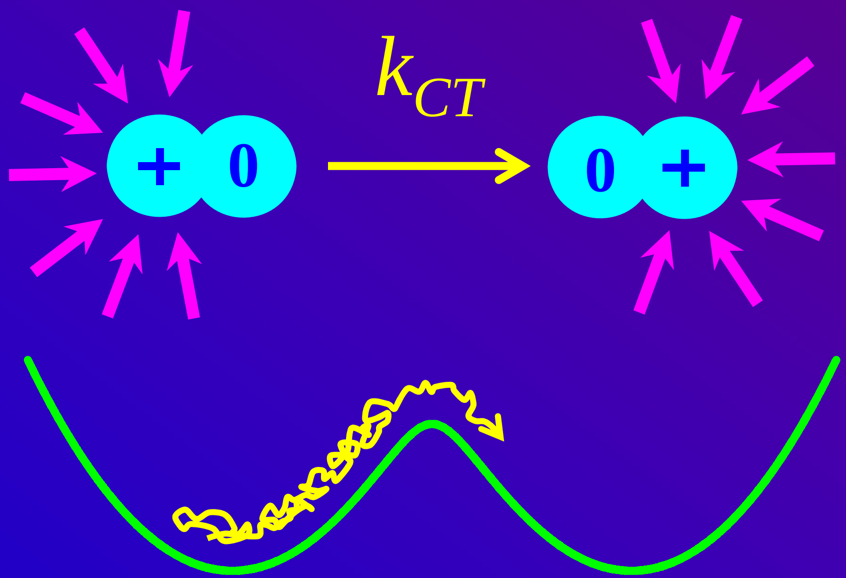
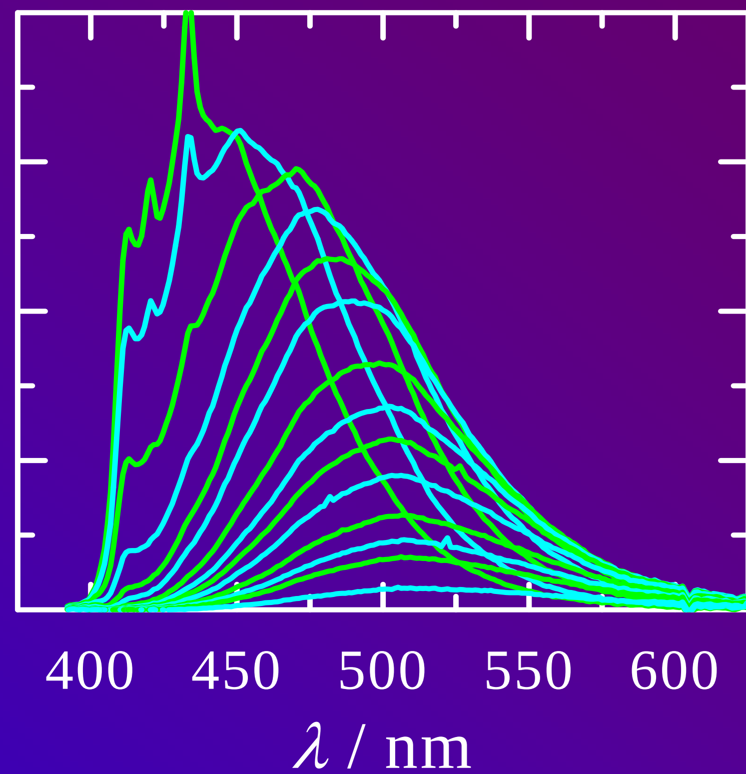
Dynamic Spectroscopy of Charge-Transfer Processes





Some Predecessors:

Zusman, Rips, Fonseca, Hynes, Barbara, Fleming, Nordio …

Free Energy Surfaces*

- adiabatic reaction on 1d surface
- relevant nuclear coordinate is the "solvation coordinate" μ_s
- free energies are quadratic in μ_s:

$$F_i(\vec{\mu}_i) = U_i - \tfrac{1}{2} B_{tot} \vec{\mu}_i^{\,2} + \tfrac{1}{2} B_{nuc} (\vec{\mu}_i - \vec{\mu}_s)^2$$

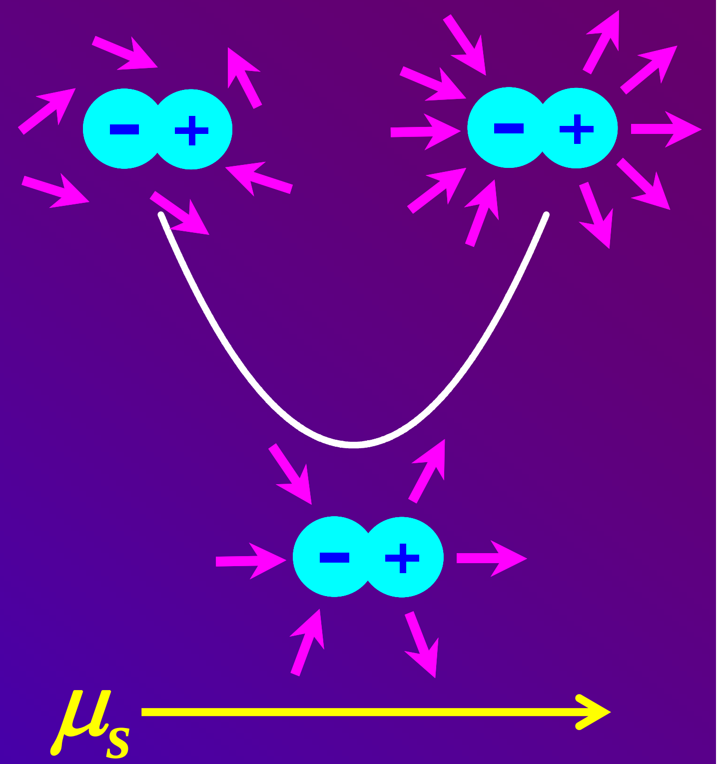
gas-phase | equilibrium solvation | non-equilibrium "strain"

$$B_{tot}^{(i)} = \frac{f_{tot}}{1 - \alpha_i f_{tot}} \qquad f_{tot} = \frac{2}{a_{cav}^3} \left(\frac{\varepsilon - 1}{2\varepsilon + 1} \right)$$

$$B_{el}^{(i)} = \frac{f_{el}}{1 - \alpha_i f_{el}} \qquad f_{el} = \frac{2}{a_{cav}^3} \left(\frac{n^2 - 1}{2n^2 + 1} \right)$$

solute polarizability (α_i) | solute radius (a_{cav})

"Solvation Coordinate"



$$B_{nuc}^{(i)} = B_{tot}^{(i)} - B_{el}^{(i)}$$

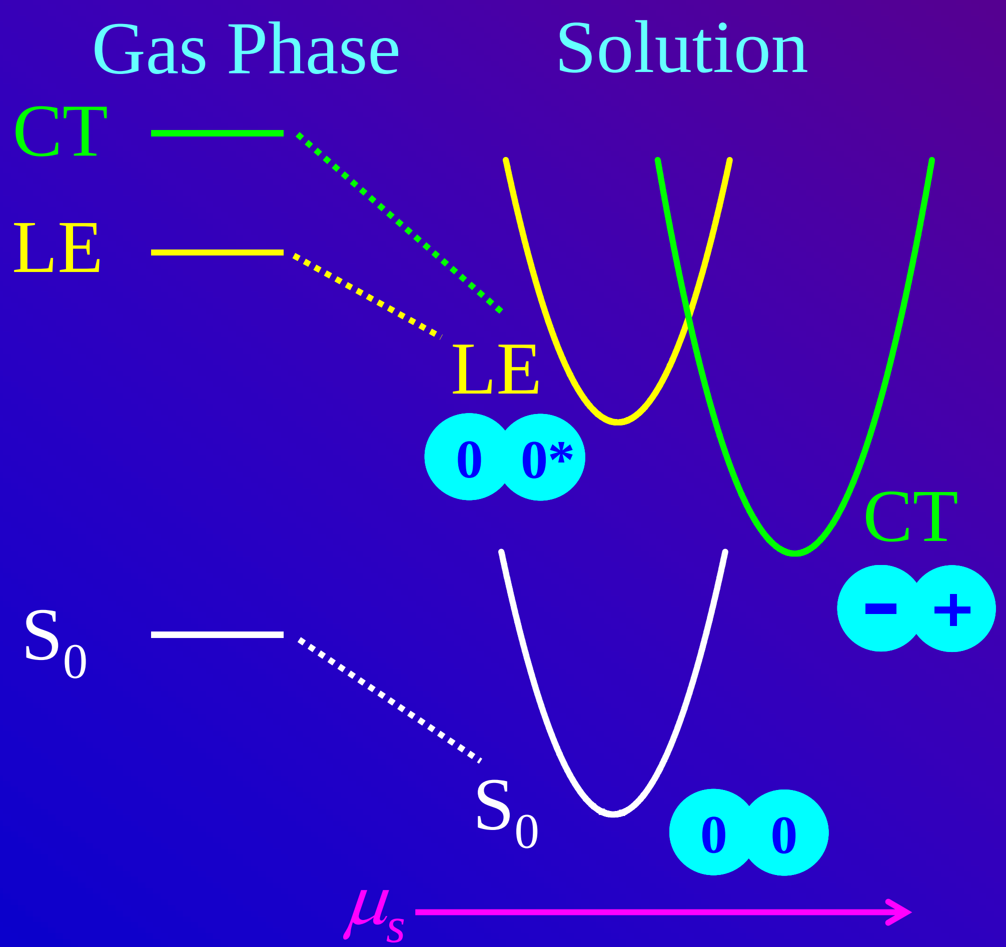
solvation force constant

*Marcus, Hynes, …

Free Energy Surfaces

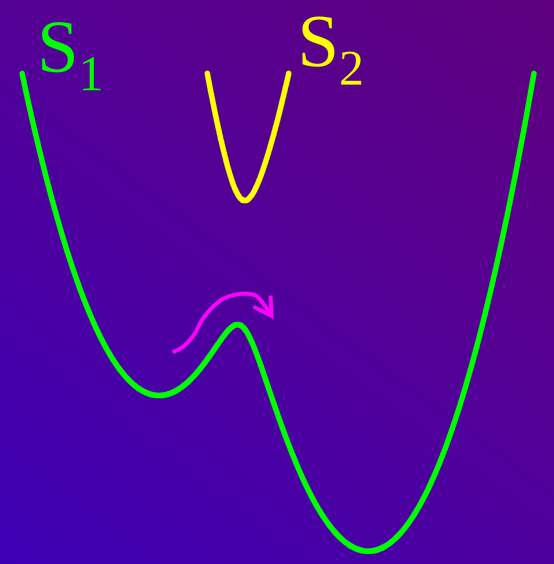
• reactive surface (S_1) results from mixing of diabatic (LE, CT) states

