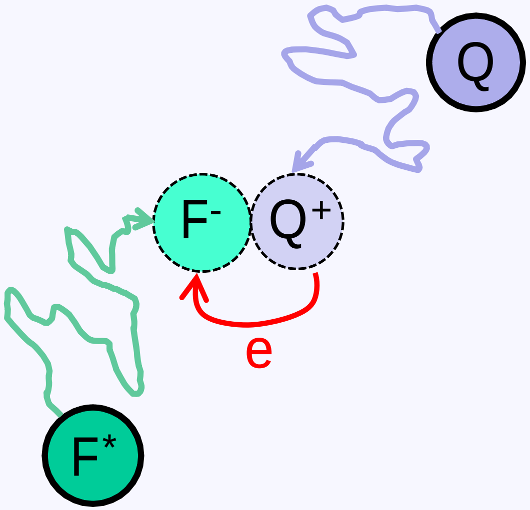
Bimolecular electron transfer kinetics and solute diffusion in ionic liquids

- Motivation
- Quenching Basics & Initial Results
- More Sophisticated Interpretations
- Missing Dynamics



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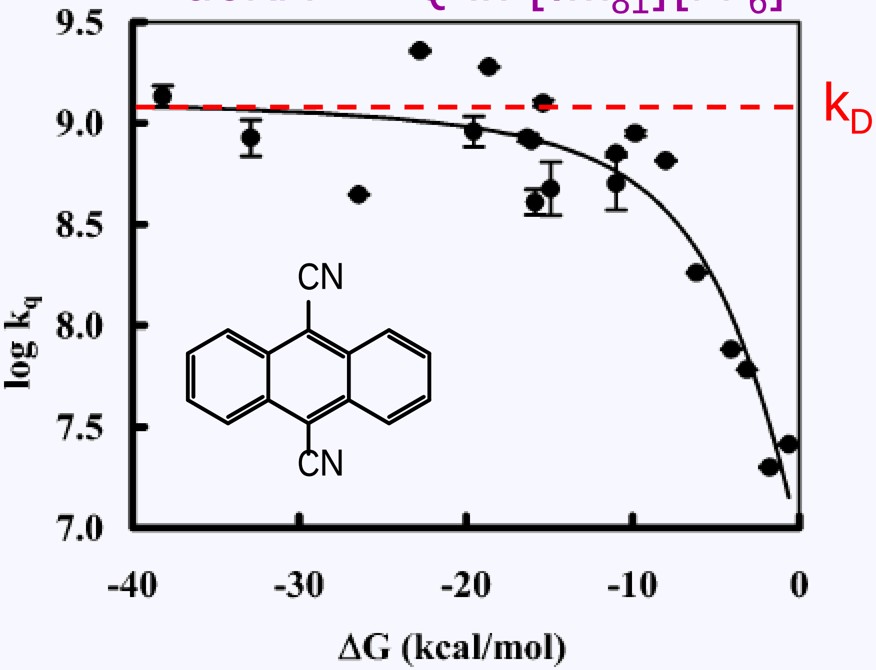
Motivation

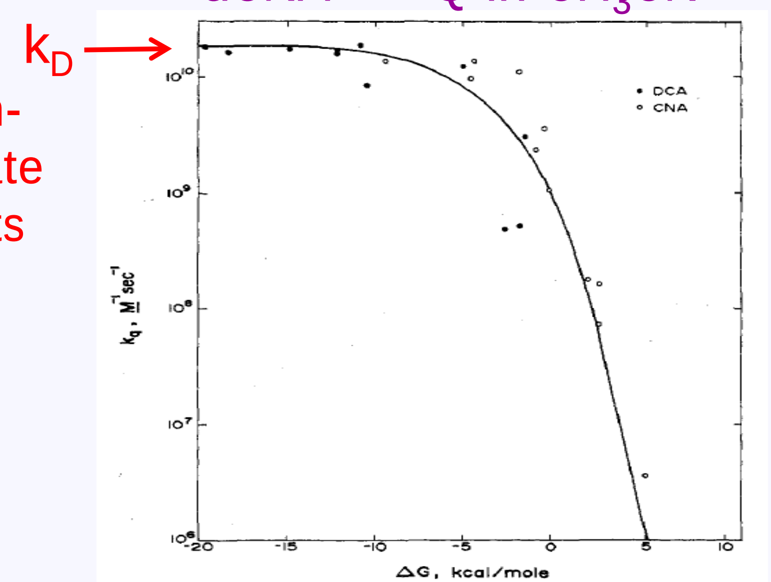
- Vieira & Falvey measured ET quenching of S_1 dicyanoanthracene (dCNA) by 21 aromatic electron donors in 2 imidazolium ILs

dCNA* + Q in $[Im_{81}][PF_6]$



diffusion-limited rate constants

dCNA* + Q in CH_3CN



Eriksen & Foote, *J. Phys. Chem.* 82, 2859 (1978).

Viera & Falvey, *J. Phys. Chem. B* 111, 5023 (2007).

Solvent	η/cP	$k_D/M^{-1}\ s^{-1}$
$[Im_{41}][PF_6]$	350	1.4×10^9
$[Im_{81}][PF_6]$	570	1.3×10^9
CH_3CN	0.34	3.6×10^{10}

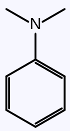
➢ compared to CH_3CN, η in ILs is greater by 10^3 but k_D is only ~20-fold smaller

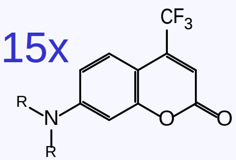
Other Diffusion-Limited Rates

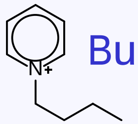
$$k_{clc} = \frac{4k_B T}{\eta}$$

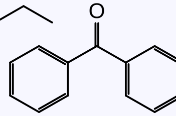
Reaction	IL	k_{obs}/k_{clc}	Technique	Ref.
$dCNA^* + D \rightarrow dCNA^- + D^+$	$[Im_{n1}][PF_6]$ n=4,8	55, 98	SS fluor.	Falvey 2007
$C15x^* + DMA \rightarrow C15x^- + DMA^+$	DAF	1.5 | 60	ps | SS fluor.	Sarkar 2009
$BuPy^\bullet + DQ \rightarrow BuPy^+ + DQ^{\bullet -}$	5 N & Pr ILs	3-9	radiolysis & ns TA	Neta 2003
$^3Bp^* + Naph \rightarrow Bp + {}^3Naph^*$	5 Im ILs	2-8	ns TA	Gordon 2002
$Py^* + DMA \rightarrow Py^- + DMA^+$	4 Im ILs	1.3-2.8	SS & ps fluor.	Samanta 2007
$I_2^- + I_2^- \rightarrow I_3^- + I^-$	6 ILs	0.8-1.2	ns TA	Takahashi 2007
$MV^+ + MV^{2+} \rightarrow MV^{2+} + MV^+$	3 Im ILs	.21-.23	ESR lineshape	Grammp 2006
$Ru(bpy)_3^{*2+} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^+$	$[Im_{41}][PF_6]$	0.8	ns TA	Gordon 2000

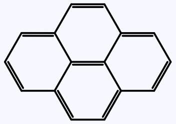
q


DMA

C15x



BuPy

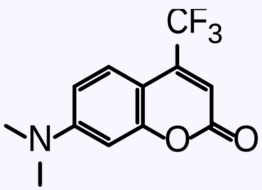

Bp

Py


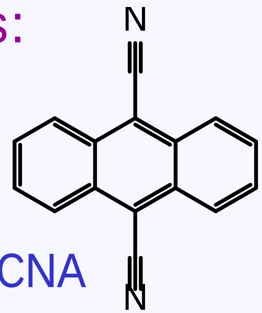
➢ rapid diffusion? solute association?

