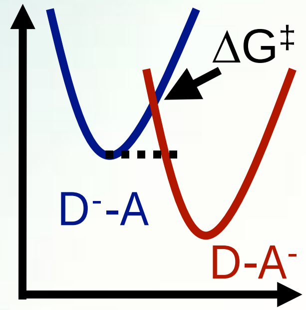
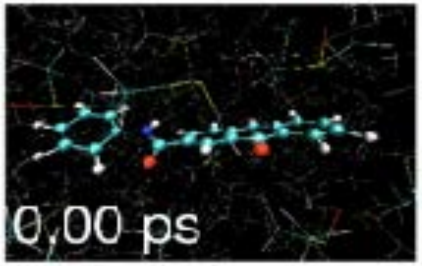
Electron Dynamics in Complex Environments: From Electron Transfer to Singlet Fission

Troy Van Voorhis
MIT Department of Chemistry
CCDM Seminar
March 3, 2017

Outline

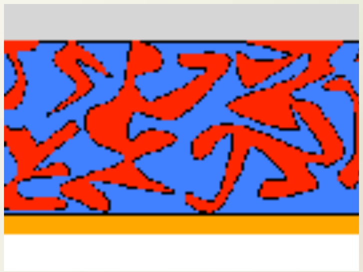


- Diabatic States for Reactions

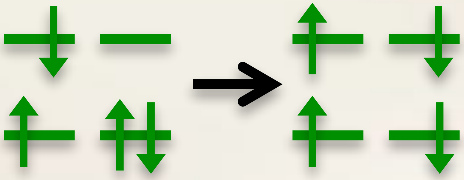


- DFT as a route to Diabatic States

- Energy Transfer in Organic Semiconductors



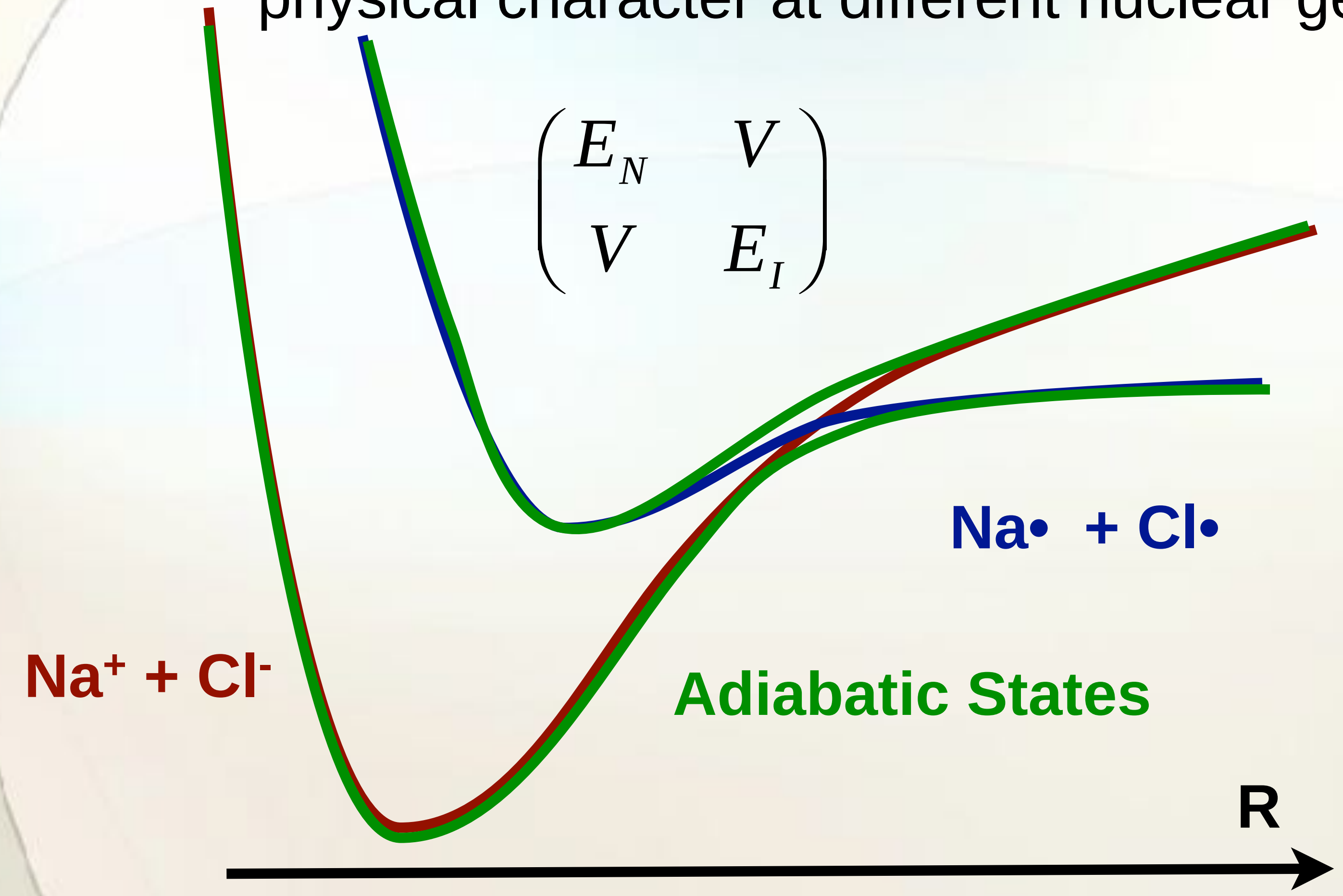
- Mechanism of Singlet Fission



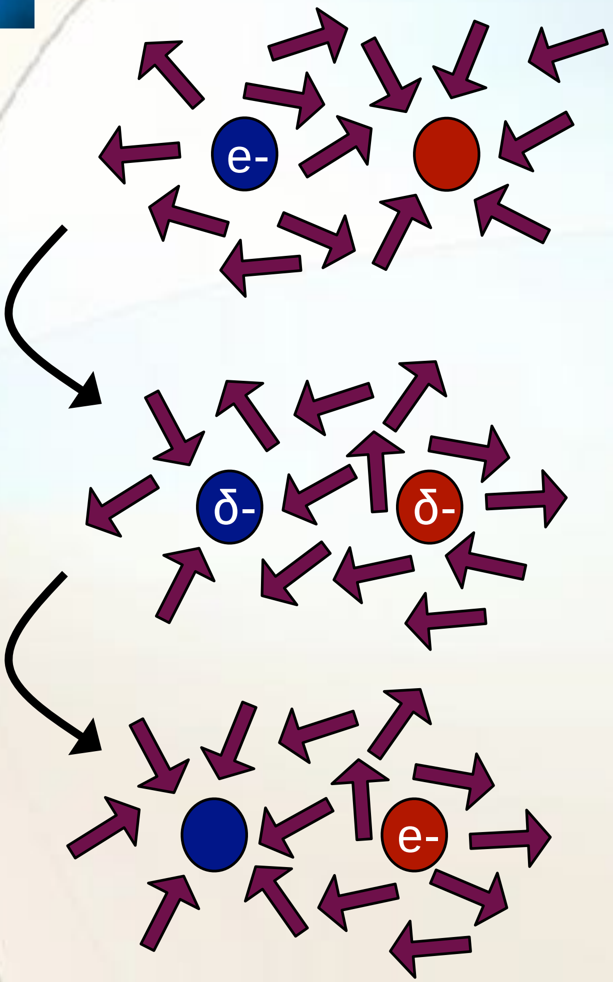
Diabatic States Idea

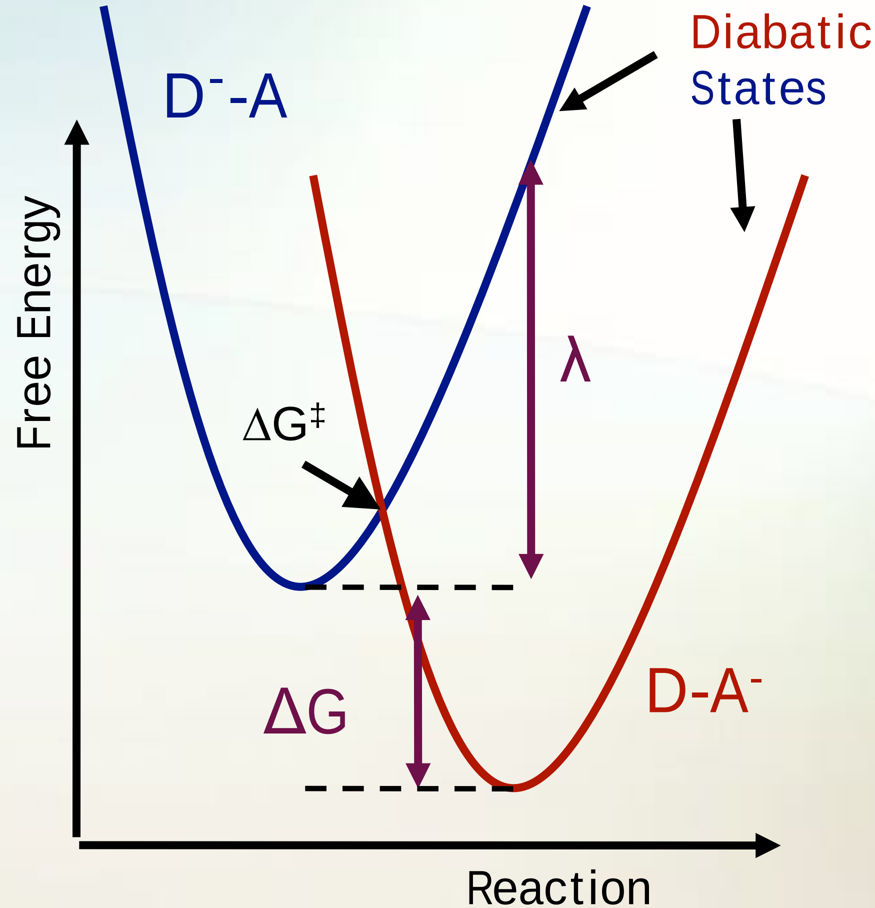
Diabatic Electronic States tend to have the same physical character at different nuclear geometries

$$\begin{pmatrix} E_N & V \\ V & E_I \end{pmatrix}$$



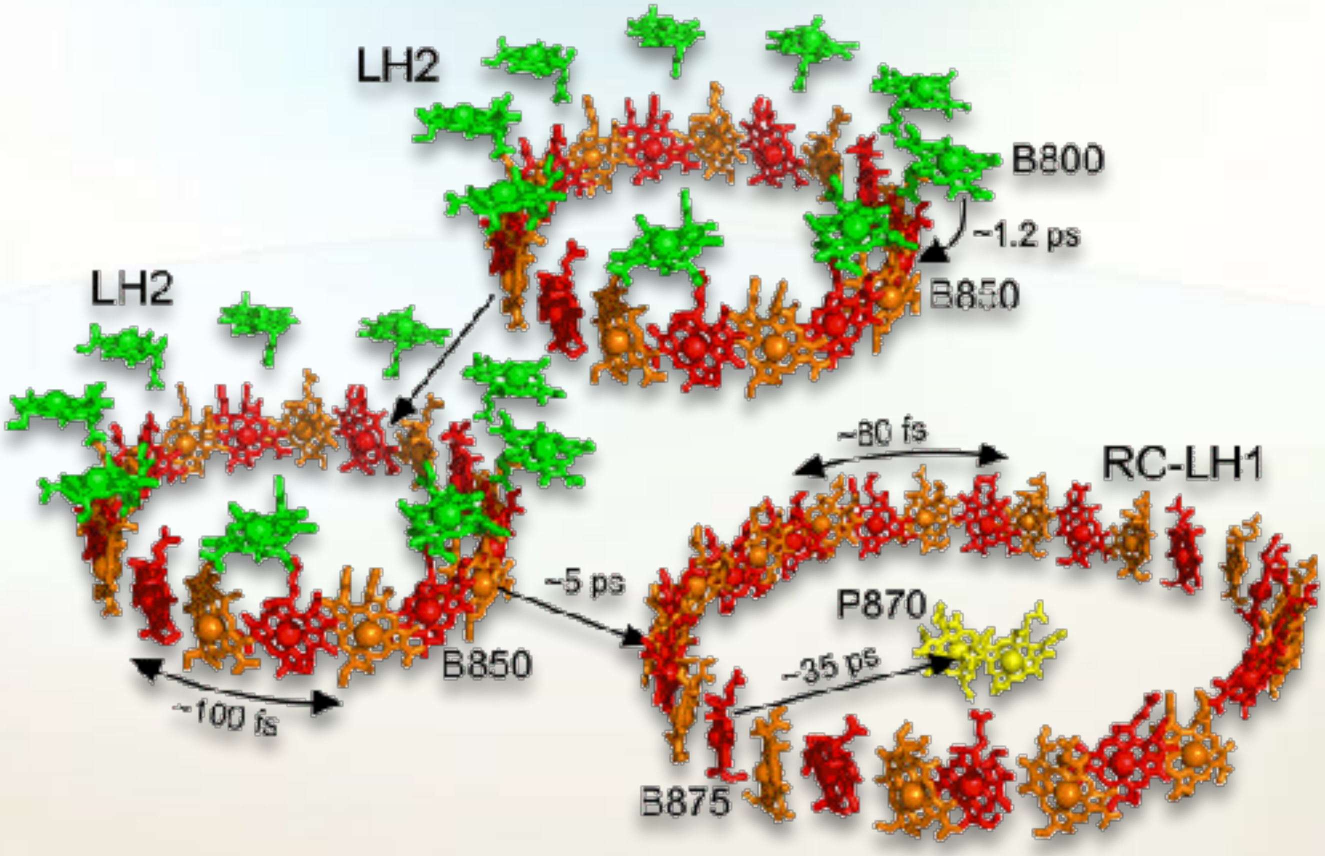
Marcus Theory





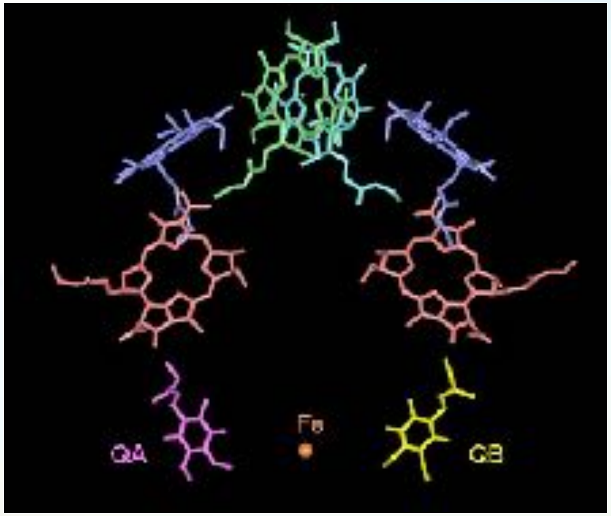
$$k_{et} \propto \left|\langle D|\hat{H}|A\rangle\right|^2 e^{-\frac{\Delta G^\ddagger}{kT}} = \left|V_{DA}\right|^2 e^{\frac{-(\Delta G+\lambda)^2}{4\lambda kT}}$$

Energy Transfer



$$V_{AB} \approx \frac{R^2 \boldsymbol{\mu}_\mathbf{A} \cdot \boldsymbol{\mu}_\mathbf{B} - 3(\boldsymbol{\mu}_\mathbf{A} \cdot \mathbf{R})(\mathbf{R} \cdot \boldsymbol{\mu}_\mathbf{B})}{R^5}$$

Outstanding Issues



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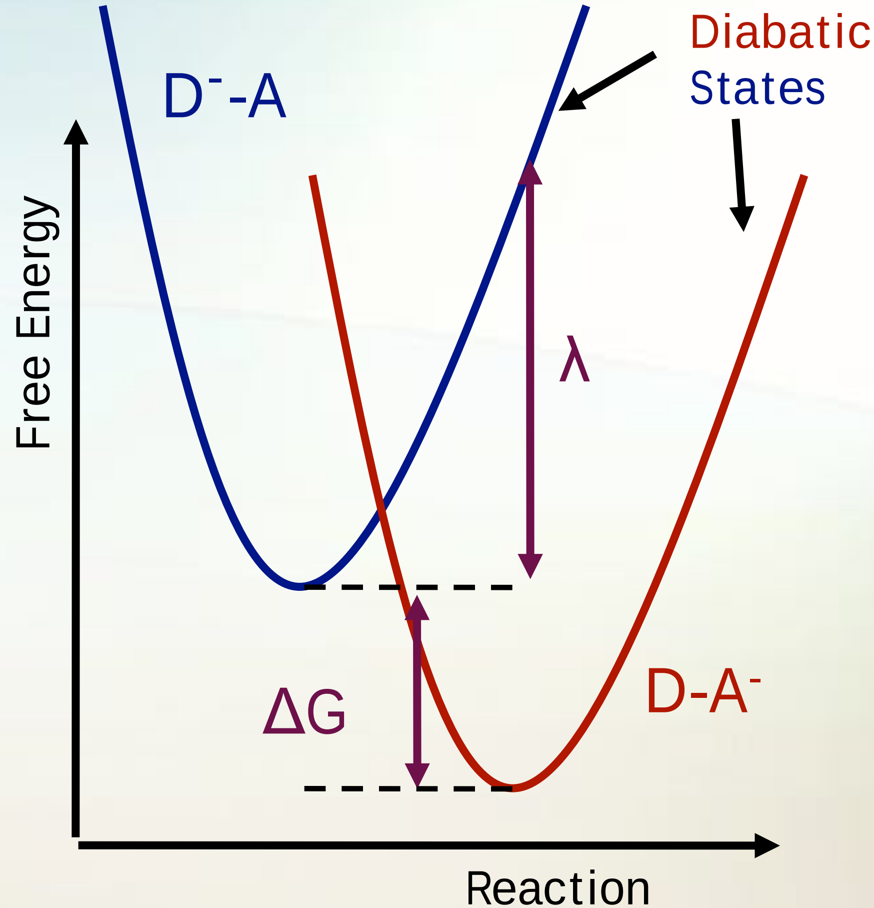

- What are these diabatic states?
- How do we explore this free energy landscape?
- How do we compute *V*?