Diabatic Surfaces: S_0, LE, CT



Adiabatic Surfaces: S_1, S_2

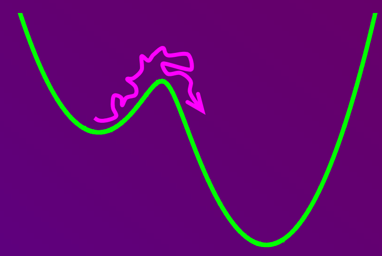
$$\begin{vmatrix} F_{LE}(\vec{\mu}_s) & V_{el} \\ V_{el} & F_{CT}(\vec{\mu}_s) \end{vmatrix} = 0$$



• assume constant V_{el}

CT Dynamics & Solvation Dynamics*

• reactive dynamics described by GLE:



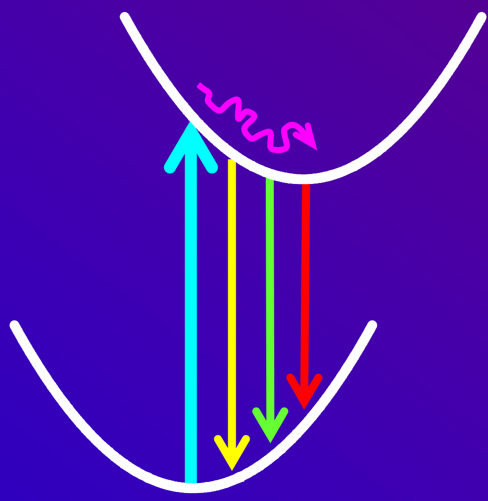
$$\ddot{\mu}_s(t) = -\int_{-\infty}^{t} dt' \underbrace{\zeta_s(t-t')}_{\text{friction}} \dot{\mu}_s(t') + \frac{1}{m_s} \underbrace{R(t)}_{\text{random force}} - \frac{1}{m_s} \underbrace{\frac{\partial F}{\partial \mu_s}}_{\text{systematic force}}$$

$$< RR(t) >= k_B T m_s \zeta_s(t)$$

• friction $\zeta_s(t)$ obtained from dynamic Stokes shift data

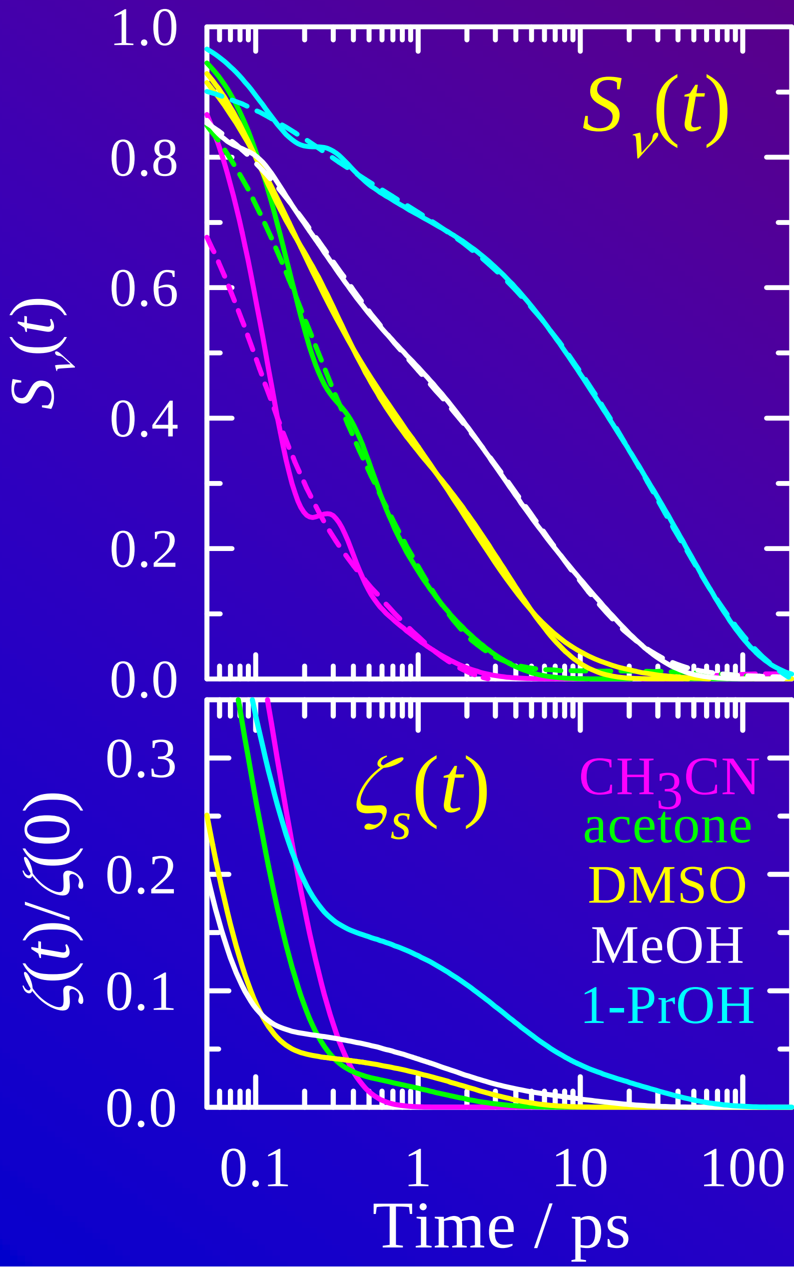
$$\tilde{\zeta}_s(z) = \frac{(z^2 + \omega_s^2)\tilde{\Delta}_s(z) - z}{1 - z\tilde{\Delta}_s(z)}$$

$$\Delta_s(t) \cong S_\nu(t) \equiv \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

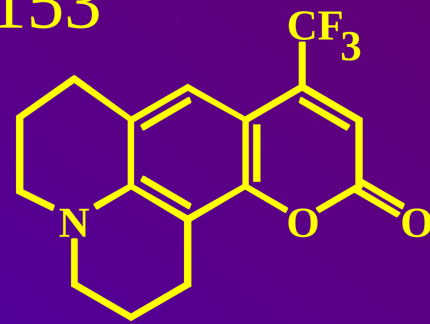


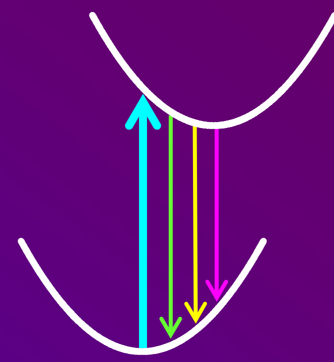
*Hynes & co.

$\zeta_s(t)$ from $S_\nu(t)$



C153





Solvation Props.			$\zeta_s(t)$ Fit				
Solvent	ω_s / ps^{-1}	$\langle\tau\rangle$ / ps	$\zeta(0)$ / ps^{-2}	a_1	τ_1 / fs	$a_{2,3}$	$\tau_{2,3}$ / ps
CH_3CN	10.9	0.26	414	.96	52	.04	.70
acetone	6.9	0.62	258	.96	70	.04	1.2
DMSO	8.2	1.7	900	.95	32	.05	1.9
CH_3OH	14.5	4.9	3670	.93	26	.05	1.3
						.02	9.2
1-PrOH	5.5	26	496	.84	64	.12	3.1
						.05	24

Spectroscopy

- spectra are in inhomogeneous broadening limit

Absorption Spectrum:

$$A(\nu) \propto \sum_{i=1}^{2} \int d\mu_s \underbrace{P_0(\mu_s)}_{S_0\text{ prob.}} \underbrace{\Delta F_{0i}(\mu_s)}_{\text{trans. }\nu} \underbrace{|M_{0i}(\mu_s)|^2}_{\text{transition moment}} \underbrace{L_{abs}(\nu - \Delta F_{0i}/h)}_{\text{abs. line shape}}$$

Equilibrated Emission Spectrum:

$$E(\nu) \propto \int d\mu_s P_1(\mu_s) \Delta F_{0i}(\mu_s)^3 |M_{0i}(\mu_s)|^2 L_{em}(\nu - \Delta F_{01}/h)$$

Model Parameters

Solute:

$U_0=0$; U_{LE}*, U_{CT}*, V_{el}*

a_{cav}, μ_0, μ_{LE}*, μ_{CT}*

(α_0, α_{LE}, α_{CT})* $\alpha/a_{cav}^3 \sim 0.3$

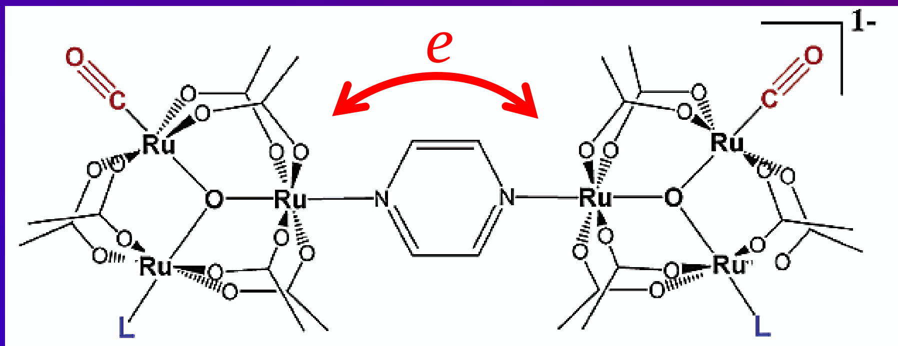
$M_{0,LE}$, $M_{0,CT}$*

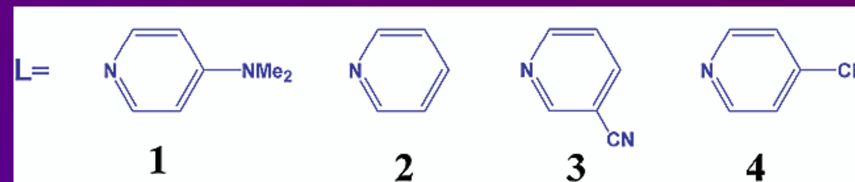
Solvent:

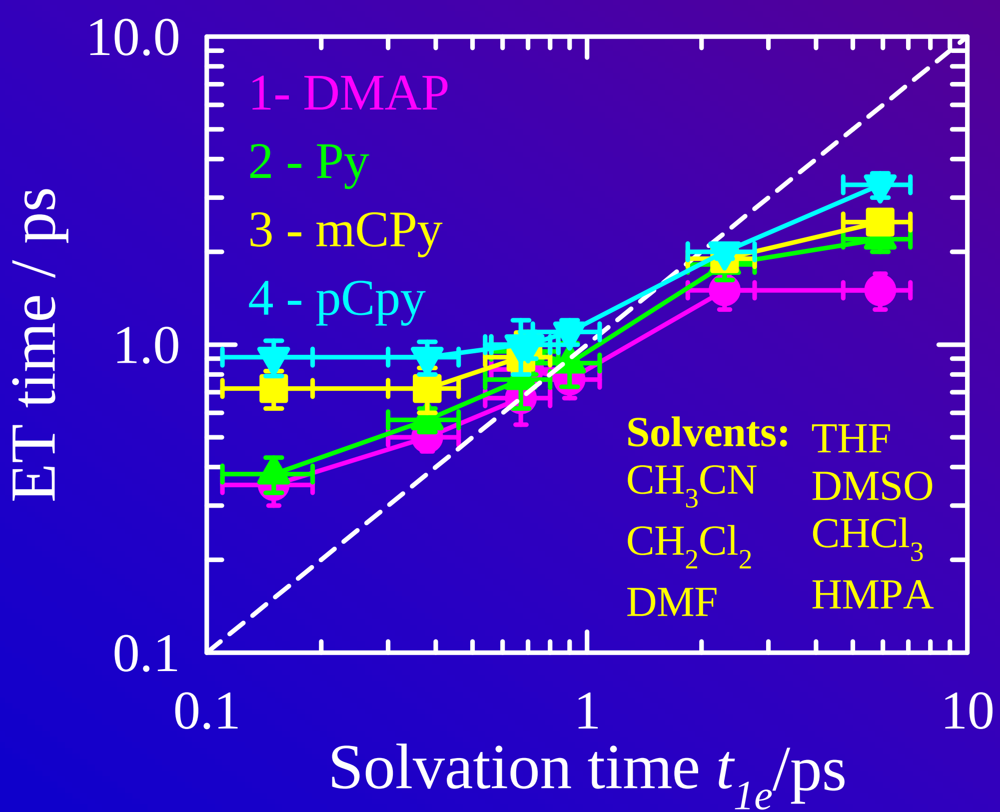
B_{nuc}, B_{el} from ε, n (or $\Delta\nu$)