Our Quenching Experiments

Fluorphores:



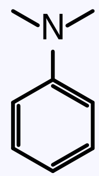
C152

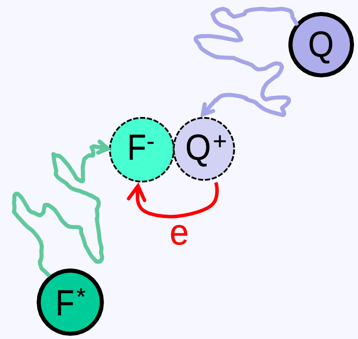


dCNA

Quencher:

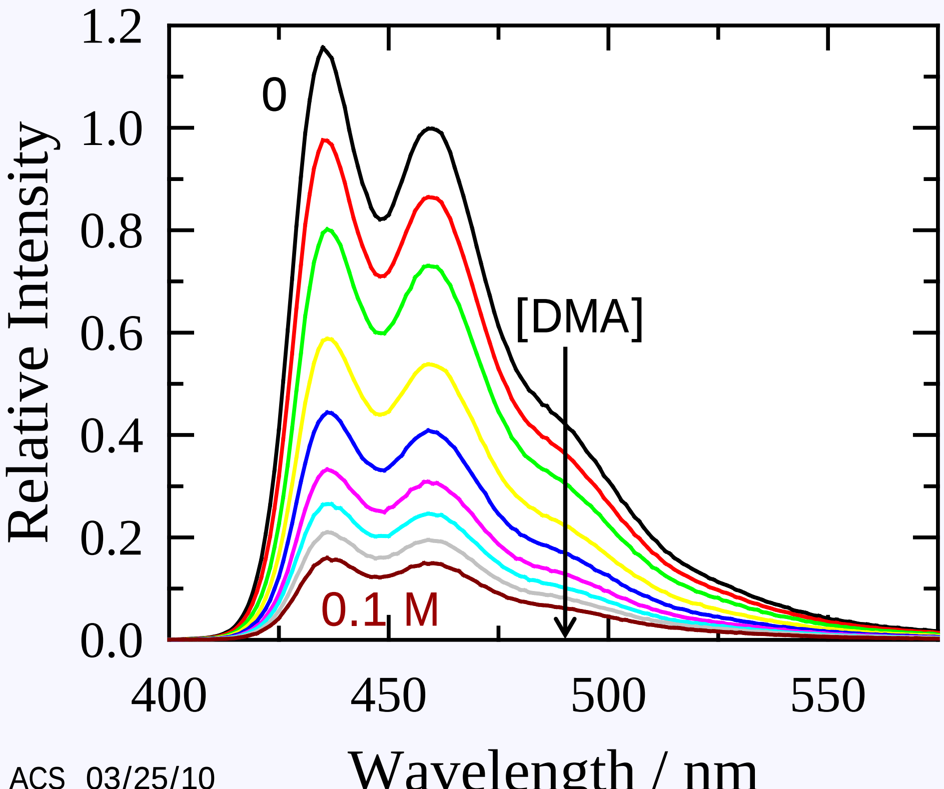
DMA

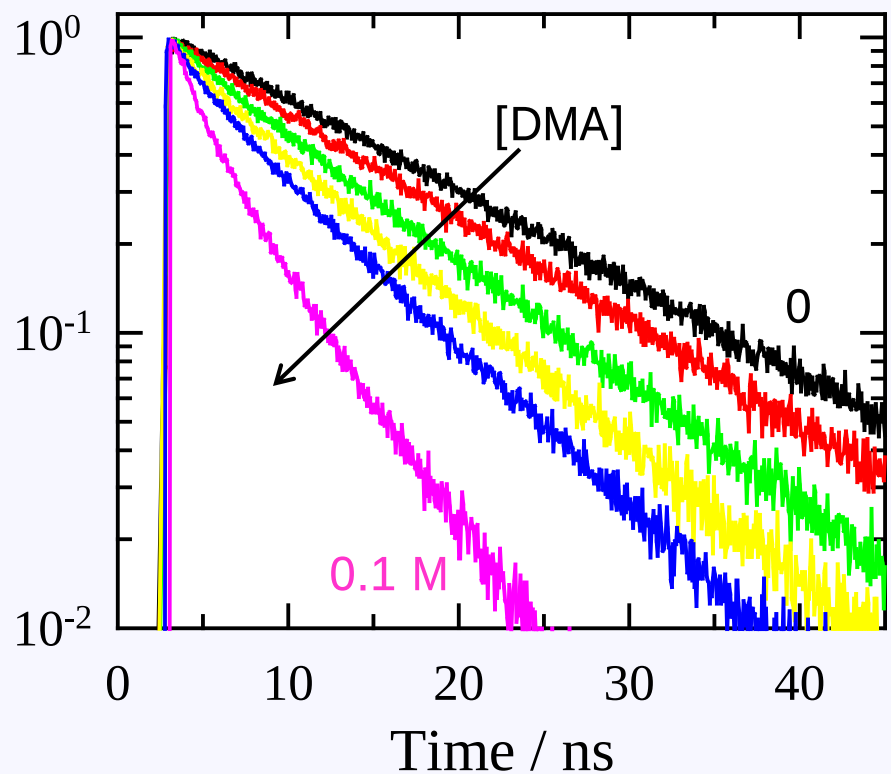




- ET mechanism
- solution & neat quencher data
- diffusion limited

Typical Data: dCNA+DMA in $[N_{3111}][Tf_2N]$





Some Basics: Stern-Volmer Kinetics & k_q

- assume quenching can be treated as a rate process:

$$\frac{d[F^*]}{dt} = k_0[F^*] + k_q[Q][F^*]$$

[F*] - fluorophore concentration
[Q] - quencher concentration
k_0 - decay const. in absence of Q
k_q - quenching rate constant

$$\frac{I(t)}{I(0)} = \frac{[F^*(t)]}{[F^*(0)]} = \exp\{-(k_0 + k_q[Q])t\}$$

emission decay

- this rate approach leads to the Stern-Volmer equation(s):

decay times

$$\frac{\tau_0}{\tau} = 1 + \underbrace{k_q\tau_0}_{K'_{SV}}[Q] \qquad (\tau_0 = k_0^{-1})$$

