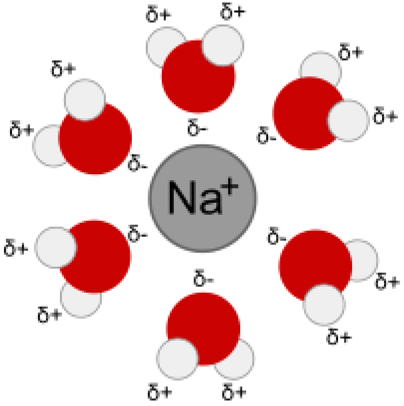
Introduction - Solvation dynamics

Solvation : response of a solvent to perturbations of a molecular solute

- important determinant of solvent effects on chemical reactions

- Good understanding in dipolar liquids

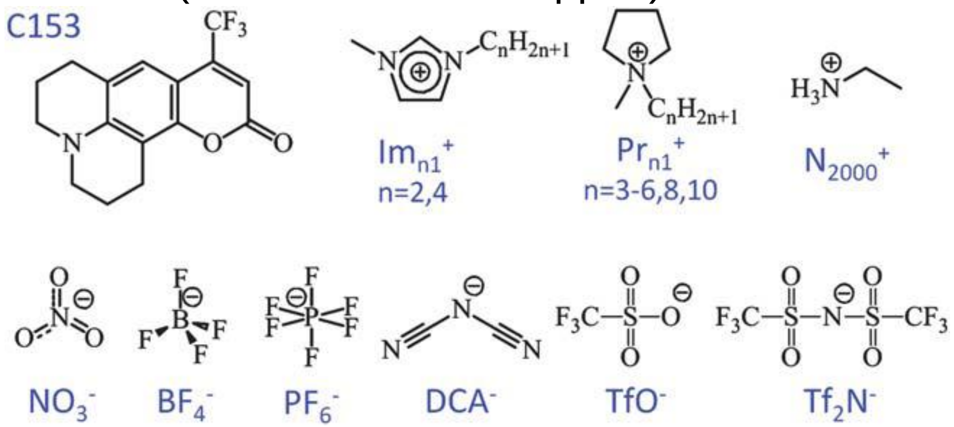
- Extend to ionic liquids



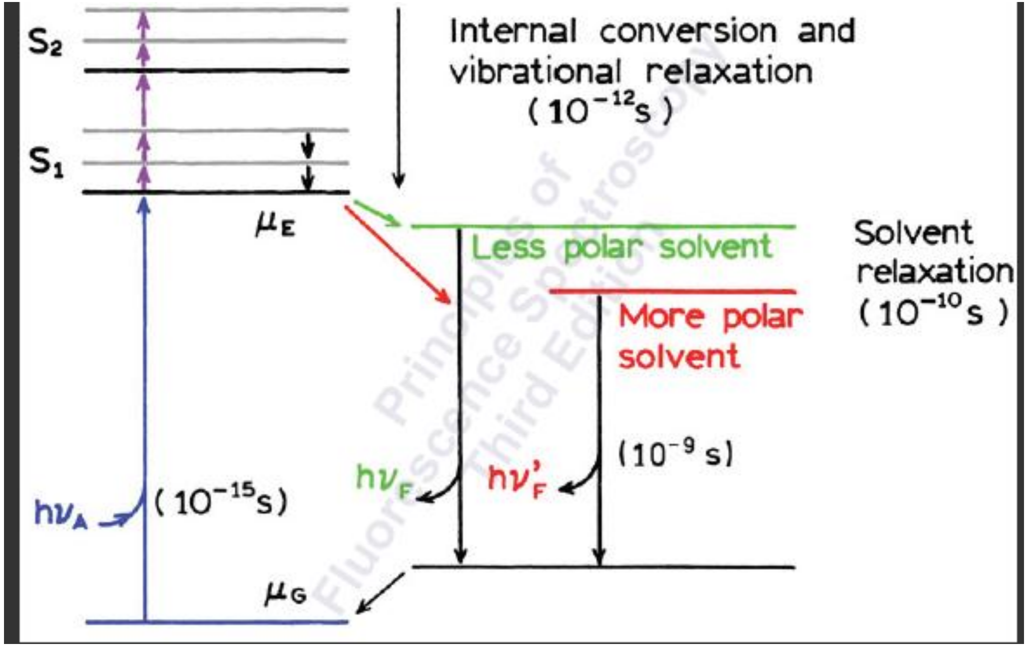
Experiments

Sample
Probe dye – Coumarin 153 (C153, laser grade, Lambda Physik & Excition)
* Coumarin dye is highly sensitive to solvent polarity