$\zeta_s(t)$ from C153 $S_\nu(t)$

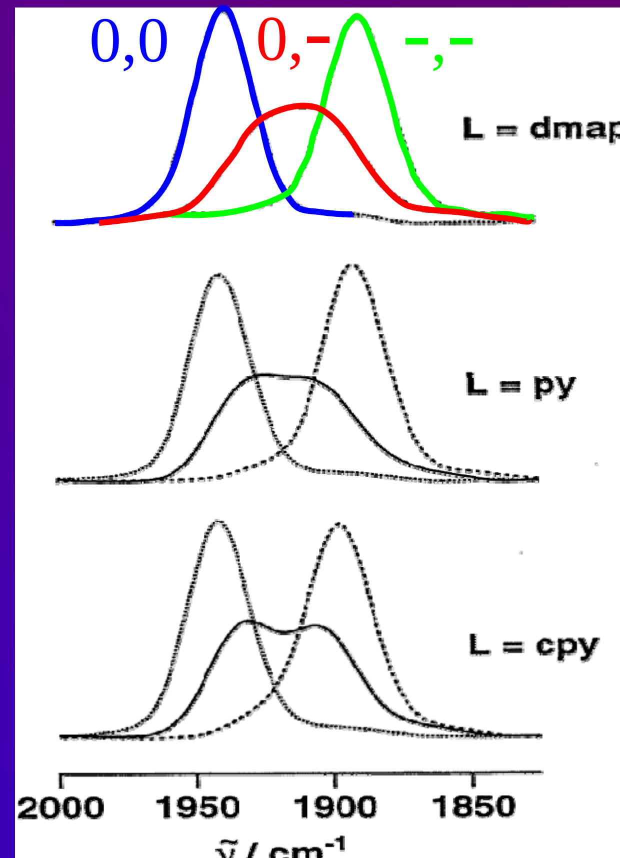
System #1: “HDR” Complexes*





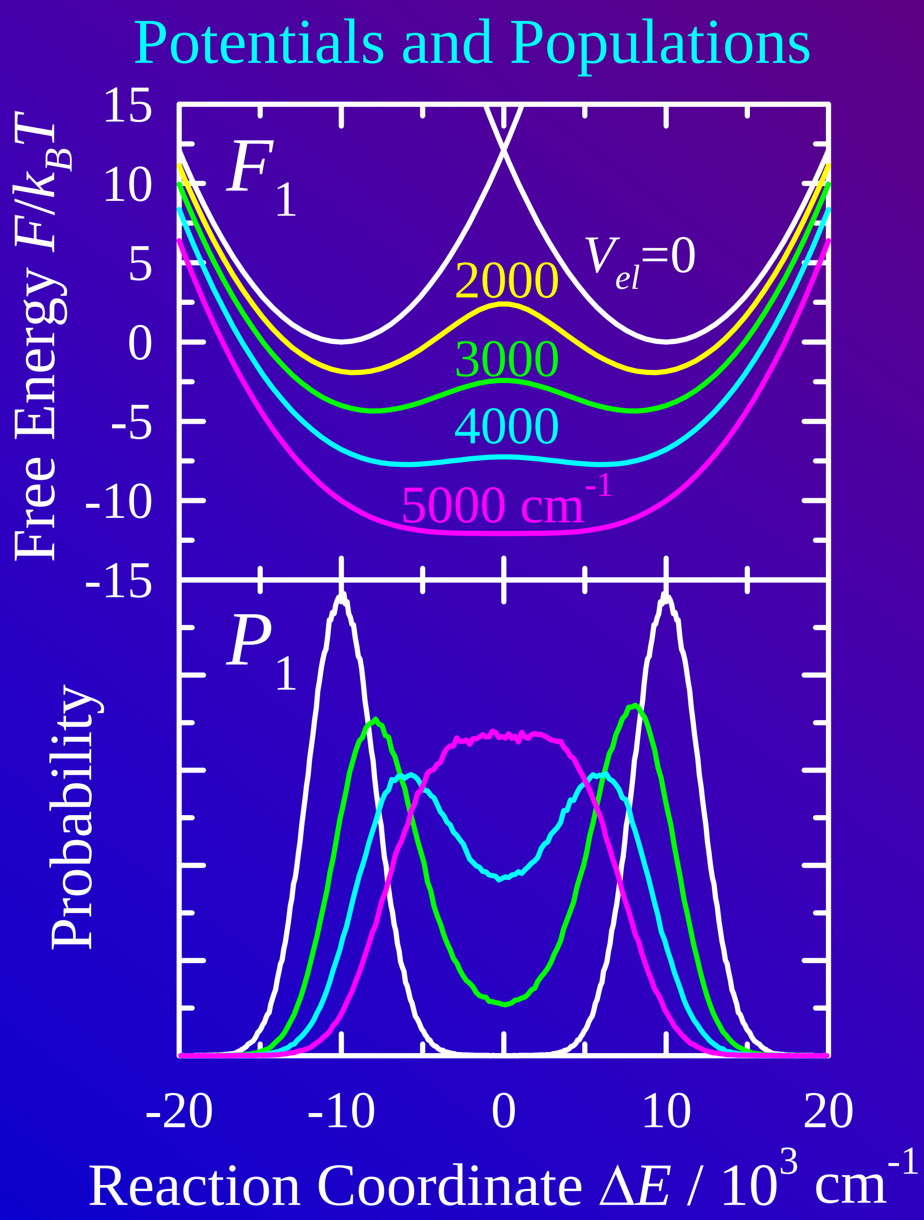


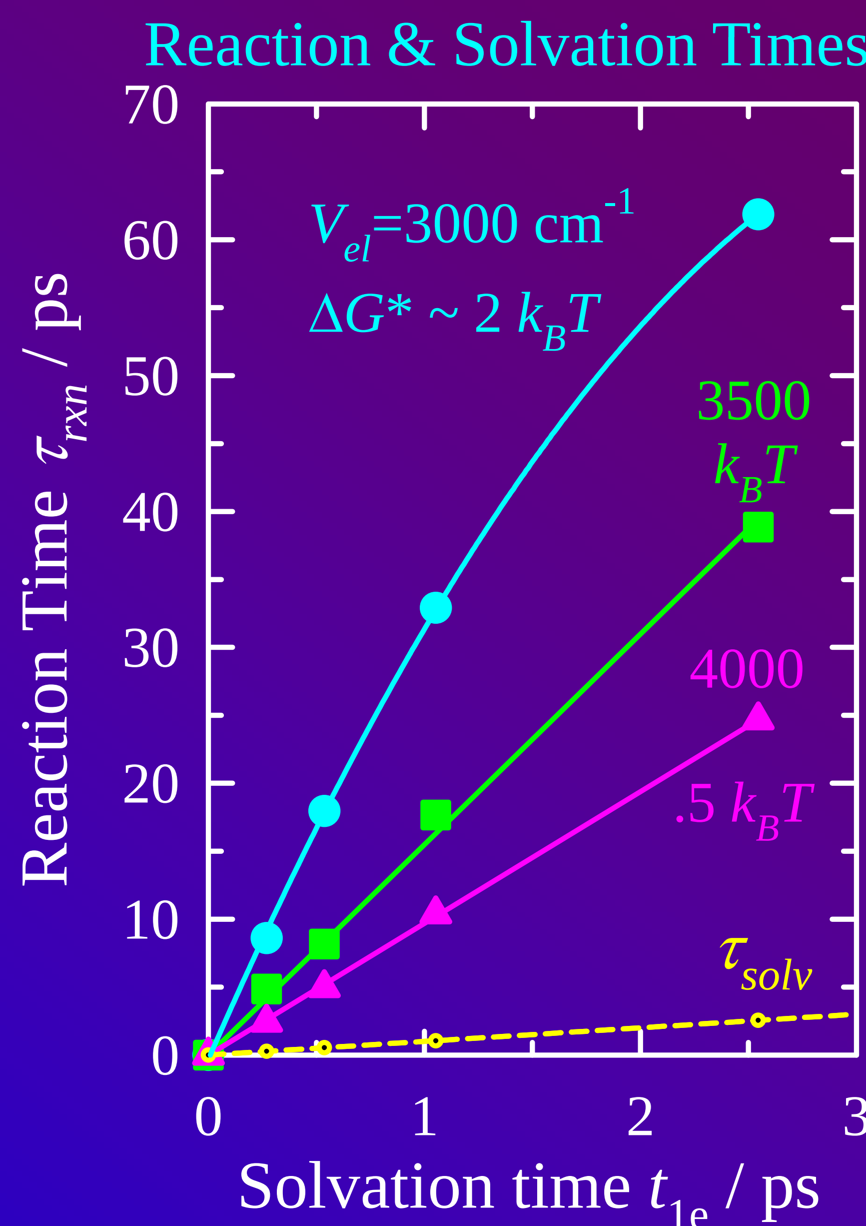
IR Band Coalescence



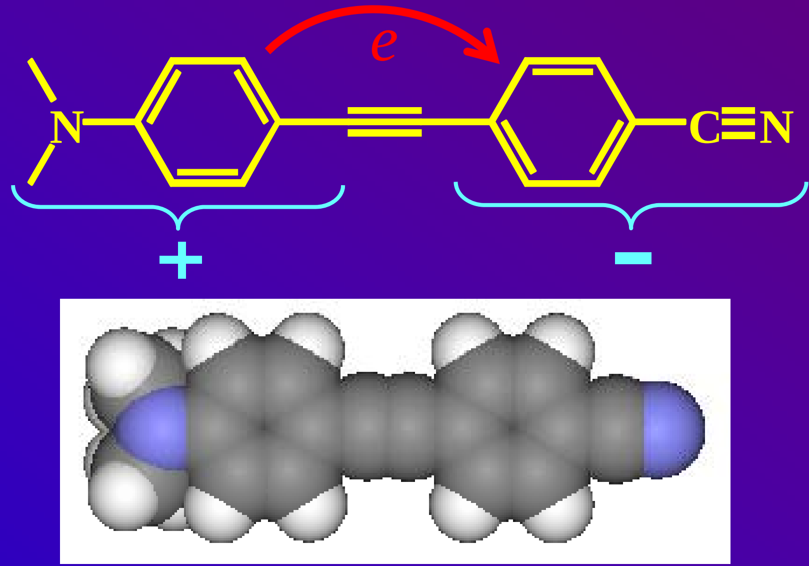
*data of Londergan, Kubiak *et al*., JACS 124, 6236 (2002).