SS intensities

$$\frac{I_0}{I} = 1 + \underbrace{k_q\tau_0}_{K_{SV}}[Q]$$

O_2 Quenching of Tryptophan

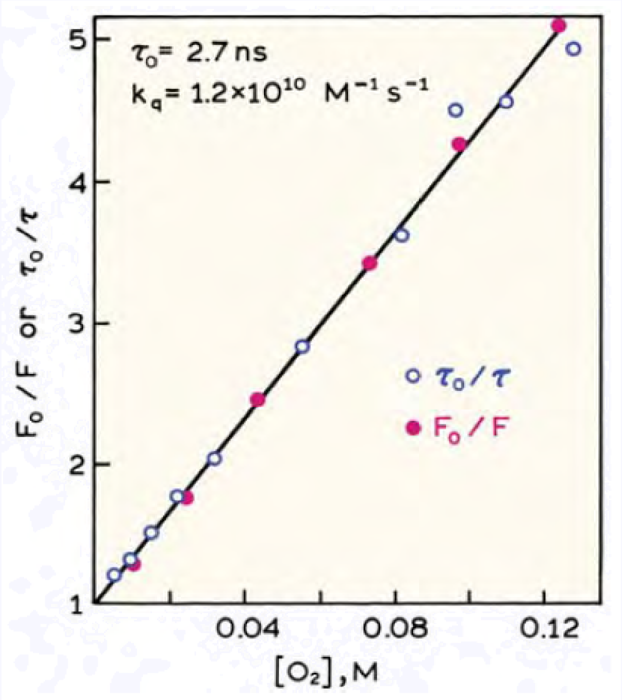


fig. from Lakowicz, *Principles of Fluorescence Spectroscopy* (Springer, 2006)

k_q at the Diffusion Limit

- envision quenching as a 2-step irreversible rate process:

$$F^* + Q \underset{k_{-D}}{\overset{k_D}{\rightleftarrows}} \{F^*Q\} \xrightarrow{k_{rxn}} F^-Q^+$$

diffusion | encounter pair | reaction

- applying the SS approximation, for rapid reactions ($k_{rxn} >> k_{-D}$), quenching is a pseudo-first order process with rate constant

$$k_q = k_D(1 + k_{-D}/k_{rxn})^{-1} \cong k_D$$

- k_D can be modeled using the Smoluchowski approach [immobile F, independent Qs, continuum fluid, $k_{rxn}(r)=\delta(R_{rxn})$] which, in the absence of a Q-F potential, provides the simple "Smoluchowski" eqn:

$$k_q = k_D = 4\pi(D_F + D_Q)R_{rxn}$$

D_i – diffusion coefficient of i
R_{rxn} – reaction distance

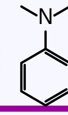
k_q at the Diffusion Limit (cont.)

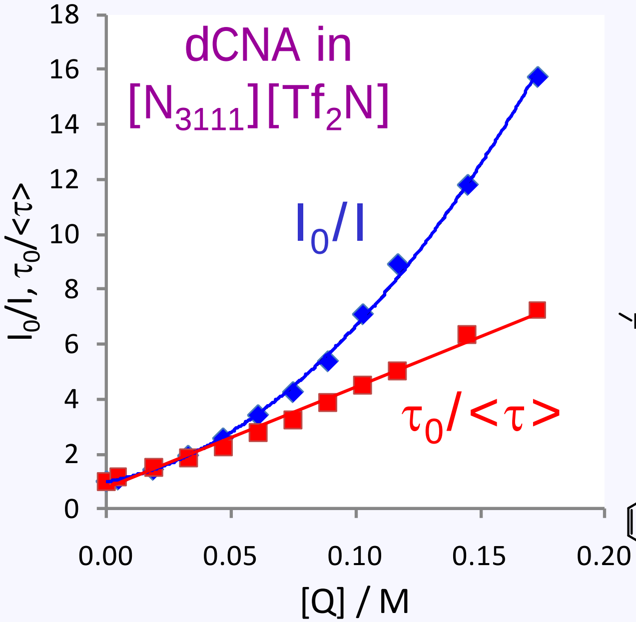
- finally, modeling the D_i using the Stokes-Einstein equation (slip BCs),

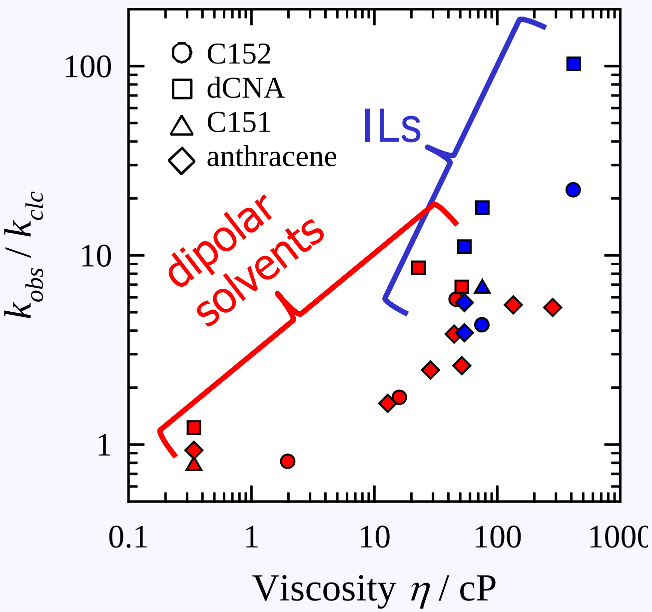
$$D_i = \frac{k_B T}{4\pi R_i \eta}$$

and assuming $R_F \cong R_Q \cong R_{rxn}/2$, one obtains the simplest prediction for a diffusion-limited reaction:

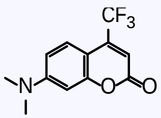
$$\boxed{k_q = k_D \cong \frac{4k_B T}{\eta}}$$

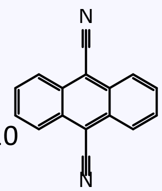
Quenching Rates (Q= , 298 K)





$$\text{obs/clc} \equiv k_{obs} / (4k_B T / \eta)$$





			$\tau_0/<\tau>$		I_0/I (0.1 M)	
F*	solvent	η / cP	k_{obs}	obs/ clc	k_{obs}	obs/ clc
C152	acetonitrile	0.3	~350	~1	158	1
C152	$[N_{3111}][Tf_2N]$	76	6	10	21	16
C152	$[P_{14,666}][Tf_2N]$	418	5	22	10	43
dCNA	acetonitrile	0.3	357	1	349	1
dCNA	$[Pr_{31}][Tf_2N]$	54	20	11	34	18
dCNA	$[N_{3111}][Tf_2N]$	76	23	18	40	31
dCNA	$[P_{14,666}][Tf_2N]$	418	24	100	63	270
C152	ethylene glycol	16	13	2	56	9
C152	1,3-propanediol	47	12	6	25	12
dCNA	1,3-propanediol	23	39	9	109	24
dCNA	EG+Gly	51	13	7	33	17

k_{obs} units 10^{-8} M^{-1} s^{-1}

- k_q in ILs is 10-100× larger than predicted
- related to high viscosities in ILs