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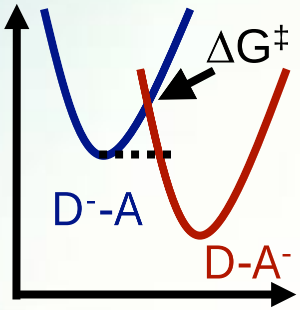

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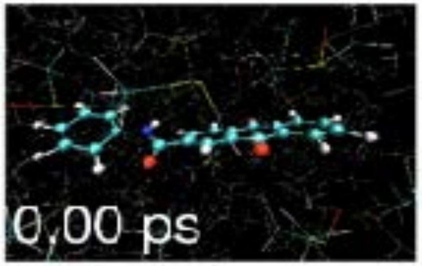
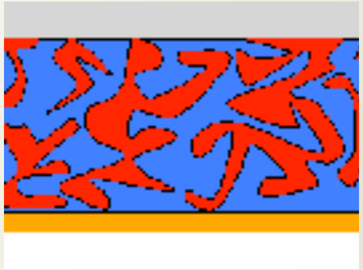


- Energy Transfer in Organic Semiconductors



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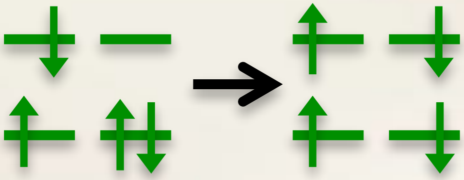
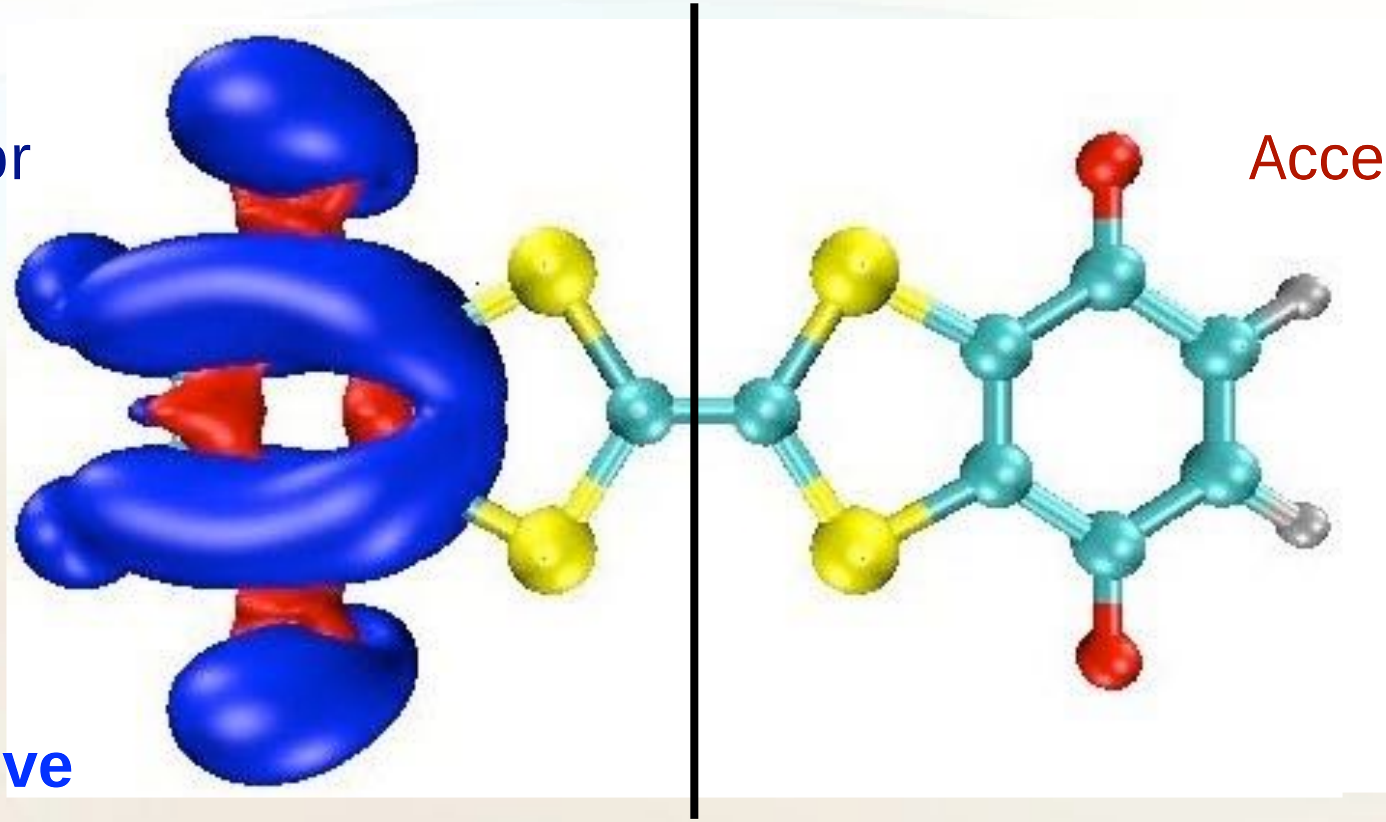


Constrained DFT

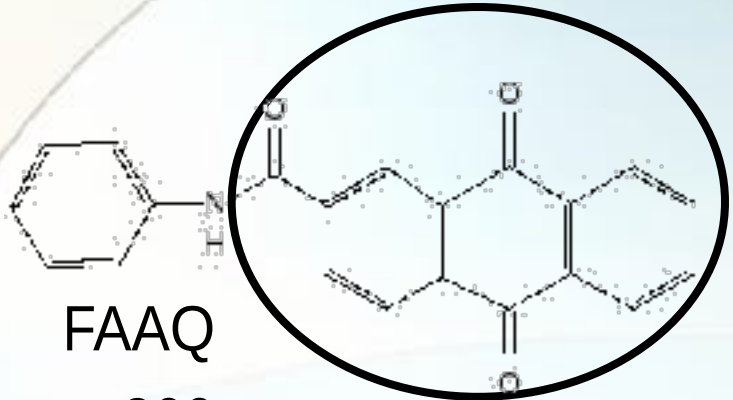
- The diabatic state D^+A can be obtained by constraining a positive charge on the donor

$$W[\rho, V_D] = E[\rho] - V_D\left(\int \rho(\mathbf{r}) O(\mathbf{r})\, d\mathbf{r} - N_D\right)$$



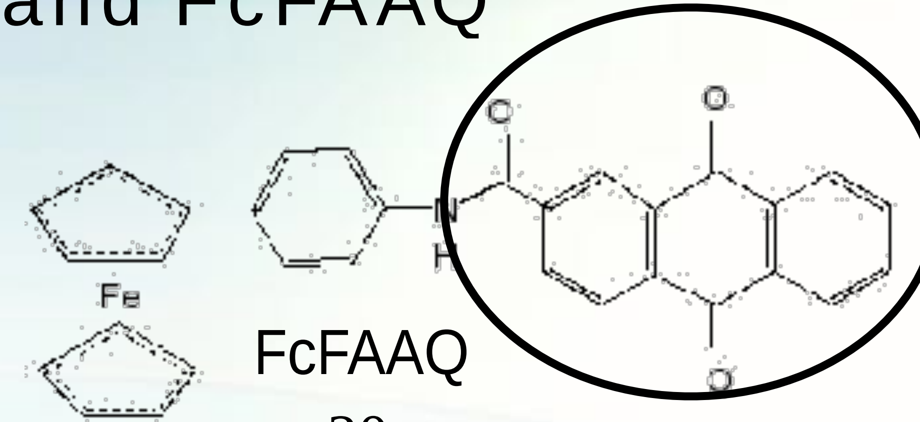
Implemented Charge & Spin Constraints in NWChem and QChem

FAAQ and FcFAAQ



FAAQ

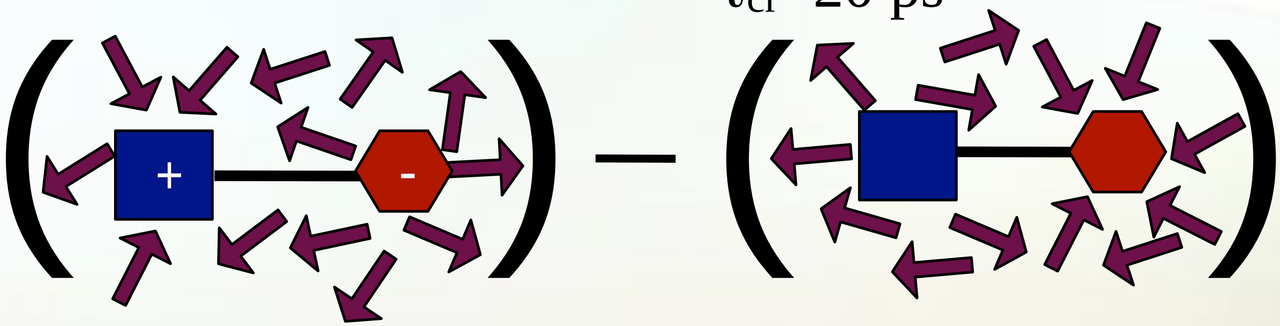
τ_{cr}>900 μs



FcFAAQ

τ_{cr}=20 ps

ΔG=

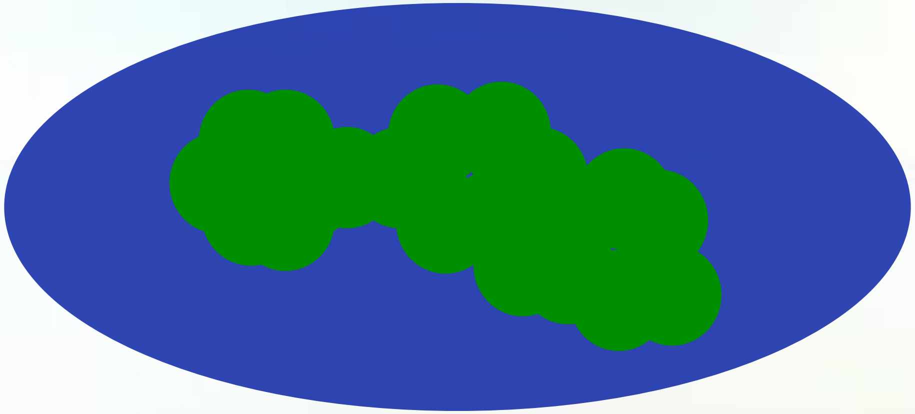


- Using CDFT (B3LYP/6-31G*/COSMO), one finds

	FAAQ (Expt)	FcFAAQ (Expt)
ΔG=	2.36 eV (2.24 eV)	1.12 eV (1.12 eV)

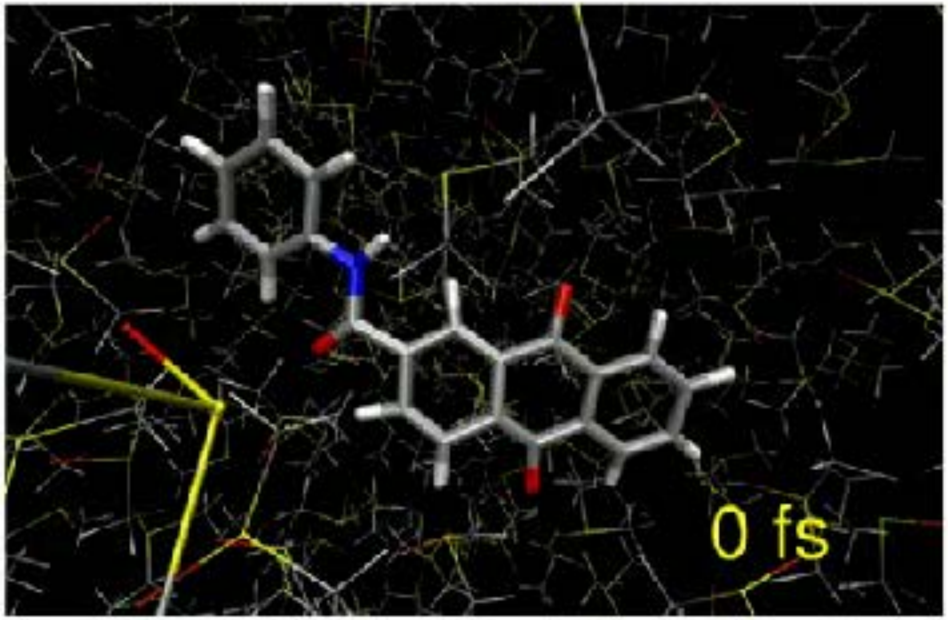
Continuum Dielectric Solvation

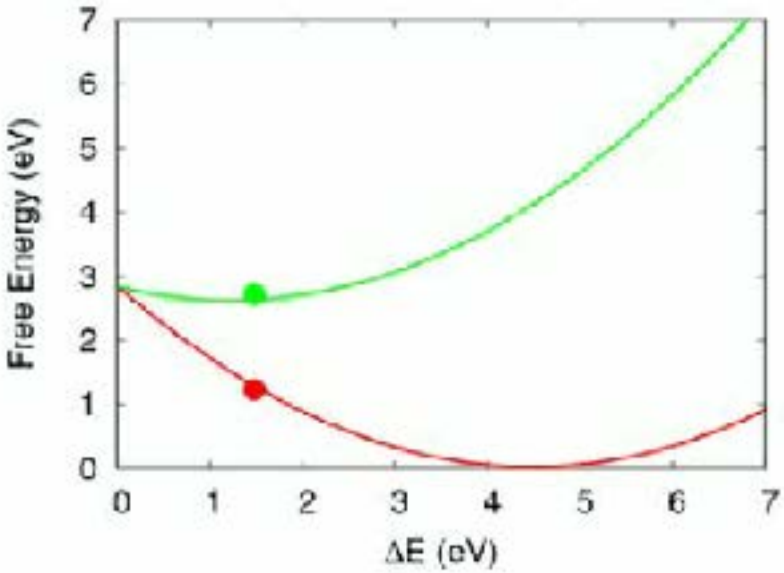
- Step 1: Enclose Molecule in a Cavity



- Step 2: Fill the rest of space with a material that has a constant dielectric, ε
- Step 3: Solve Self-Consistently for the charge density and the polarization P(ε)

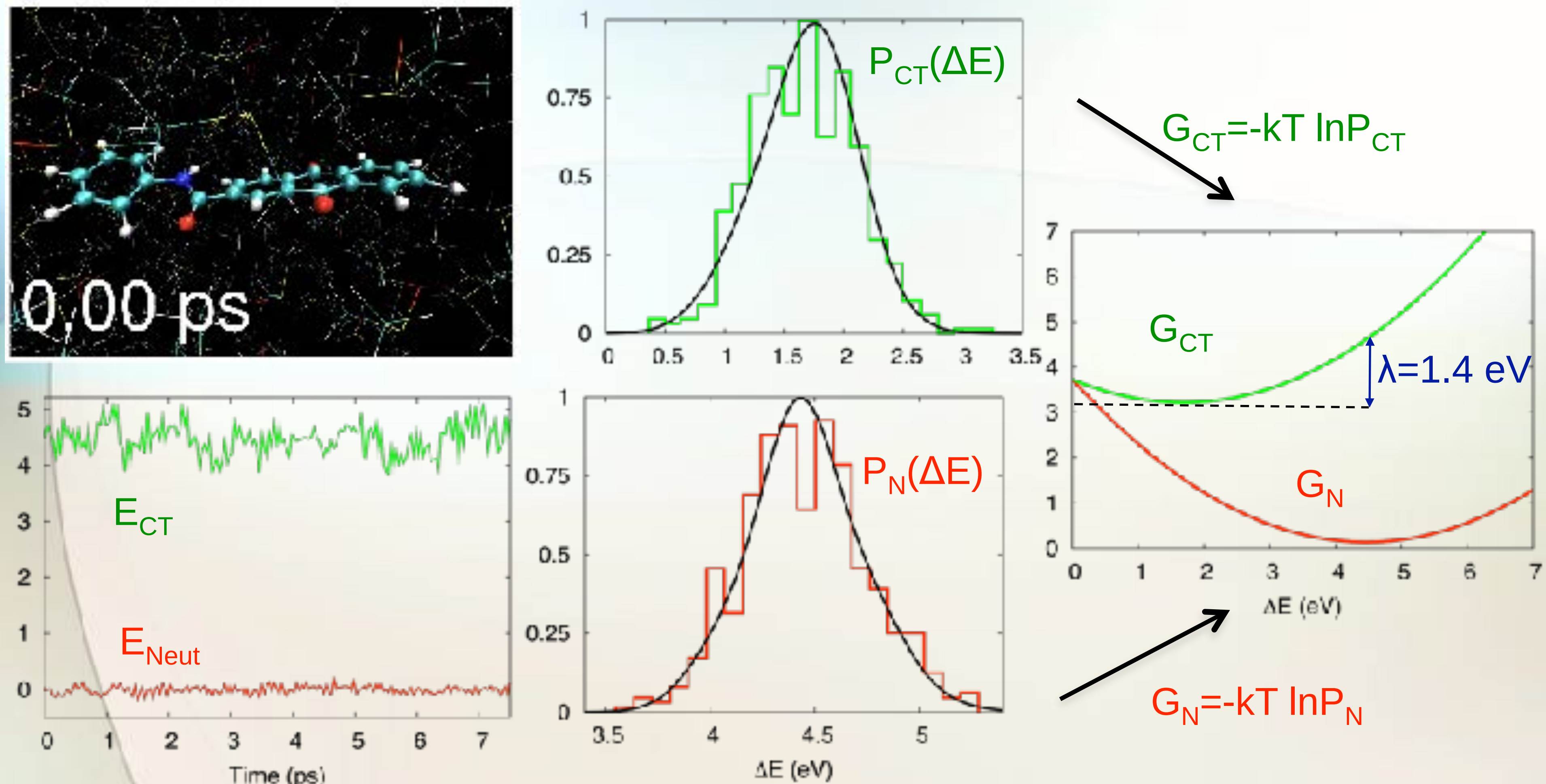
Explicit Solvation





A QM/MMpol Molecular Dynamics Trajectory (B3LYP/3-21G)

Exploring The Free Energy Landscape



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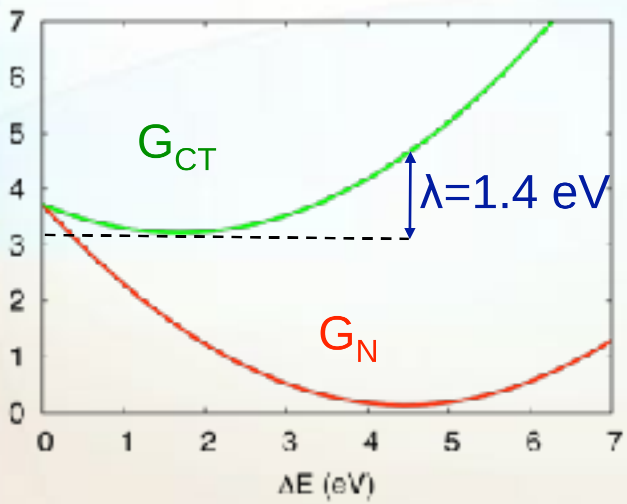

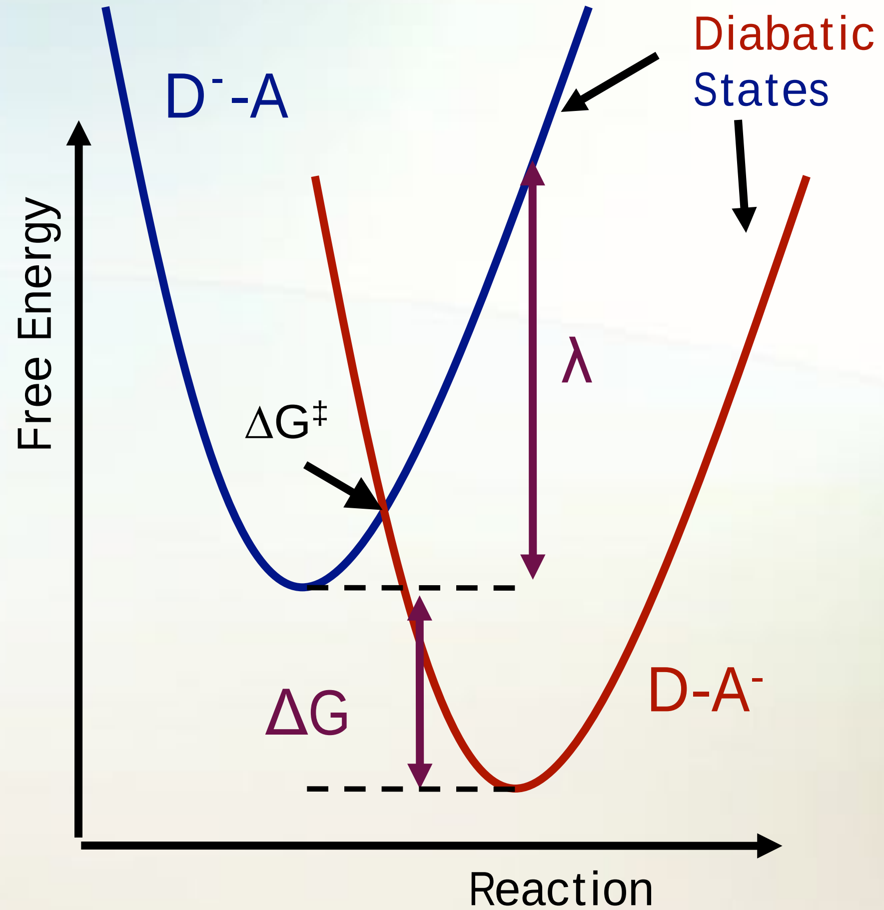

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Determining Diabatic Couplings

$$\mathbf{H} = \begin{pmatrix} E_R & V_{RP} \\ V_{PR} & E_P \end{pmatrix}$$

CDFT

- The coupling, V_{RP}, is a functional of the constrained densities and can be re-written in the suggestive form:

$$\langle R | \varepsilon_R$$

$$V_{RP} = \langle R | \hat{H} | P \rangle = \langle R | \left(\hat{H} + \hat{v}_R \right) - \hat{v}_R | P \rangle$$

$$\rightarrow V_{RP} = \langle R | \varepsilon_R - \hat{v}_R | P \rangle = \varepsilon_R \langle R | P \rangle - \langle R | \hat{v}_R | P \rangle$$

