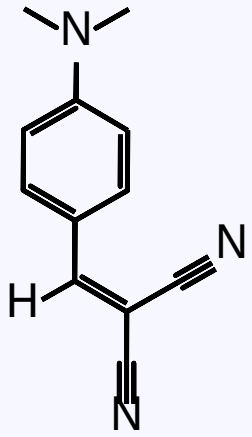
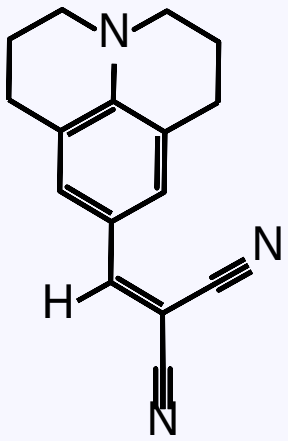
Benzylidene Malononitriles as Local Friction Probes

- Experimental Characterization
- Electronic Structure Calculations
- Simulations of Solution-Phase Dynamics

DMN



JDMN



Chet Swalina, Hui Jin, Min Liang,
Durba Roy, & Mark Maroncelli
The Pennsylvania State University

"Push-Pull" "Molecular Rotors"

- significant CT character to $S_0 \rightarrow S_1$; large β

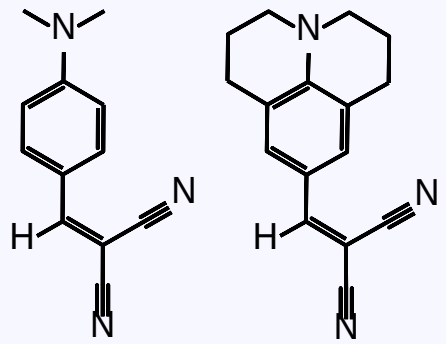
  μ_0~9 D, μ_1~18 D

- weakly fluorescent in most solvents

  φ_f ~10^{-3}-10^{-4}; τ_f ~1 ps

- $S_1 \rightarrow S_0$ sensitive to local fluidity or free volume of environment
- used to probe liquids, polymers & biological systems*

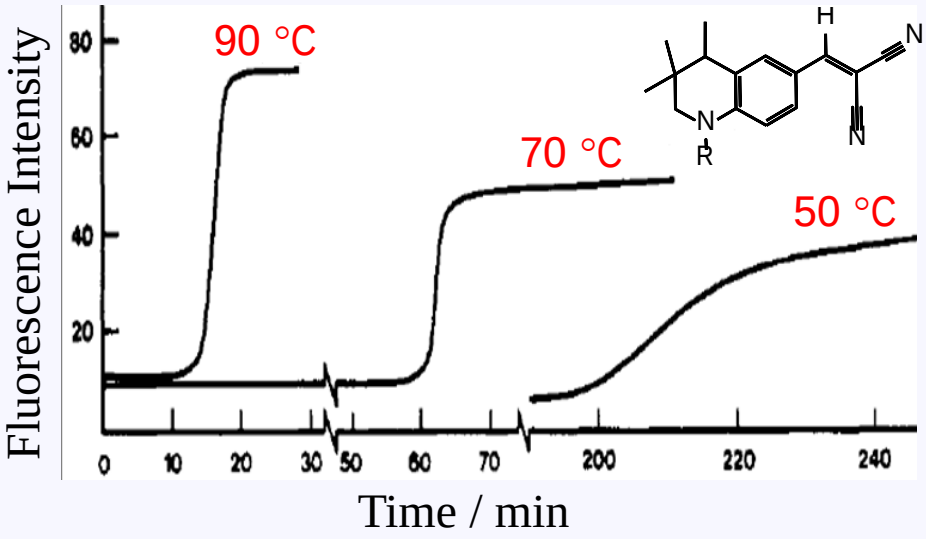
DMN JDMN



Our Interests:

- determine deactivation mechanism & better define what is being sensed
- learn about reactive friction

Polymerization of MMA

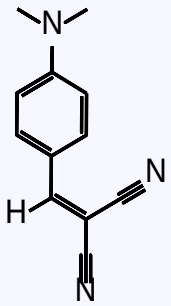


Loutfy, *Macromolecules* **14**, 270 (1981).

*Haidekker & Theodorakis, *Org. Biomol. Chem.* **5,** 1669 (2007).