Why the Deviations?

$$k_q = k_D \overset{?}{\cong} \frac{4k_B T}{\eta}$$

Three approximations might be inappropriate for these ET reactions in ILs:

1. neglect of the transient portion of the reaction (and treatment as a simple rate process)

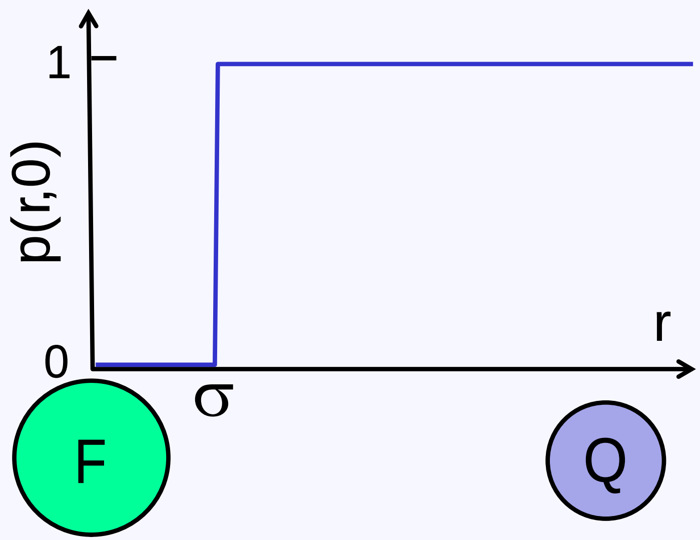
2. assuming a contact model for the ET process

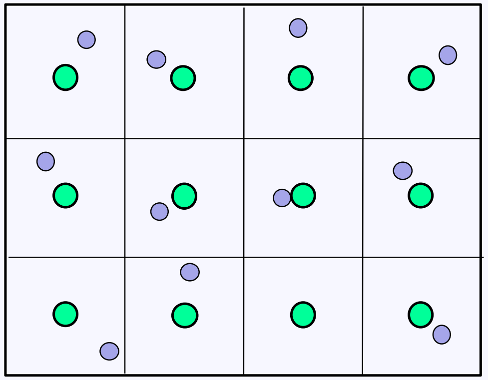
3. using Stokes-Einstein hydrodynamic predictions

The Transient Effect

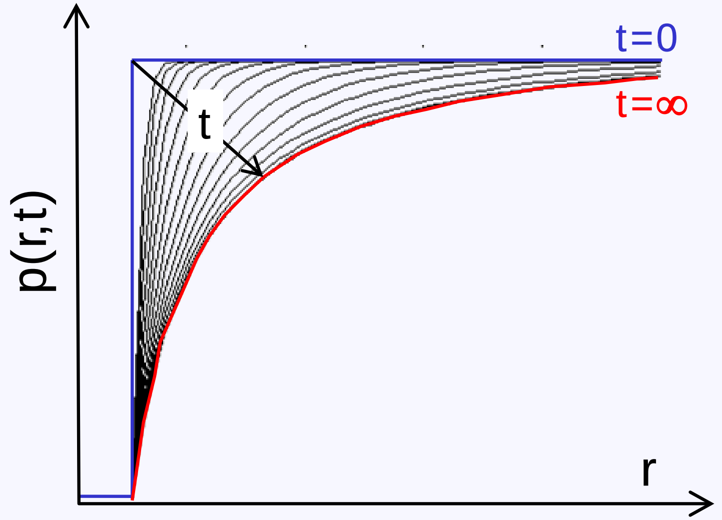
- diffusion-influenced reactions can be described by rate laws only after a transient time during which $k_q=k(t)$

The F-Q Spatial Distribution





Time Evolution of p(r,t)



- increasing η lengthens the transient time thereby increasing its relative importance

A More Complete Analysis

$$\frac{\partial}{\partial t}p(r,t)=\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2 D\frac{\partial}{\partial r}-\kappa(r)\right]p(r,t)$$

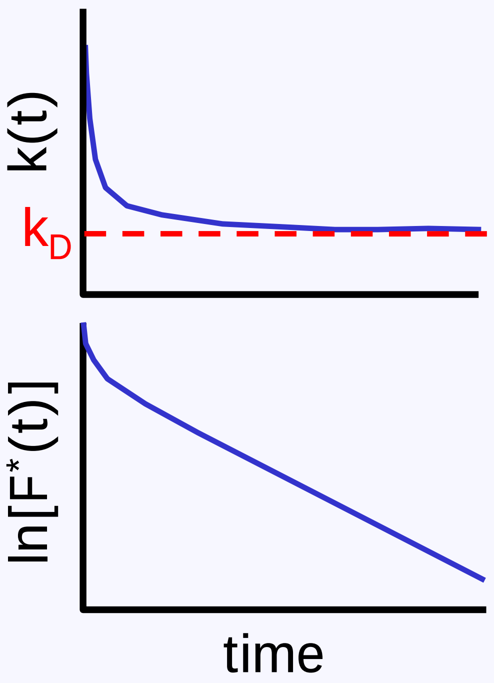
spherically symmetric diffusion equation for p(r,t)

reaction model

$$k(t)=4\pi\int_{\sigma}^{\infty}\kappa(r)\,p(r,t)\,r^2\,dr$$

time-dependent rate constant

$$[F^*(t)]=[F^*(0)]\exp\left\{-\frac{t}{\tau_0}-[Q]\int_0^t k(t')\,dt'\right\}$$



Smoluchowski (1917): $\kappa(r)=\infty$ for $r=\sigma$

$$k(t)=k_D\left\{1+\sqrt{\frac{\sigma^2}{\pi D t}}\right\}\qquad k_D=4\pi\sigma D=4\pi\sigma(D_F+D_Q)$$

$$\frac{[F^*(t)]}{[F^*(0)]}=\exp\left\{-\frac{t}{\tau_0}-[Q]\left[k_D t+8\sigma^2\sqrt{\pi D t}\right]\right\}$$

Diffusion Equation Modeling

$$\frac{\partial}{\partial t} p(r,t) = \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 D(r) g(r) \frac{\partial}{\partial r} \frac{1}{g(r)} - \kappa(r) \right] p(r,t)$$

Smoluchowski
Collins & Kimball
Fixman
Szabo
Tachiya
Burshtein
⋮

$p(r,t)$ – F*-Q pair distribution function

$g(r)$ – equilibrium F-Q pair distribution function

* $\kappa(r)$ – distance-dependent reaction rate *

$D(r)$ – diffusion coefficient (distance dependent)

Dudko & Szabo[1] (2005): approximate analytic results for arbitrary $\kappa(r)$ & $g(r)$

$$k(t) = k(\infty)[1 + \alpha_1 e^{-\gamma_1^2 t} erfc(\sqrt{\gamma_1^2 t}) + \alpha_2 e^{-\gamma_2^2 t} erfc(\sqrt{\gamma_2^2 t})]$$

1 - O. K. Dudko & A. Szabo, J. Phys. Chem. B 109, 5891 (2005).

