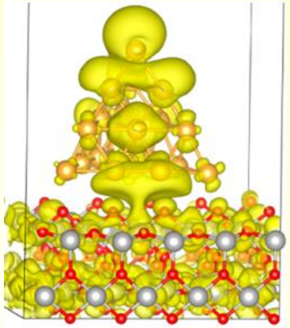
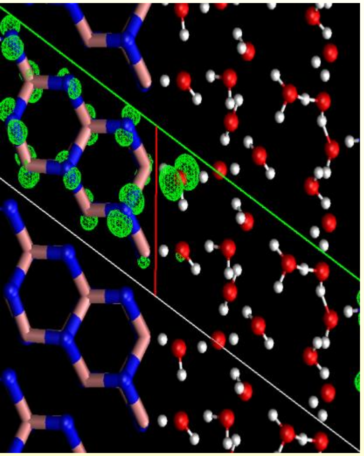
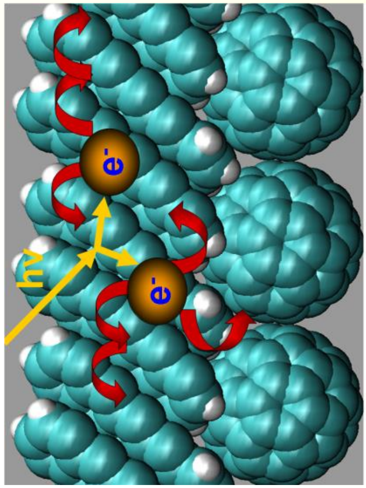
Excitation Dynamics in Nanoscale Hybrids



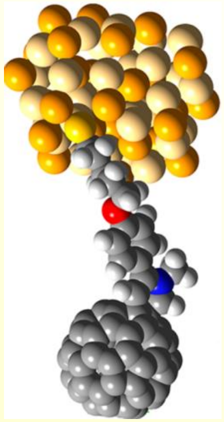
Oleg Prezhdo

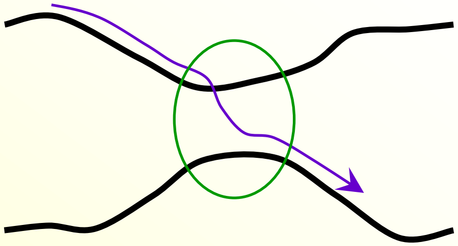
U. Southern California

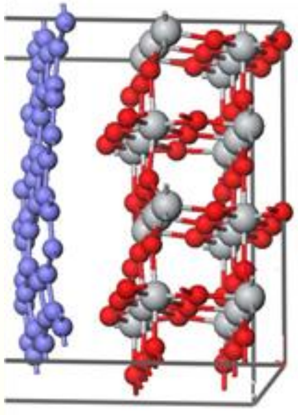




Moscow
Dec 10, 2014



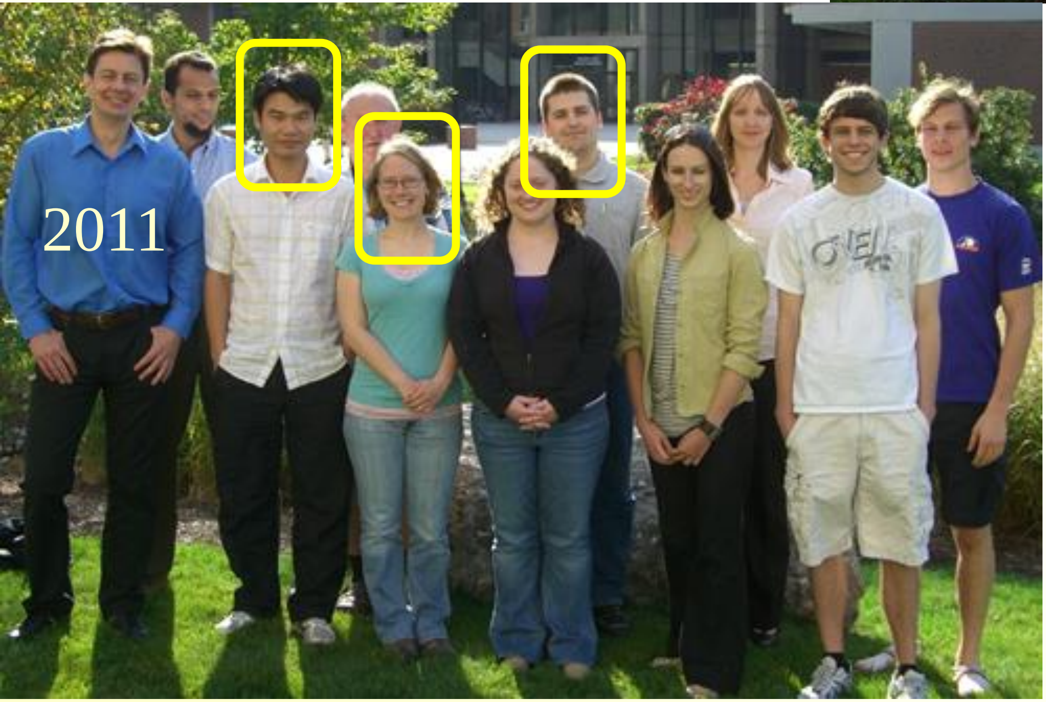




Group Members

Dr. Alexey Akimov
Dr. Run Long
Dr. Vitaly Chaban
Amanda Neukirch

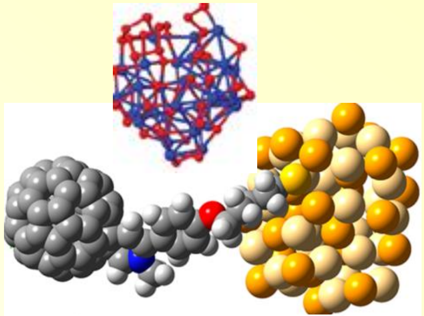
2013

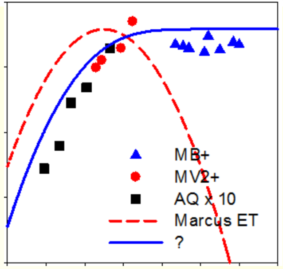


2011

We have graduate student and postdoc openings

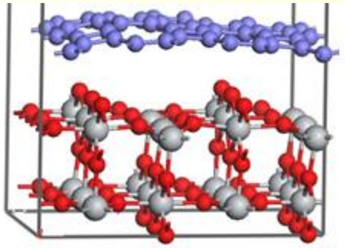
Outline

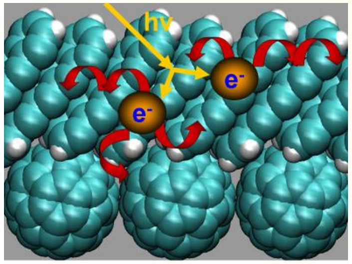


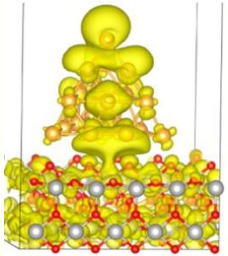


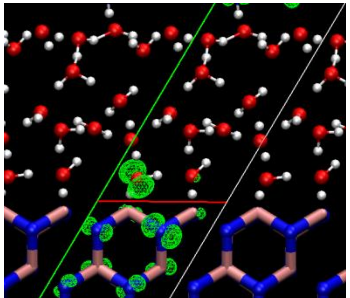
- Nonadiabatic Molecular Dynamics & Time-Dependent Density Functional Theory

- Applications
  - Are defects good or bad for QD applications?
  - Why long bridge accelerates ET from QD to C_{60}?
  - Lack of Marcus inverted regime – Auger assisted ET
  - Why graphene (metal!) can be used as light-harvester?
  - Instantaneous plasmon-driven ET
  - Dimensionality and ET mechanism
  - Exploiting asymmetry of ET in CNT/polymer systems
  - Why H_2O splitting is not efficient on GaN?
  - Singlet fission vs. charge transfer?