Average V_{RP} & V_{PR}

$$V_{RP} = \frac{\varepsilon_R + \varepsilon_P}{2} \langle R | P \rangle - \langle R | \frac{\hat{v}_R + \hat{v}_P}{2} | P \rangle$$

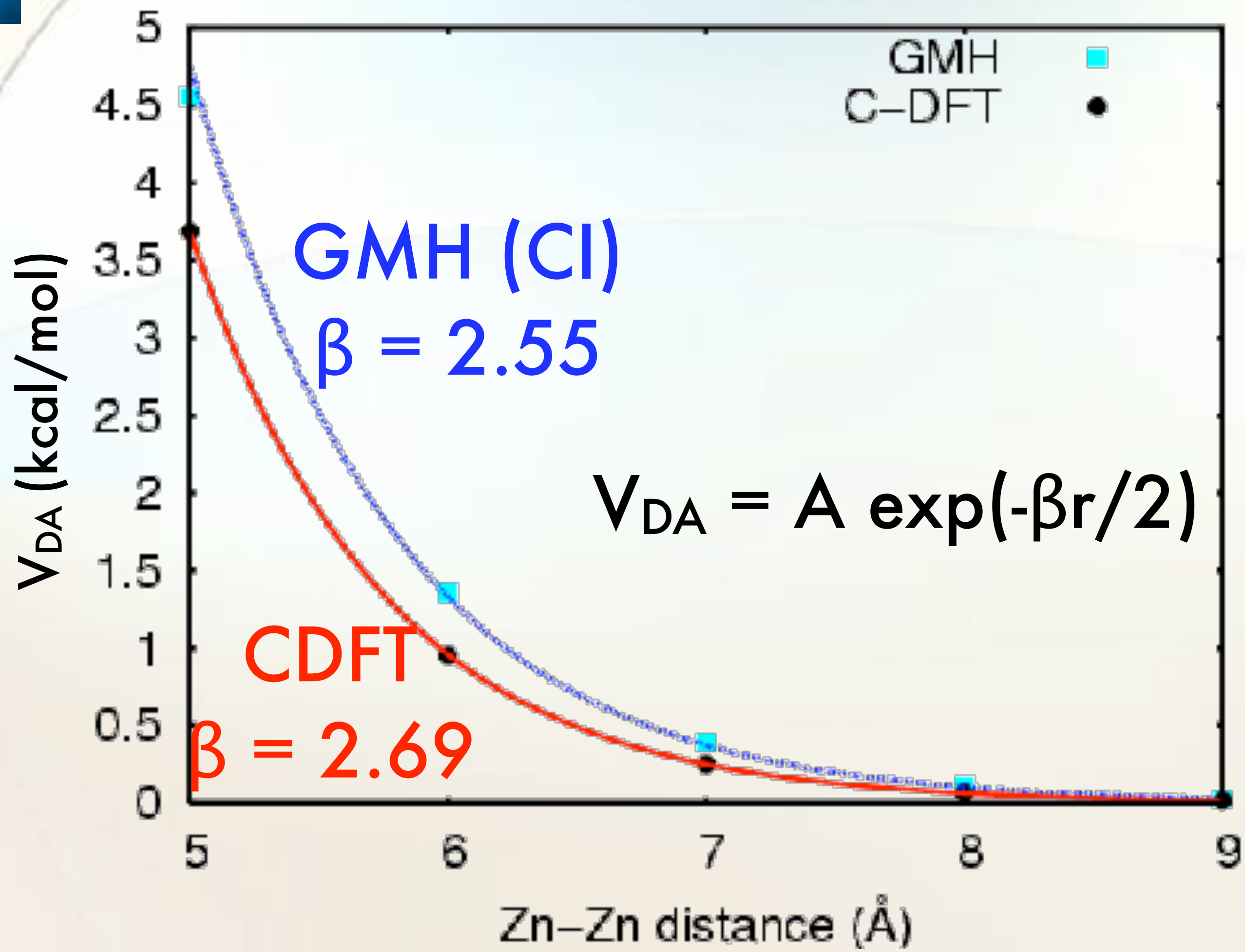
- Good Approximation: Use KS wavefunctions for *R* and *P*

Wu and Van Voorhis *JCP* 125 164105.

MIT

Zn^{+}-Zn ↔ Zn-Zn^{+}

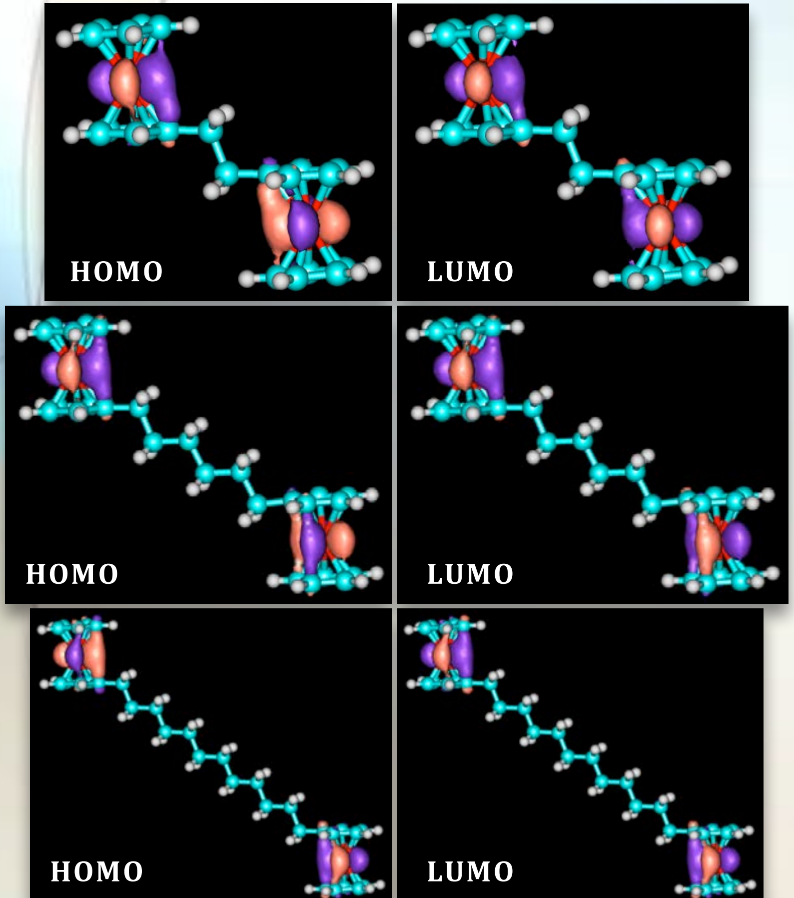
$$\mathbf{H} = \begin{pmatrix} E_R & V_{RP} \\ V_{PR} & E_P \end{pmatrix}$$



GMH data from Cave and Newton, *JCP*, 106, 9213 (1997)

Fc-Bridge-Fc^+ Coupling

CDFT



H_{ab}= 0.88 kcal/mol

H_{ab}= 0.15 kcal/mol

H_{ab}= 0.03 kcal/mol

B3LYP/6-31G*

Ding et al *JPCA* **114** 6039 (2010)

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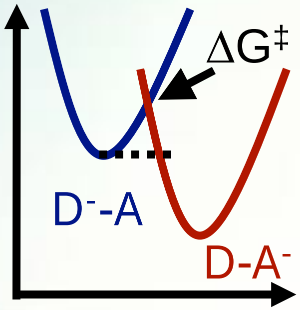

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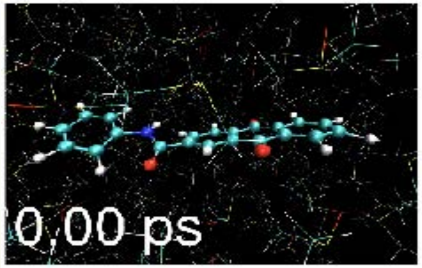

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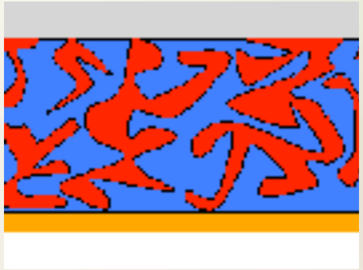

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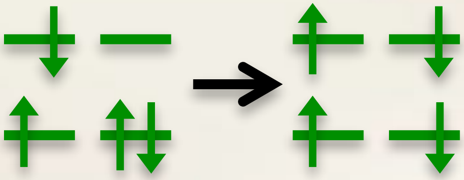
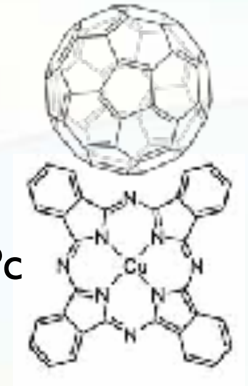


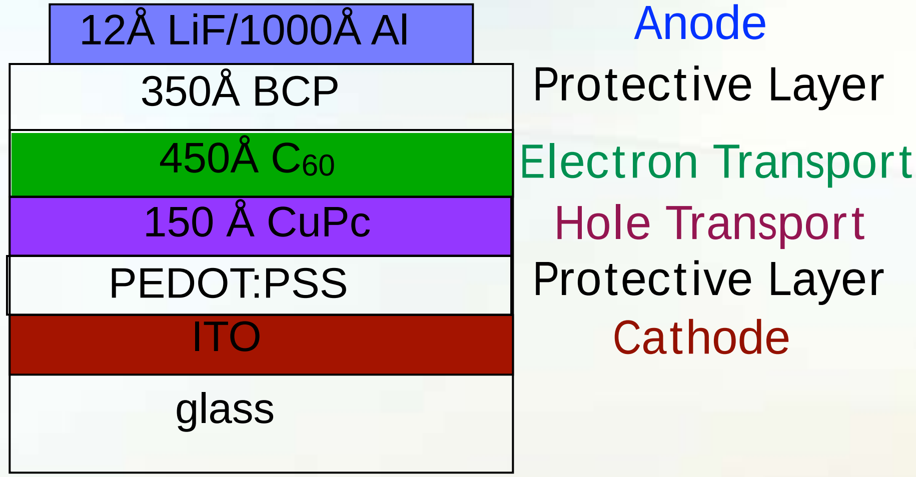
Organic Solar Cells

Planar Heterojunction Cells (~4% Power Efficiency)

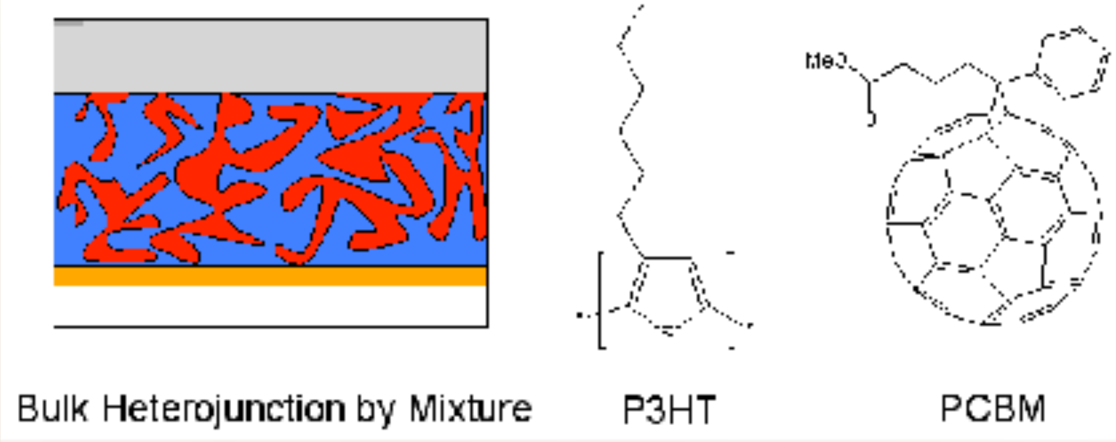
C_{60}

CuPc

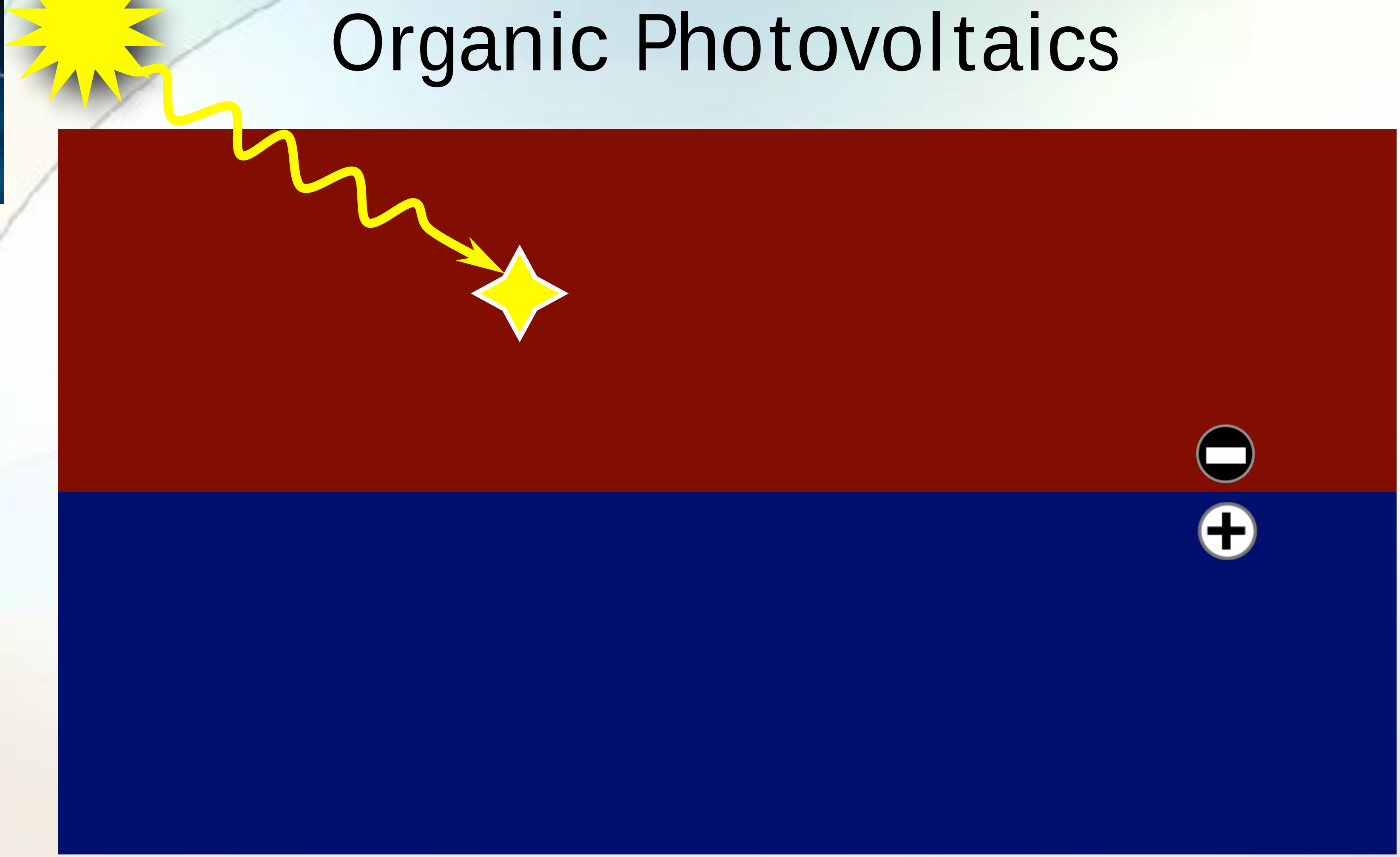




Bulk Heterojunction Cells (~8% Power Efficiency)