Cations
Methylimidazolium, Ethylammonium, Pyrrolidnium (water content <100ppm)



Fluorescence with solvent relaxation



Fluorescence lifetimes (few ns)

Solvent relaxation lifetime (10-100 ps)

-> emission spectra of fluorophores are representative of solvent relaxed state

Lippert-Mataga equation

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hc}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)\frac{(\mu_E - \mu_G)^2}{a^3}$$

the Lippert-Mataga equation

$E_{dipole} = -\mu F$
E_{dipole} : the energy of dipole in an electric field
F : relative reaction field in the dielectric induced by the dipole

$$F = \frac{2\mu}{a^3} f$$

f : polarizability of the solvent
a : cavity radius

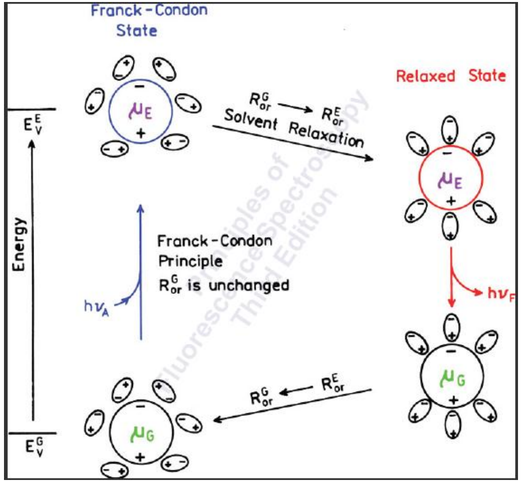
At high frequency

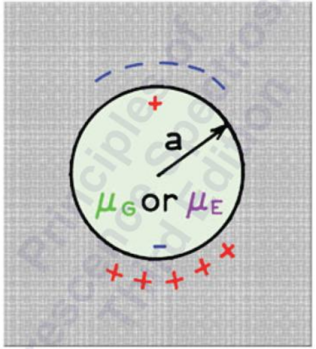
$$f(n) = \frac{n^2 - 1}{2n^2 + 1}$$

At low frequency

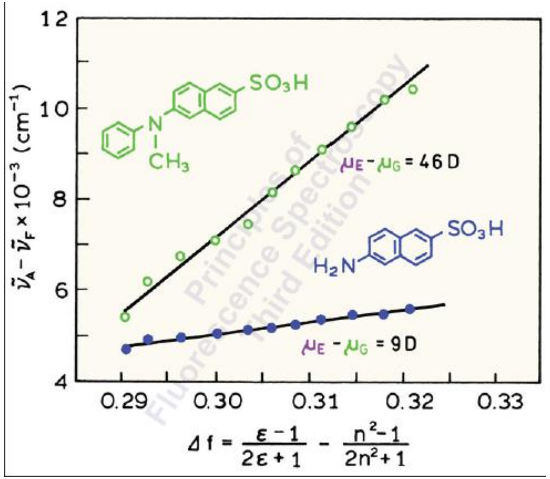
$$f(\varepsilon) = \frac{\varepsilon - 1}{2\varepsilon + 1}$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$





the Lippert-Mataga equation



$$F_{el}^{G} = \frac{2\mu_G}{a^3} f(n)$$

$$F_{el}^{E} = \frac{2\mu_E}{a^3} f(n)$$

$$F_{or}^{G} = \frac{2\mu_G}{a^3} \Delta f$$

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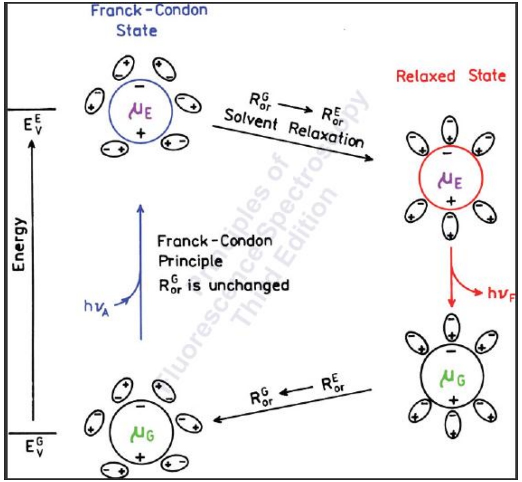