Spectra & Solvatochromism

DMN



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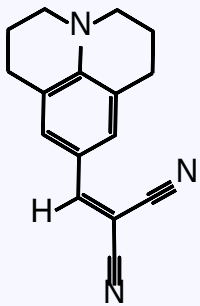
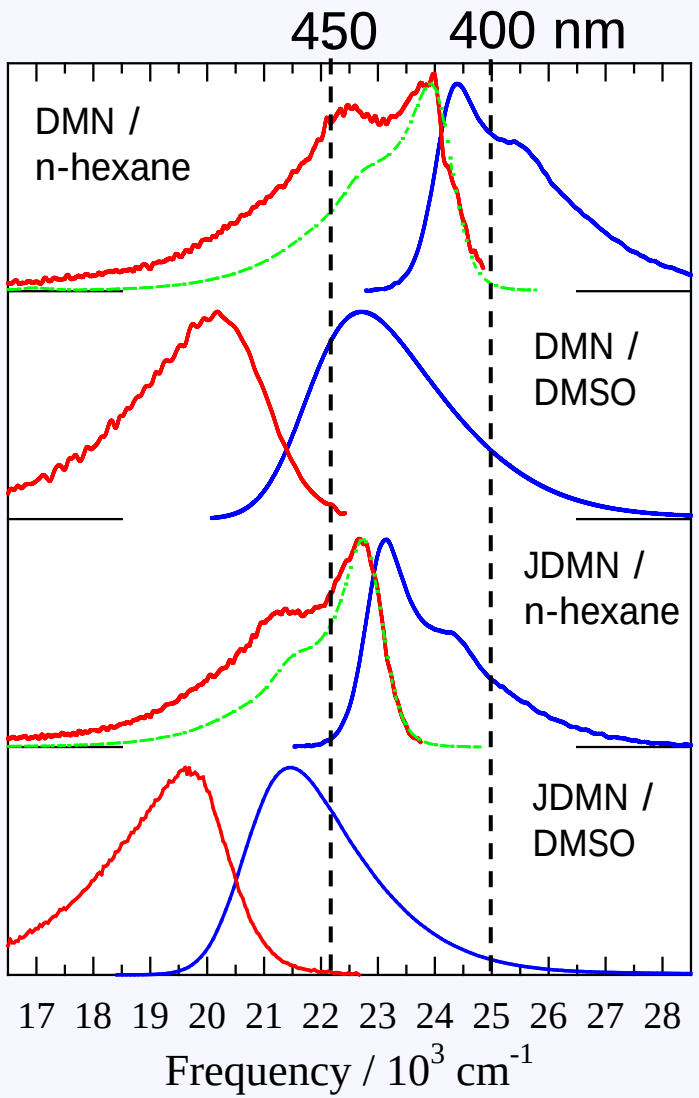
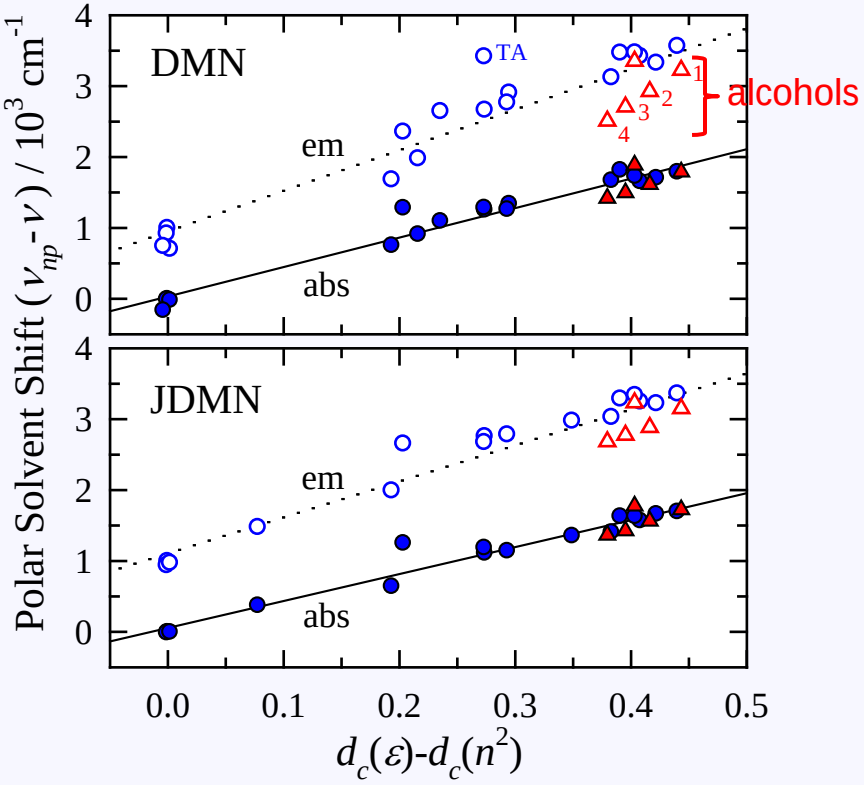




Jin et al., *JPCB* **114**, 7565 (2010).