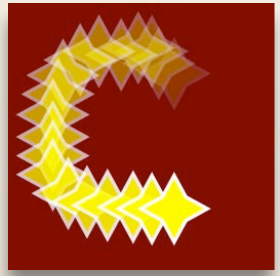


Organic Photovoltaics

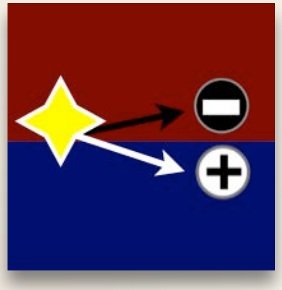


Absorption Spectra

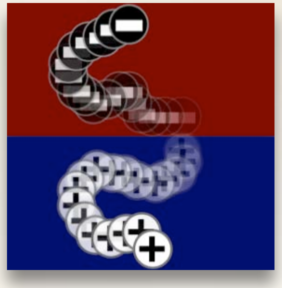
Exciton Diffusion



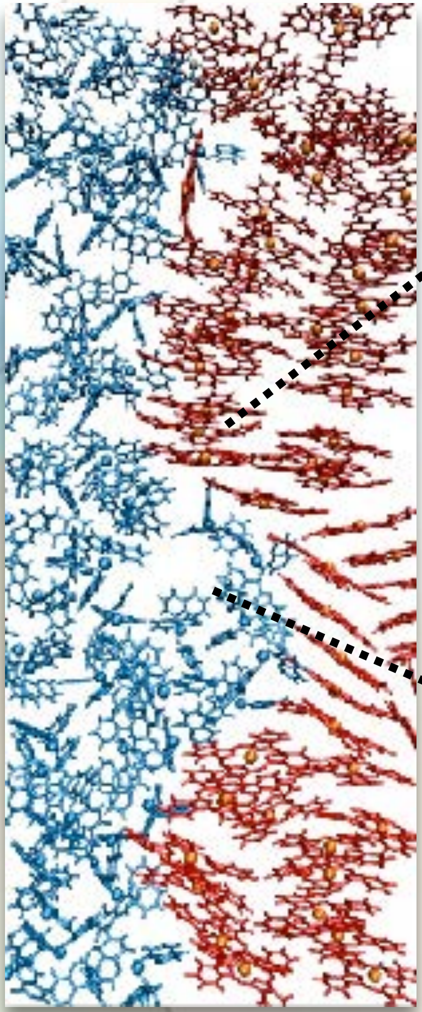
Charge Transfer



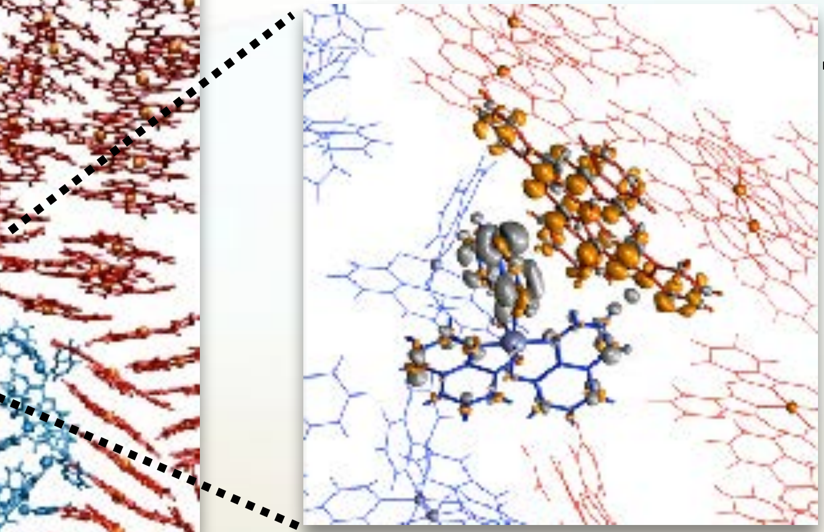
Charge Mobility



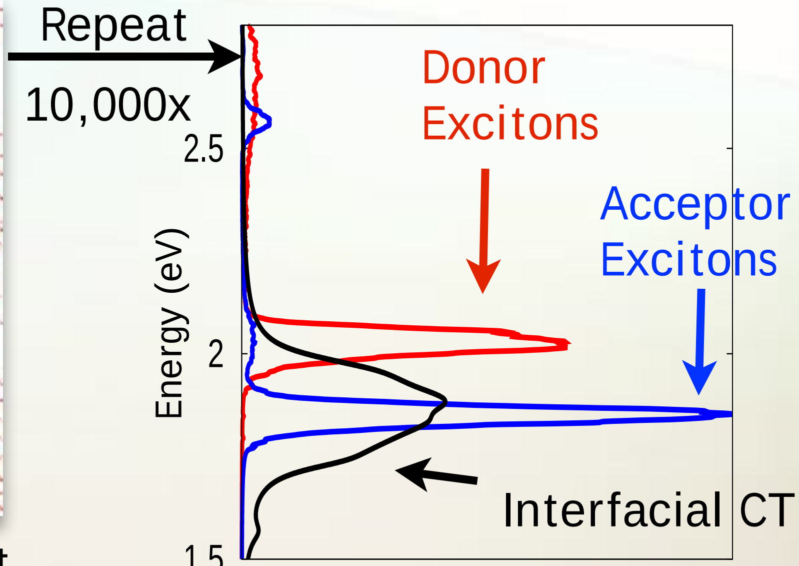
QM/MM Model of Interfaces



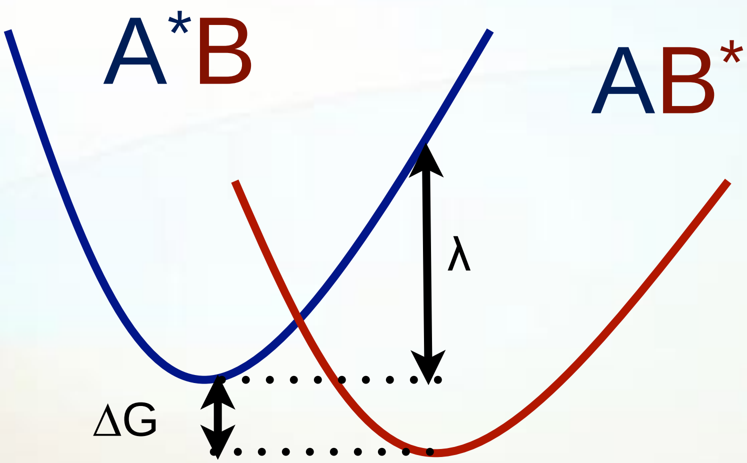
Classical Force Field (MM) on nm length scale

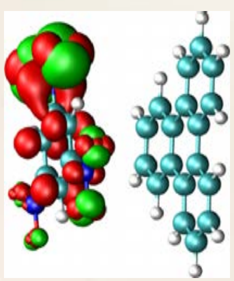


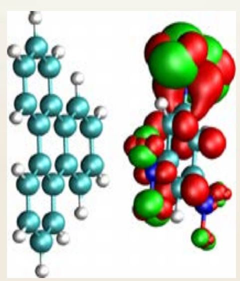
Subsystem of interest
QM/MMpol Electrostatic Embedding



Application: Triplet Excitation Energy Transfer





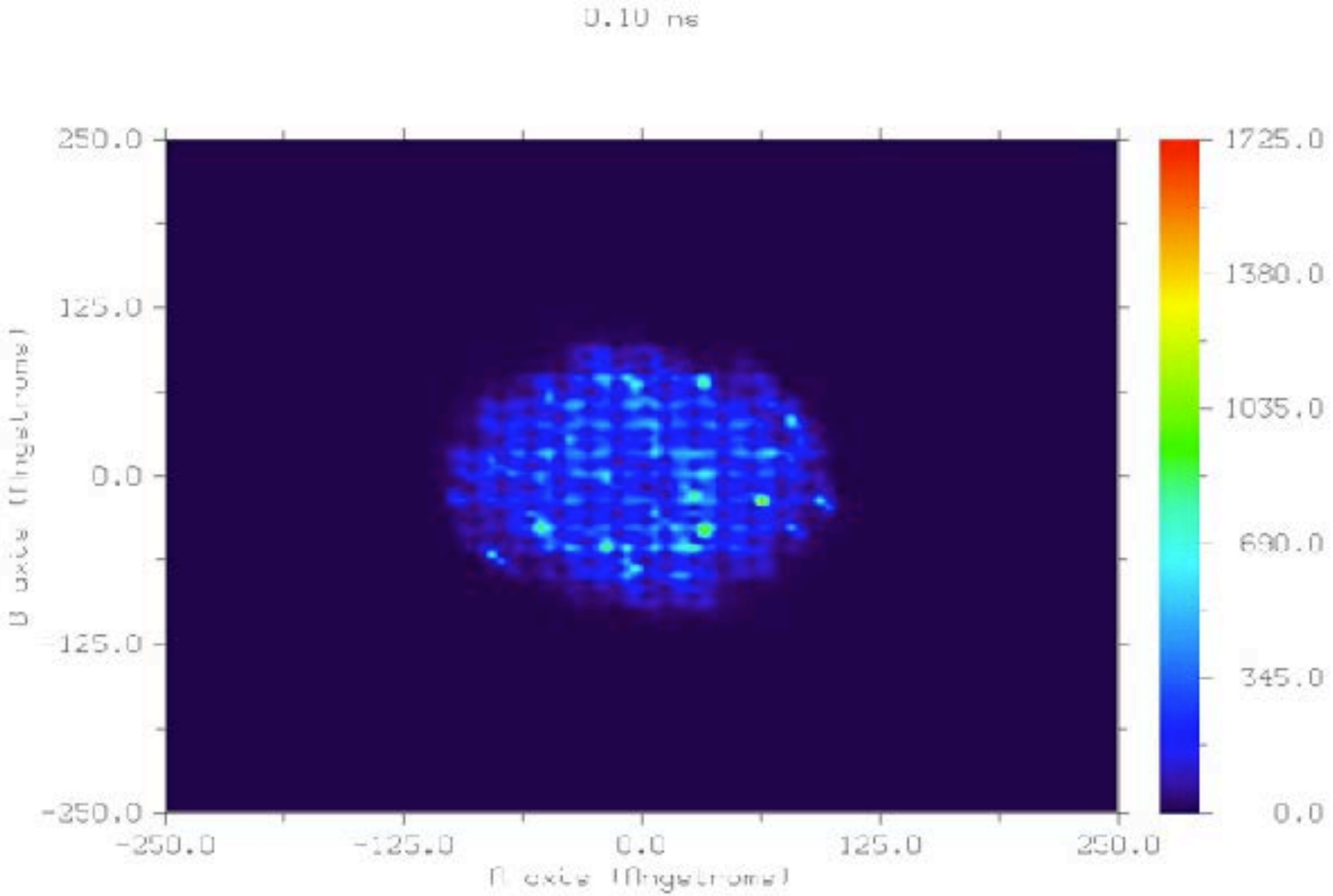


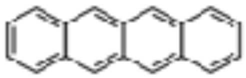
$$k_{TEET} \propto |V_{AB}|^2 e^{-\frac{(\Delta G+\lambda)^2}{4\lambda kT}}$$

- Obtain localized states by constraining the spin
- Compute coupling Directly:

$$V_{AB} \equiv \langle A^* B | \hat{H} | AB^* \rangle$$

Triplet Diffusion in Crystalline Tetracene

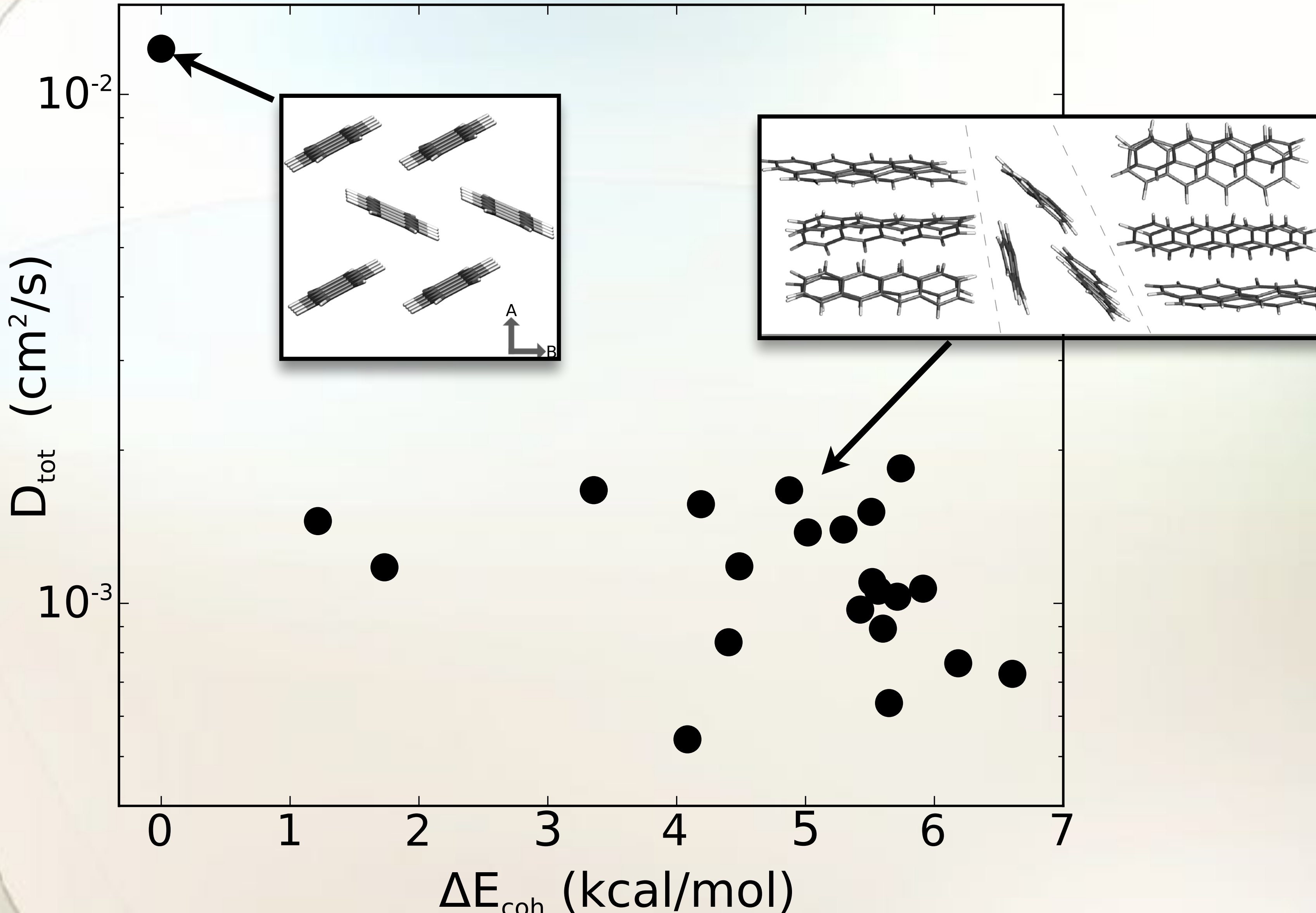




<u>Tetracene</u> A/B/C (μm) (λ=0.33 eV)

L_D Expt: --/18/-- L_D Theory: 20/25/.09

Disordered Tetracene Films



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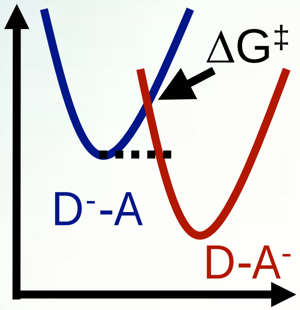

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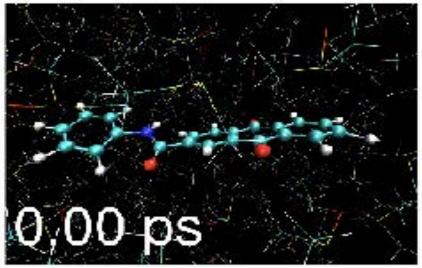

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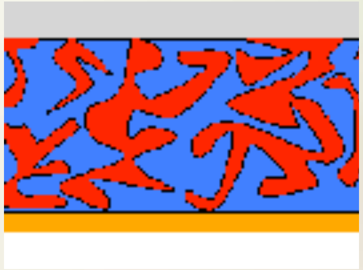

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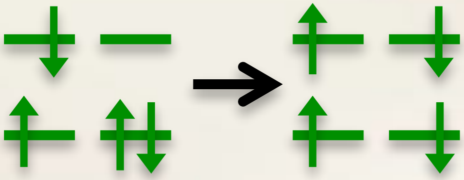
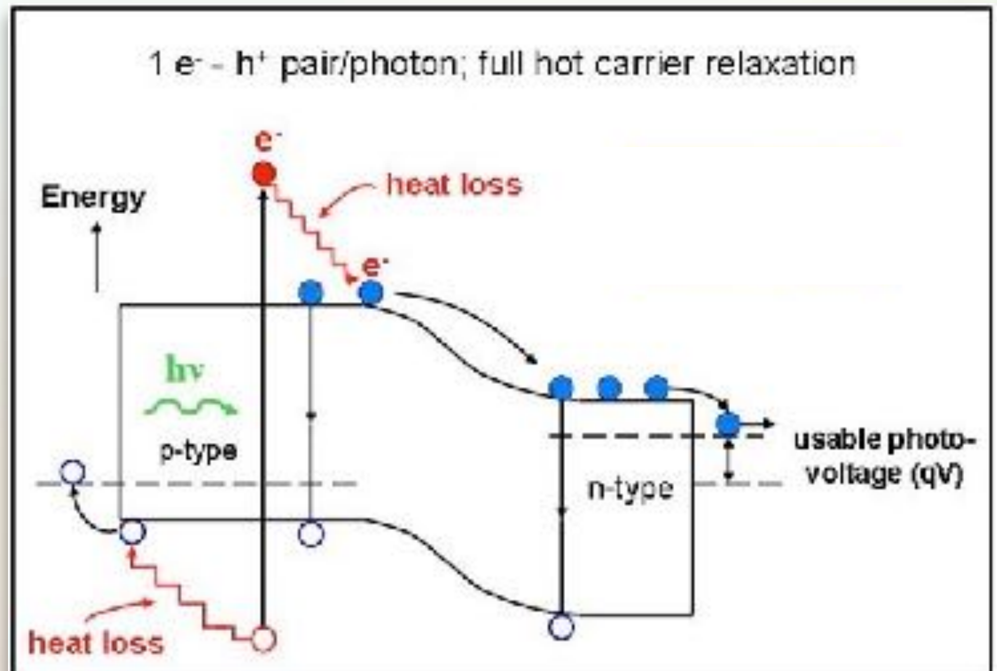


Photovoltaics: Capture&Conversion

(*Photos*=Light *Volta*=Inventor of the first electrical battery)

90% of the market is Silicon

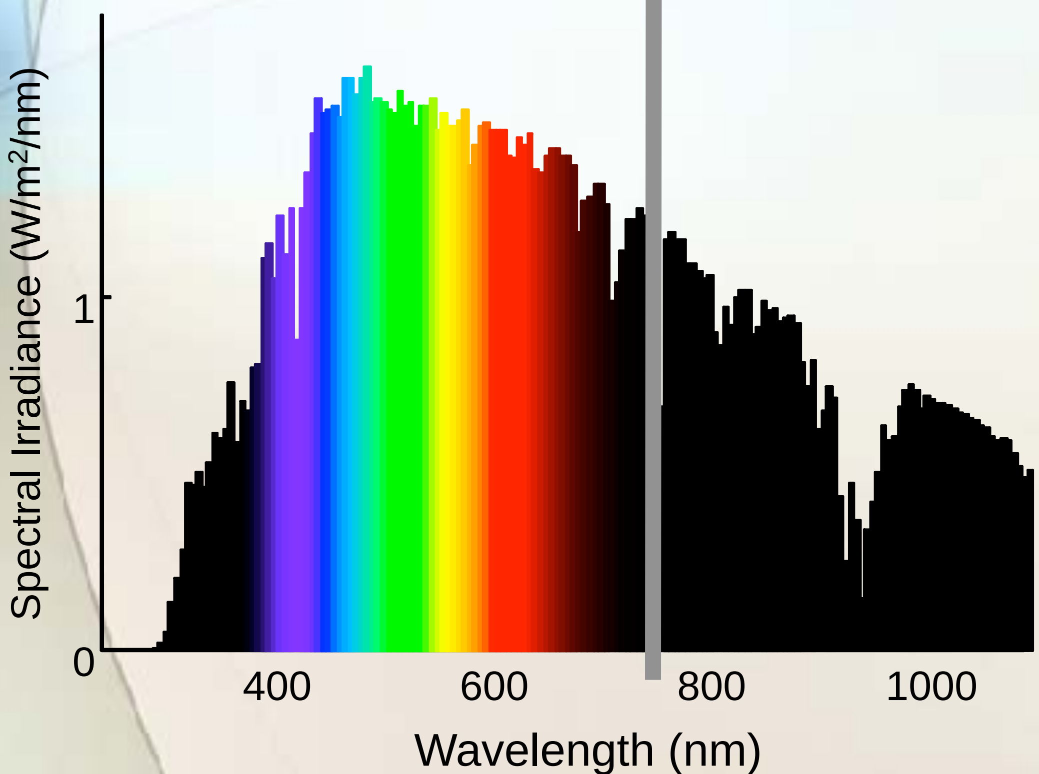
Si solar panels convert light to electricity by creating a junction