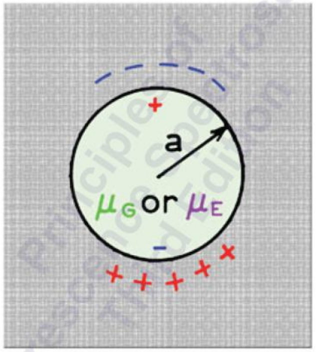

Lippert-Mataga equation

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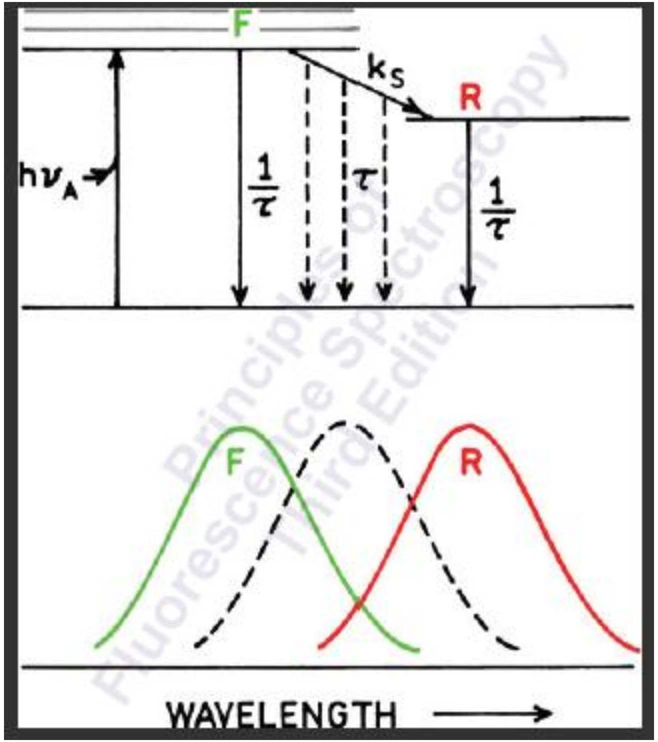
the Lippert-Mataga equation

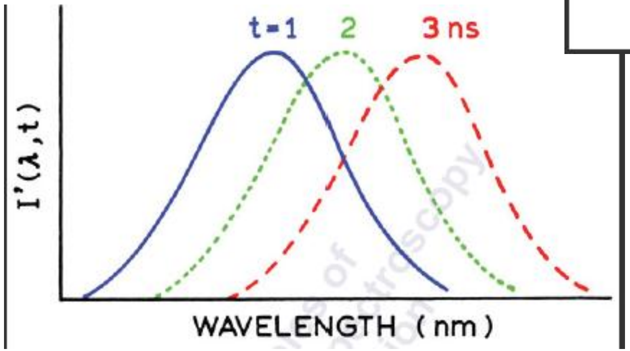
Limitation (assumption)

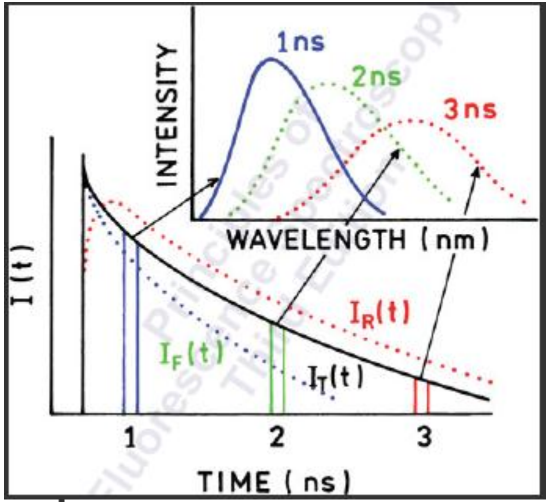
Describing only polarity effect

Spherical fluorophore
No specific interaction between fluorophore and solvent
Ignore polarizability of fluorophore
Ground and excited state dipole moment point in the same direction
…