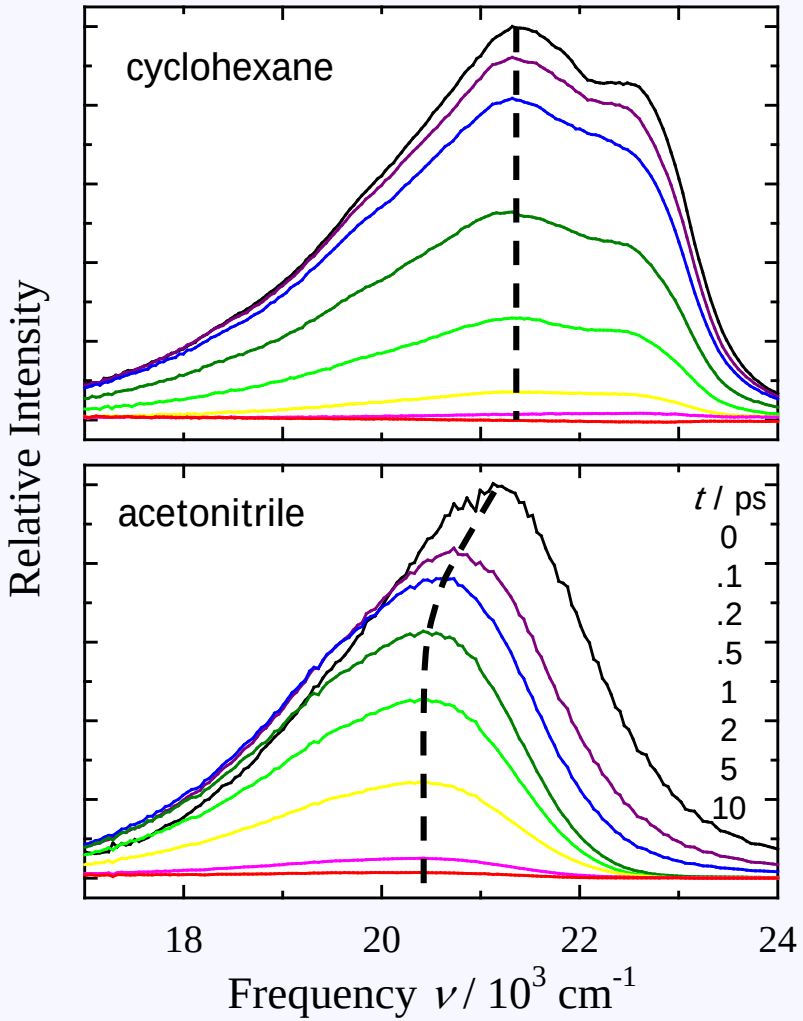
Dielectric Correlations



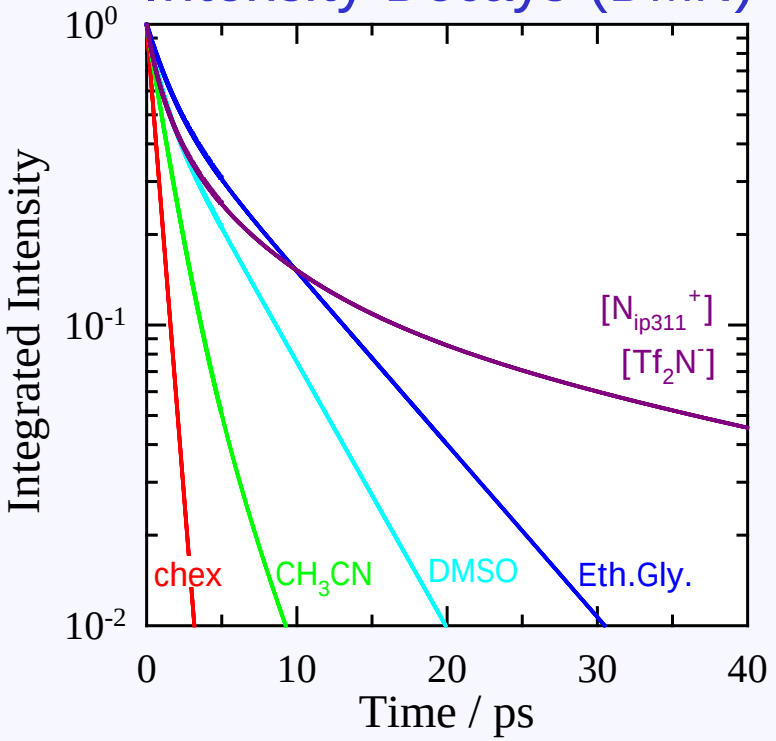
- vibronic widths in $S_1 > S_0$
- absorption shifts indicate $\Delta\mu$=7-8 D, consistent with electrochromism
- emission shifts smaller than expected

fs-Time-Resolved Emission (25 °C)

Kerr Gated Emission of DMN



Intensity Decays (DMN)

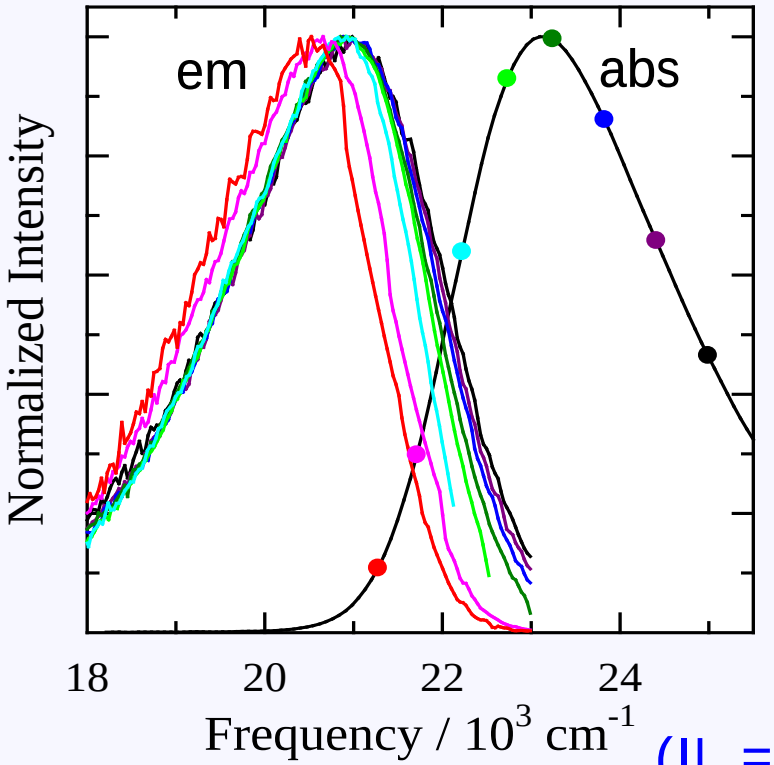


Solvent	η/cP	τ_0/ps	β	<τ> /ps
cyclohexane	0.9	0.7	1	0.7
CH_3CN	0.3	1.5	0.94	1.5
DMSO	2	3.0	0.79	3.4
ethylene elycol	17	3.9	0.75	4.6
$[N_{ip311}^+]$ $[Tf_2N^-]$	113	2.5	0.63	3.5

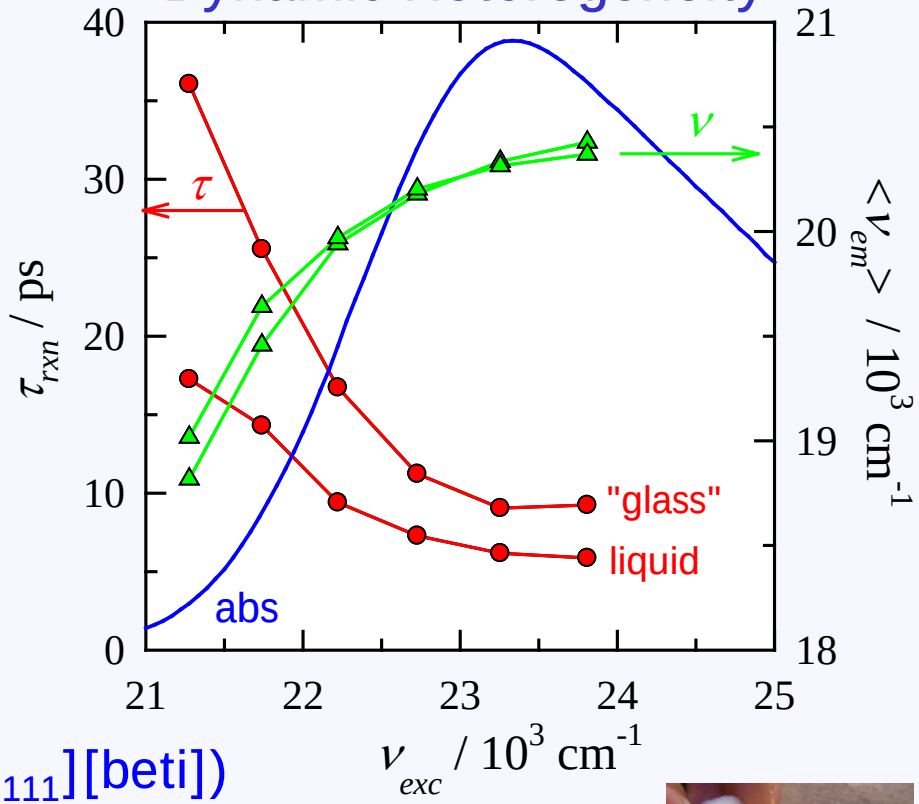
Jin et al., *JPCB* **114**, 7565 (2010).