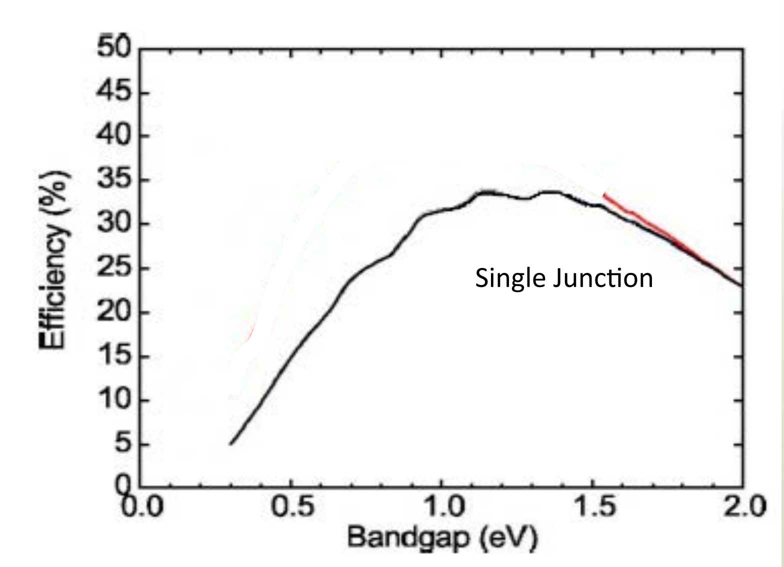


Shockley-Quiesser Limit

Excess Energy Loss

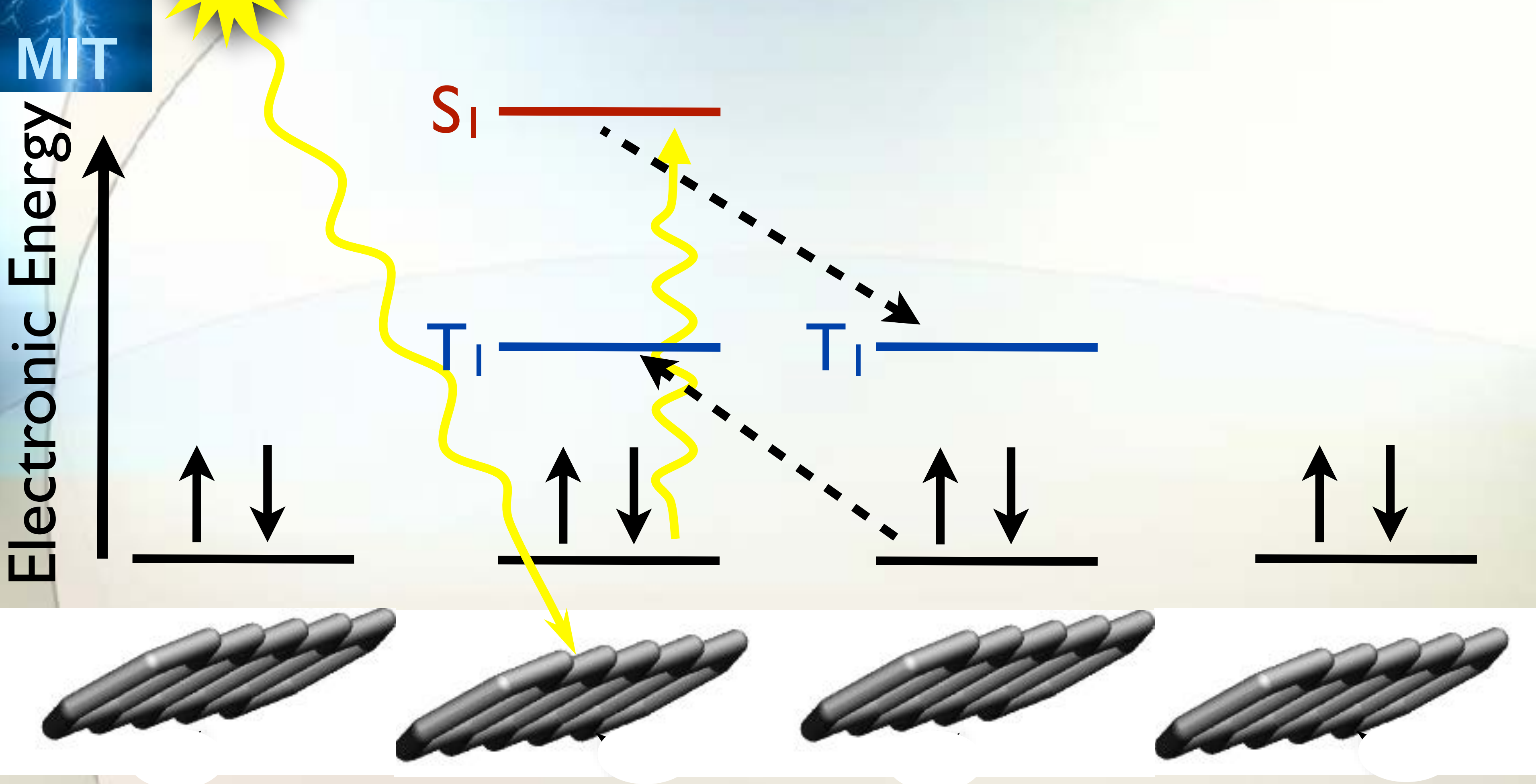
Light Not Absorbed





"Impossible" to make PV's that are > 33% efficient

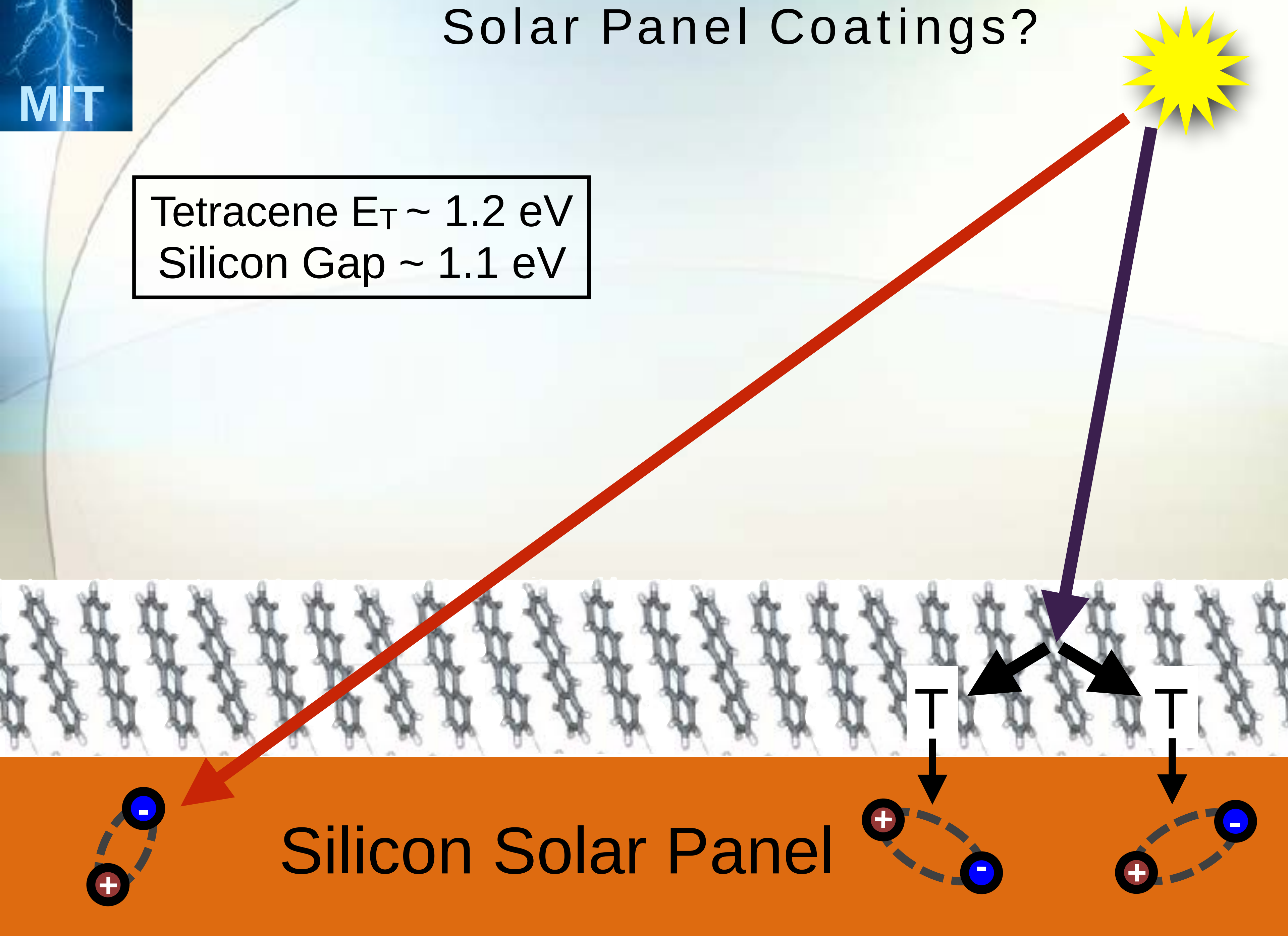
Singlet Fission



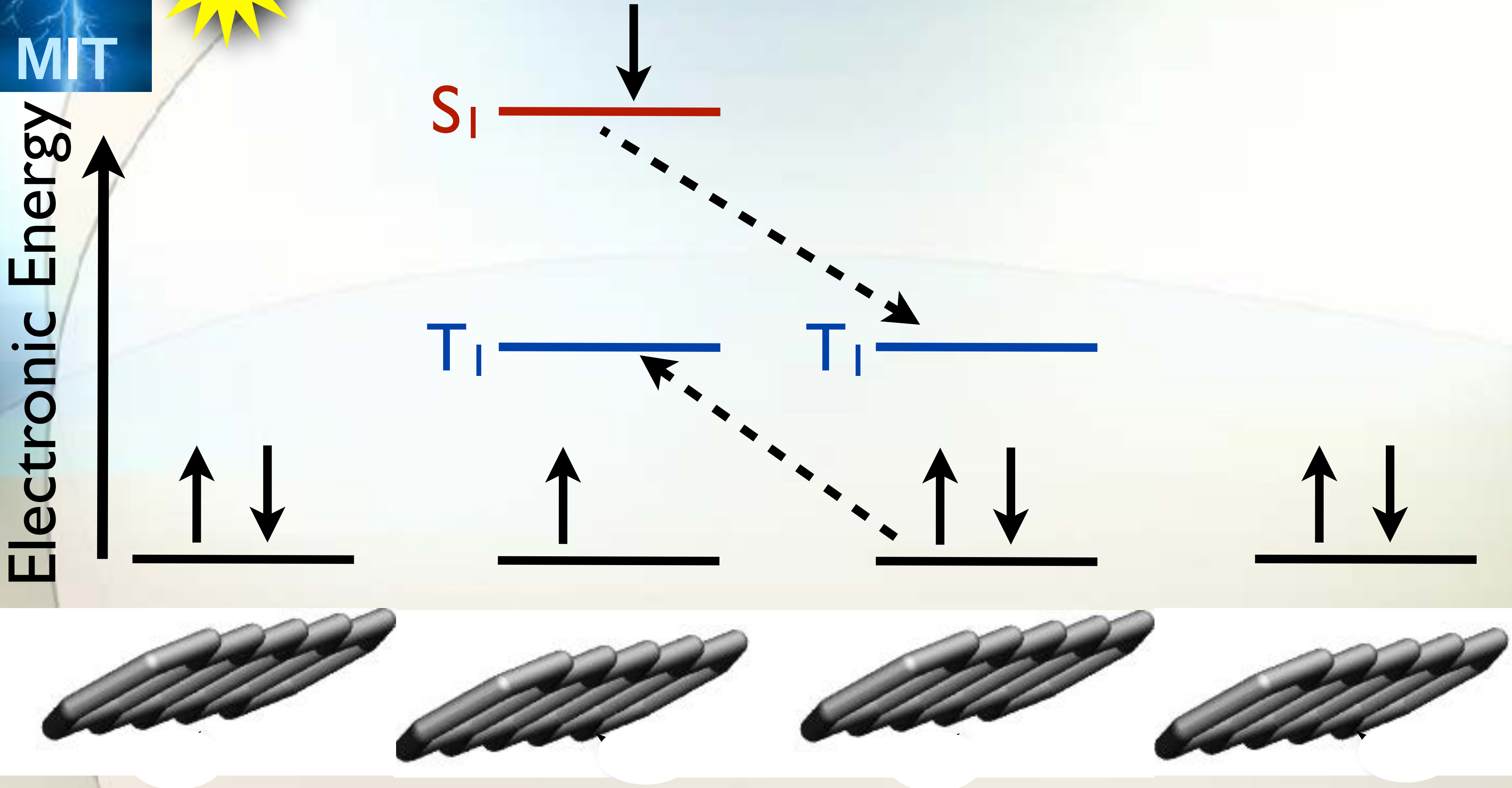
- Fission is spin allowed
- Observed in a handful of organic materials
  - Acenes, isobenzofurans, polyacetlyene
- Analogous to Multiple Exciton Generation in Quantum Dots

Solar Panel Coatings?

Tetracene $E_T \sim 1.2$ eV
Silicon Gap ~ 1.1 eV



Singlet Fission



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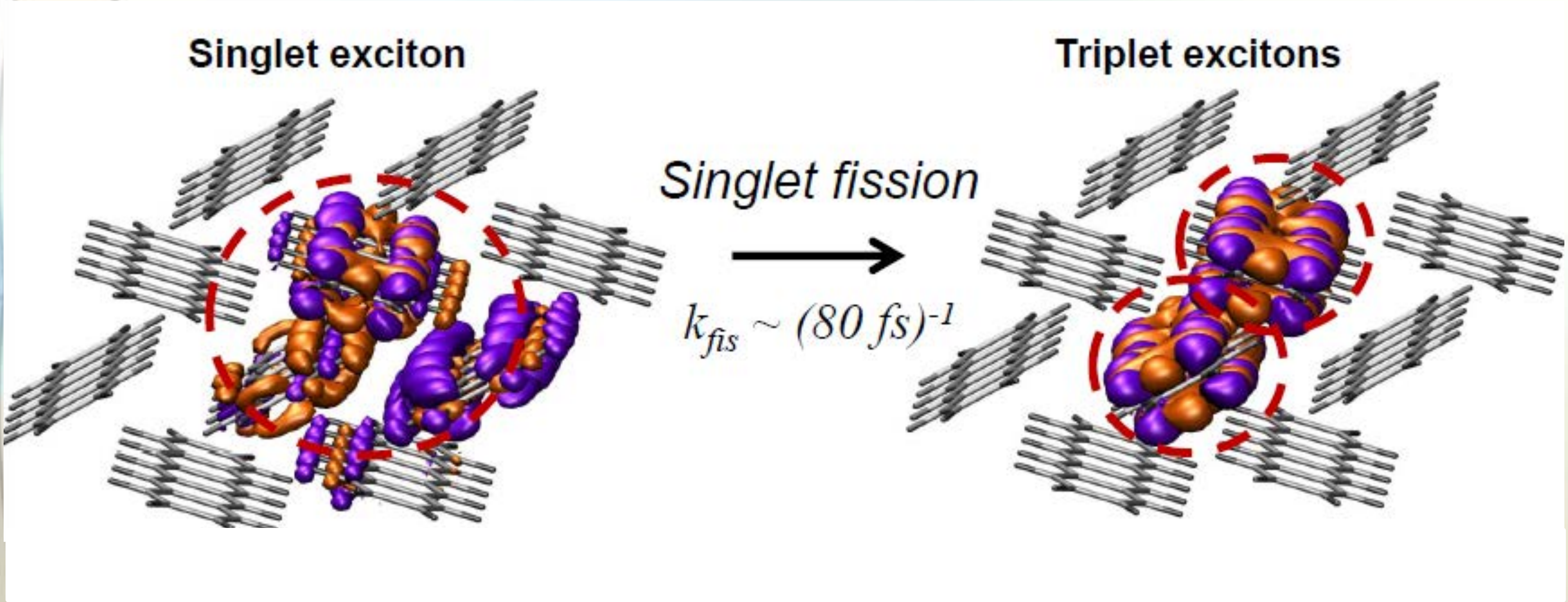
Fission Can Be Ultrafast

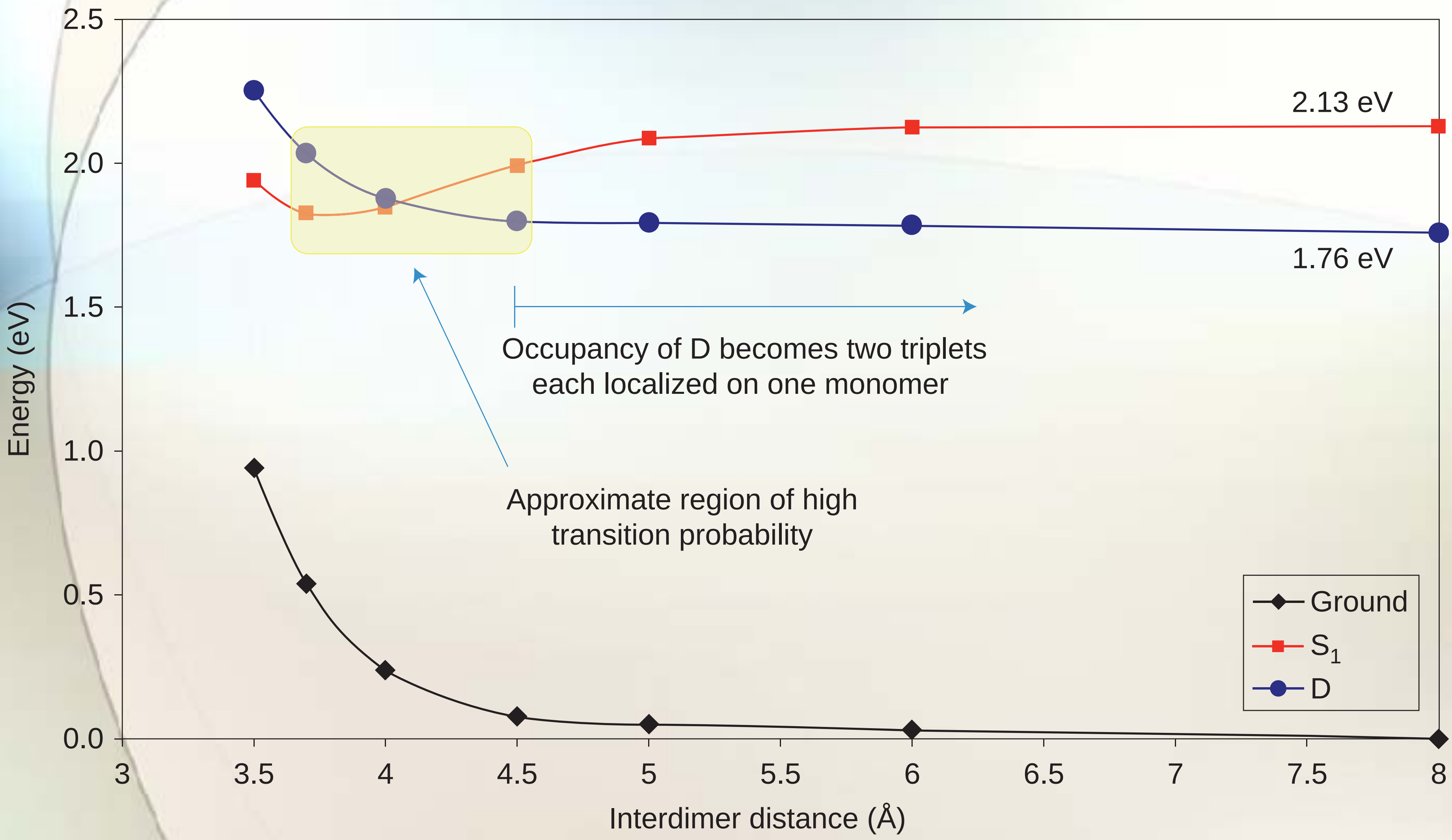


Transient measurements **estimate** the fission yield at 200%.

M. W. B. Wilson et al., *J. Am. Chem. Soc.*, 133, no. 31, *11830* (2011).
W.-L. Chan, et al, *Science*, 334, no. 6062, *1541*, (2011).

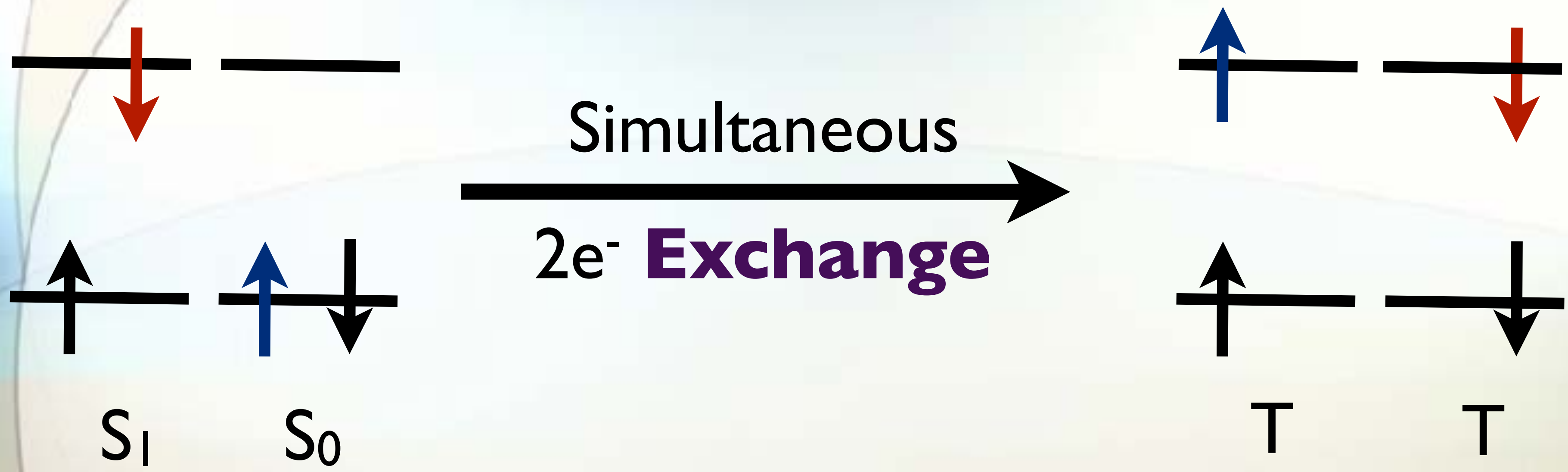
Why is it so fast?