Dynamic Stokes shift



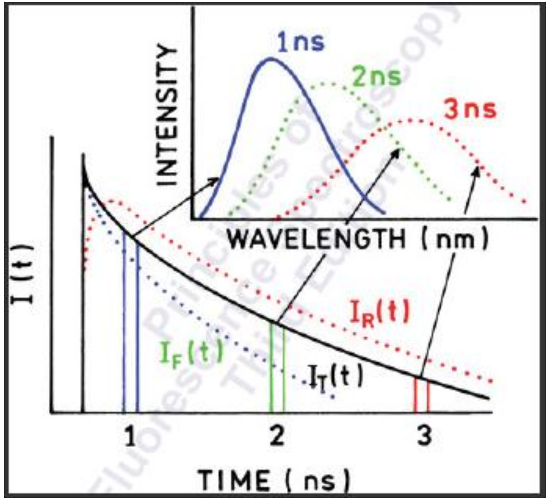




Dynamic Stokes shift

$$\tau_S \sim \tau_D \frac{2\varepsilon_\infty + \varepsilon_C}{2\varepsilon_0 + \varepsilon_C} \sim \tau_D \frac{2n^2 + 1}{2\varepsilon + 1} \sim \frac{n^2}{\varepsilon} \tau_D$$

τ_S : spectral relaxation time
τ_D : dielectric relaxation time
ε_C : dielectric constant of the cavity containing the fluorophore (~1)



Experiments

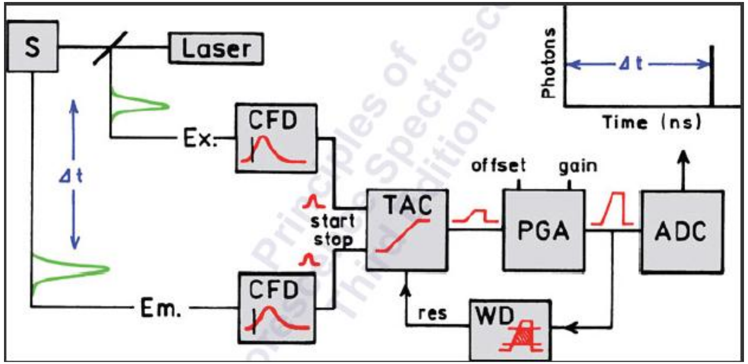
Steady-State measurement - Spex Fluorolog 212 spectrometer (2nm resolution)

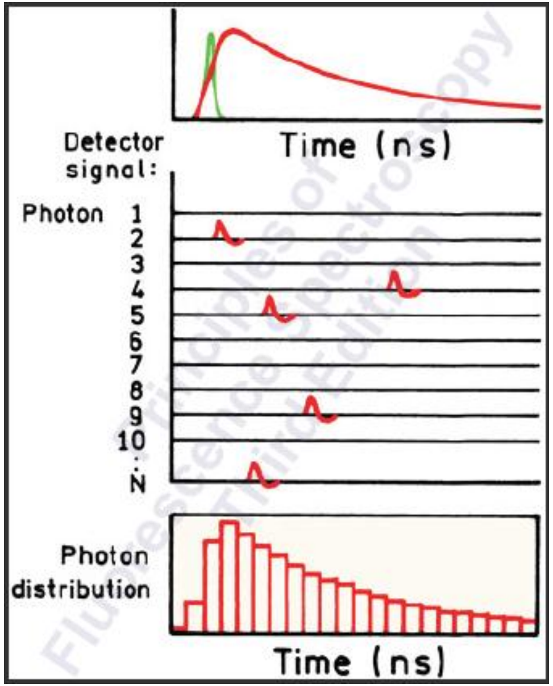
Ps-ns time-resolved measurement - Time-correlated single photon counting
Frequency doubled Ti:Sapphire oscillator

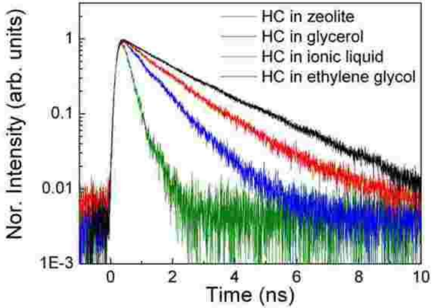
Fs time-resolved measurement - Broadband fluorescence up-conversion spectrograph