An Electron Transfer Model for κ(r)

- use classical Marcus theory to estimate distance-dependent reaction rate κ(r):

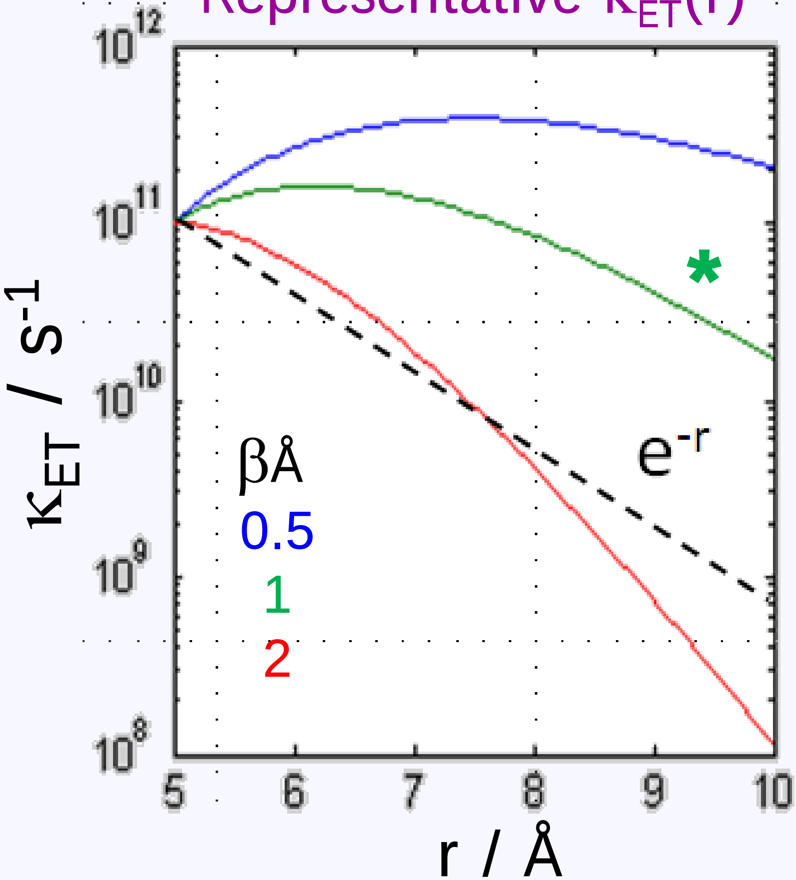
$$\kappa_{ET}(r) = \frac{V^2 e^{-\beta(r-r_0)}}{h\sqrt{4\pi\lambda k_B T}} \exp\left\{-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right\}$$

$$\lambda_{sol}(r) = e^2 \left\{\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}}\right\}\left\{\frac{1}{n^2} - \frac{1}{\varepsilon}\right\}$$

$$\Delta G(r) = \Delta G_0 - \frac{e^2}{\varepsilon r_{DA}}$$

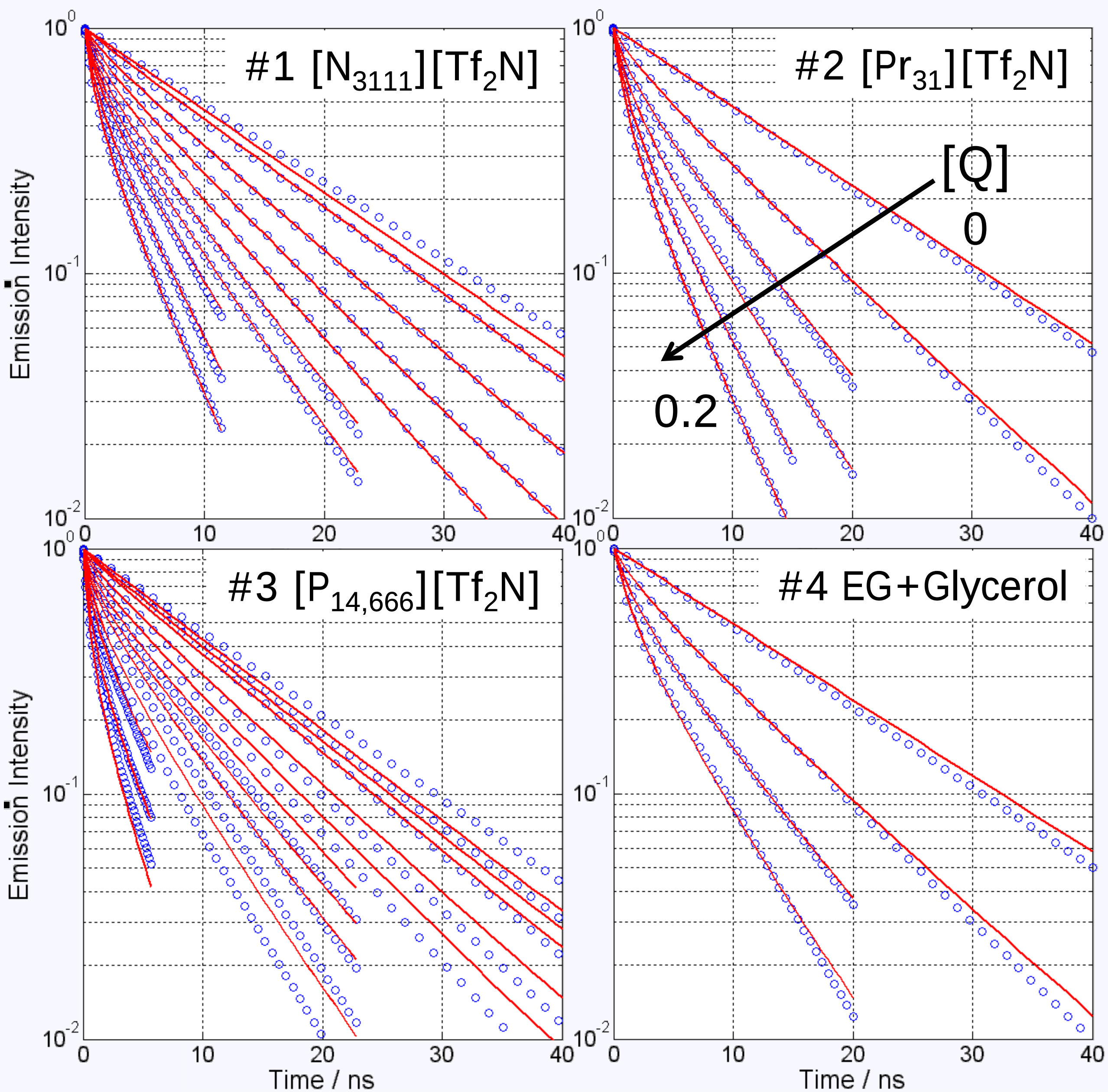
$$\Delta G_0 = E(D/D^+) - E(A/A^-) - E_{00}$$