Is it Dynamics?



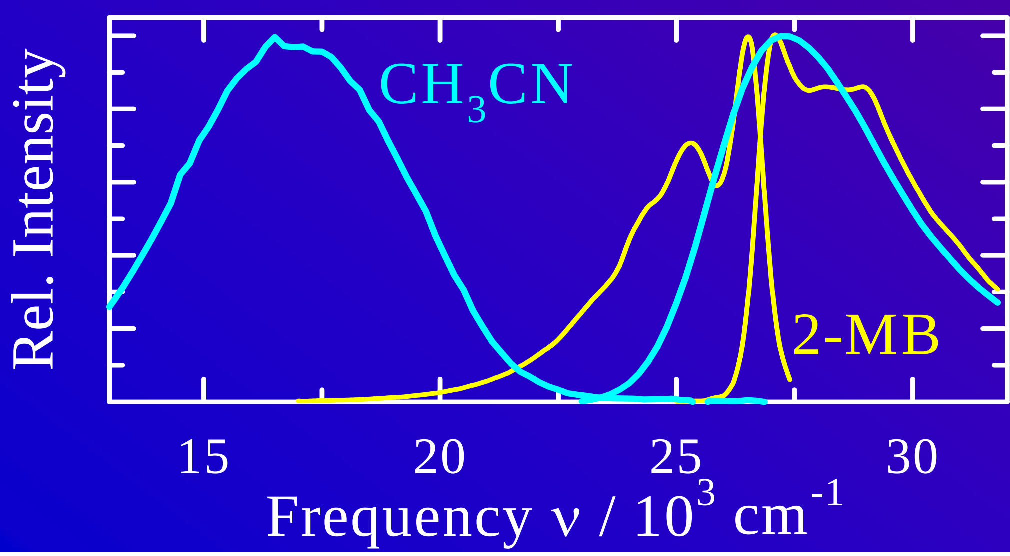


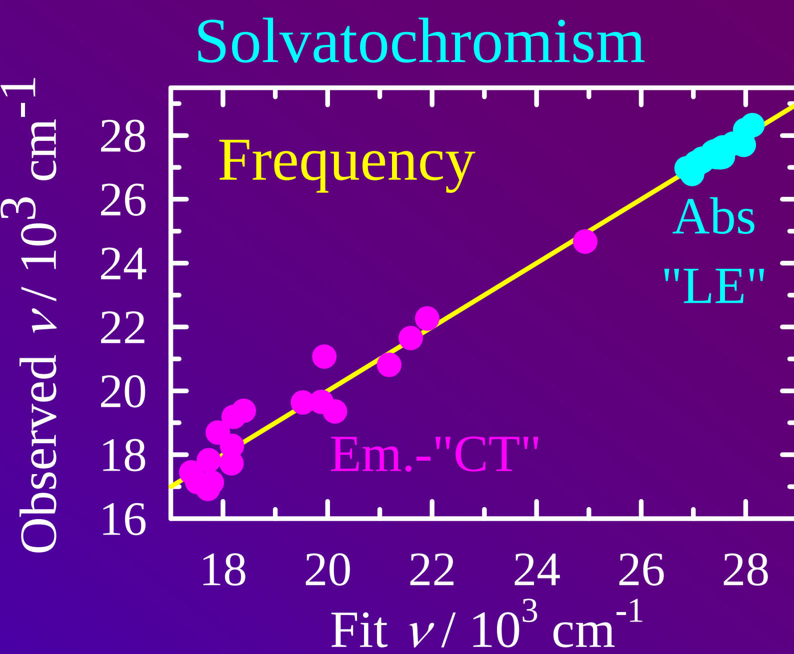
System #2: "DTN"

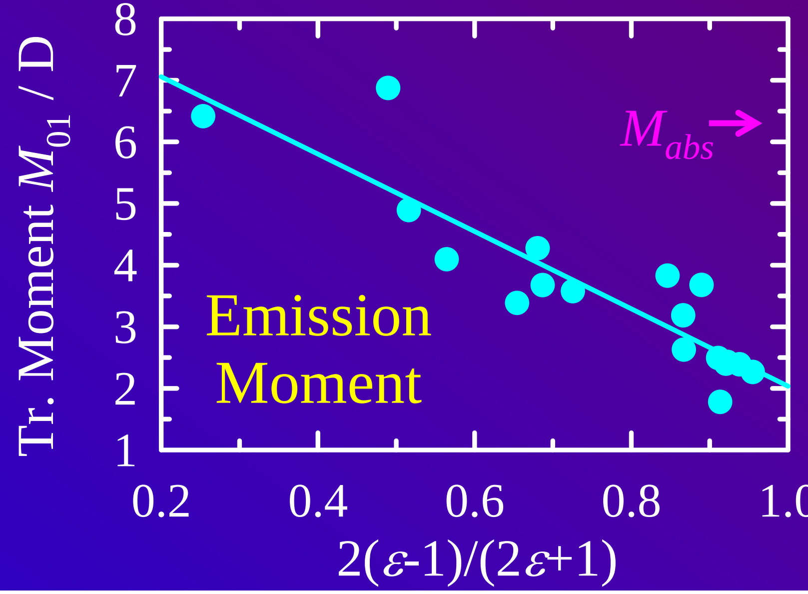


μ_0 = 8.7 D, ω =19° (MP2/6-311G)

$\mu_{LE} \sim \mu_0$; $\mu_{CT} \sim 2\mu_0$ (AM1/CI)