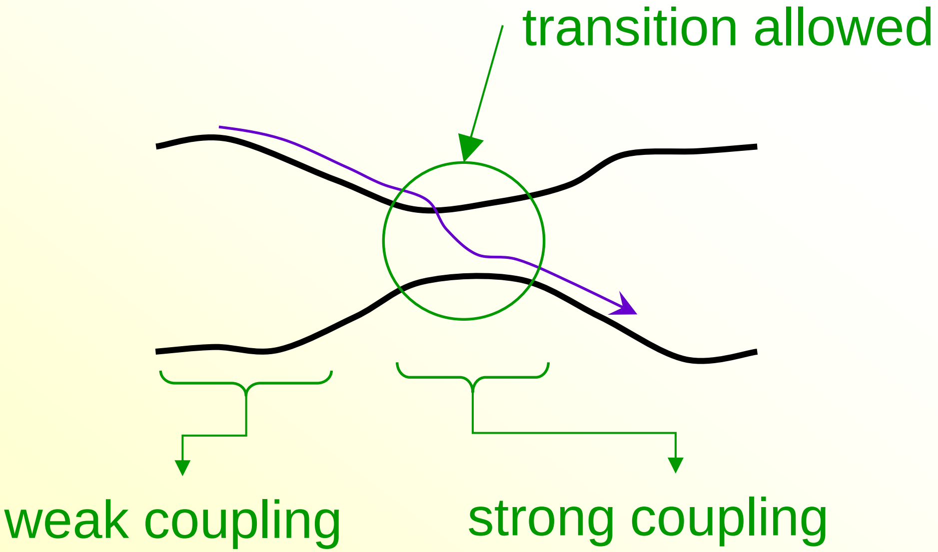


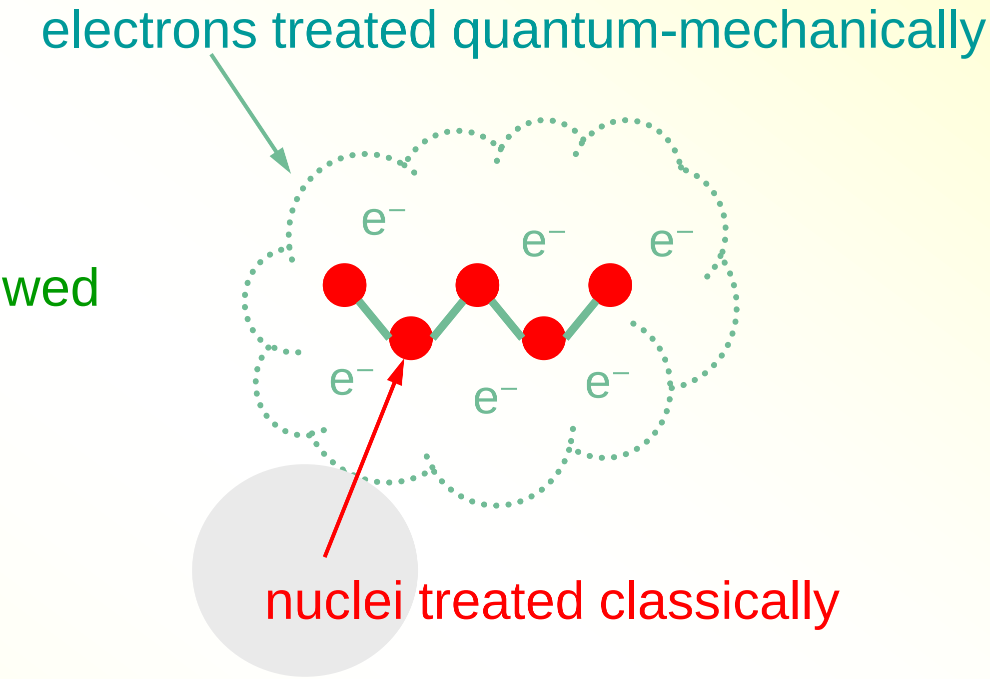




Nonadiabatic Molecular Dynamics

<u>Nonadiabatic MD:</u> Coupling between potential surfaces opens channels for system to change electronic states.





Time-Domain DFT for Nonadiabatic Molecular Dynamics

Craig, Duncan, Prezhdo *Phys. Rev. Lett.* **95,** 163001 (2005)

Electron density derives from Kohn-Sham orbitals

$$\rho(x) = \sum_p \left|\varphi_p(x)\right|^2 \qquad \left|\Psi\right\rangle = \left|\varphi_p(x_1,t)\varphi_q(x_2,t)\ldots\varphi_v(x_N,t)\right\rangle_{SD}$$

DFT functional *H* depends on nuclear evolution *R(t)*

Variational principle gives $$i\hbar\frac{\partial\varphi_p(x,t)}{\partial t} = H\varphi_p(x,t) \quad p = 1,2\ldots$$

Orbitals are expanded in adiabatic KS basis $$\varphi_p(x,t) = \sum_\alpha c_p^\alpha(t)\chi^\alpha(x)$$

$$i\hbar\dot{c}^\alpha = \sum_\beta c^\beta\left(\varepsilon^\beta\delta_{\alpha\beta} - \boxed{i\hbar\left\langle\chi^\alpha\middle|\vec{\nabla}_R\middle|\chi^\beta\right\rangle\cdot\dot{\vec{R}}}\right)$$

non-adiabatic coupling

Theoretical Questions

✓ How to couple quantum and classical dynamics?
quantum back-reaction on classical variables

✓ Can one do better than classical mechanics for nuclear motion?
zero-point motion, tunneling, branching, loss of coherence

<u>Recently developed methods</u>

Decoherence induced surface hopping (DISH) *JCP* **137**, 22A545 (2012)
Self-consistent FSSH (SC-FSSH) *JPC-L* **5**, 713 (2014)
Global flux surface hopping (GFSH) *JCTC*, in press
Coherence penalty functional (CPF) *JCP* **140**, 194107 (2014)
Second quantized surface hopping (SQUASH) *PRL*, in press

PYXAID: PYthon eXtension of Ab Initio Dynamics

Akimov, Prezhdo, *J. Theor. Comp. Chem.* **9**, 4959 (2013);
ibid. **10**, 789 (2014)

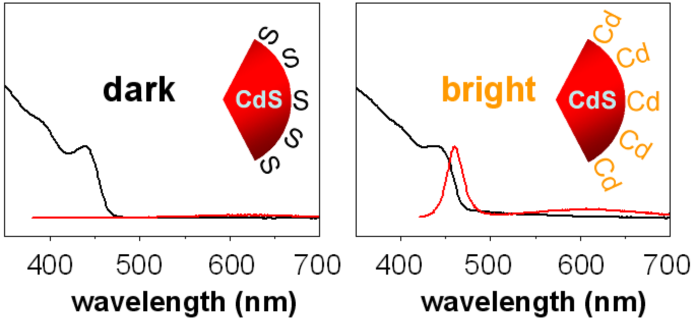
Set of Python scripts, currently interfaced with Quantum Espresso, can be trivially interfaced with other DFT codes, e.g. VASP

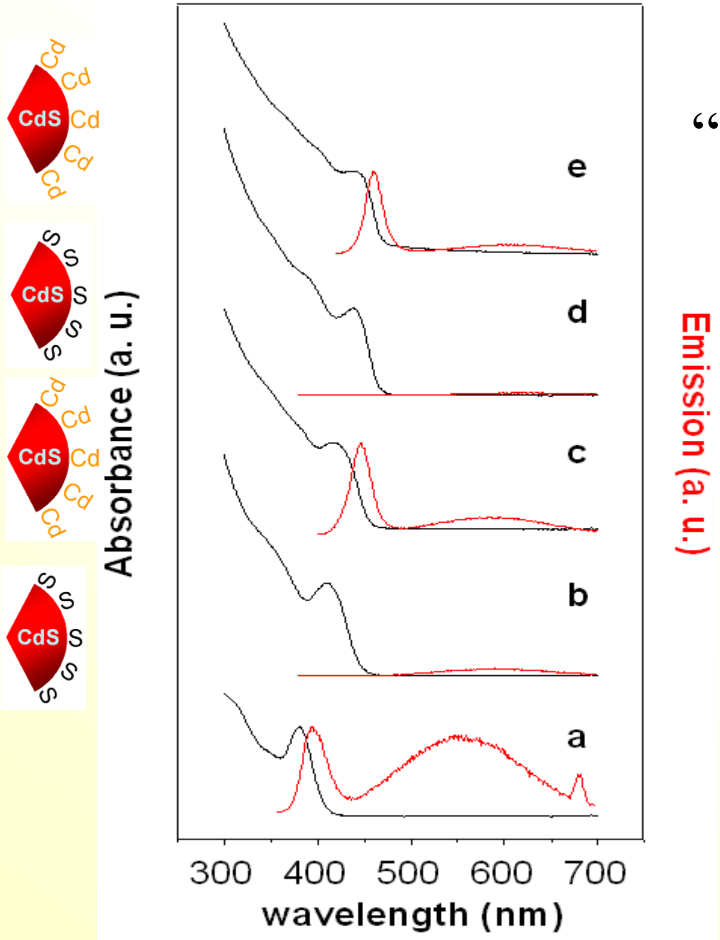
http://gdriv.es/pyxaid

by Dr. Alexey Akimov

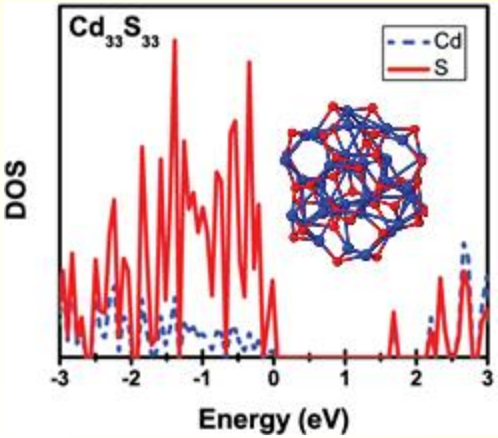
Surface Chemistry Controls Relaxation

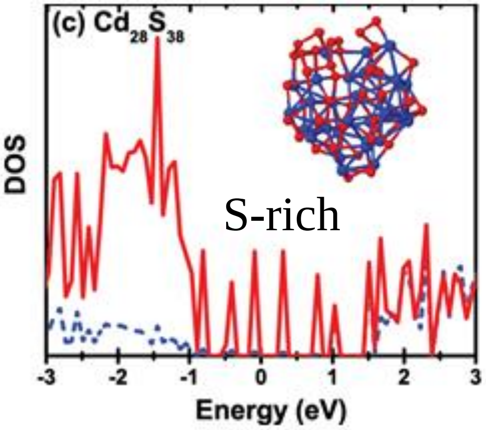
Wei, Evans, Swartz, Neukirch, Young,
Prezhdo, Krauss, *Nano Lett* **12**, 4465 (2012)