Heterogeneous Spectra & Kinetics in ILs

REE Shifts of Emission



Dynamic Heterogeneity



(IL = $[N_{10,111}][beti]$)

- red-edge shifts observed in slower solvents at RT (ILs, n-alcohols,...)
- τ_{rxn} is also λ_{exc} dependent: “dynamic heterogeneity”

τ_{rxn} & Fluorescence Quantum Yields

- can estimate reaction times ≅ lifetimes from QYs if k_{rad} is known

$$\tau_f^{-1} = k_{rad}(\varphi_f^{-1} - 1) \cong \tau_{rxn}^{-1}$$

k_{rad} from time-resolved emission:

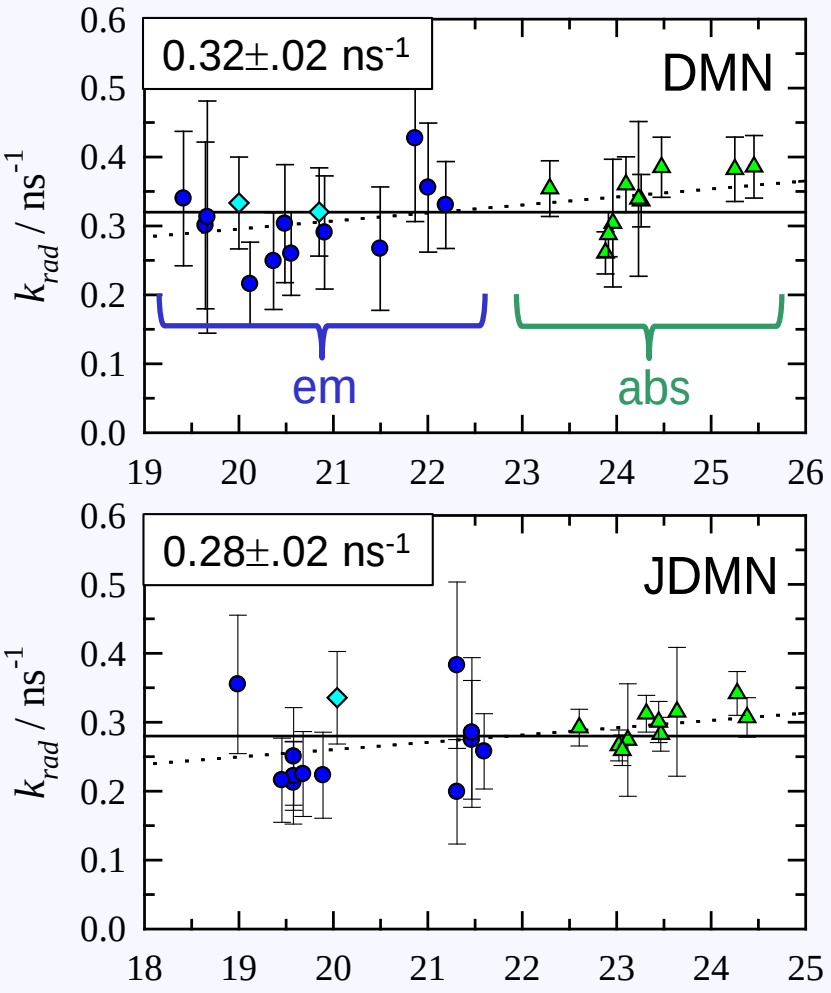
$$k_{rad} = \frac{\varphi_f}{<\tau_f>}$$

k_{rad} from absorption:

$$k_{rad}\,/\,\mathrm{s}^{-1} \cong 2.88\times10^{-9} n^2 (\tilde{\nu}_{em}^3\,/\,\mathrm{cm}^{-3}) \otimes \int_{S_1} \frac{\varepsilon(\nu)/(\mathrm{M}^{-1}\mathrm{cm}^{-1})}{\nu} d\nu$$

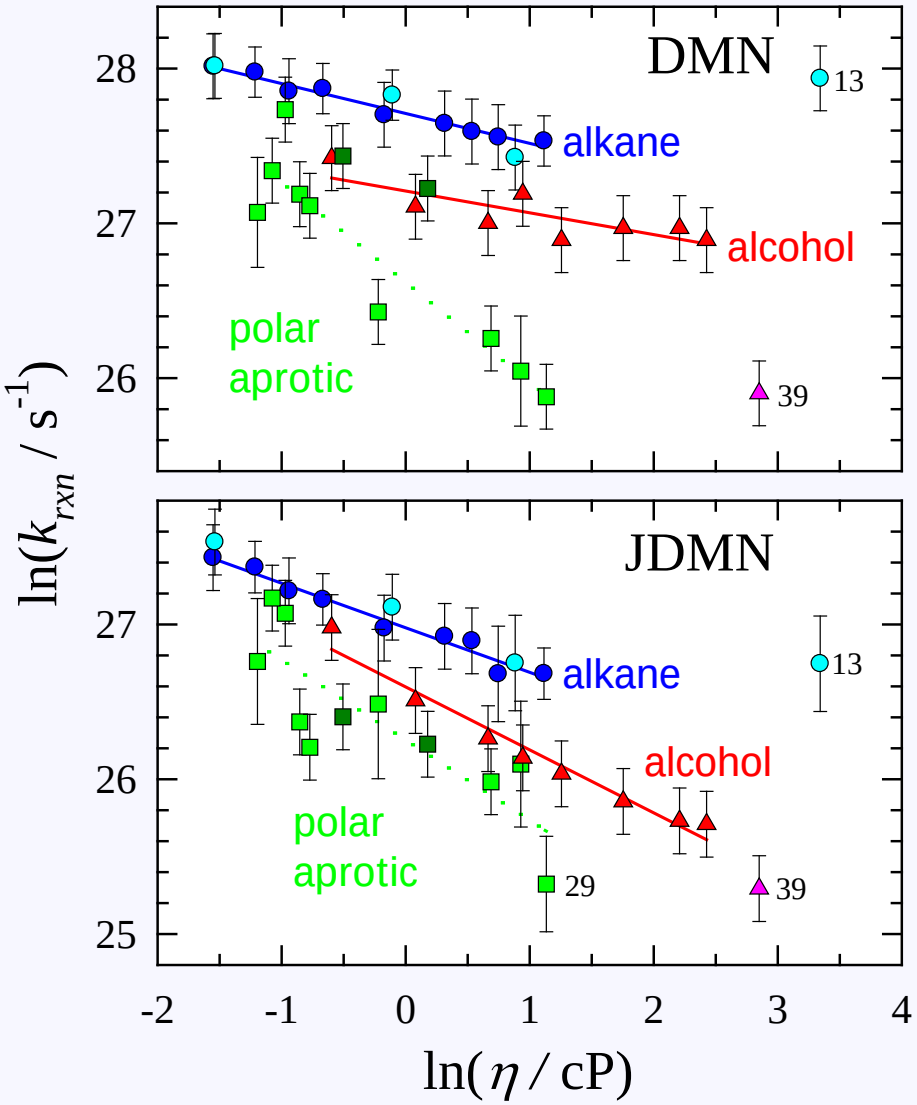
- (φ_f difficult to measure)
- k_{rad} solvent independent
- $M_{01}=M_{10}=6.6 \pm 0.2$ D, the same for both solutes