Crossing Between S_1 and TT



Zimmerman *et al* *Nat. Chem.* **2**, 648 (2010)

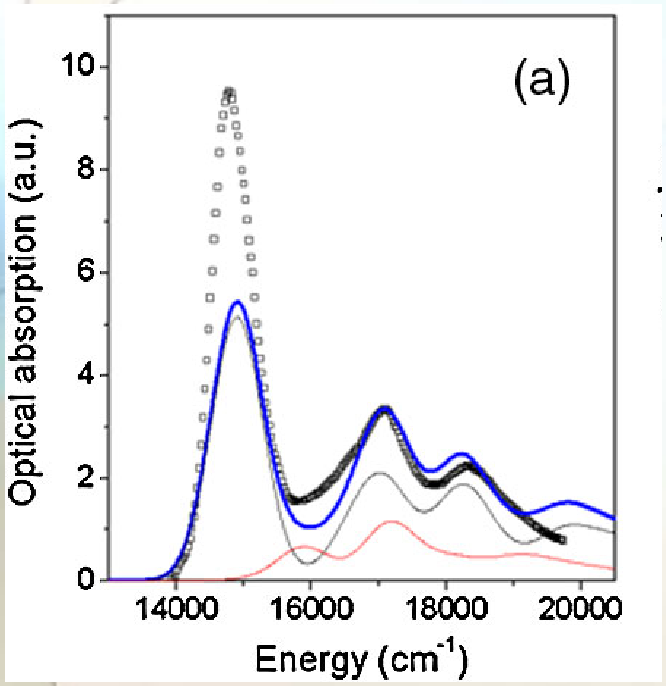
Hypothesis 1: Direct Fission

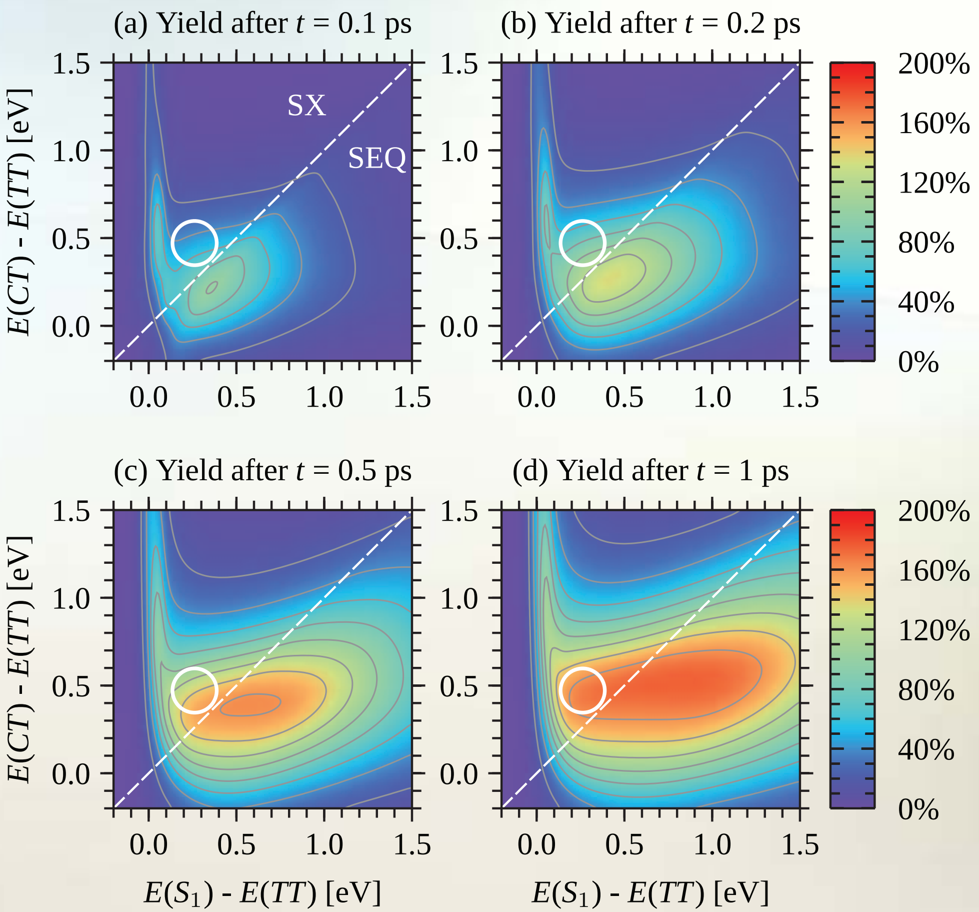


- Analogous to kinetic exchange in magnetic complexes
- Governed by:

$$V \equiv \langle S_1 S_0 | \hat{H} | TT \rangle \approx \langle LUMO_L \, \overline{HOMO}_R | \overline{LUMO}_L \, LUMO_R \rangle$$

Charge Transfer States

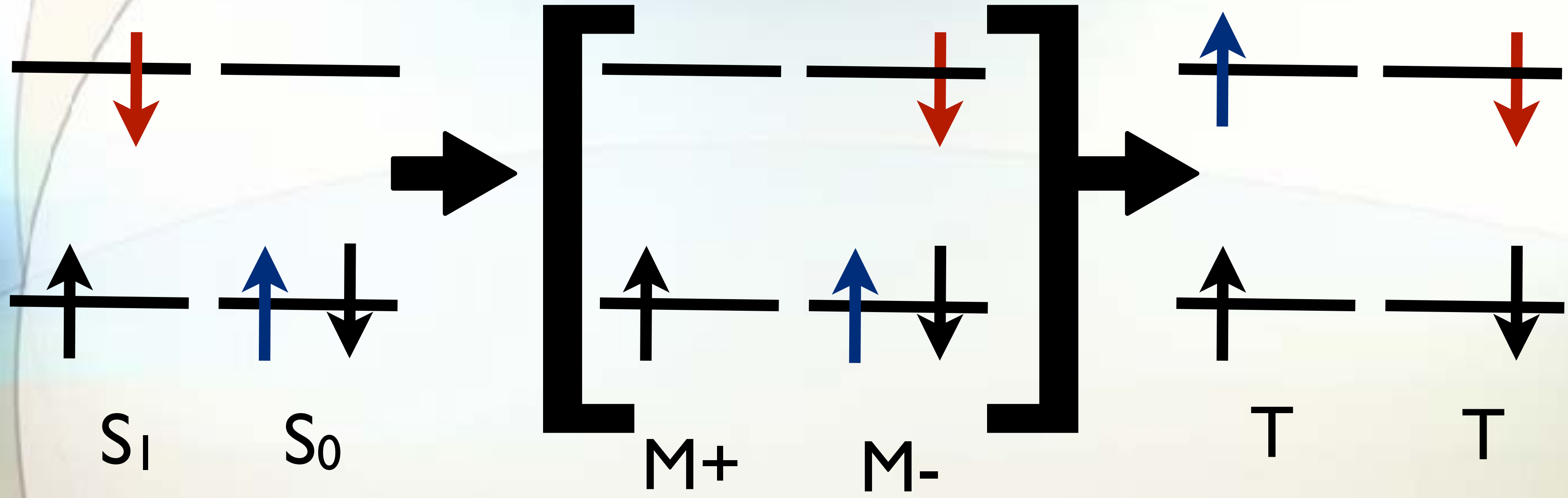




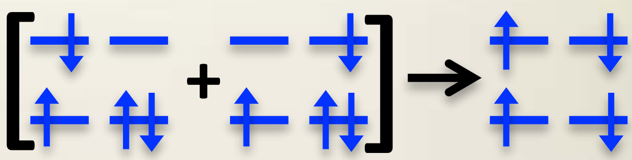
Beljonne *et al Phys. Rev. Lett.* ***110*** 226402 (2013)

Berkelbach&Reichman *JCP* **138** 114103 (2013)

Hypothesis 2: CT Mediated Fission

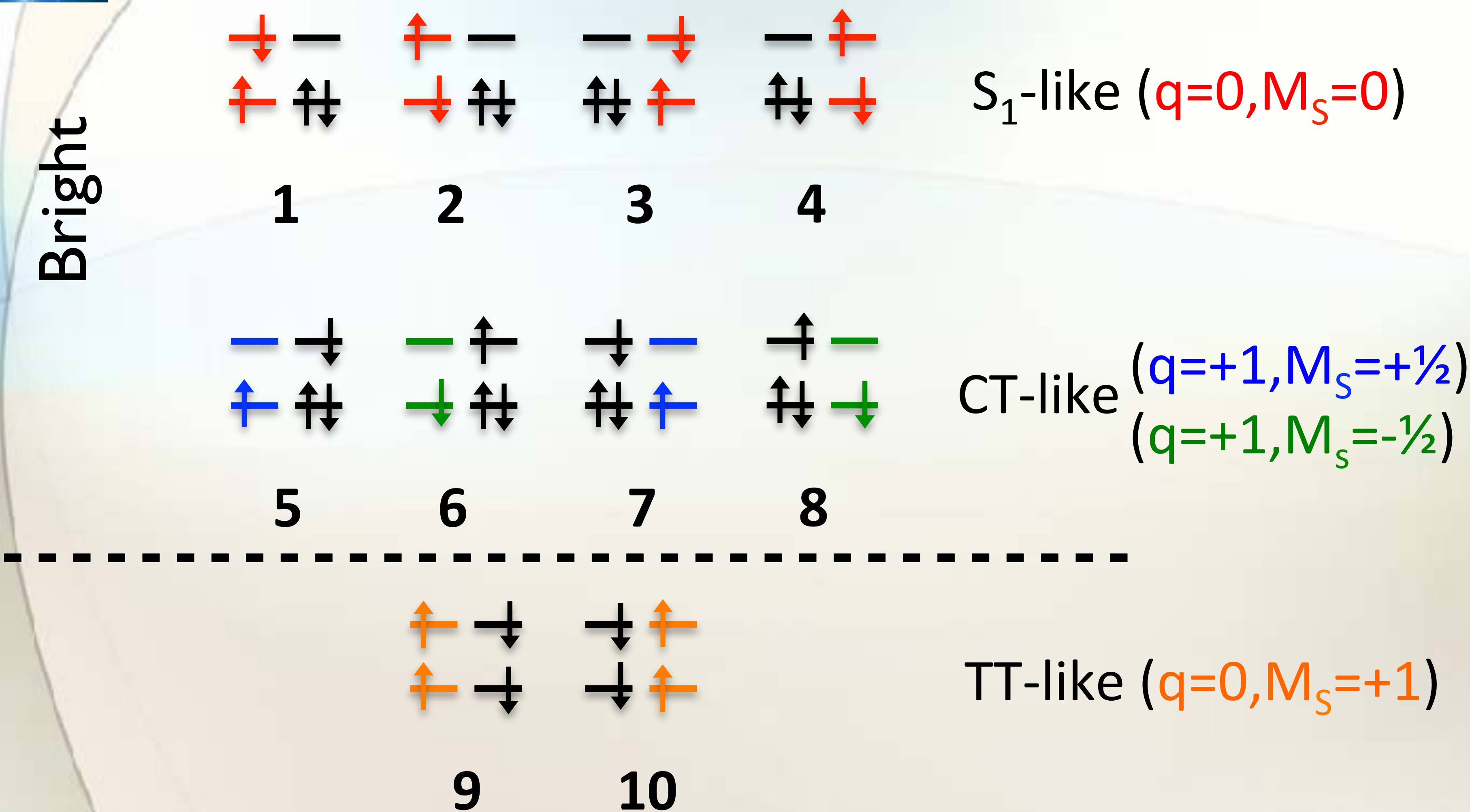


- Analogous to Superexchange
- Direct+CT Fission governed by combined coupling:



$$V \equiv \langle Bright | \hat{H} | TT \rangle$$

The Excited States Involved



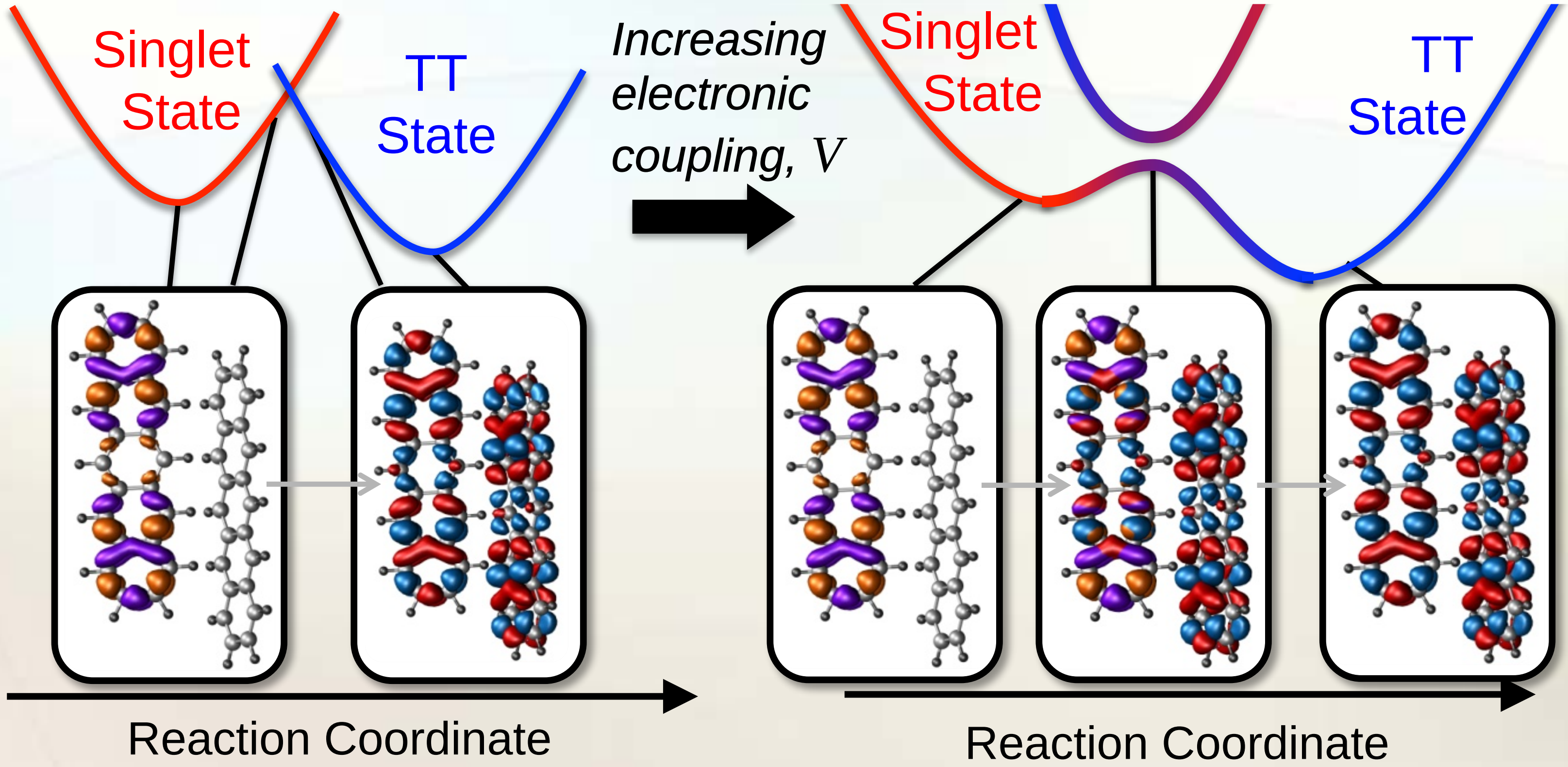
$$V \equiv \langle Bright | \hat{H} | TT \rangle$$

The Expected Rates

$$V = \langle S_1 S_0 | \hat{H} | TT \rangle$$

Nonadiabatic: $k_{fis} \propto V^2$

Adiabatic: $k_{fis} \sim \tau_{ad}^{-1}$

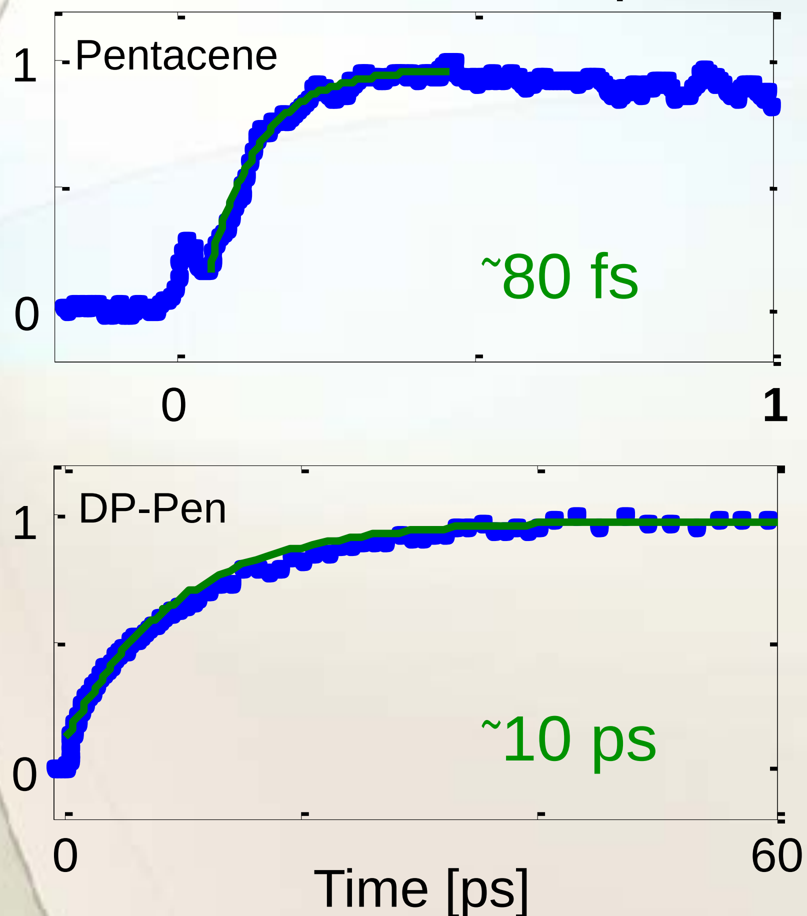


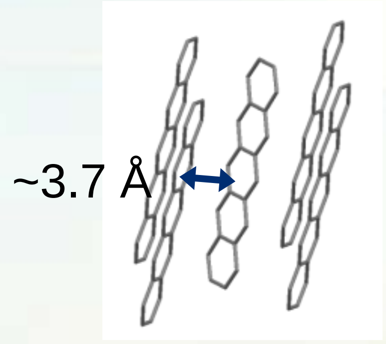
Expected Rate Expression: $k_{fis} = \sum_n \frac{k_n V^2}{1 + \tau_n^{ad} V^2}$