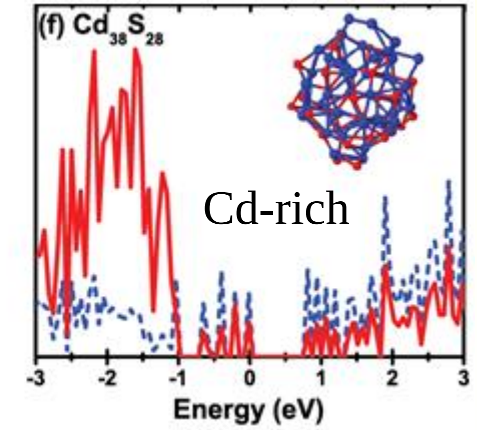


Metallic Cd
“heals” dangling bonds
Covalent S does not





S-rich

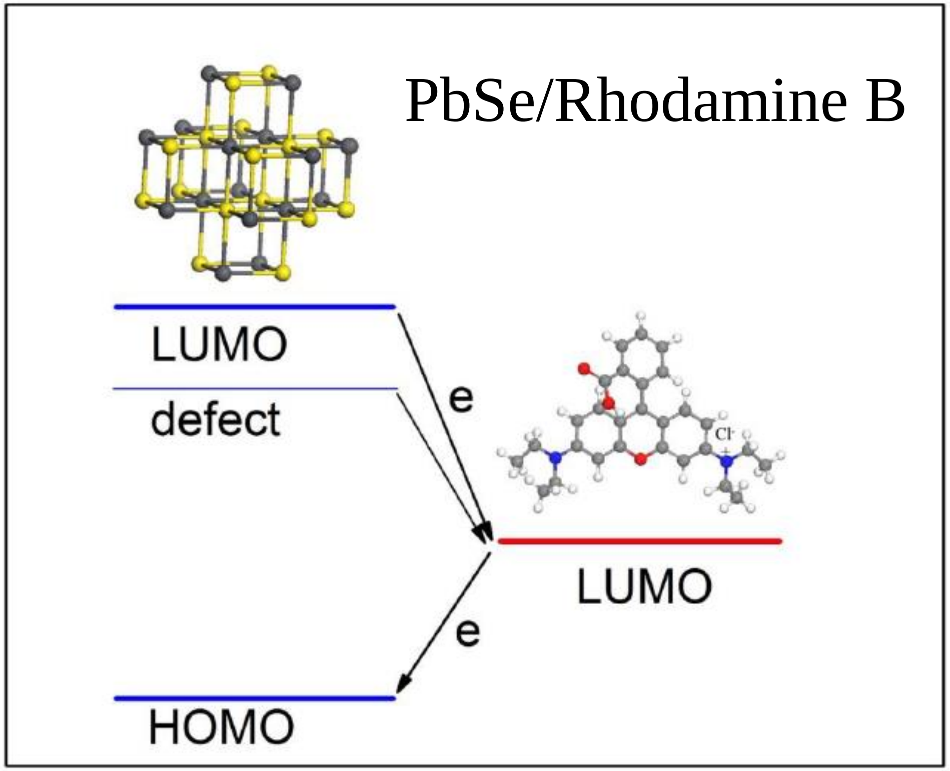


Cd-rich

Surface states facilitate non-radiative relaxation

Defects Help Charge Separation

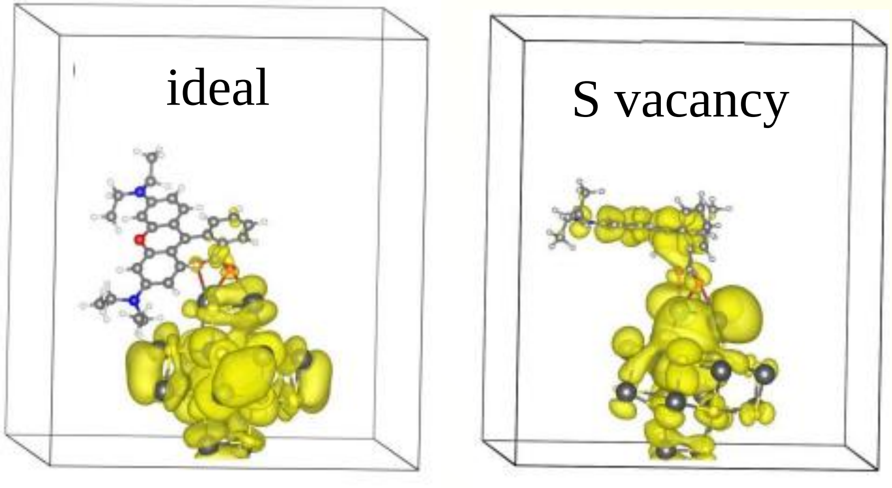
L. Run, N. English, O. V. Prezhdo *J. Am. Chem. Soc.* **135**, 18892 (2013)



Sulfur vacancy lowers donor-acceptor energy gap (20%) and increases NA coupling (factor of 2)

<u>ET time</u> (ps)

	forward	backward
Exp:	0.4	9
Ideal:	3.4	10
Defect:	1.0	



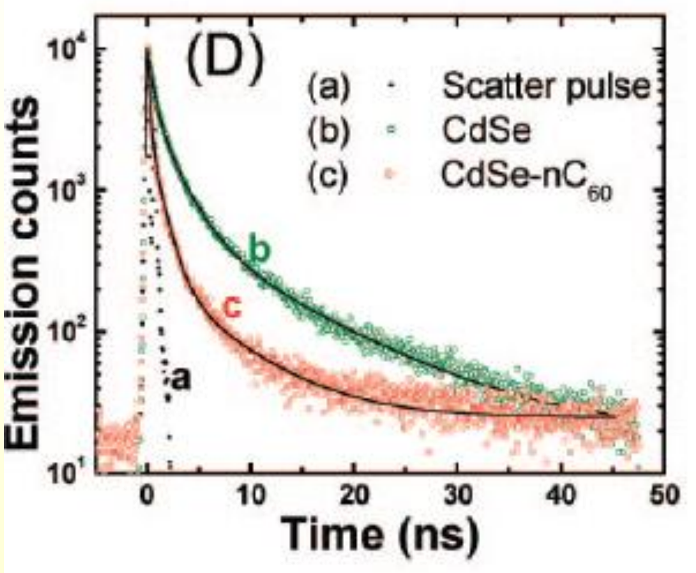
QD LUMO

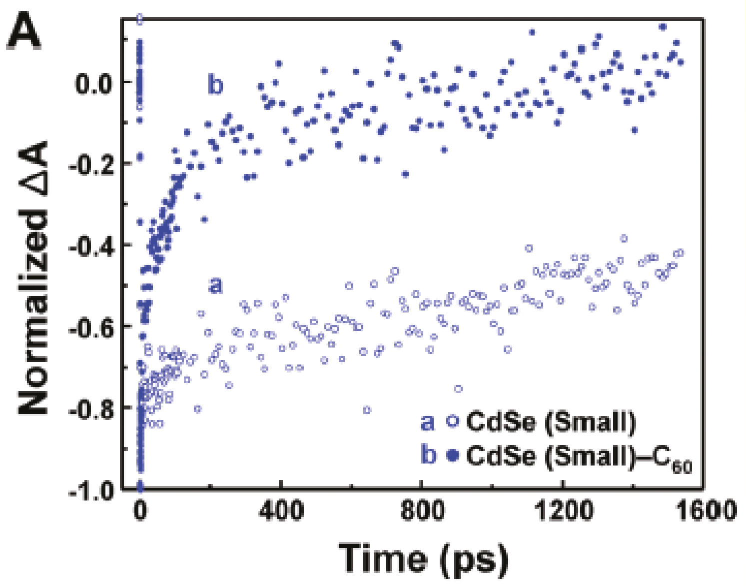
ET between CdSe QD and C_{60}

Chaban & Prezhdo, *J. Phys. Chem. Lett* **4**, 1 (2013)