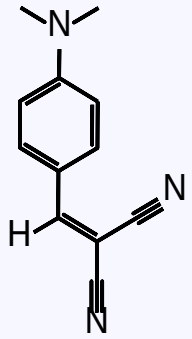
k_{rad} in Assorted Solvents

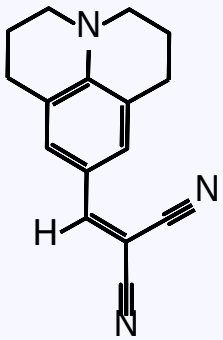


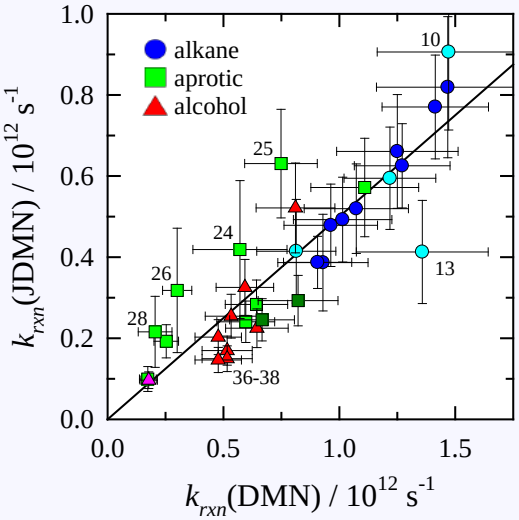
Survey of Reaction Rates

33 Solvents (25 °C)







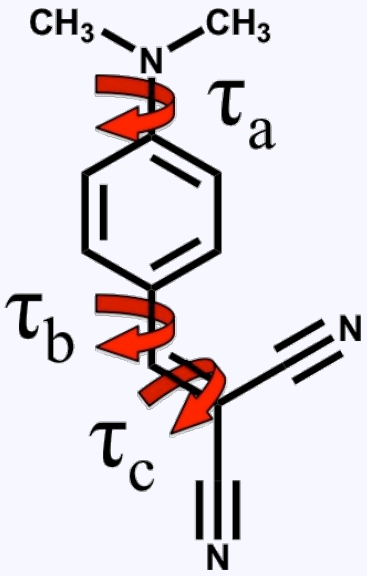


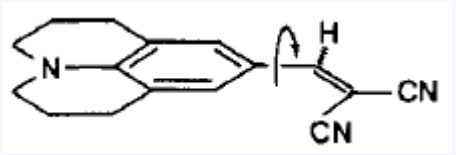
- k(DMN)~2k(JDMN)
- $k_{rxn} / T \propto \eta^{-p}$

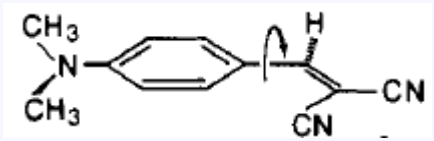
Exp. p	DMN	JDMN
n-alkanes	.19	.29
n-alcohols	.14	.41
mTHF (T)	.69	.78
1-PrOH (T)	.39	--

- solvent polarity?

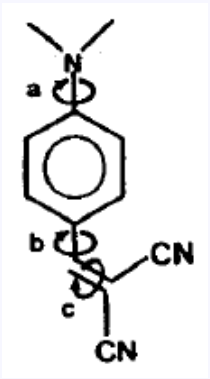
What's the Mechanism?

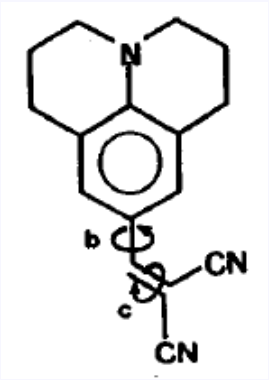




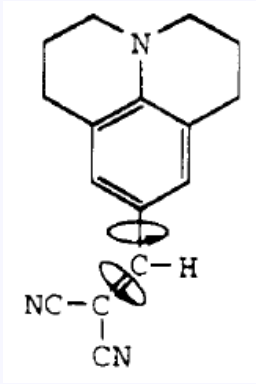


Loutfy (1982)

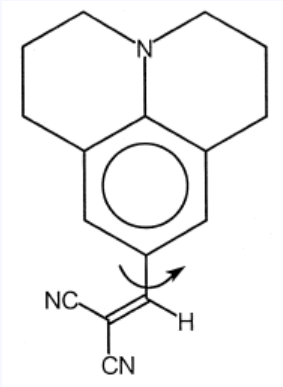


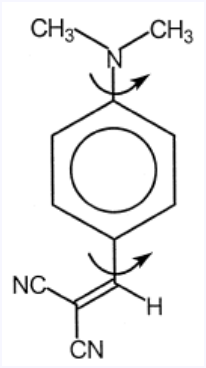


Mqadmi (1990)

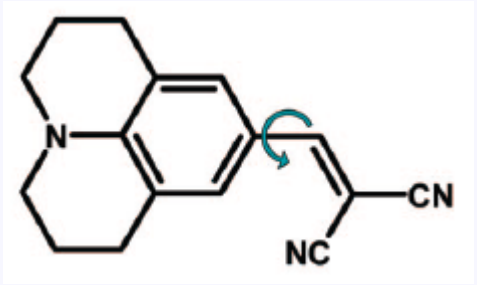


Torkelson (1995)

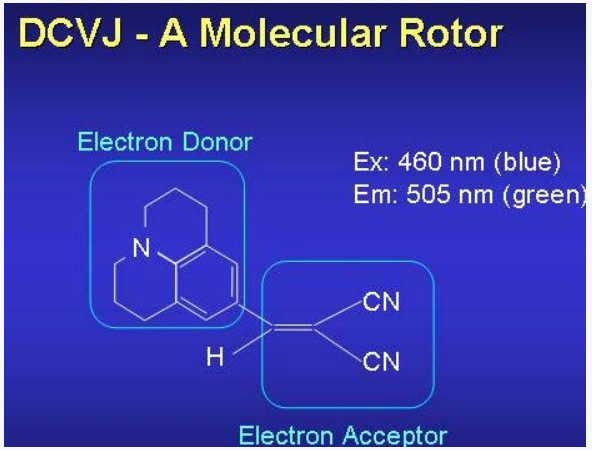




Drickamer (1998)