DTN: Modeling Steady-State Spectra

U_{LE}* = 27.578 cm^{-1}

U_{CT}* = 31,840 cm^{-1}

μ_{LE}* = 12.5 D

μ_{CT}* = 22.8 D

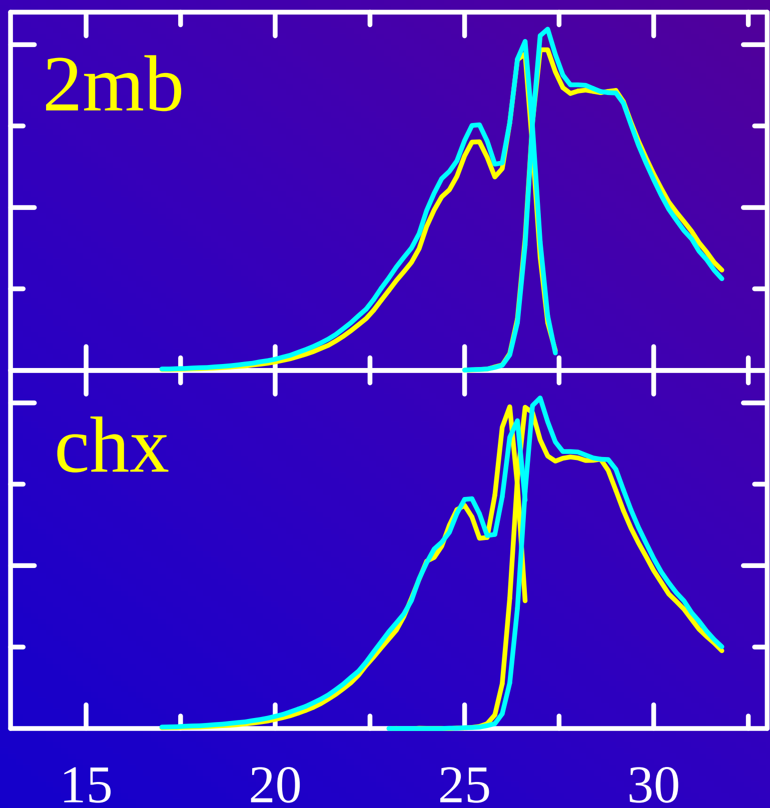
a_{cav} = 5.1 Å

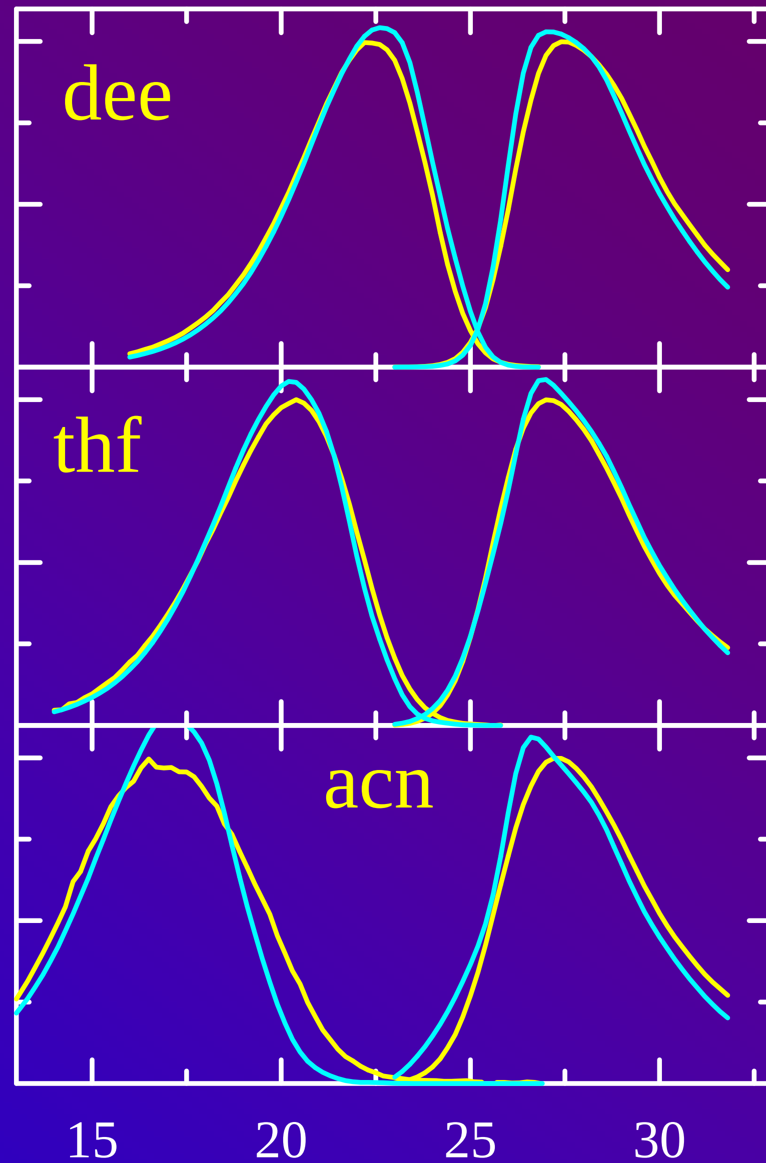
α_i/a^3 = 0.26

V_{el}* = 0.635

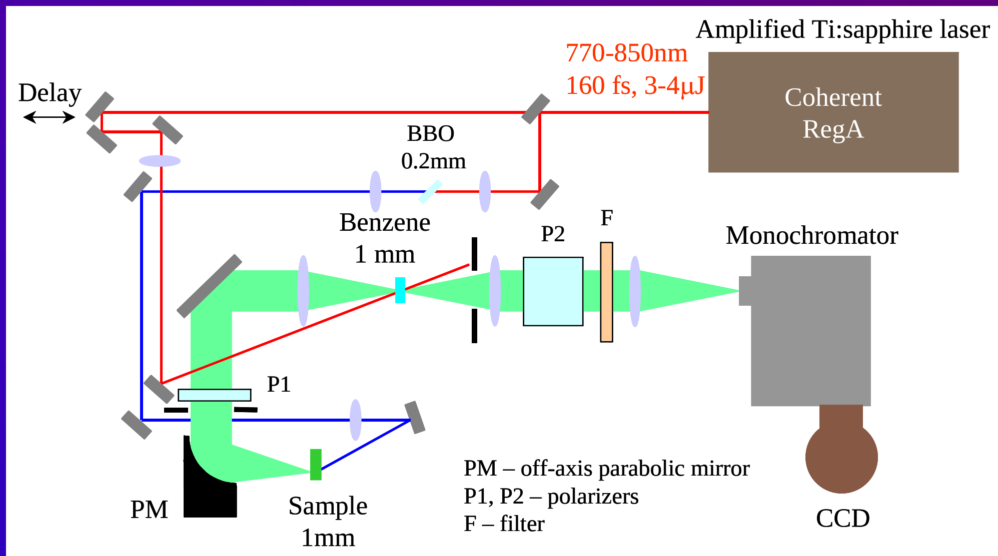
M_{LE} = 6.3 D

M_{CT}* = 2.4 D

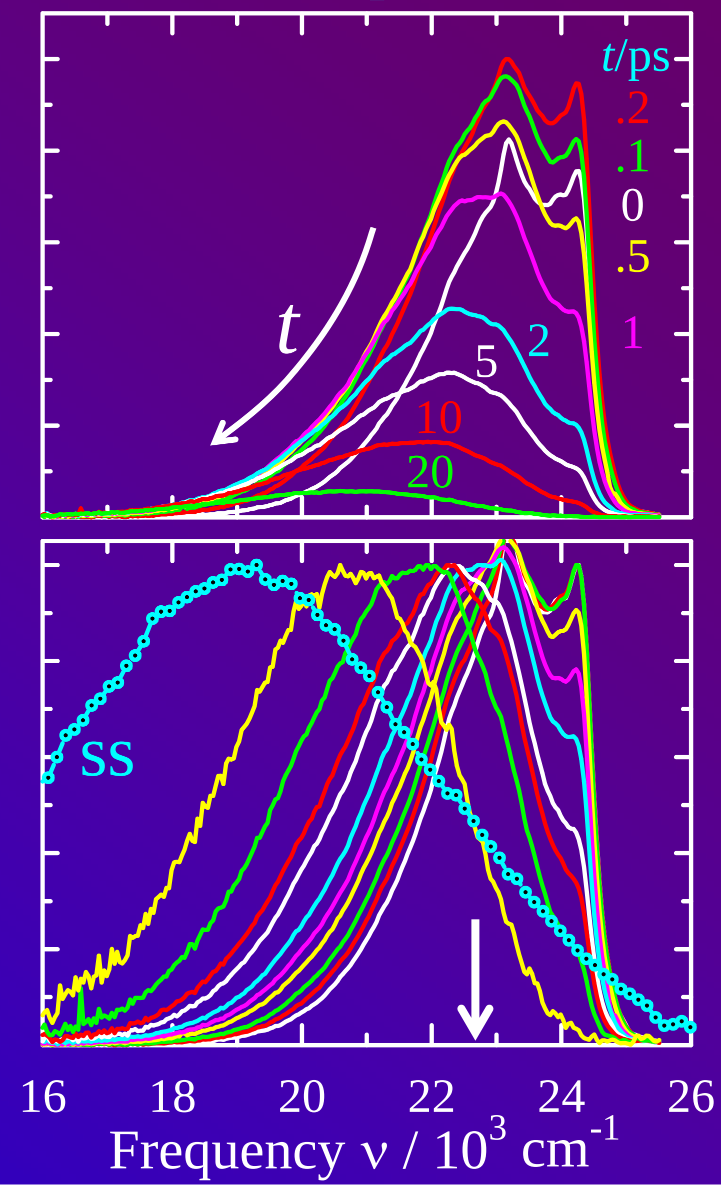




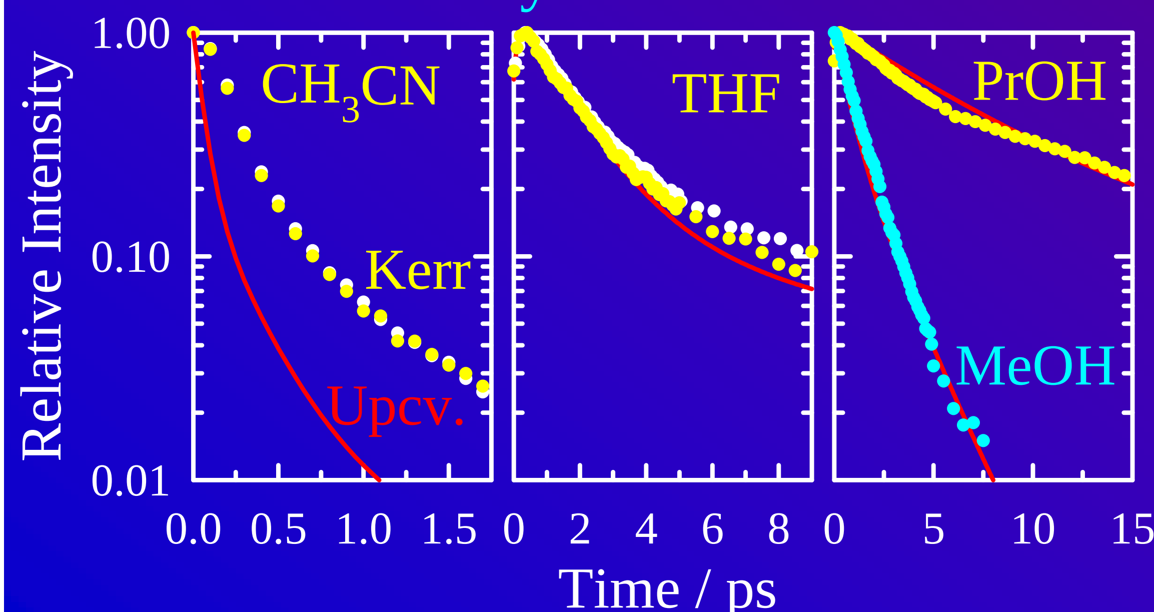
Kerr-Gated Spectroscopy



DTN / 1-Propanol

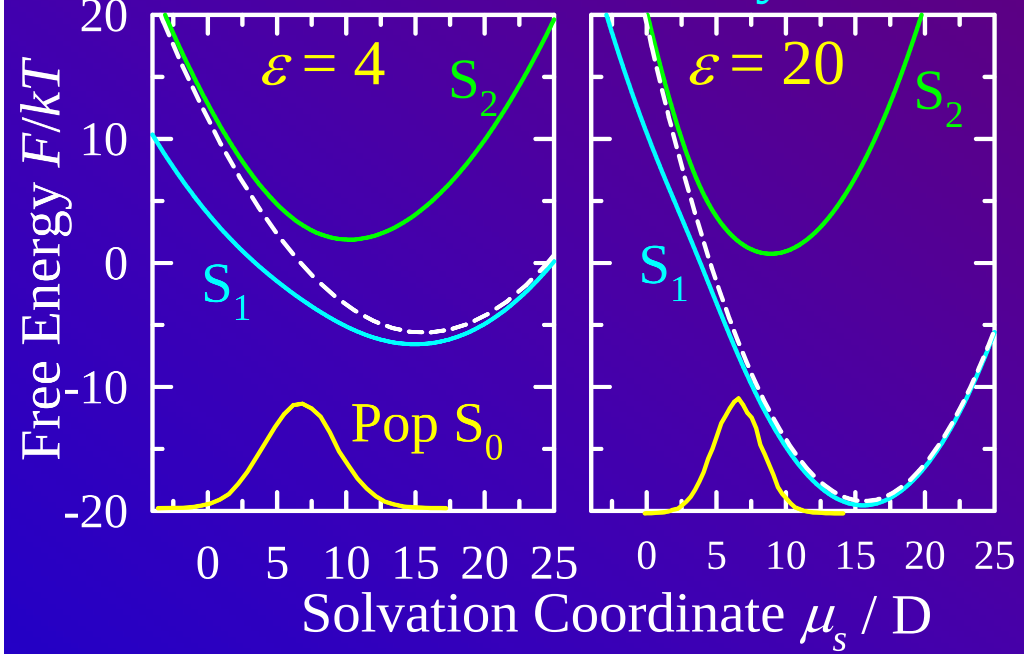


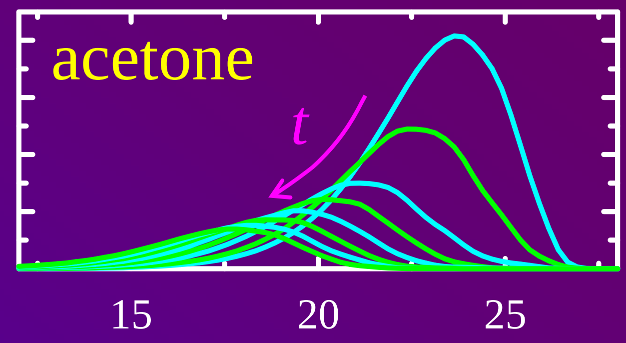