Mechanical mixture: 10ns

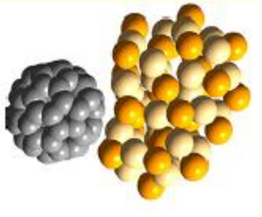
Bridged: 10-100ps



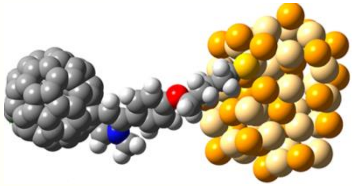


Brown & Kamat, *JACS* **130**, 8891 (2008)

Bang & Kamat, *ACS Nano* **12**, 9421 (2011)

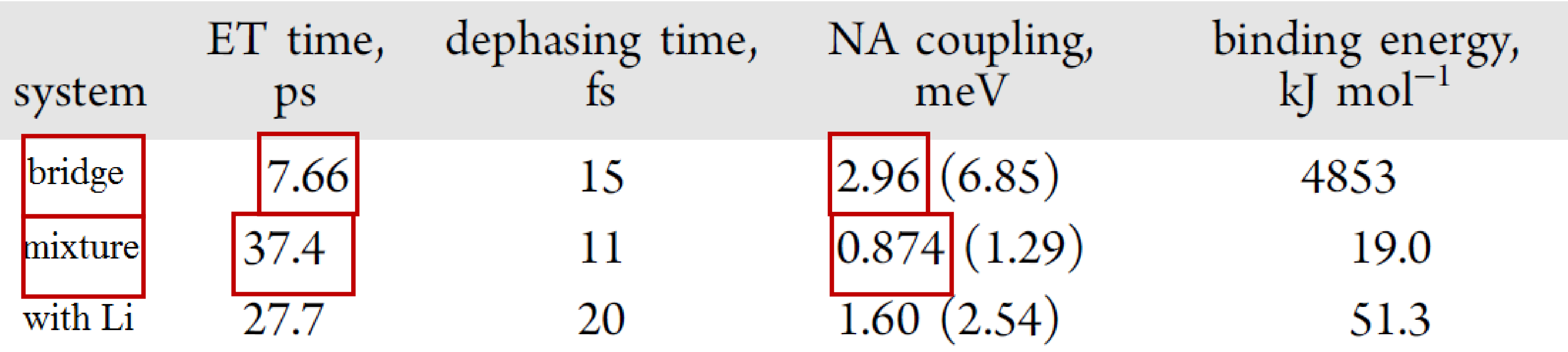


<= closer contact
faster dynamics =>

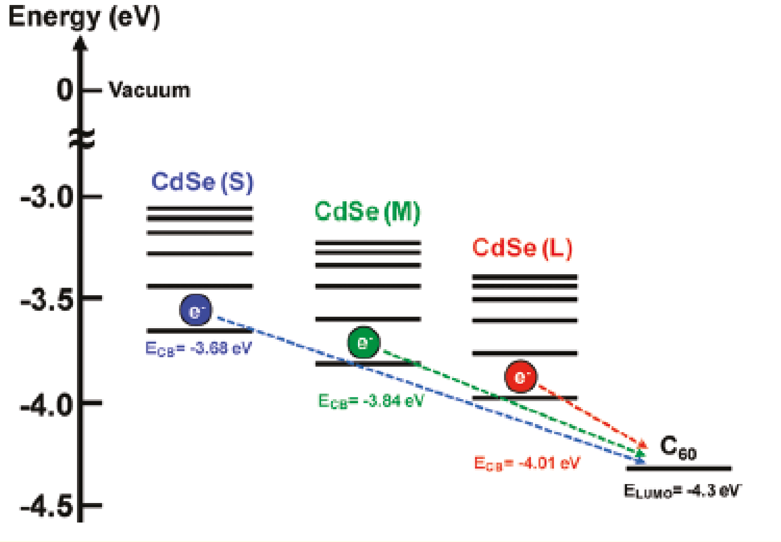


ET between CdSe QD and C$_{60}$

Chaban & Prezhdo, *J. Phys. Chem. Lett* **4**, 1 (2013)



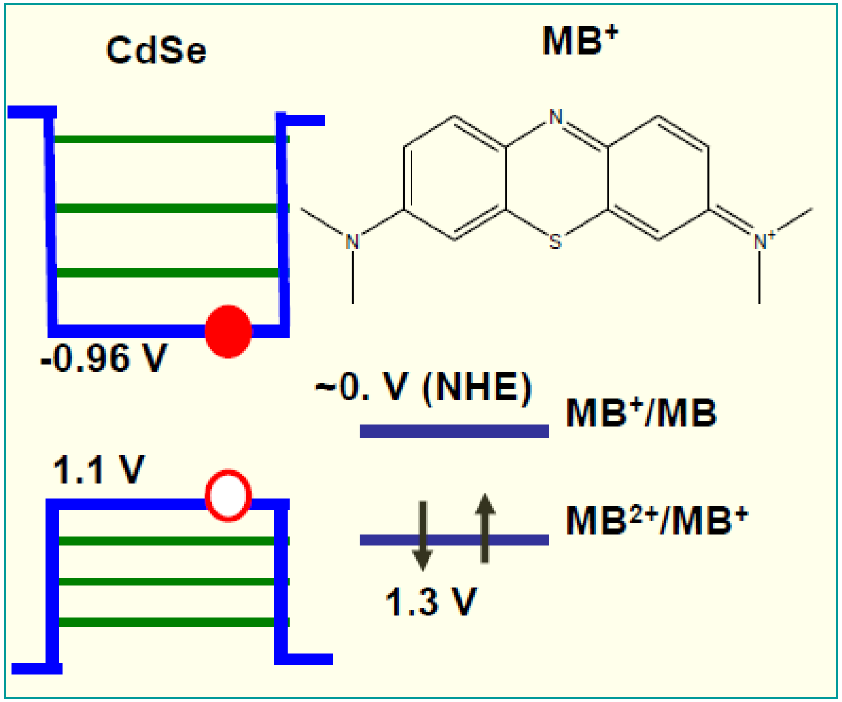
system	ET time, ps	dephasing time, fs	NA coupling, meV	binding energy, kJ mol^{-1}
bridge	7.66	15	2.96 (6.85)	4853
mixture	37.4	11	0.874 (1.29)	19.0
with Li	27.7	20	1.60 (2.54)	51.3

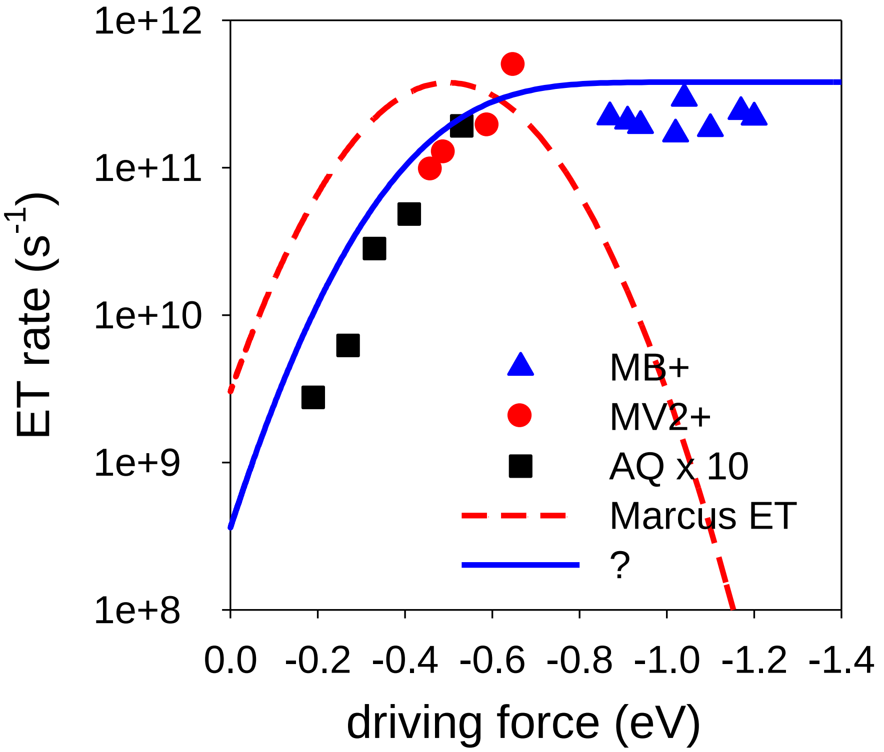


Bridge provides strong
NA electron-phonon coupling
needed to remove
excess electron energy

Auger-assisted ET

Zhu, Yang, Hyeon-Deuk, Califano, Song, Wang,
Zhang, Prezhdo, Lian, *Nano Lett.* **14**, 1263 (2014)