Representative $\kappa_{ET}(r)$



similar $\kappa_{ET}(r)$ modeling also by Fayer, Tachiya, Burshtein, Grammp

Fitting Emission Decays – dCNA+DMA



Fixed Parameters

ΔG^0 = -1.0 eV

β = 1.0 Å^{-1}

λ_{in} = 0.3 eV

g_{max} = 2.0

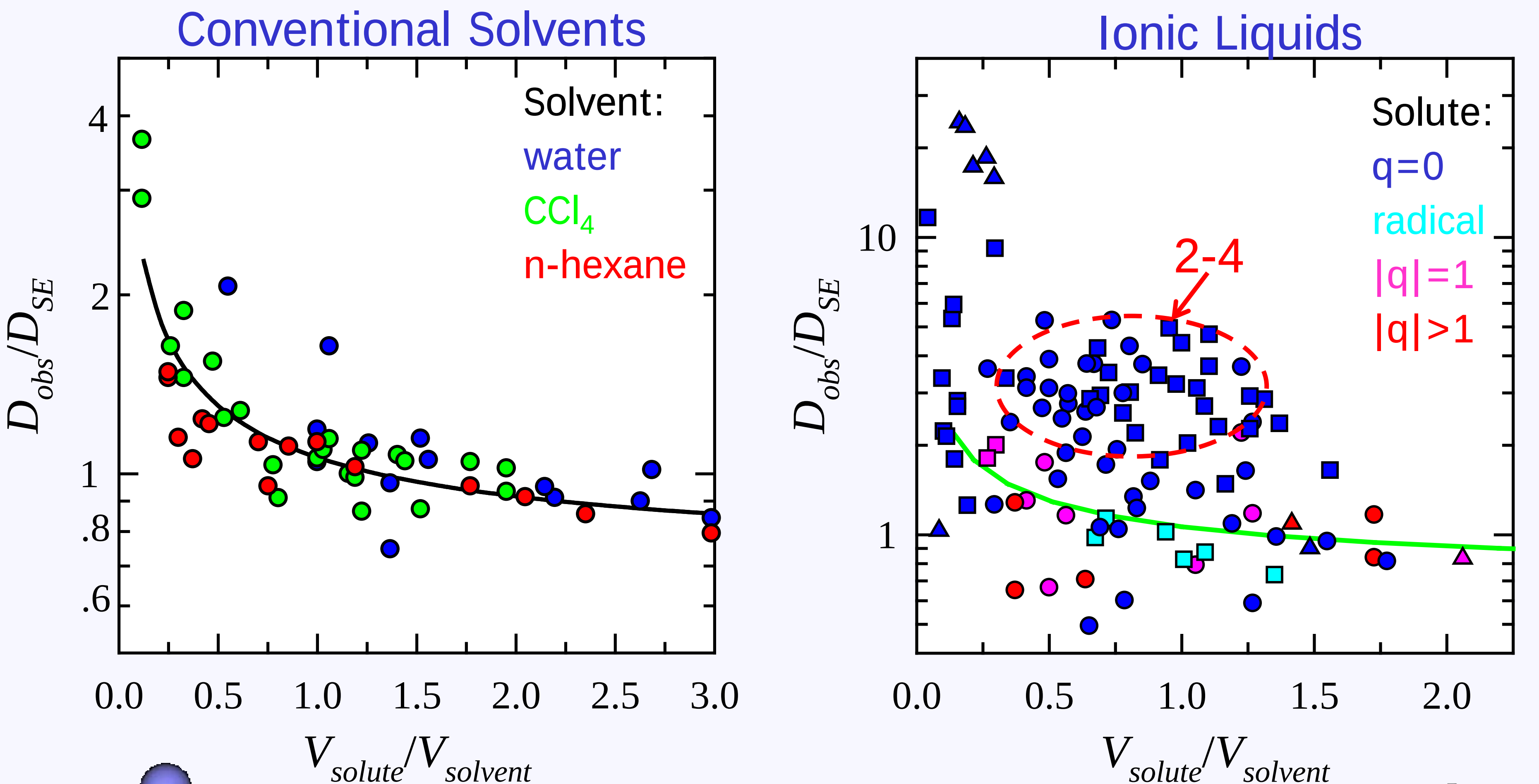
r_0 = 6.5 Å

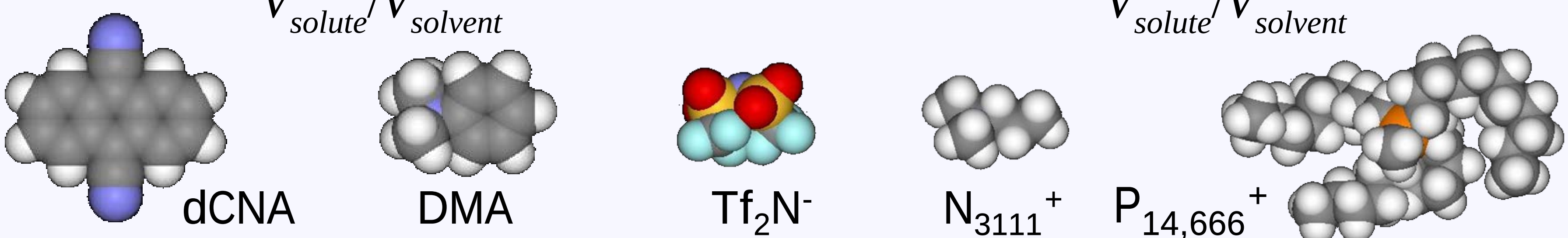
ε = 35, n_D = 1.4

Variable Parameters

#	V_{el} /cm^{-1}	D_{opt} /D_{SE}
1	66	5
2	58	3
3	(75	16)
4	48	2

Solute Diffusion Coefficients & SE





dCNA (211)

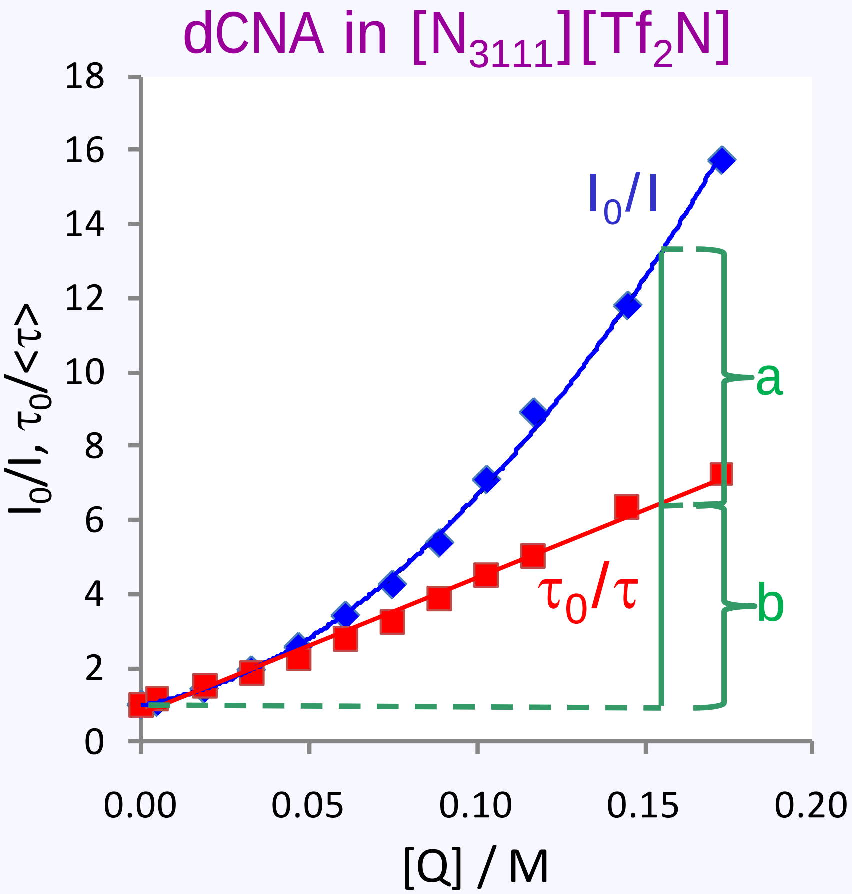
DMA (131)