440 nm decays

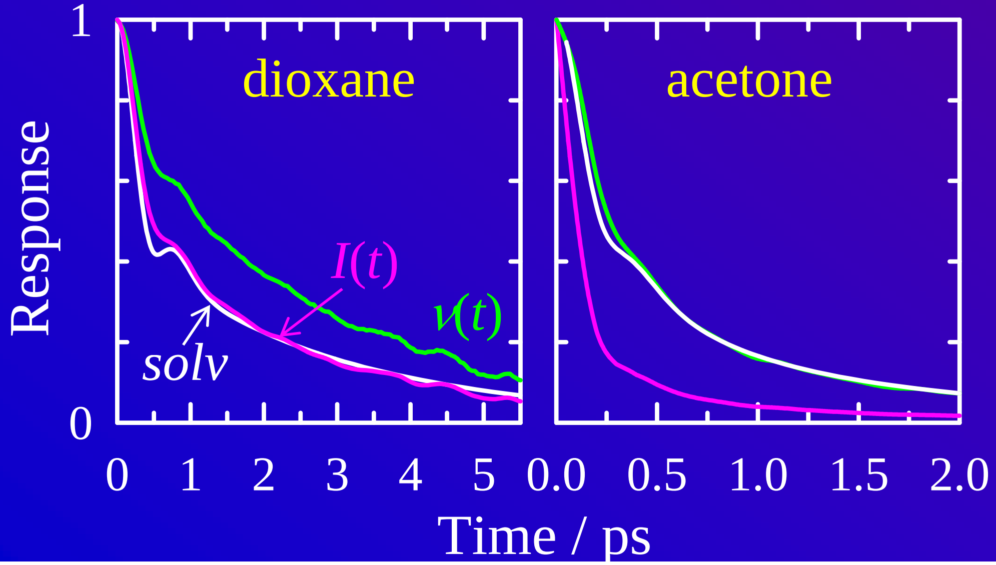


DTN Model Dynamics

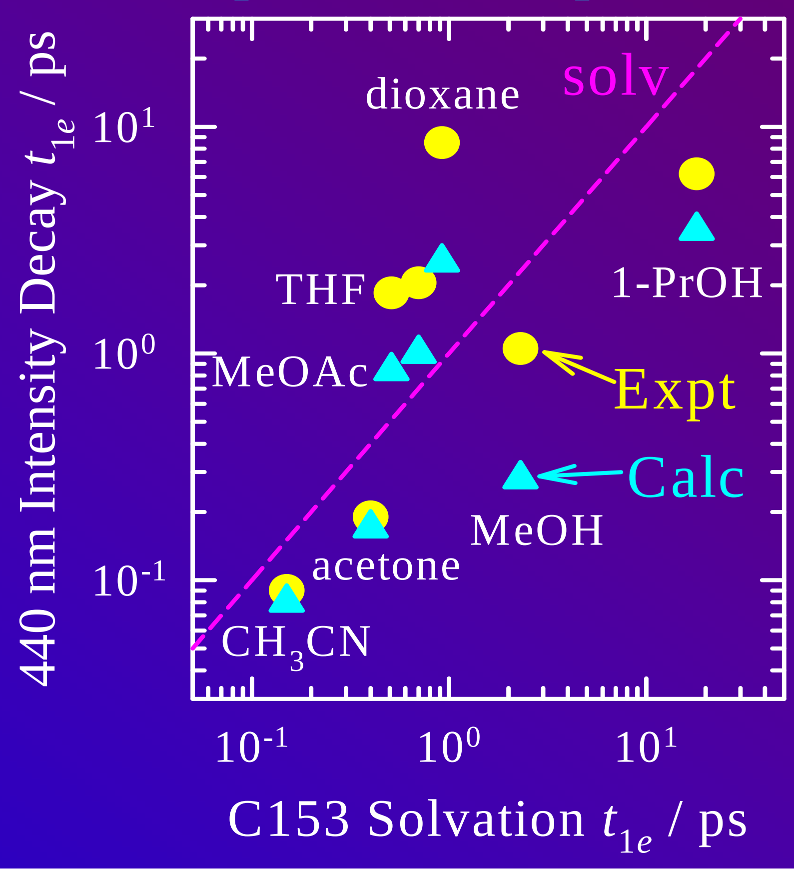
Model Potentials and Dynamics



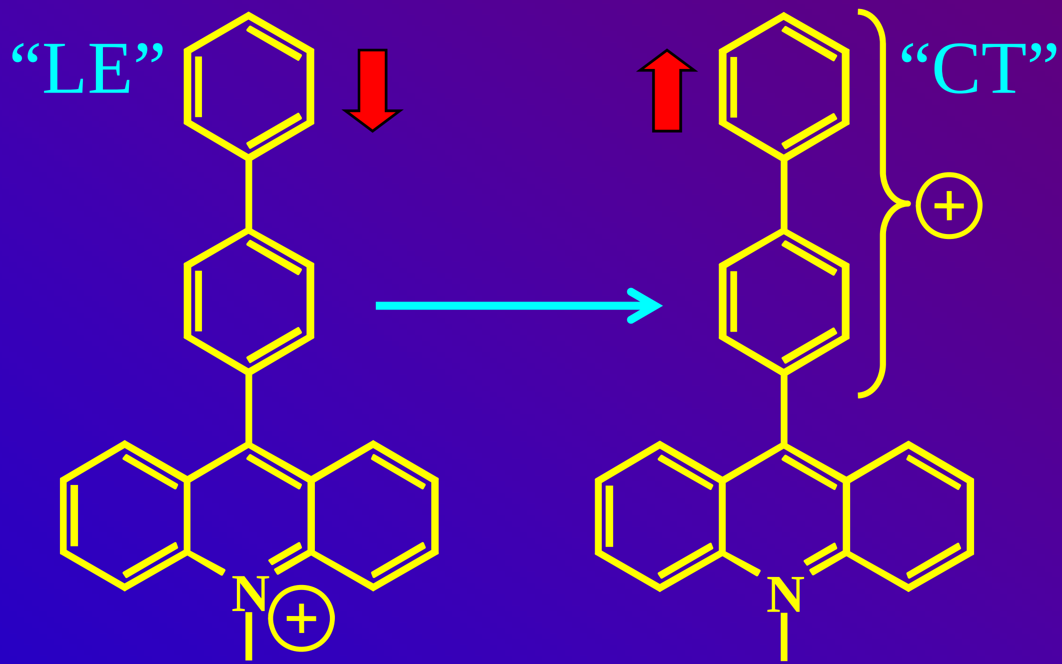


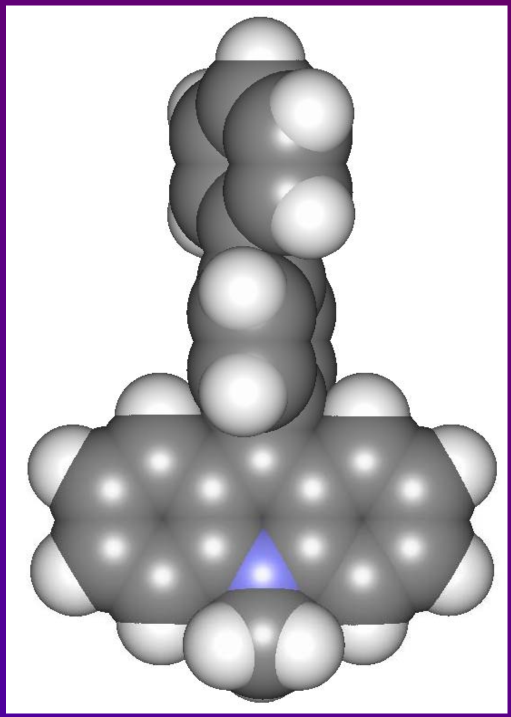


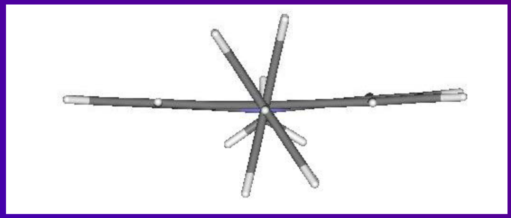
Comparison to Experiment



System #3: "BPAc"

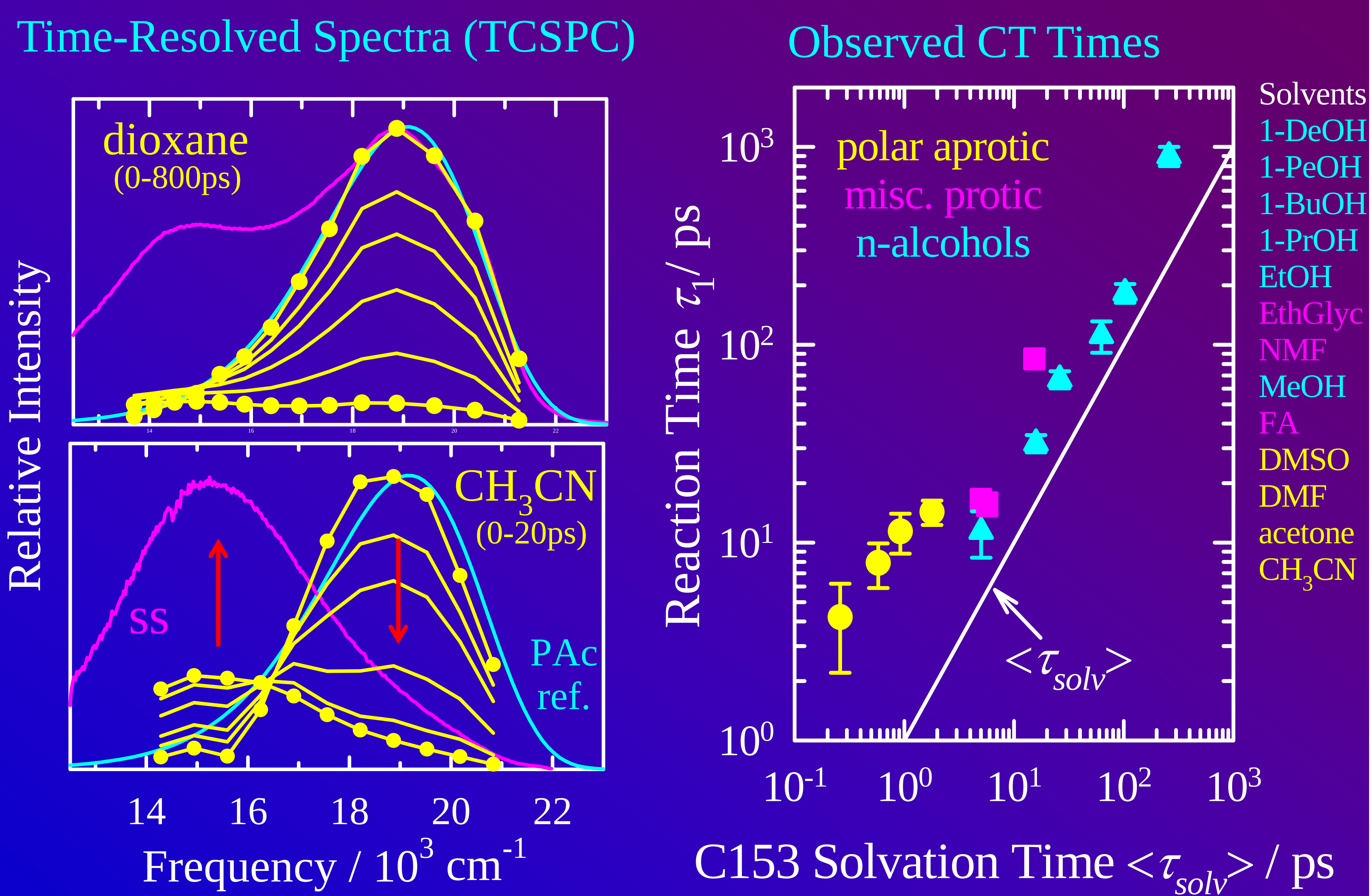






- *charge shift* means energetics are relatively solvent independent
- equivalent to -9 D $\rightarrow$ +9 D change in μ (AM1/CI)
- V_{el} ~ 750 cm^{-1} (AM1/CI)