Time-resolved Single Photon Counting

Ps-ns time-resolved measurement - Time-correlated single photon counting

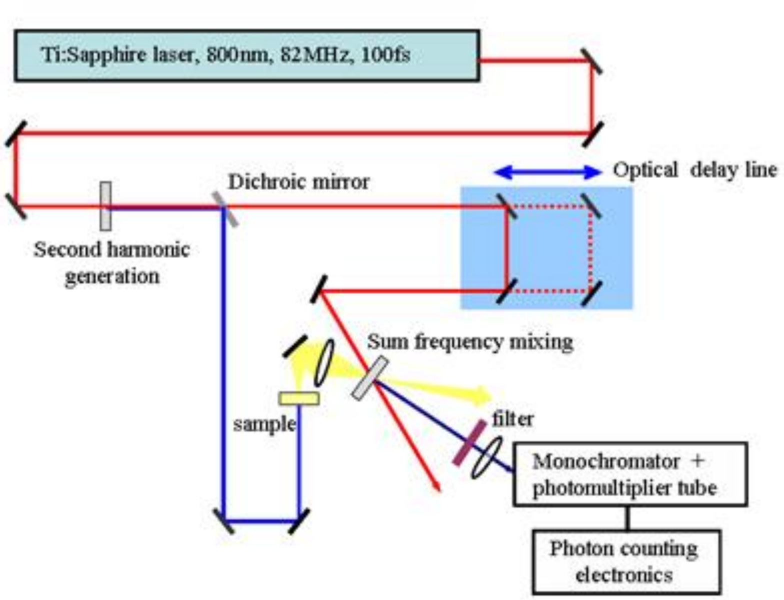


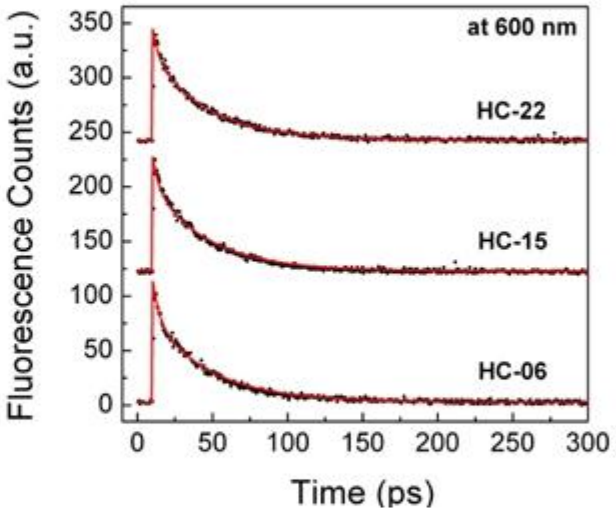




Fluorescence Up-conversion

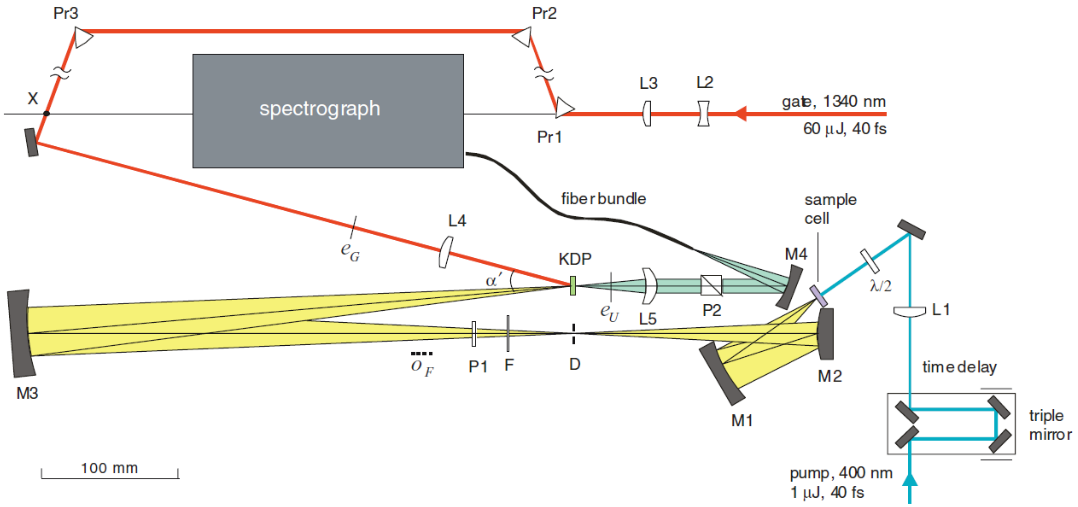
Fs time-resolved measurement - Broadband fluorescence up-conversion spectrograph