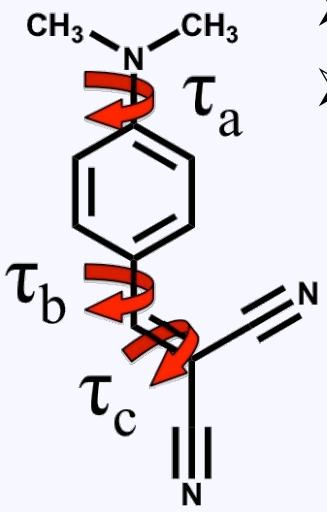


Samanta (2008)



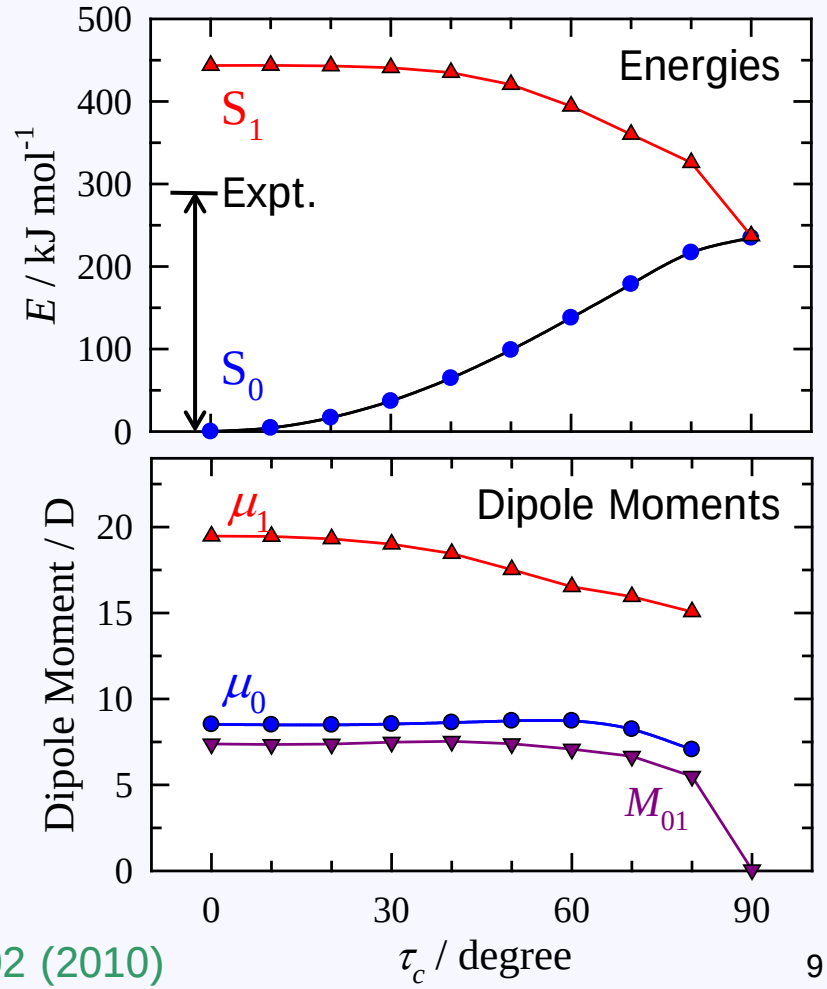
Haidekker (2009)

Gas-Phase Torsional PES of S_1 DMN



- τ_c is primary reaction coordinate
- scanned at SA2-CAS(12,11)/6-31G(d) level (S_0 optimized geometries)

CAS-SCF Predictions



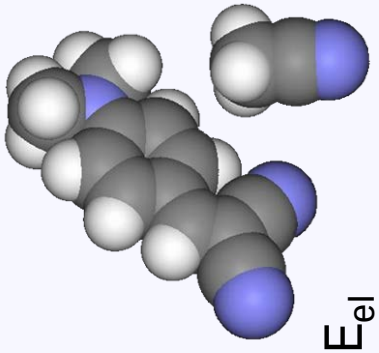
Details of PES Search

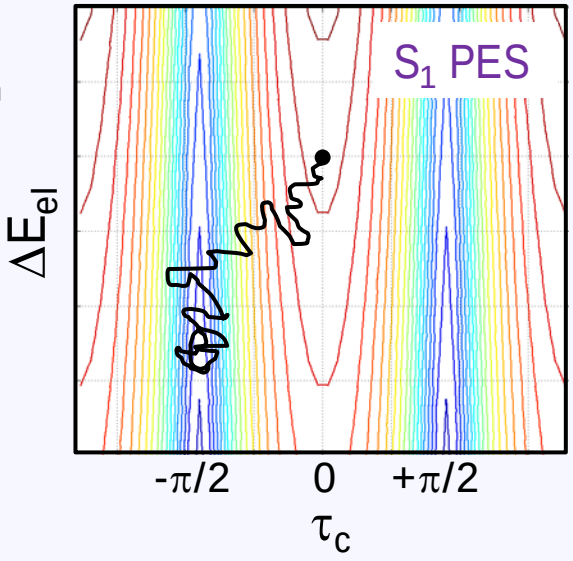
- search of S_1 @ RI-CC2/def2-TZVP level located minima at τ_a=90° and $\tau_b \sim \tau_c \sim$20°, but no τ_b=90° TICT state
- (a TD-B3LYP located a τ_b-TICT state, but LC corrections eliminated it)
- a CIS search did not reveal a τ_b TICT state; instead a conical intersection with S_0 was found at τ_c=90°