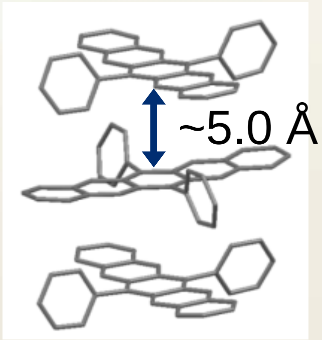
(Bixon&Jortner)

Experimental Fission Rates

Triplet-Triplet Photoinduced Absorption





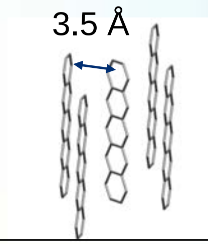
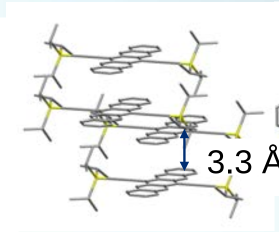
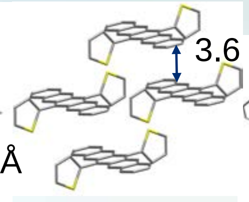
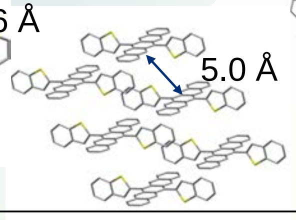
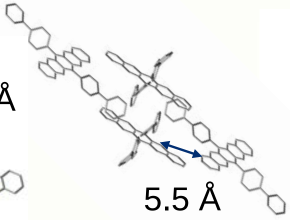
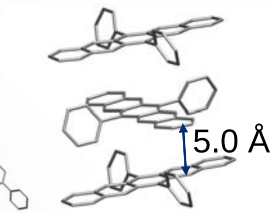


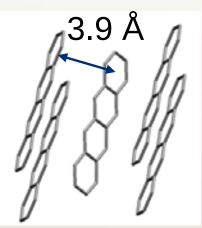
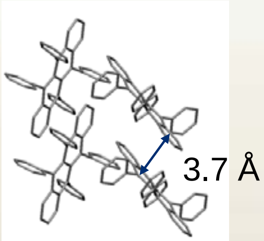
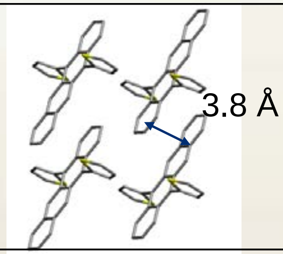
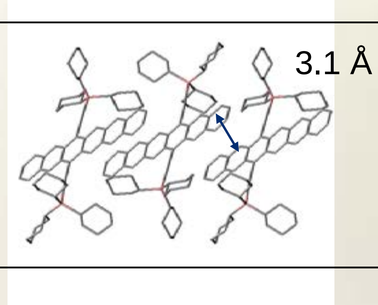
Device Measurements: Prof. Marc Baldo

Synthesis: Prof. Tim Swager

Ultrafast: Prof. Richard Friend

Fission Rates And Couplings

	Pentacene	TIPS-P	DTP	DBTP	DBP	DPP
Crystal Structure						
Structure Type	Herringbone	2D π stack	Slip stacked	Displaced slip stack	Displaced slip stack	Orthogonal π stacked
V (meV)	84	72	16	5.4	2.0	0.82
k_{fis} (ps^{-1})	12.5	10	6.25	1.11	0.26	.085

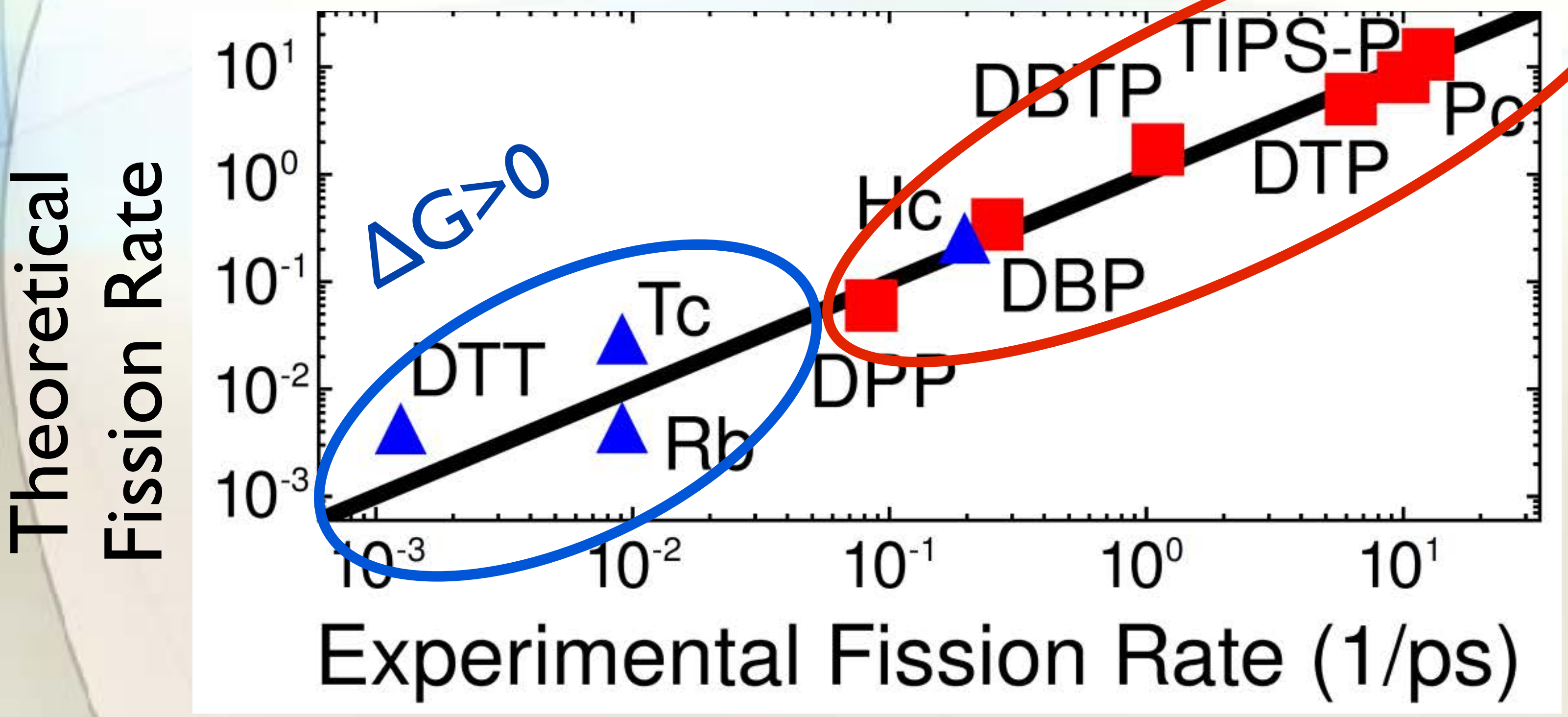
	Tetracene	Rubrene	DTT	Hexacene
Crystal Structure				
Structure Type	Herringbone	Slip stacked	Slip stacked	Slip stacked
V (meV)	83	5.9	6.2	44
k_{fis} (ps^{-1})	0.0091	0.0091	0.0025	0.196

Yost, et al *Nat. Chem.* **6** 492 (2014)

Bixon-Jortner Agrees With Experiment

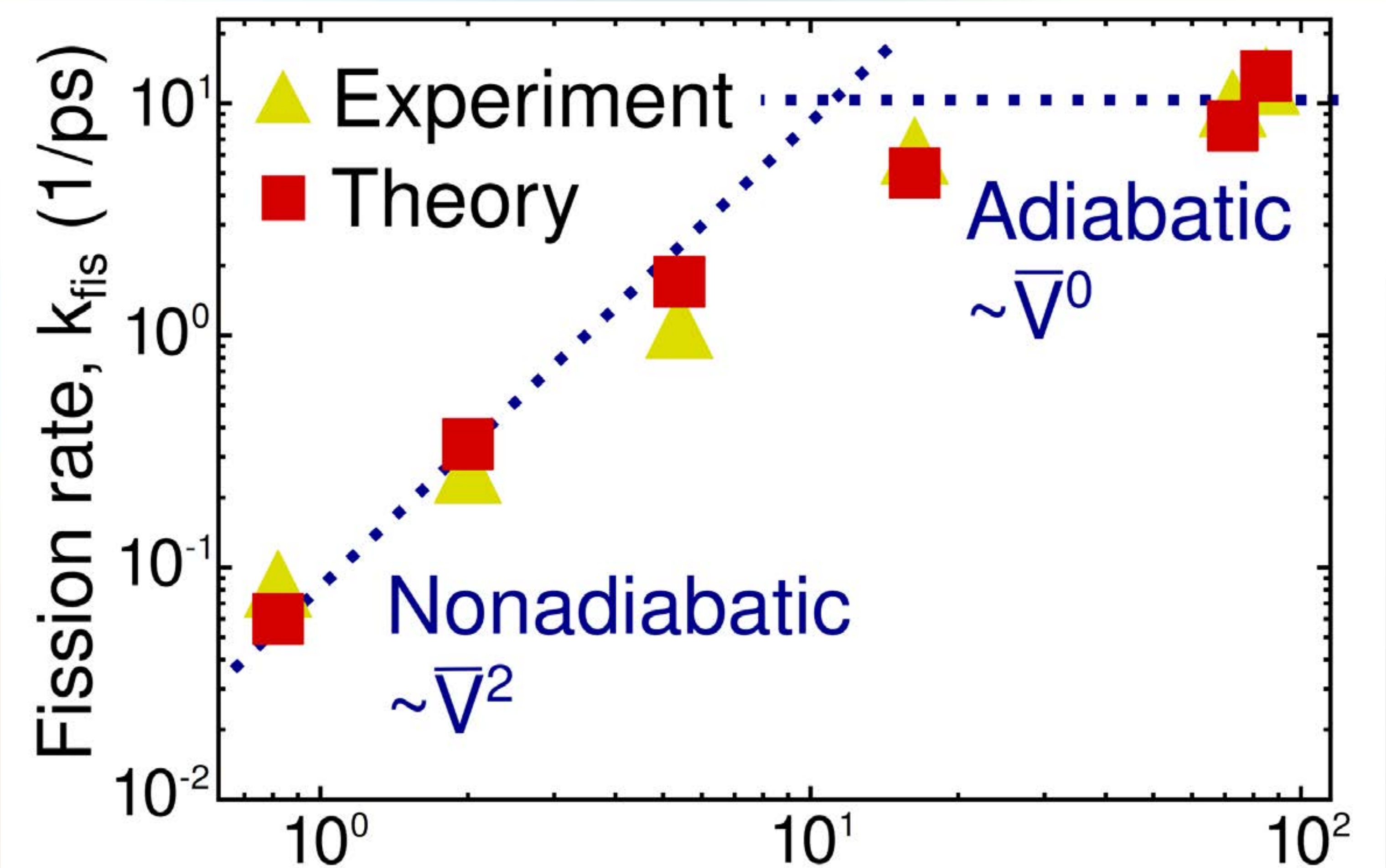
Tetracene&Hexacene Derivatives

Pentacene Derivatives



<u>Observation:</u> ΔG Dominates Fission Rate

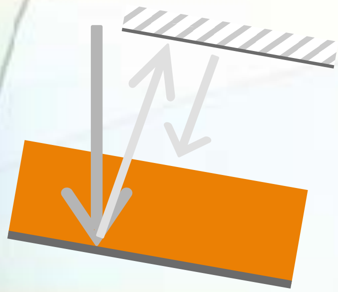
Pentacene Data



Electronic Coupling *V* (meV)

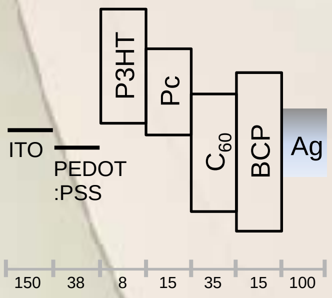
Yost, et al *Nat. Chem.* **6** 492 (2014)

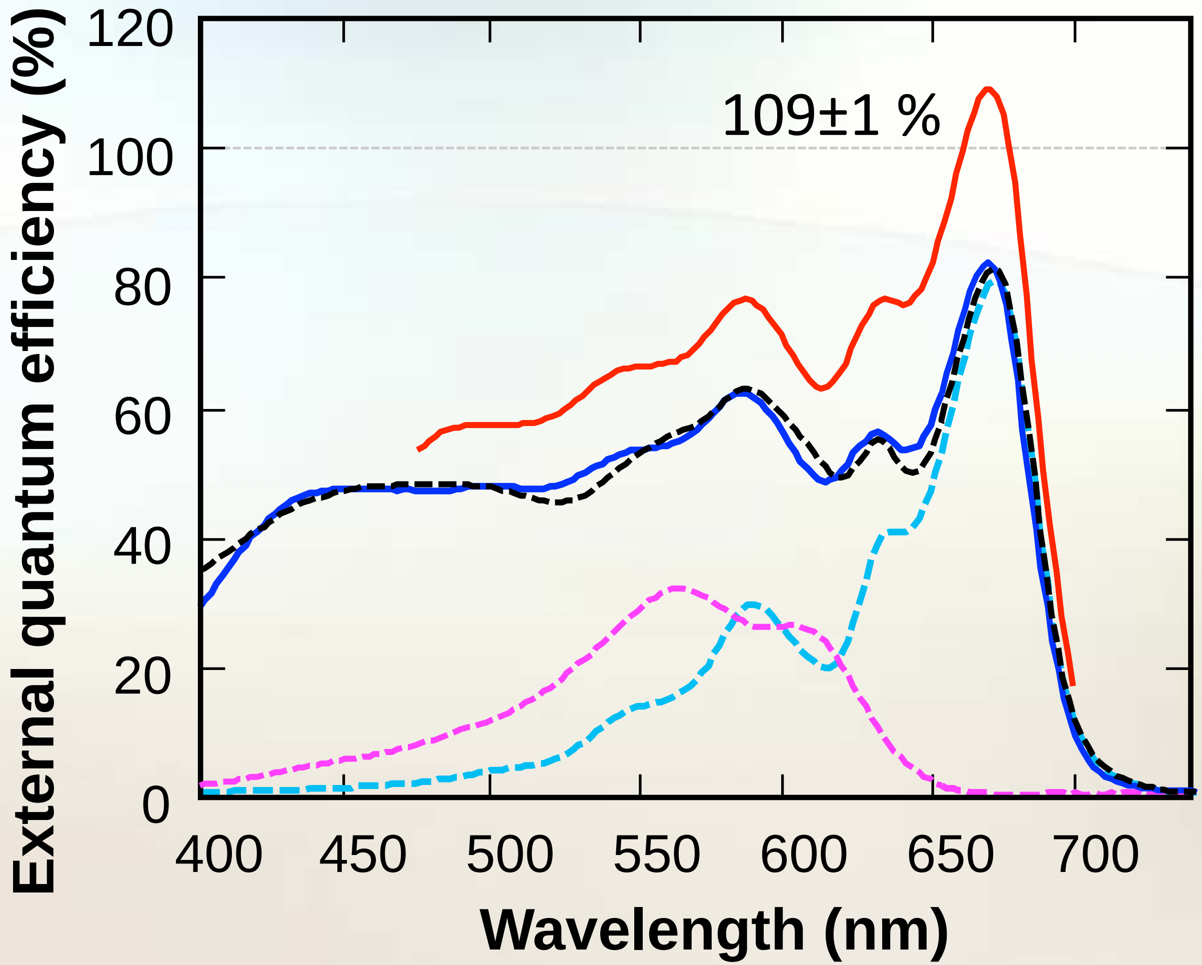
More than 1 Electron per Photon



Pc Abs = 71%

Pc IQE = 150±10 %

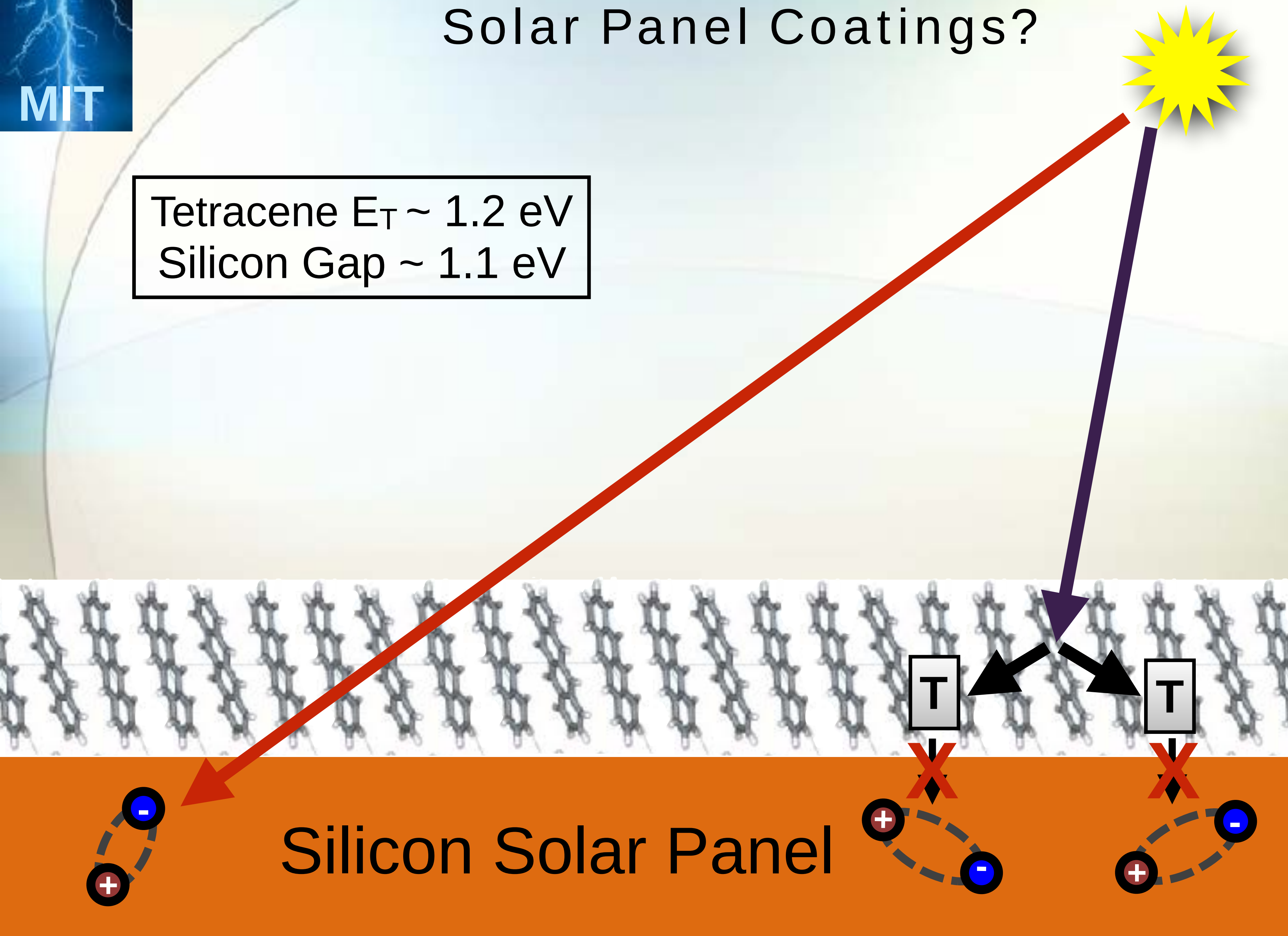




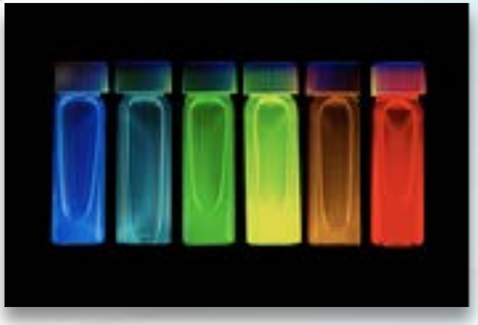
Congreve, *et al Science* **340** 334-337 (2013).