BPAc Experimental Results



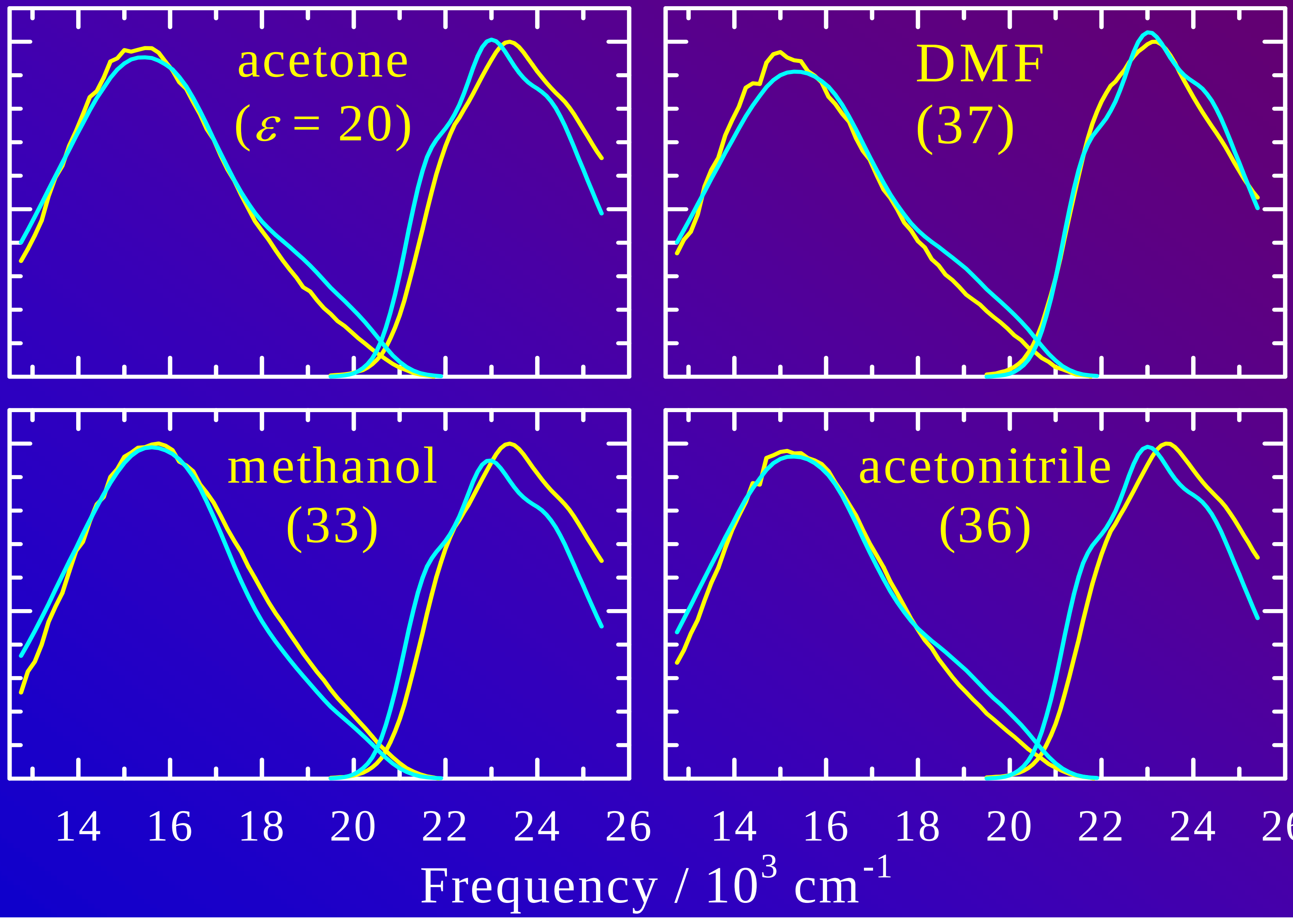
BPAc: Fits to Steady-State Spectra

U_{LE}* = 20,970 cm^{-1} μ_{LE}* = 20,970 cm^{-1} a_{cav} = 5.2 Å M_{LE} = 1.0 D

U_{CT}* = 19,870 cm^{-1} μ_{CT}* = 19,870 cm^{-1} α/a^3* = .1, .3, .3 M_{CT} = .64 D