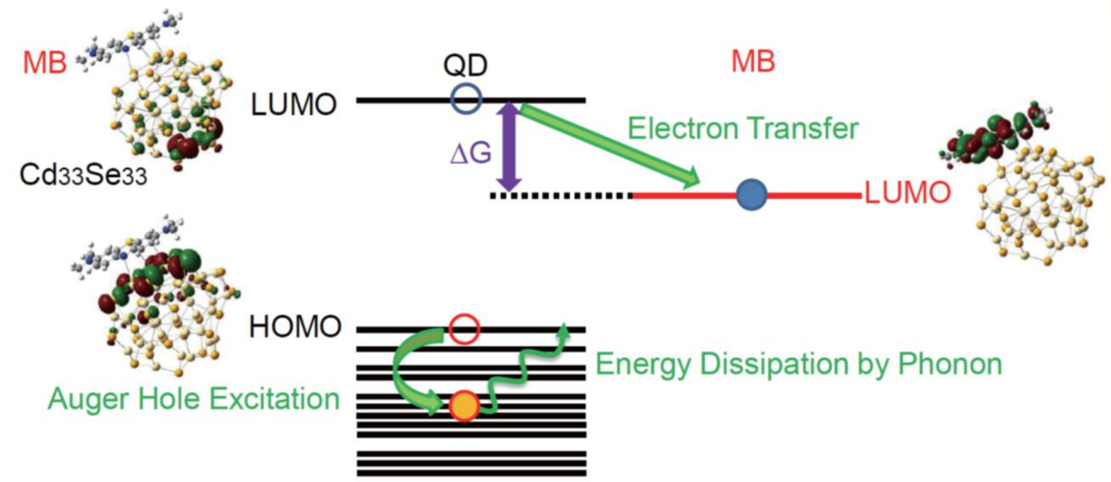


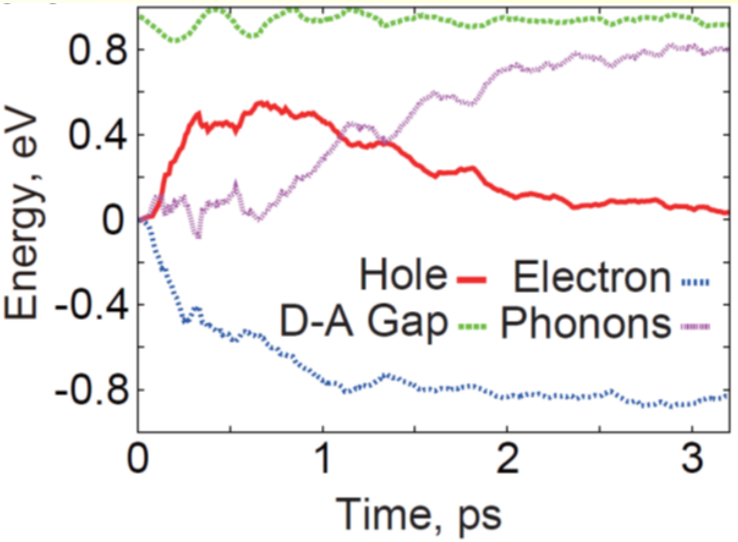
Why is there no Marcus inverted region?

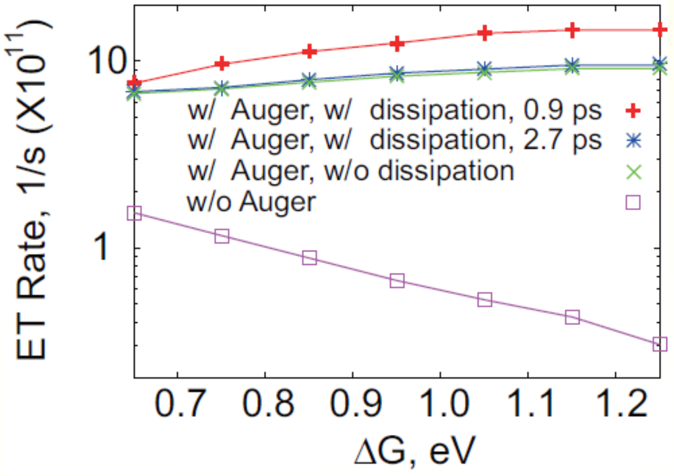
$$k(r) \propto e^{-\frac{[\Delta G(r)+\lambda]^2}{4\lambda RT}}$$

Auger-assisted ET

Zhu, Yang, Hyeon-Deuk, Califano, Song, Wang,
Zhang, Prezhdo, Lian, *Nano Lett.* **14**, 1263 (2014)



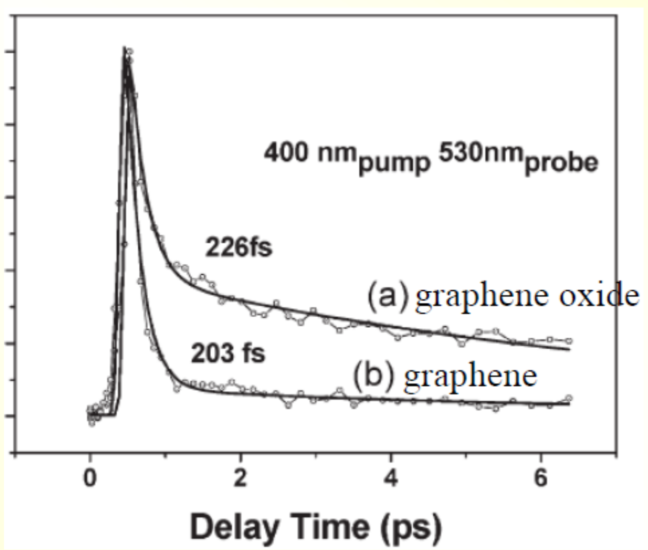




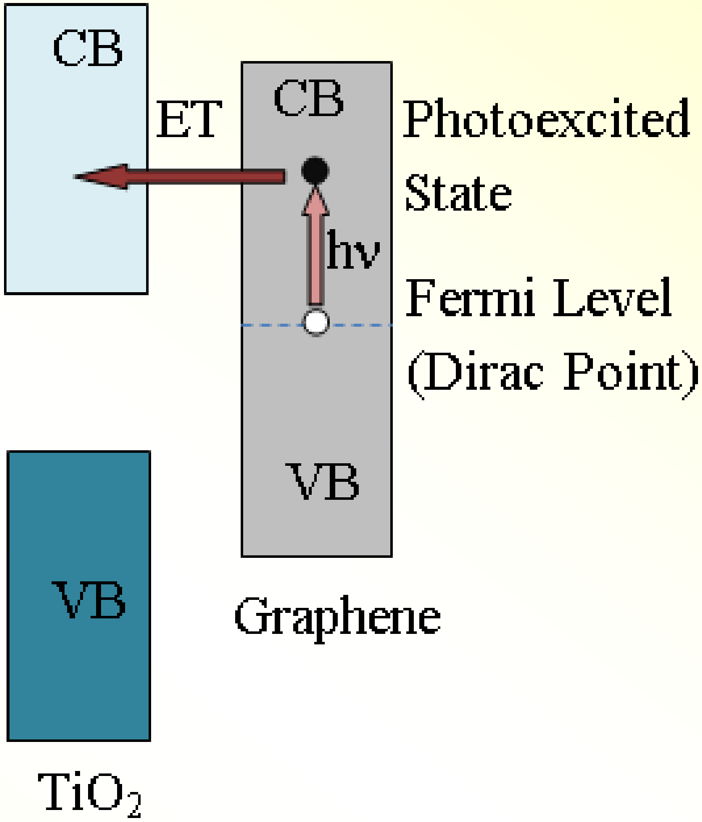
- Normally, excess energy goes to phonons
- In QDs, hole excitation accompanies ET
- Then, hole transfers energy to phonons

ET in Graphene-TiO_2

Long, English, Prezhdo *JACS* **134**, 14238 (2012)
chosen for *JACS* Spotlight



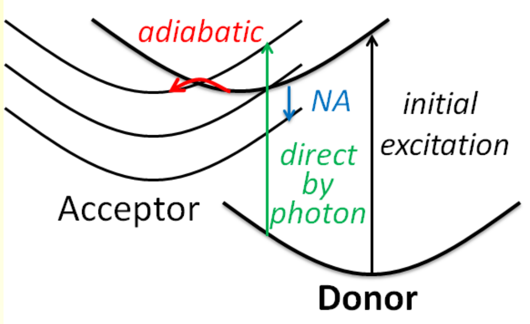
Manga, Zhou, Yan, Loh
Adv. Funct. Mat. **19** 3638 (2009)

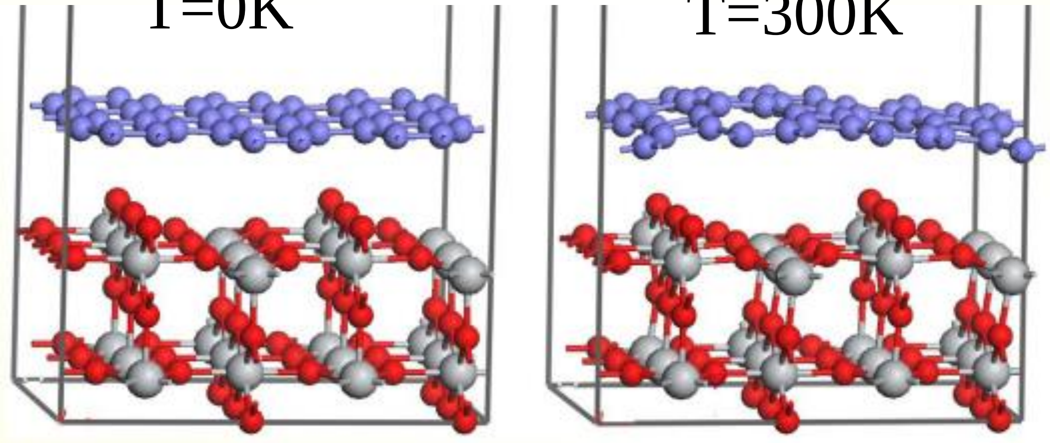


Graphene is an excellent hole conductor (e.g. no need for electrolyte),
However, it is a metal: electrons and holes can annihilate, not separate
Can electrons transfer into TiO_2 before they relax?