Tf_2N^- (163)

N_{3111}^+ (129)

$P_{14,666}^+$ (638)

"Static" Quenching



% Missed by TCSPC ([Q]=.1 M)

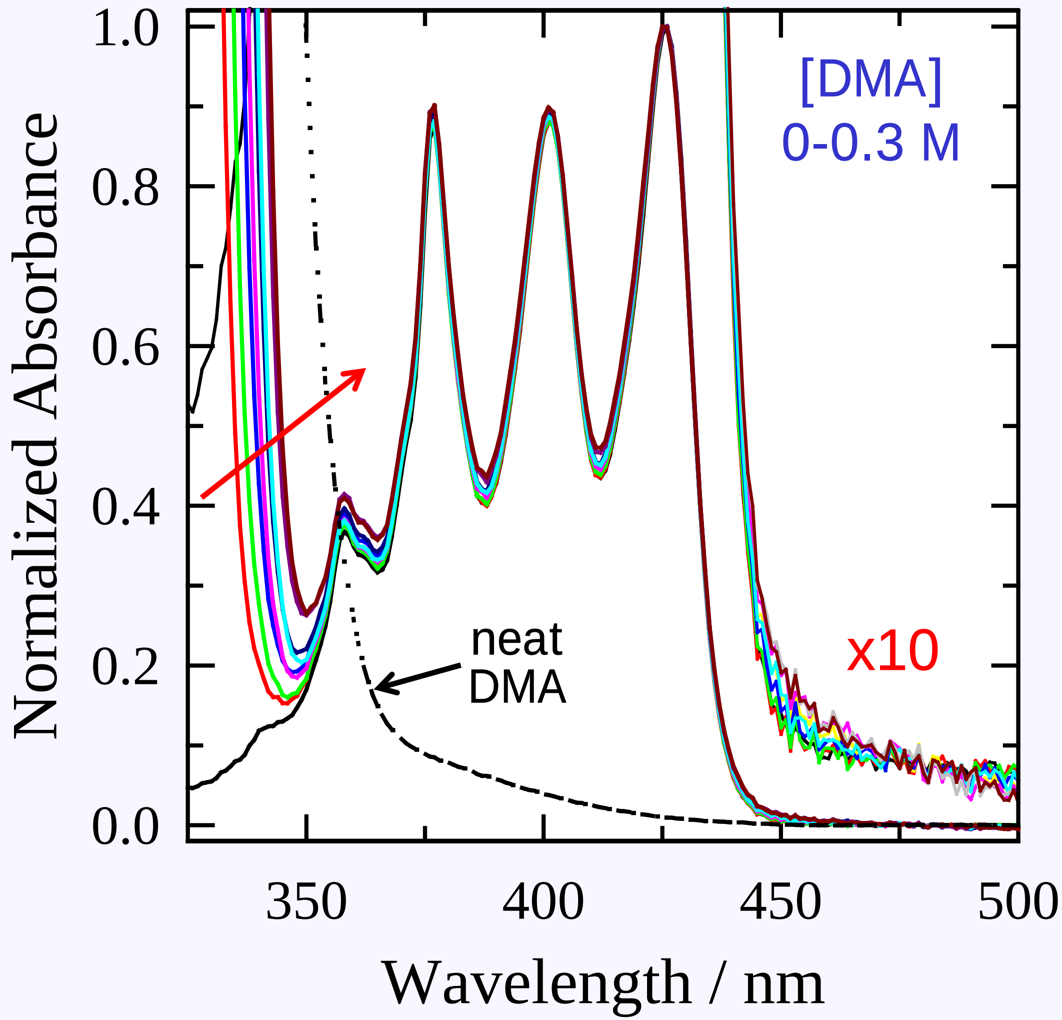
F*	solvent	η / cP	% missed
C152	$[N_{3111}][Tf_2N]$	76	73
C152	$[P_{14,666}][Tf_2N]$	418	49
dCNA	$[Pr_{31}][Tf_2N]$	54	39
dCNA	$[N_{3111}][Tf_2N]$	76	42
dCNA	$[P_{14,666}][Tf_2N]$	418	61
C152	ethylene glycol	16	78
C152	1,3-propanediol	47	49
dCNA	1,3-propanediol	23	62
dCNA	EG+Gly	51	60

% missed = $100 \times a/(a+b)$

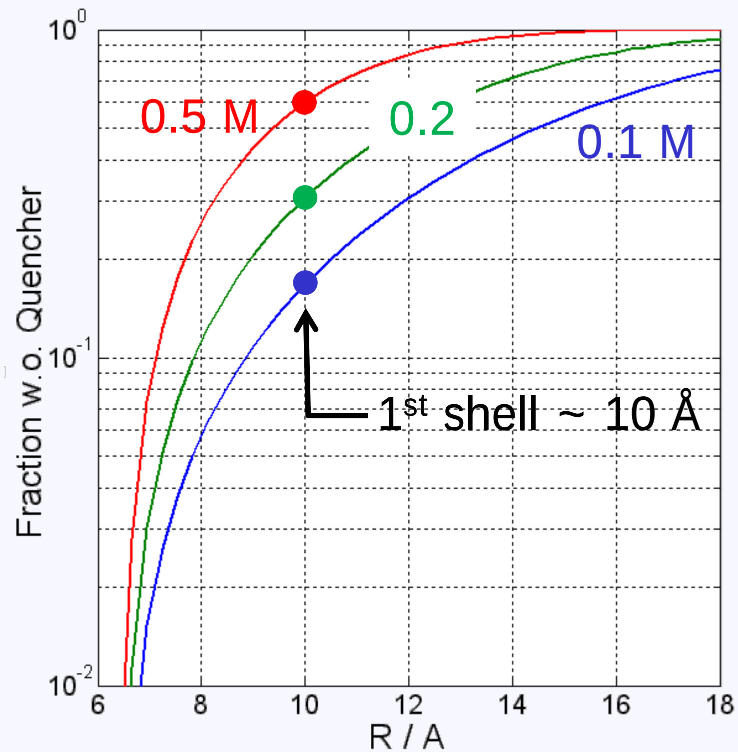
- TCSPC indicates substantial <5 ps ET even at [Q]=0.1 M
- for this reason SS Stern-Volmer analysis greatly exaggerates k_D

Ground-State Association?