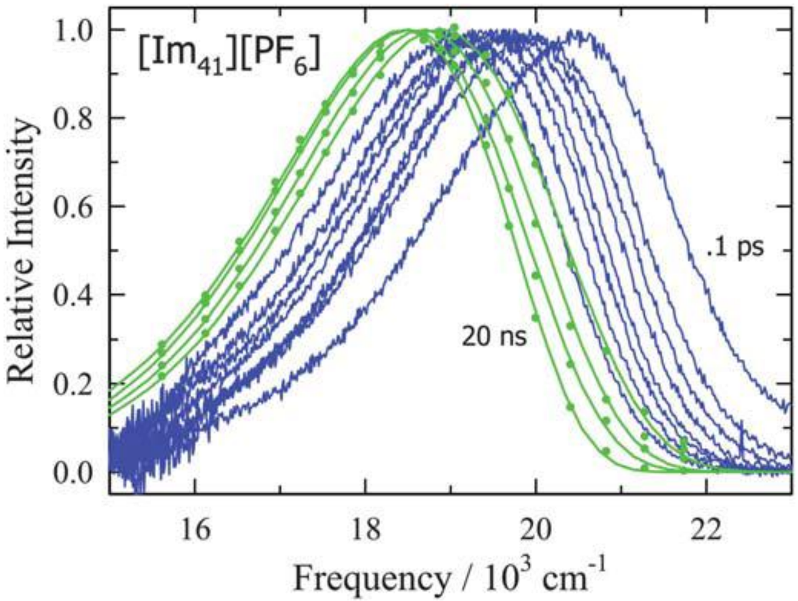
Broadband Fluorescence Up-conversion

Fs time-resolved measurement - Broadband fluorescence up-conversion spectrograph



Results – Dynamic Stokes shift

Time-resolved emission spectra of C153 in $[Im_{41}][PF_6]$
Blue : FLUPS (0.1 to 500 ps)
Green : TCSPC (1 to 20 ns)