Graphene-TiO_2

Long, English, Prezhdo *JACS* **134**, 14238 (2012)
chosen for *JACS* Spotlight



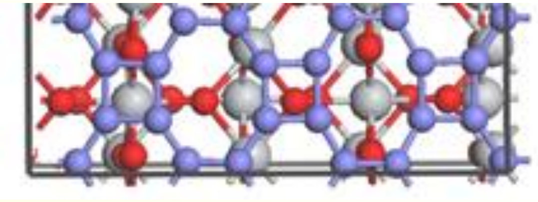


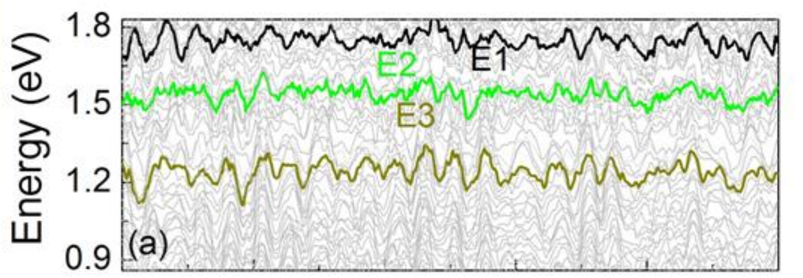
T=0K

T=300K

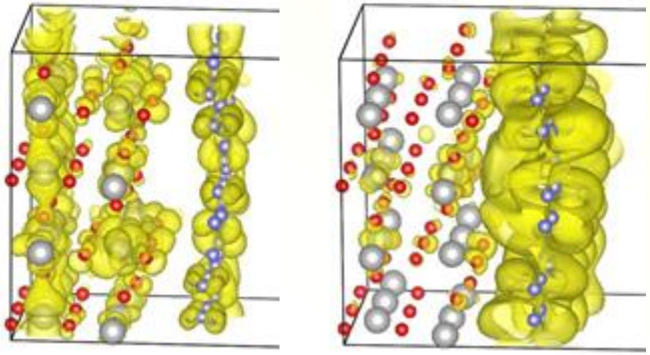
Chemisorption

at room T





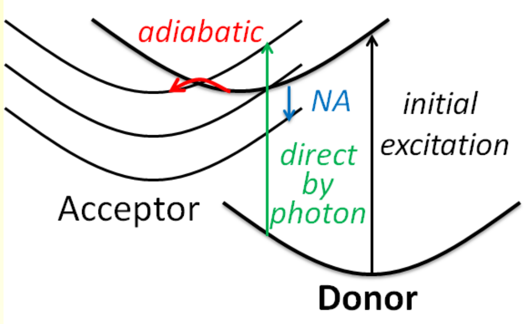
Photoexcited states

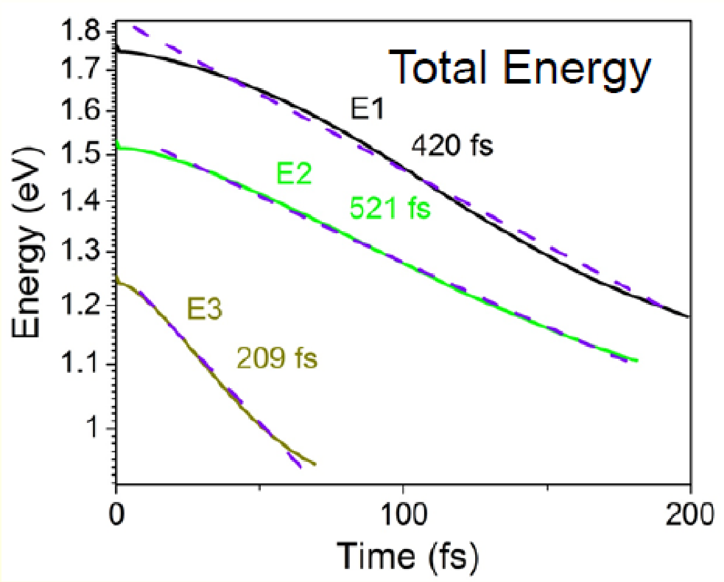


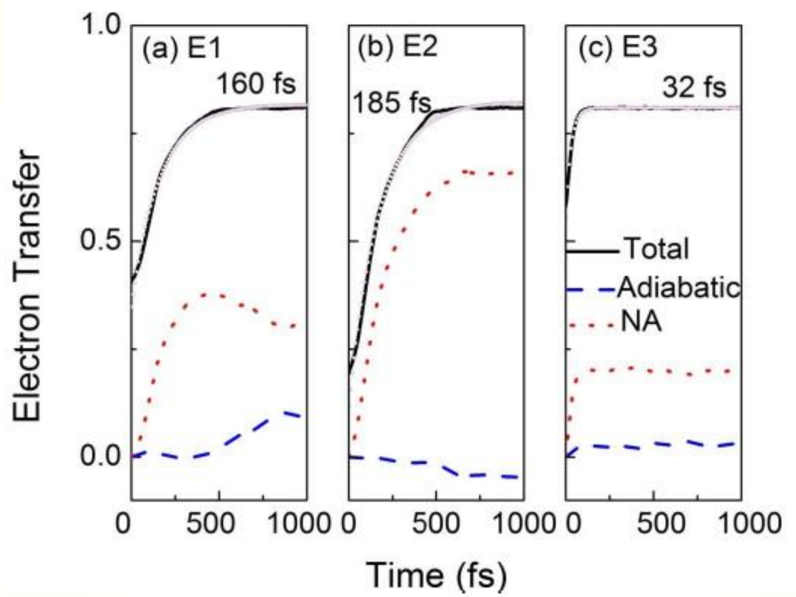
“Direct” ET

Graphene-TiO_2

Long, English, Prezhdo *JACS* **134**, 14238 (2012)
chosen for *JACS* Spotlight



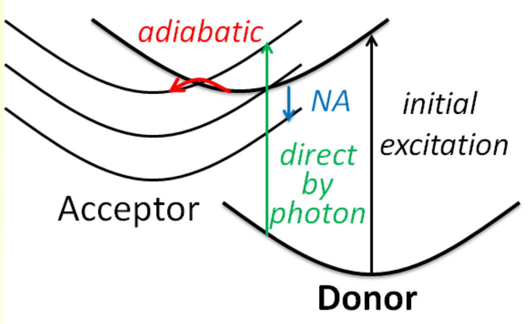


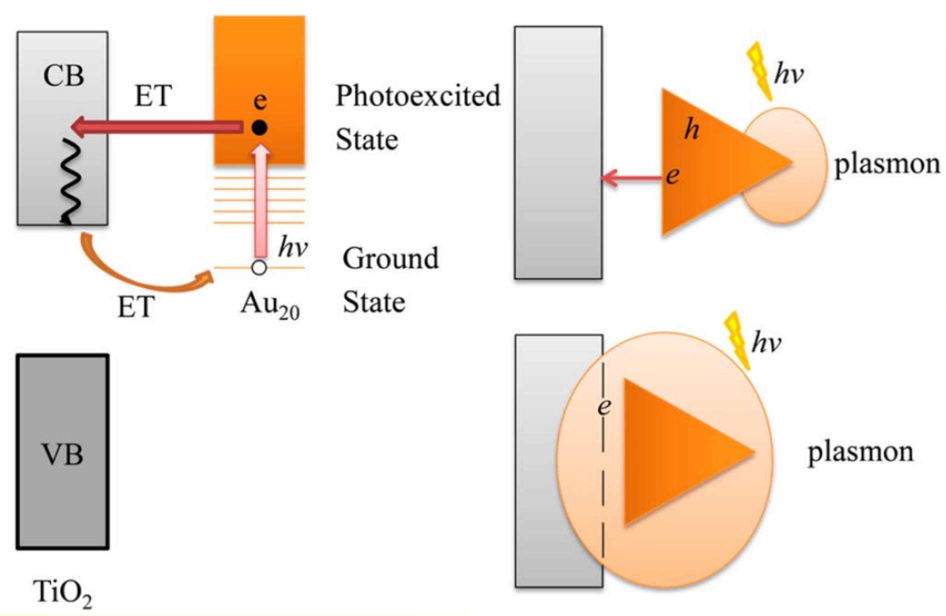


- ET consistently faster than energy loss
- Fast ET due to strong donor-acceptor coupling
- NA ET, though coupling is strong; dense state manifold
- 30-60% of direct ET, delocalized excited state