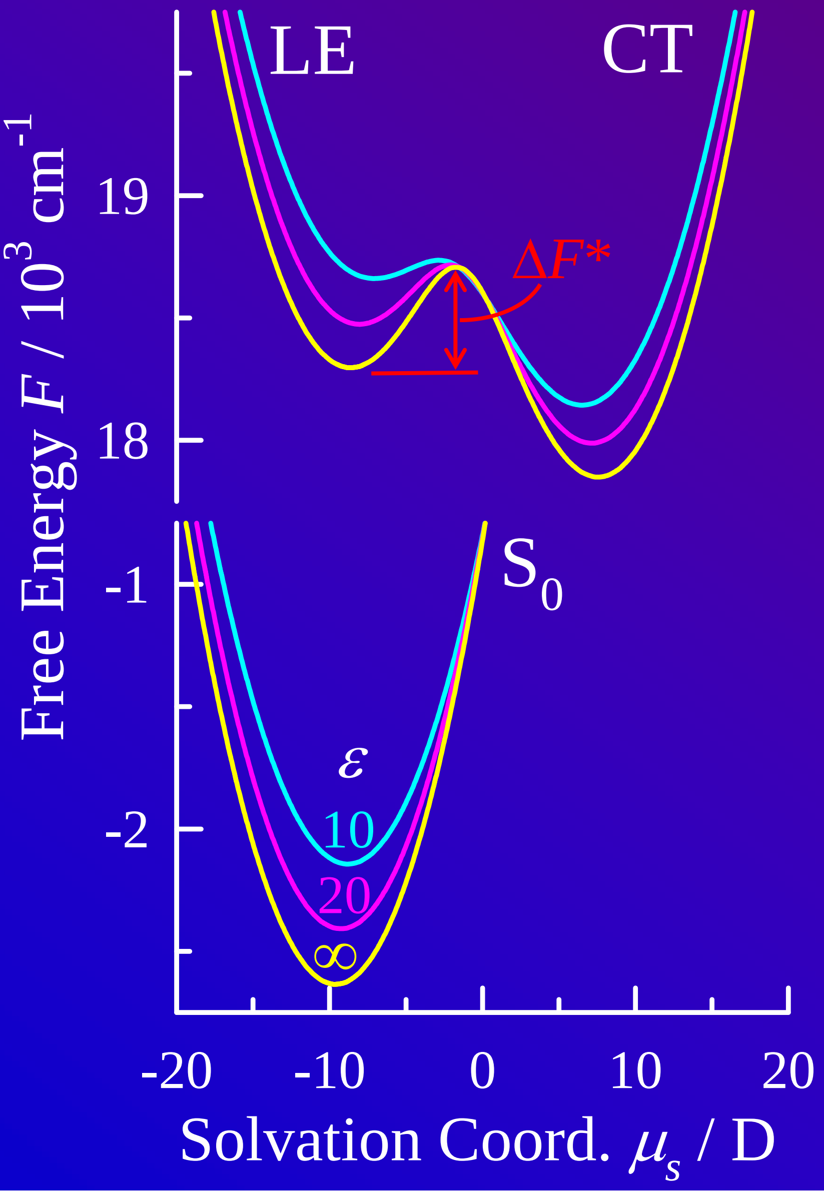
V_{el} *= 1,000 cm^{-1}

*

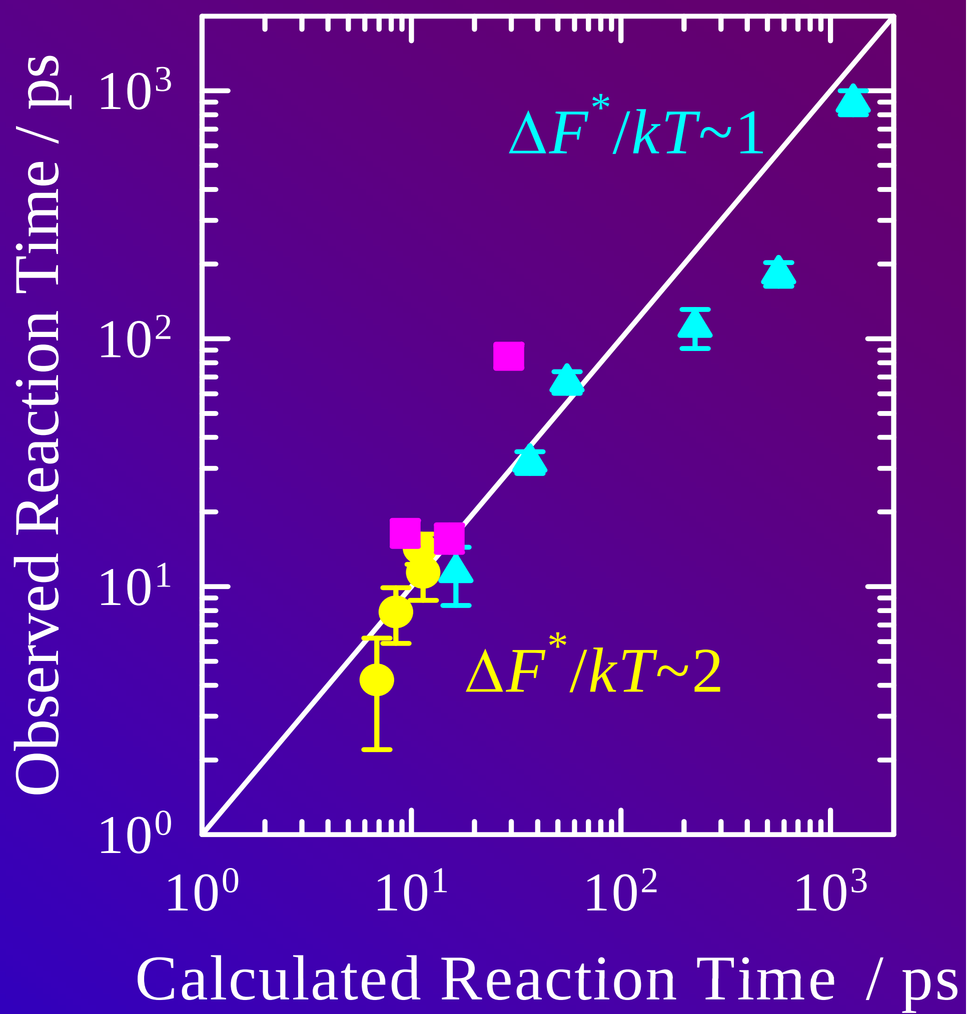


BPAc: Model Results

Free Energy Surfaces

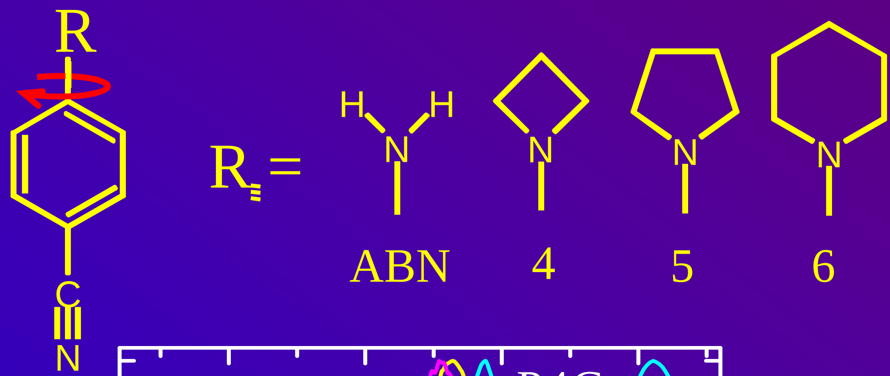


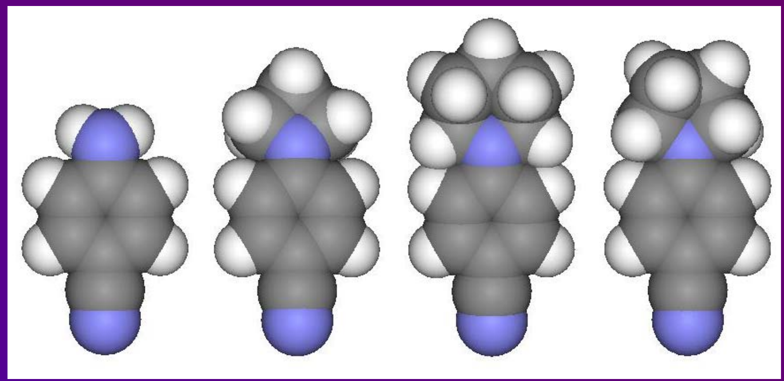
Predicted Dynamics

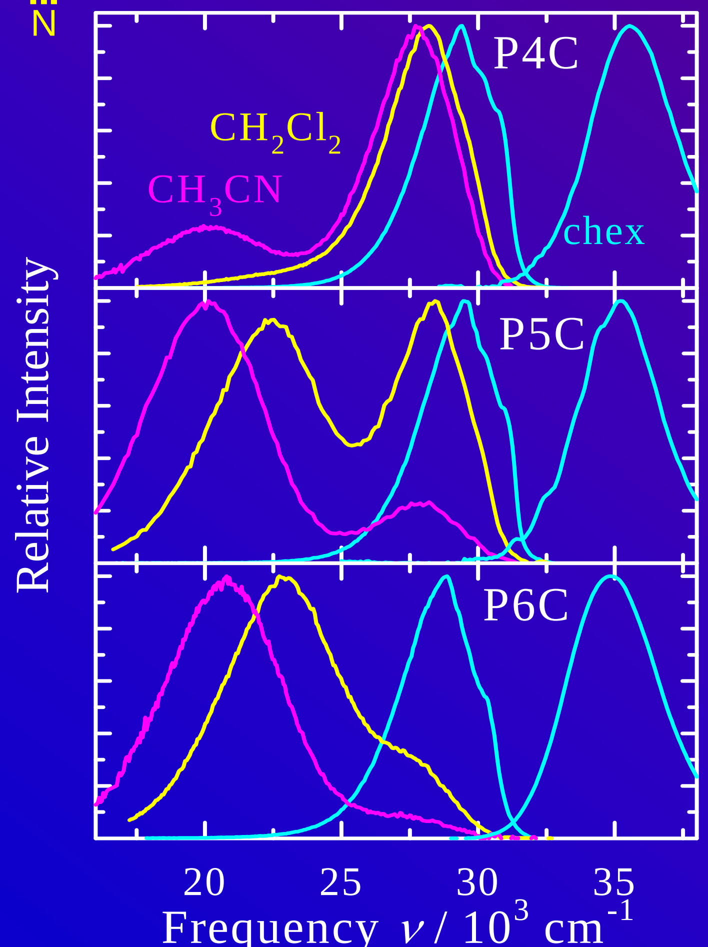


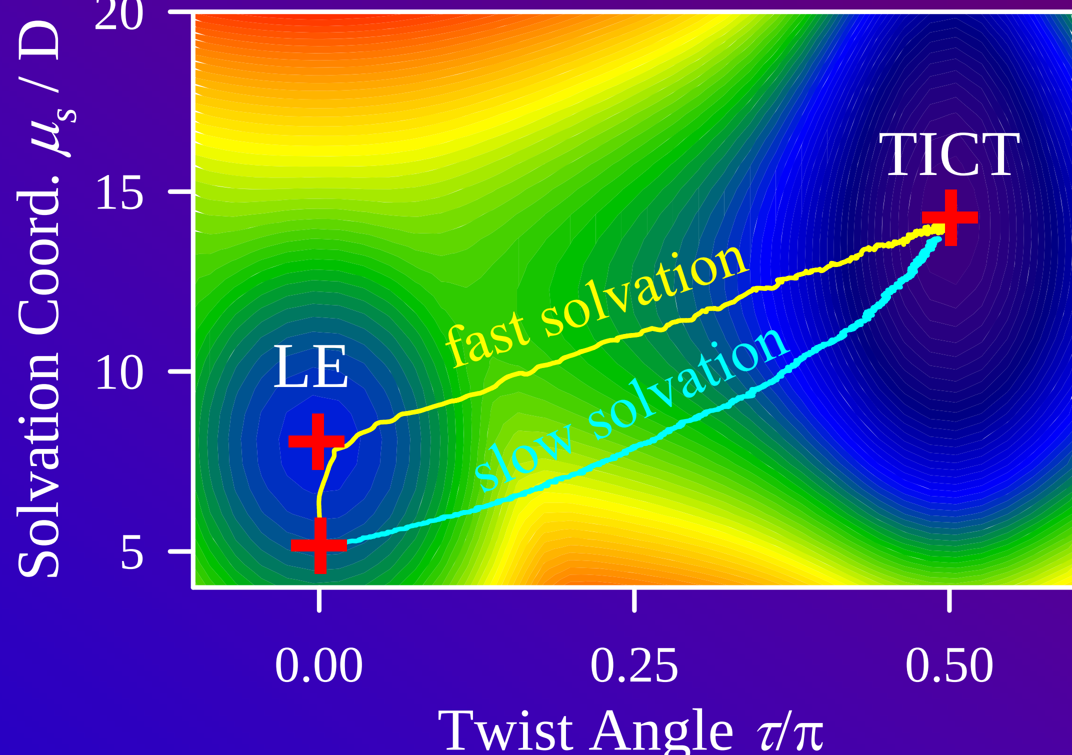
- exponential for $\Delta F^* \sim kT$

2d Systems: “PnC” Series









Summary & Conclusions

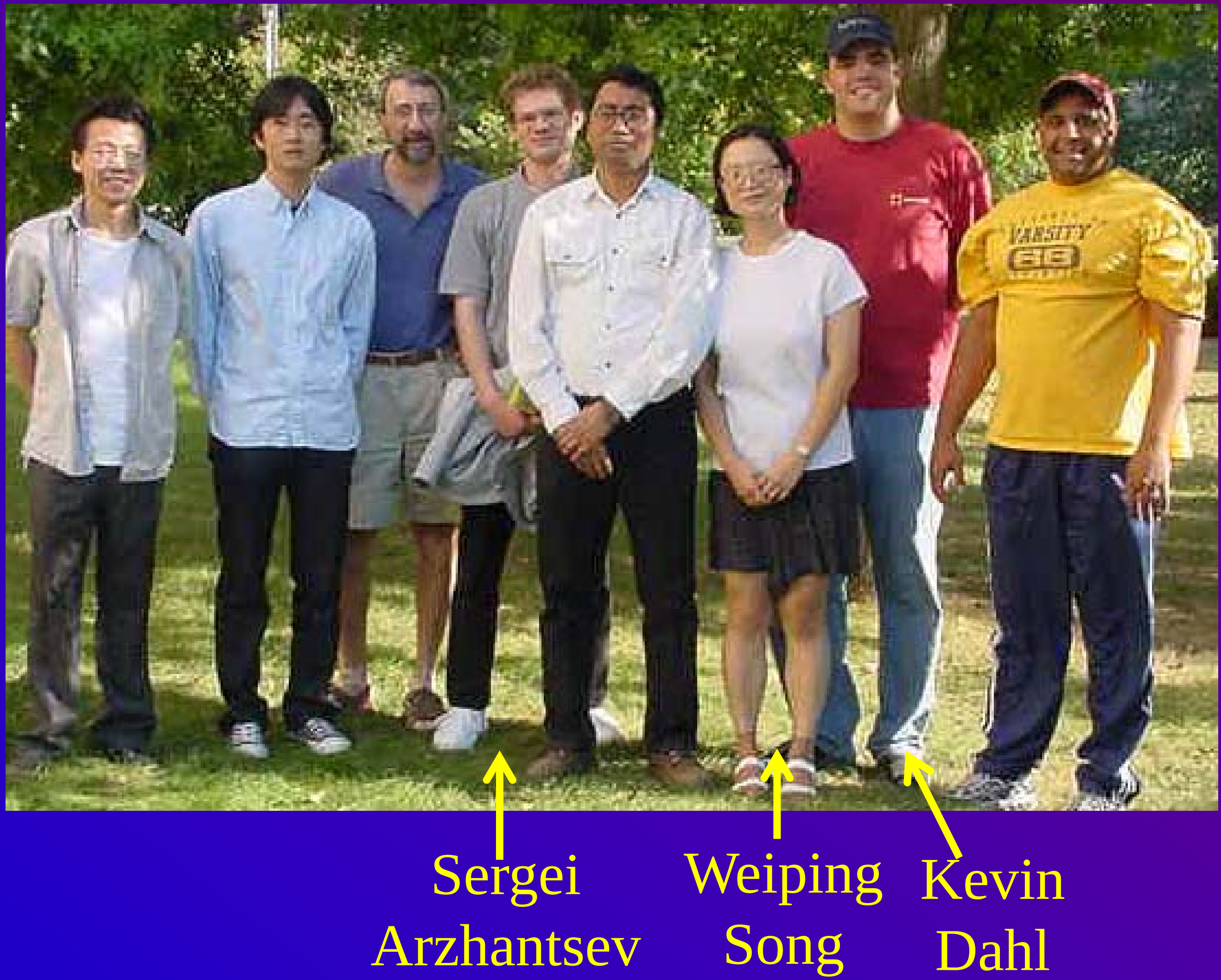
- "Photodynamic model" of time-resolved CT spectra based on the theoretical work of Hynes and others
  - adiabatic rxn, reaction coordinate $\Leftrightarrow \mu_s$
  - free energies quadratic in μ_s
  - dielectric continuum estimates of energetics B_{el}, B_{nuc}
  - GLE with $\zeta_s(t)$ from $S_\nu(t)$

- 1d approach is reasonably successful in capturing solvent's role in some systems: "DTN", "BPAc"; provides an important interpretive tool in others: "HRD"

- (Kerr spectroscopy offers potential for highly detailed comparisons between experiment and model calculations)

- 2d modeling of TICT reactions of "PnC" series is underway

Acknowledgements



Others: Joe Gardecki, Gil Jones (BU), Casey Londergan & Cliff Kubiak (UCSD), DOE