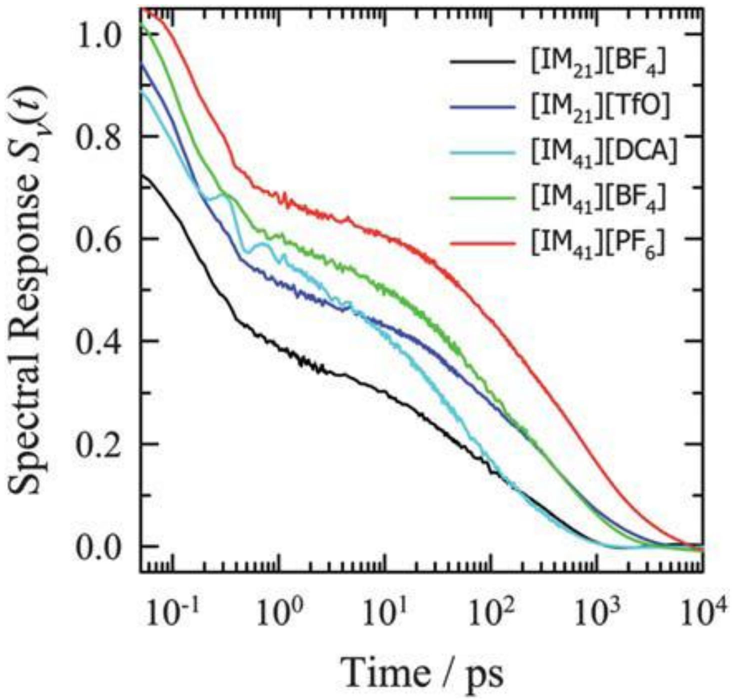


Results – Spectral Response

Correlation function

$$S_\nu(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

Short time component :
inertial properties of the solvent ions



Results – Comparing with simple dielectric model

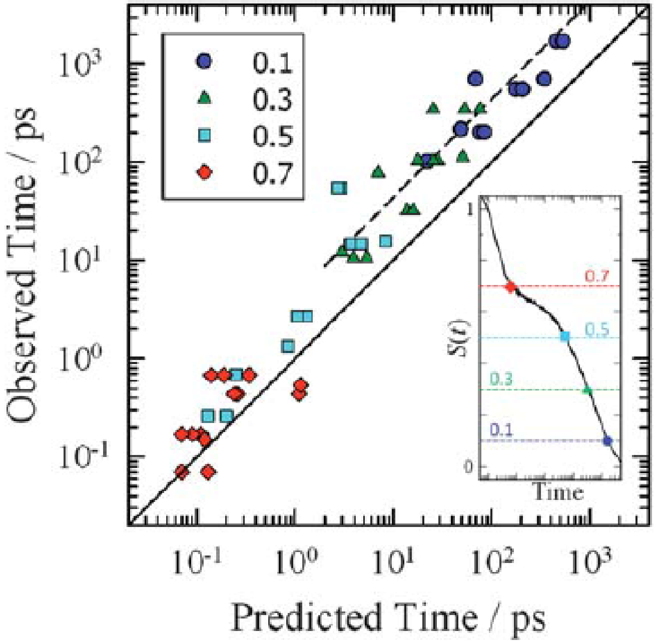
$$S_{dc}(t) = \frac{L_p^{-1}\left\{\left[\hat{\chi}(\infty) - \hat{\chi}(p)\right]/p\right\}}{\hat{\chi}(\infty) - \hat{\chi}(0)}$$

$$\hat{\chi}(p) = \frac{\hat{\eta}(p) - 1}{\hat{\eta}(p) + \frac{1}{2}\varepsilon_u}$$

Table 1 Dielectric sources and frequency ranges covered[a]

Ionic liquid	Frequency range	ε_0	ε_∞	n_D	$\Delta\varepsilon$	Reference
$[Im_{21}][BF_4]$	100 MHz–10 THz	15.9	1.94	1.391	0.0	T′09[34]
	1 MHz–20 GHz	13.6	6.7	1.411	4.7	N′10[35]
$[Im_{21}][TfO]$	100 MHz–10 THz	17.7	2.12	1.433	0.1	B′11[59]
$[Im_{41}][BF_4]$	100 MHz–3 THz	12.2	1.06	1.420	−1.0	S′08[33]
	200 MHz-20 GHz	11.0	4.08	1.421	2.1	S′07[30]
	1 MHz–20 GHz	14.1	5.45	1.421	3.4	N′10[35]
$[Im_{41}][PF_6]$	100 MHz–3 THz	11.8	2.1	1.409	0.1	St′08[33]
	1 MHz–20 GHz	14.1	4.8	1.407	2.8	N′10[35]
	40 MHz–40 GHz	12.4	3.26	1.409	1.3	M′10[36]
$[Im_{41}][DCA]$	100 MHz–10 THz	12.3	2.36	–		T′09[34]
	100 MHz–3 THz		2.13	–		St′08[33]
$[Im_{41}][Tf_2N]$	200 MHz-20 GHz	11.5	3.03	1.427	1.0	D′06[29]
	1 MHz–20 GHz	13.7	4.25	1.426	2.2	N′10[35]
	40 MHz–40 GHz	12.7	2.7	1.426	0.7	M′10[36]
$[Pr_{41}][Tf_2N]$	200 MHz-20 GHz	11.7	2.42	1.423	0.4	W′07[31]
$[N_{2000}][NO_3]$	10 MHz–1 THz (wet)	26.4	3.2	1.452	1.1	K′10[32]

[a] All dielectric data correspond to a temperature of 25 °C. Mizoshiri *et al.* (M′10)[36] recorded data between 30–70 °C and in this case we extrapolated these data to 25 °C. (a) $\Delta\varepsilon = \varepsilon_\infty - n_D^2$.



Dielectric continuum calculations

- good starting point for modeling the solvation response

- Systematically faster than expt. data

WHY?

Molecular dynamics simulations

The systematic error is related to neglect of spatial dispersion in the polarization response of ionic liquid.