Plasmon-driven ET

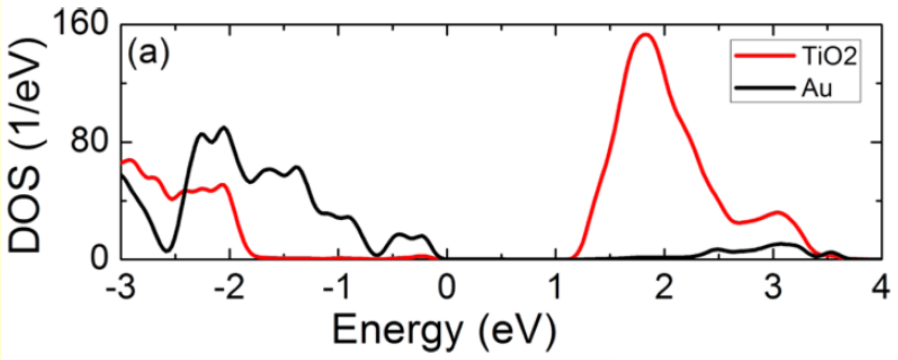
Long, English, Prezhdo *JACS* **136**, 4343 (2014)

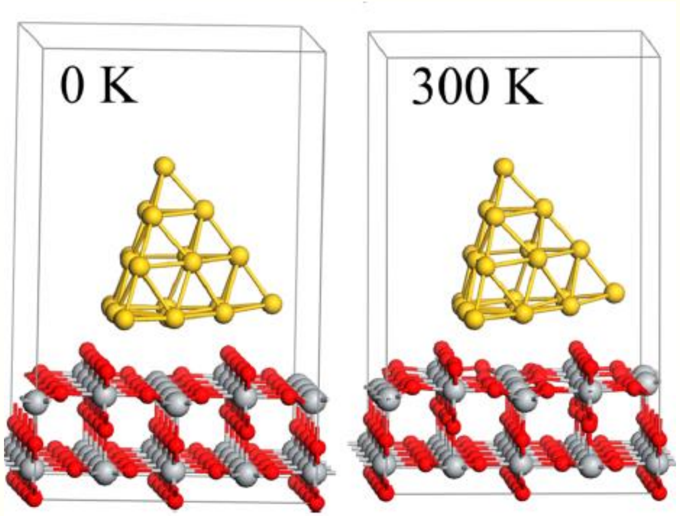




– traditional view

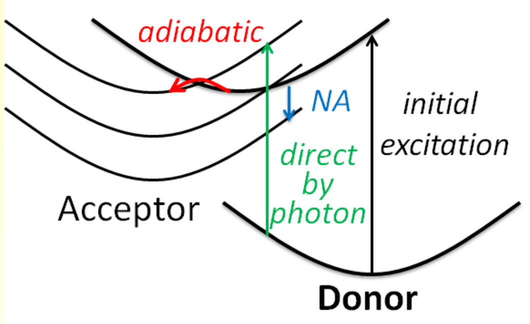
– our calculation

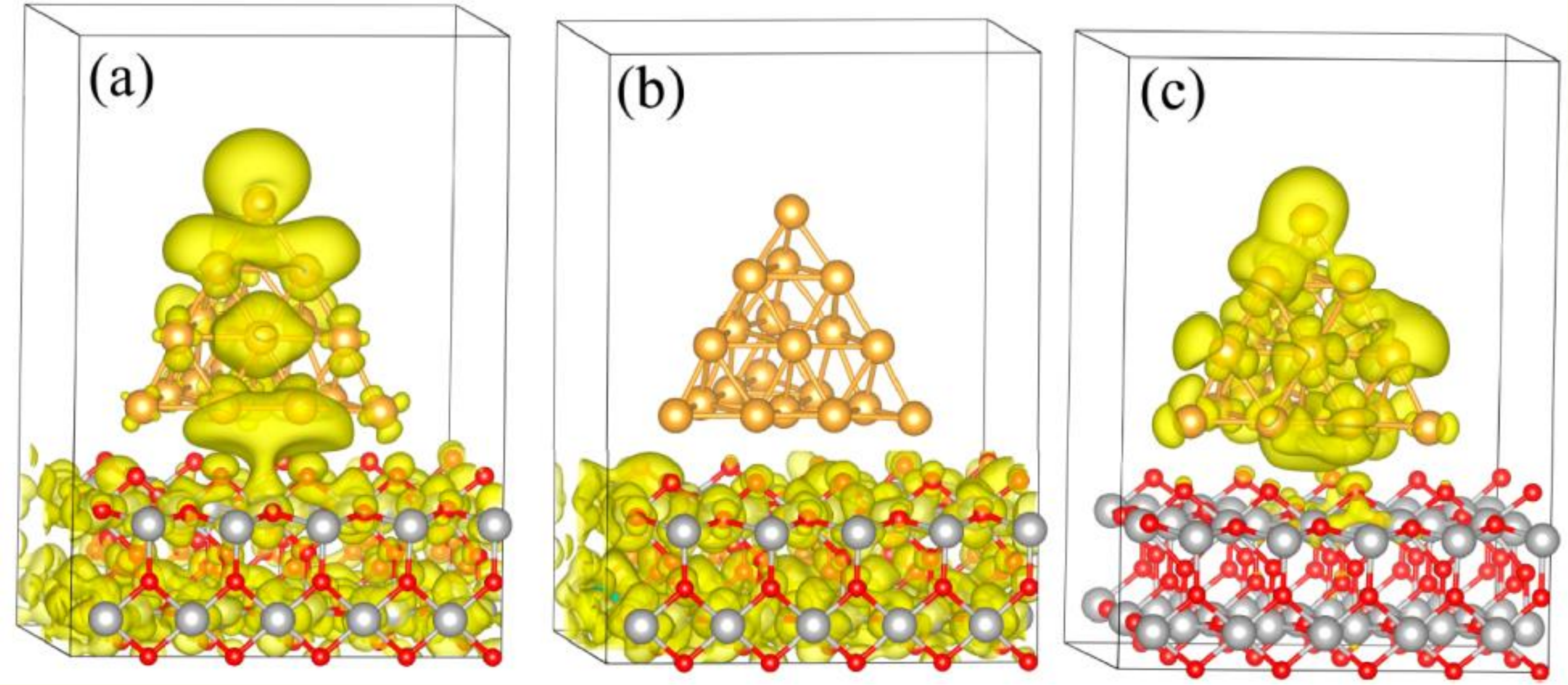




Plasmon-driven ET

Long, English, Prezhdo *JACS* **136**, 4343 (2014)