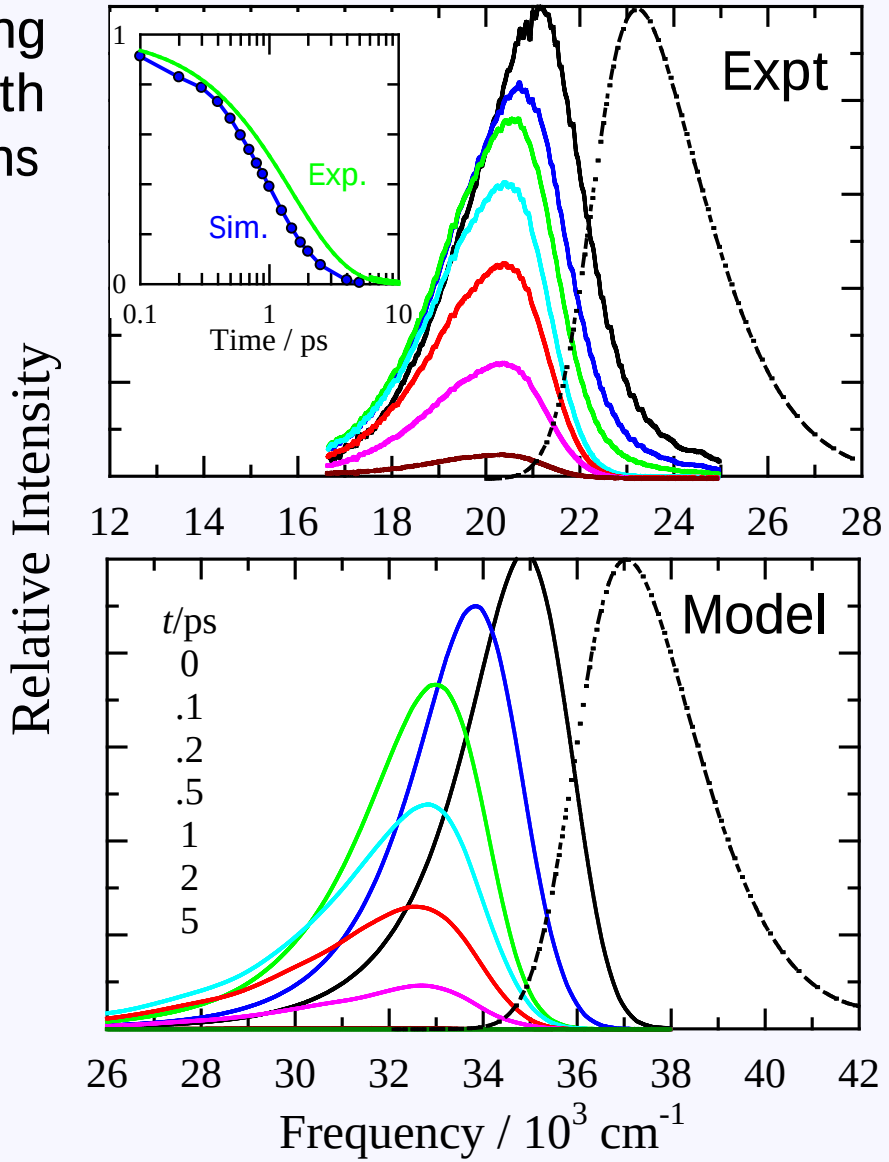
Swalina & Maroncelli, *JPCC* **114**, 5602 (2010)

Preliminary MD Simulations

- explore solvent effect by combining QM $E(\tau_c)$ with classical solvent bath via molecular dynamics simulations
- semi-rigid solute (τ_c only)
- 108 CH_3CN solvent molecules
- 2000 n.e. trajectories on U_1
- terminate when $|\tau_c|=85°$







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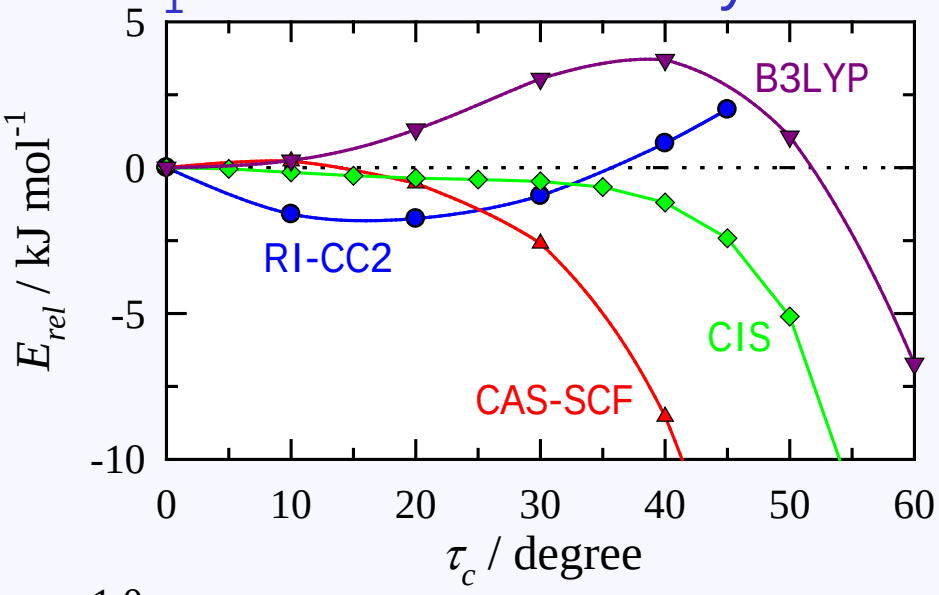
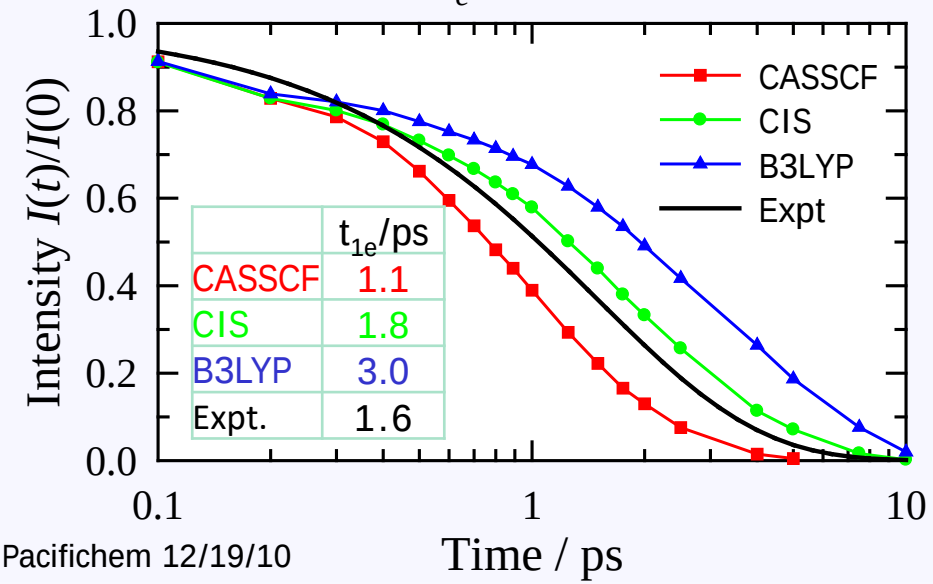
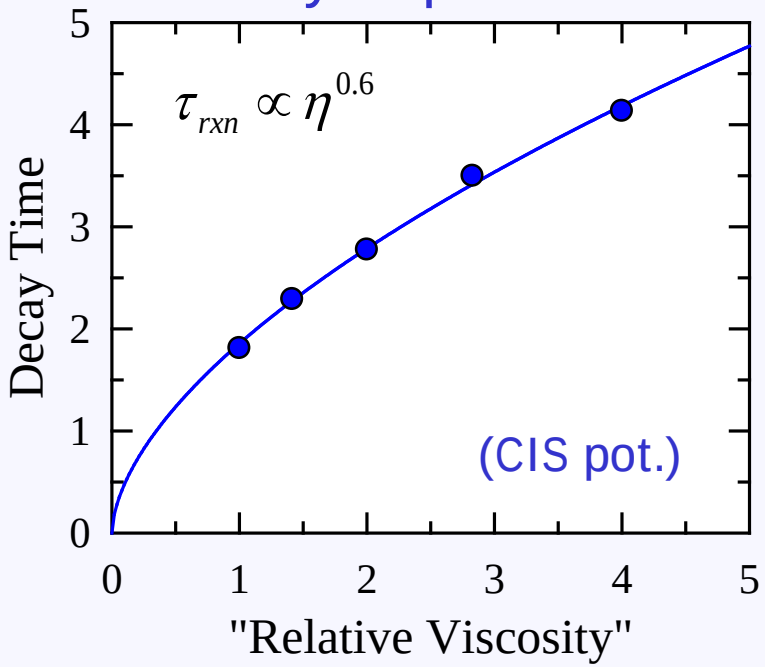
Variations with τ_c PES & Solvent