Solar Panel Coatings?

Tetracene E_T ~ 1.2 eV
Silicon Gap ~ 1.1 eV

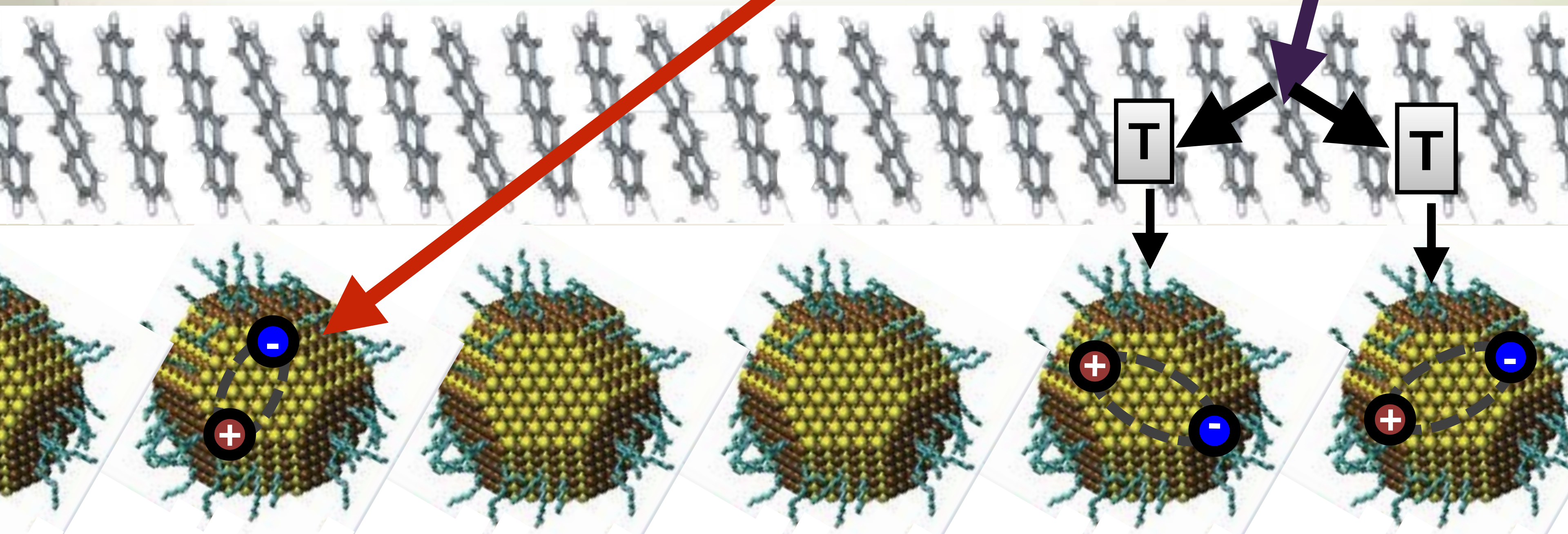


Solar Panel Coatings?

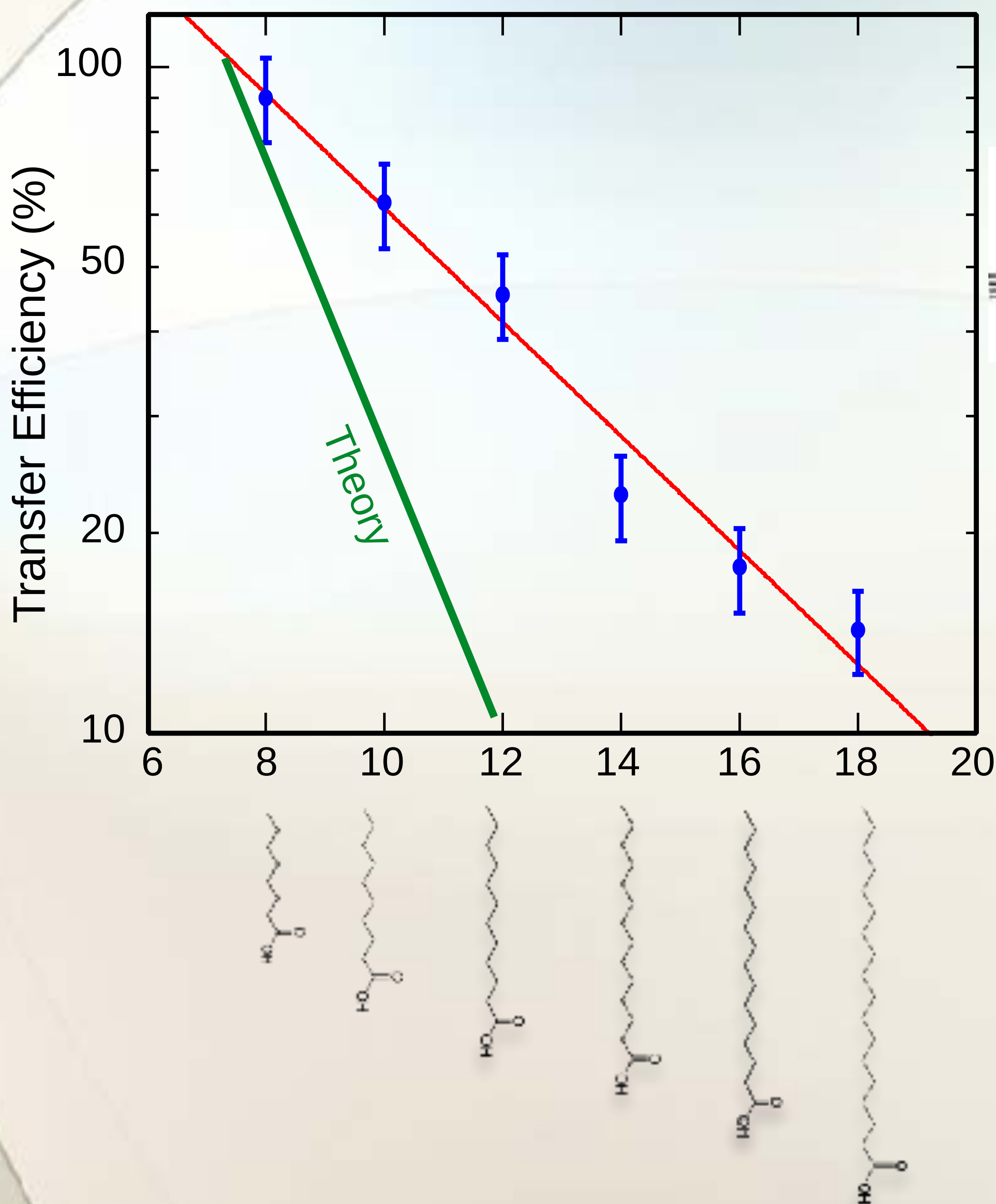


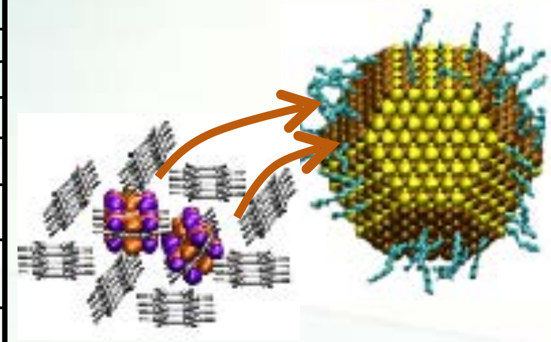
Moungi Bawendi

Tetracene E_T ~ 1.2 eV
PbS Dot Gap ~ 1.0 eV



Distance Dependence of Energy Transfer

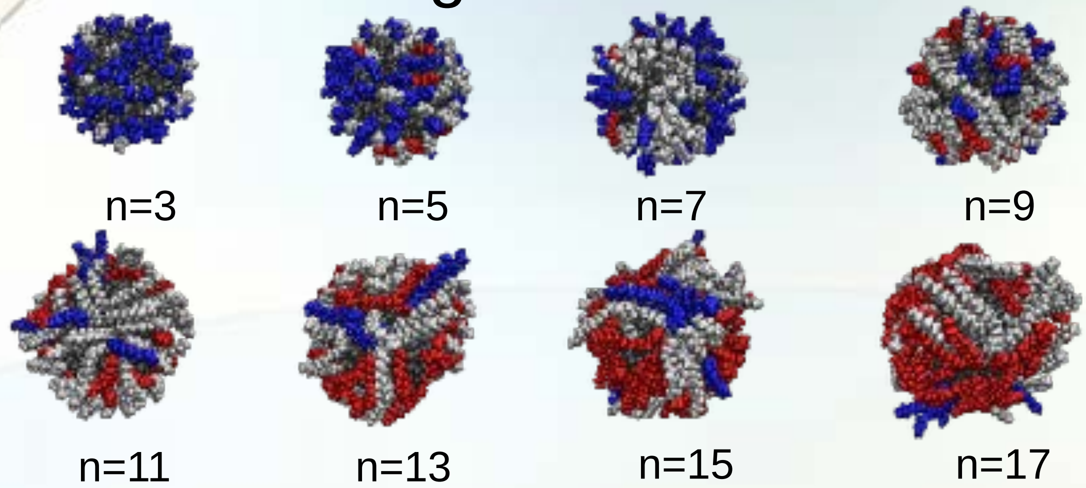




Exponential dependence on distance
➜ Wave function Overlap

But way too long-ranged!

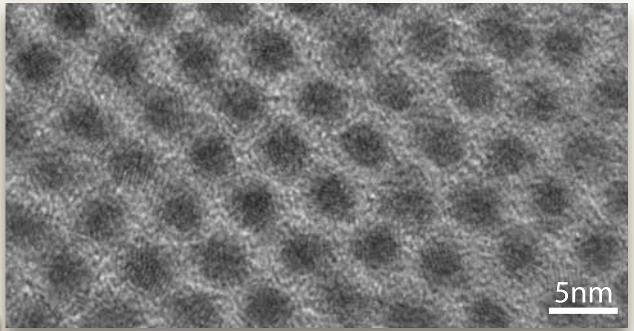
Ligand Shell Structure

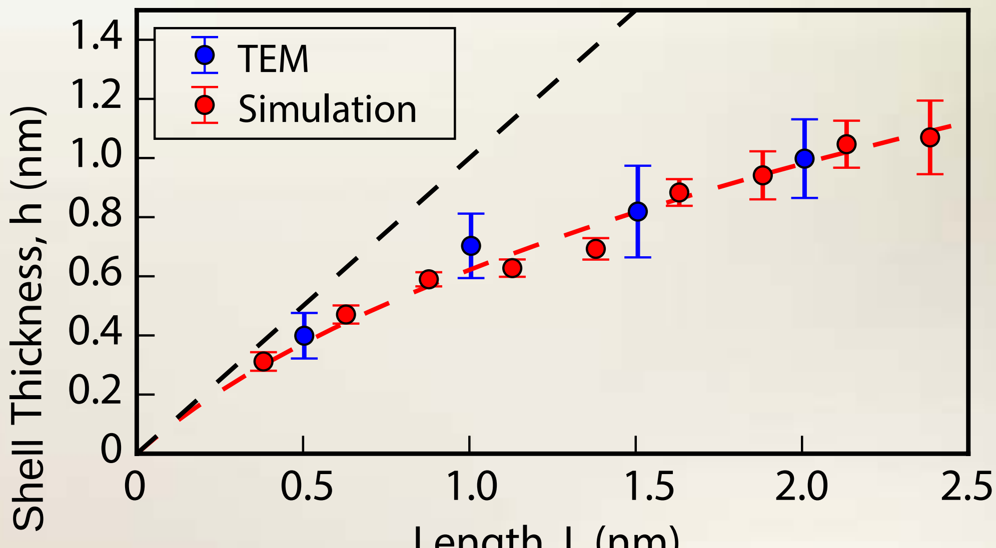


Standing Up (all anti)

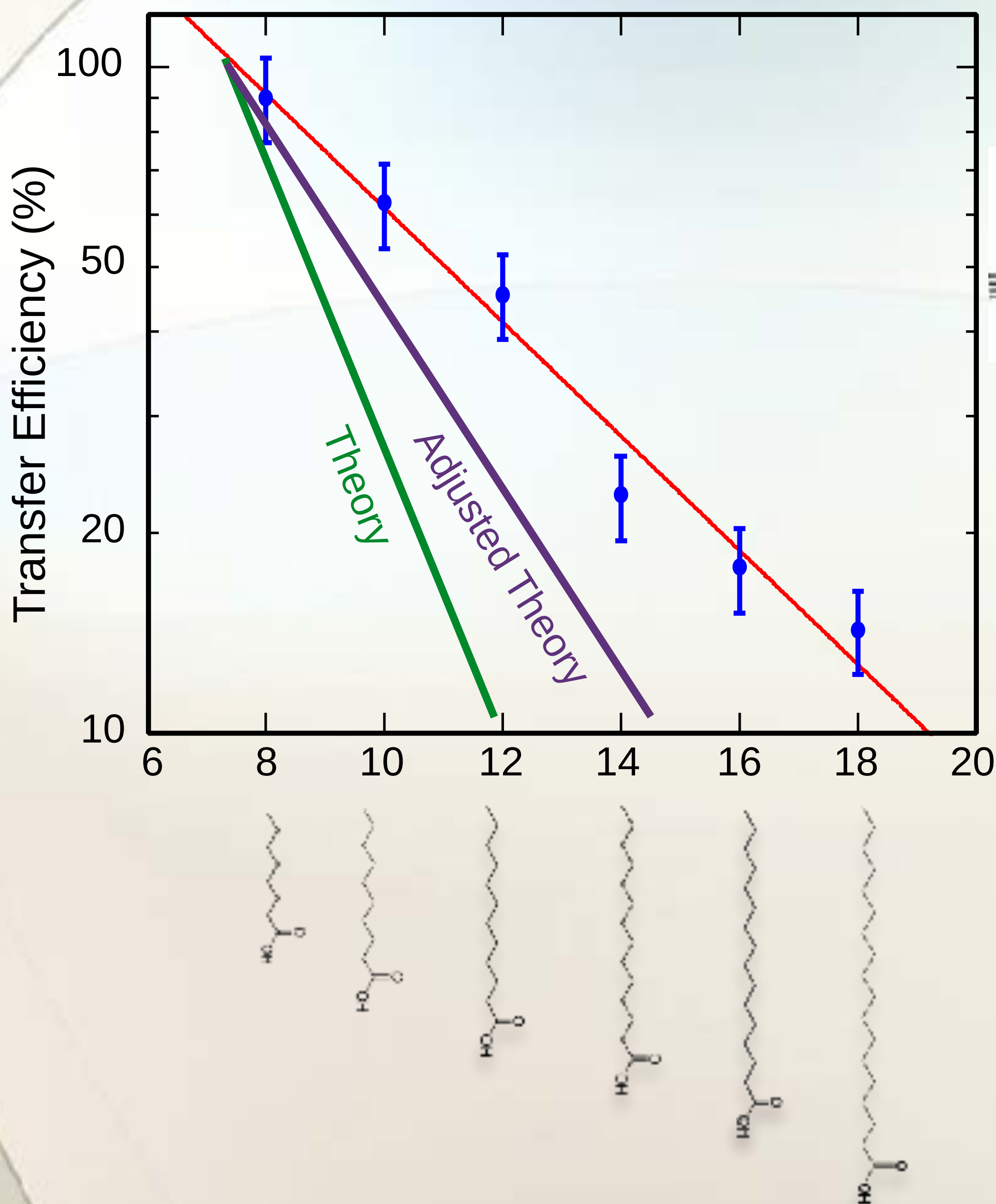
Lying Down (at least one gauche)

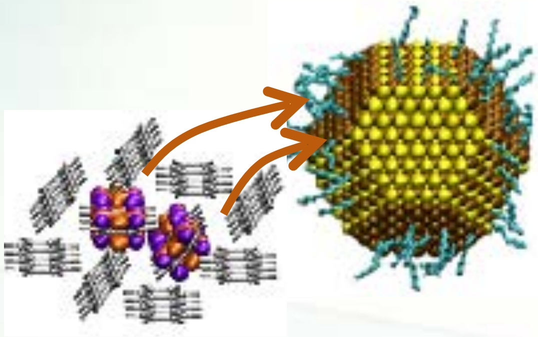
TEM of QD Array





Distance Dependence of Energy Transfer

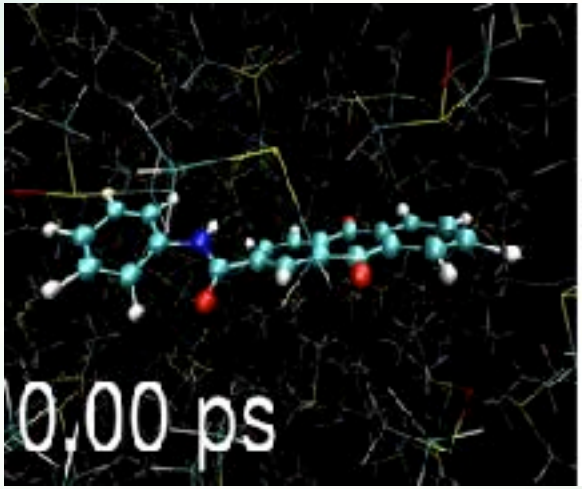




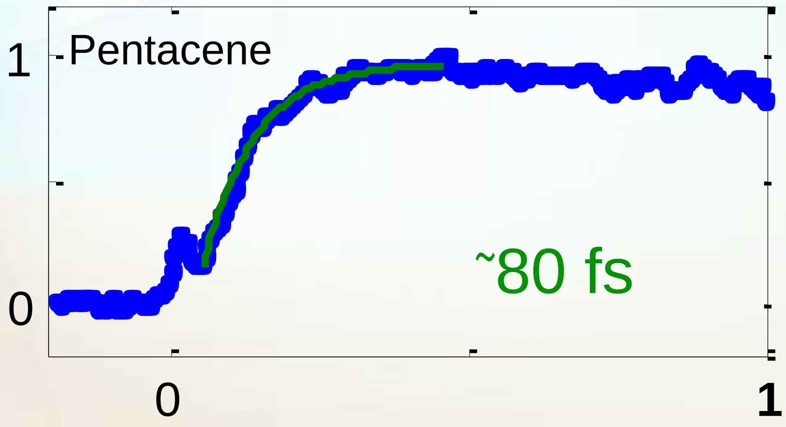
Exponential dependence on distance
➜ Wave function Overlap

But way too long-ranged!

Outlook And Future Work

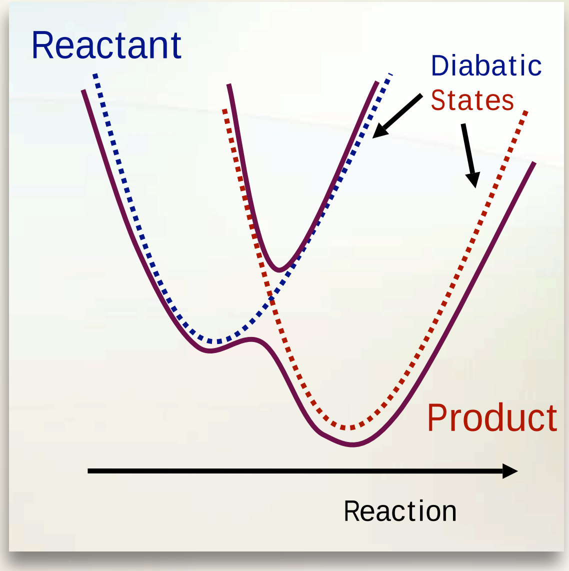


→ CDFT allows simulation of excited states in complex environments



← CDFT predicts the rate of singlet fission in devices

→ What about other types of other types of reactions?



Acknowledgements

Group Members:

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Tim Kowalczyk (FAAQ)
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