Absorption: dCNA/[N_{3111}][Tf_2N]



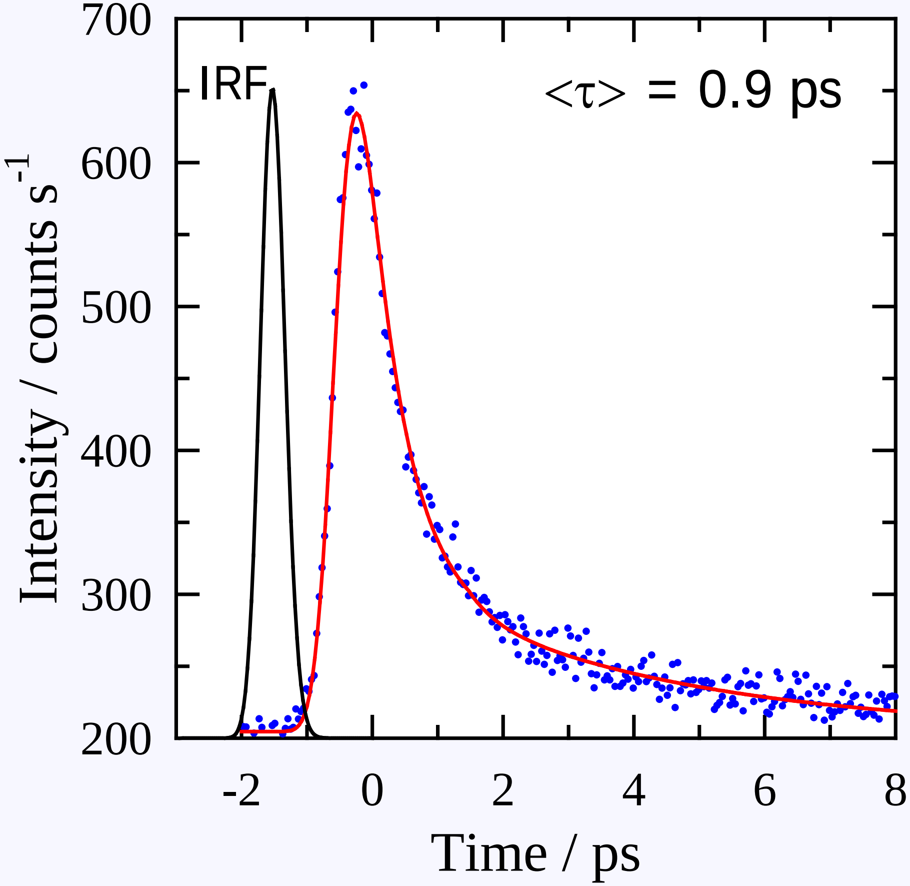
Estimated F*-Q Probabilities



Ultrafast Quenching Component

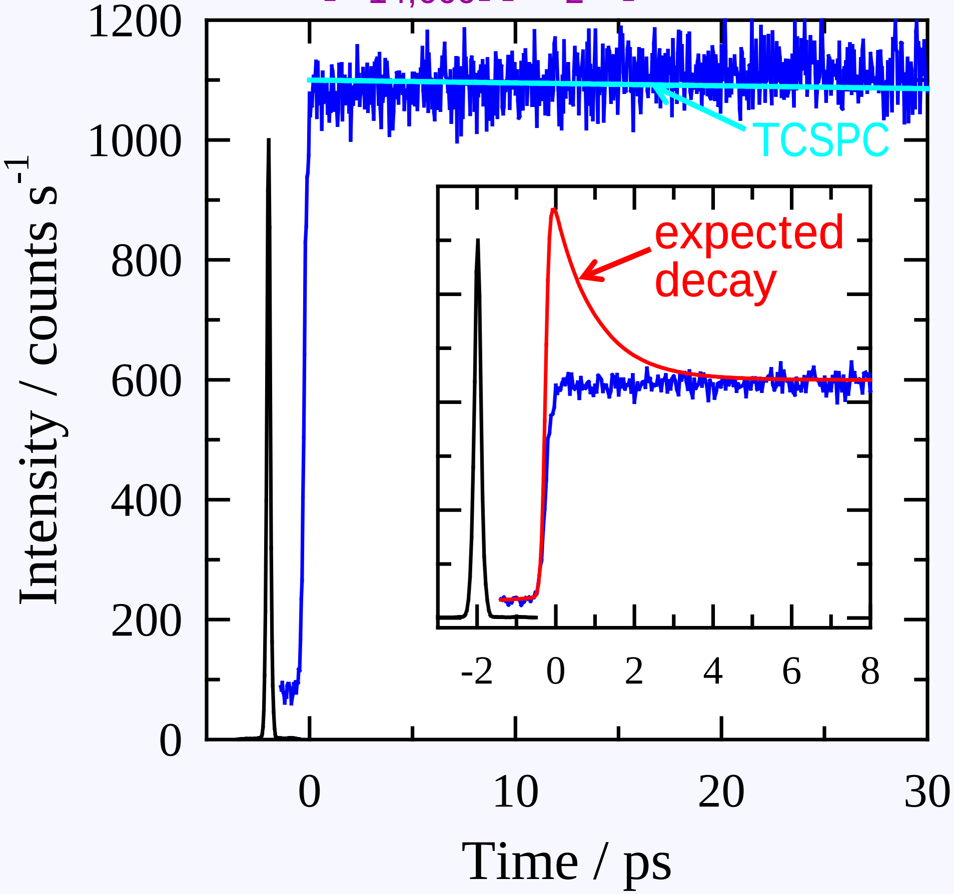
- fluorescence upconversion experiments, IRF = 200-300 fs

C152 in Neat DMA



Yoshihara & Co (1995): <τ> = 0.71 ps
Castner & Cave (2000): <τ> = 0.92 ps

C152 in $[P_{14,666}][Tf_2N]$+0.2 M DMA



➢ in 0.2 M DMA 50% of emission decay is faster than 100 fs?

Summary & Outlook

- we've begun systematic fluorescence measurements of diffusion-limited electron transfer reactions in ILs
- diffusion-limited rates are much larger than estimates based on simple Smoluchowski prediction $k_D = 4k_BT/\eta$
- several effects contribute at high η:
  - time-dependent rate [k(t)] contributions
  - long-range electron transfer [κ(r)]
  - D larger than SE predictions
- substantial "static" quenching ~50% at 0.1 M
  - no evidence for complex formation
  - quenching faster than 100 fs
- behavior is not necessarily unique to ILs

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Gary Baker (ORNL)

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