S_1 Potentials & Their Dynamics





Viscosity Dependence

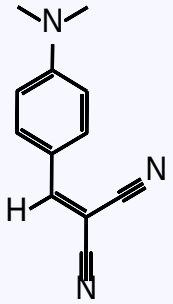


- dynamics are sensitive to k_BT-level variations in $E(\tau_c)$
- viscosity variation & DMN/JDMN difference like experiment
- overall approach is promising

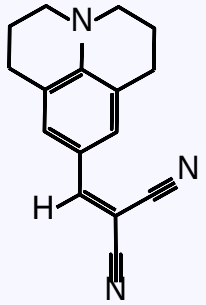
Summary & Conclusions

- DMN and JDMN characterized as environmental probes
  - first direct measurements of room-T dynamics
  - k_{rad} conveniently independent of solvent
- $\varphi_f \leftrightarrow \tau_{rxn}$ data in 33 common solvents:
  - observe $k_{rxn}/T \propto \eta^{-p}$ with 0.2<p<1 in single solvents vs. T & in homologous series
  - analogous to small-molecule rotations
  - solvent polarity likely important
- S_1 decays primarily via double-bond isomerization (τ_c)
- initial MM simulations on QM-derived τ_c surfaces exhibit proper time scale and sensitivity to solvent & solute comparable to experiment
- further simulations should provide molecular-level description of environmental friction on these reactions

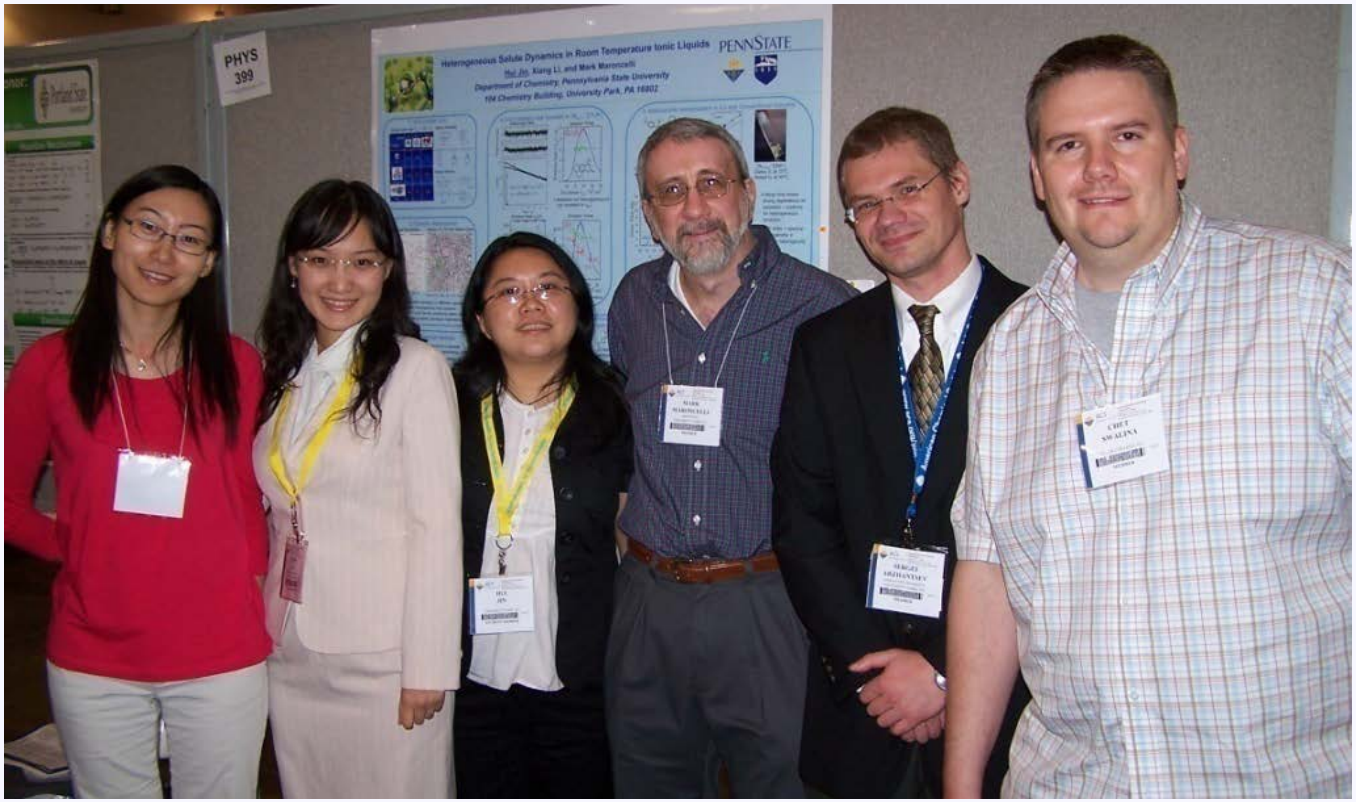
DMN



JDMN



Acknowledgements



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Lillian Li Sergei Arzhantsev

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