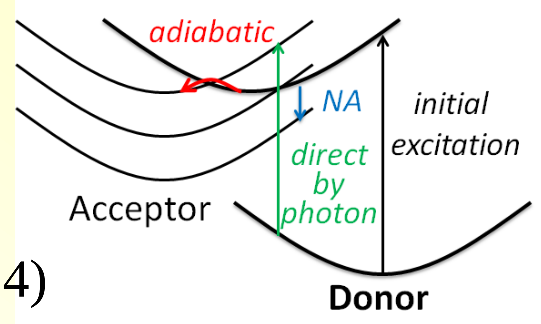
donor

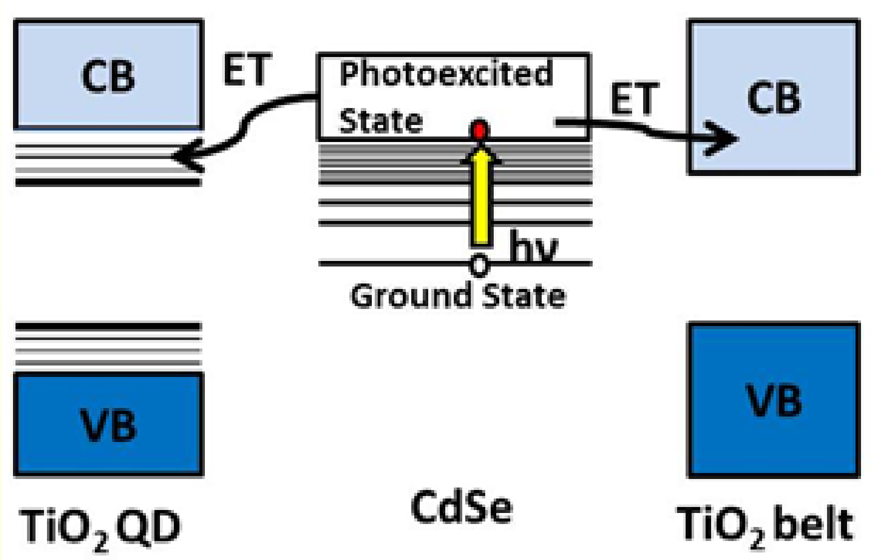
acceptor

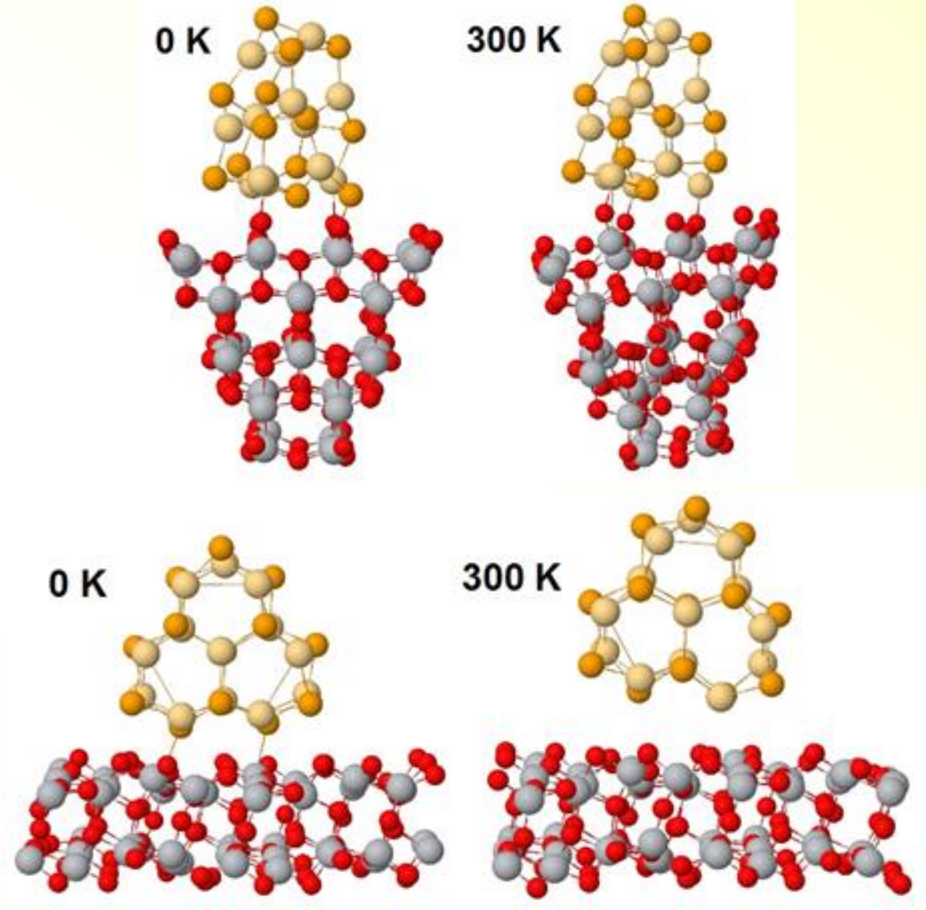
ground state

Dimensionality and ET Mechanism

Tafen, Long, Prezhdo *Nano Lett.* **14**, 1790 (2014)



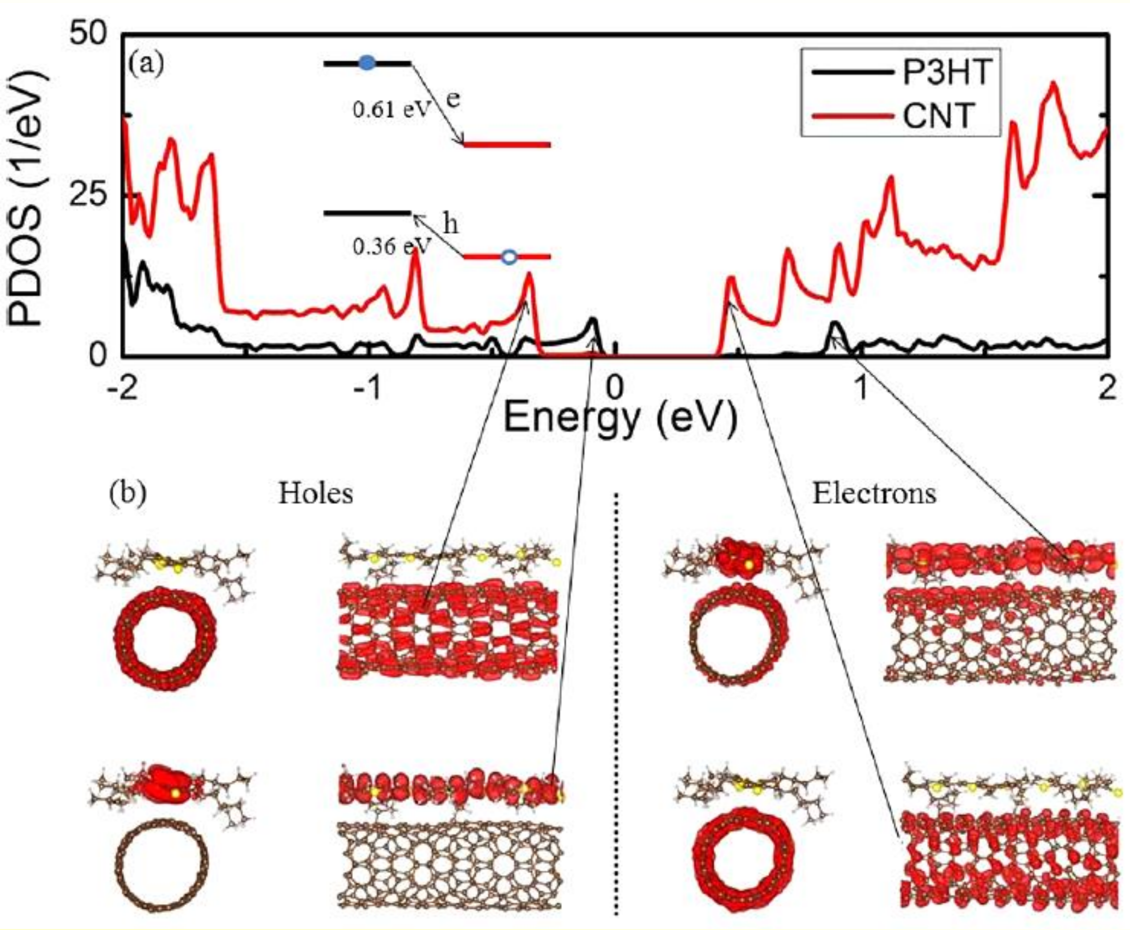


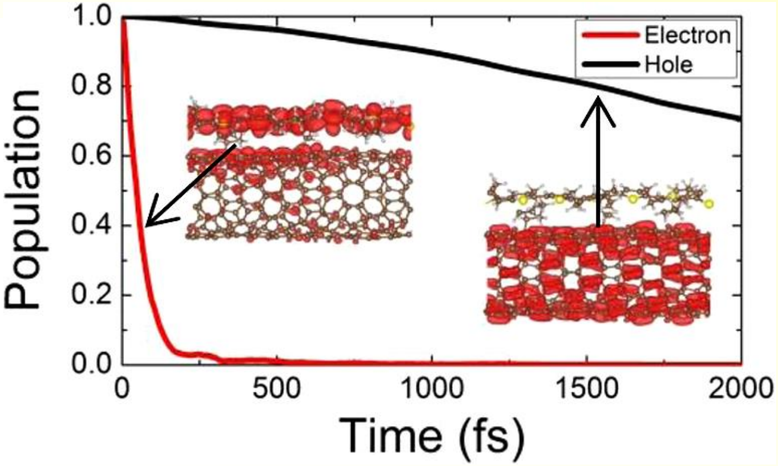


adiabatic	non-adiabatic
chemical bonding	weak coupling
low state density	high state density

CNT/Polymer Asymmetry

Long, Prezhdo *Nano Lett*, **14**, 3335 (2014)

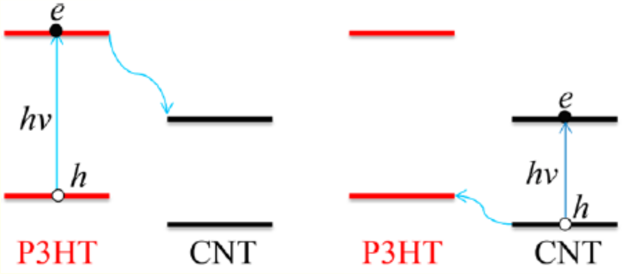


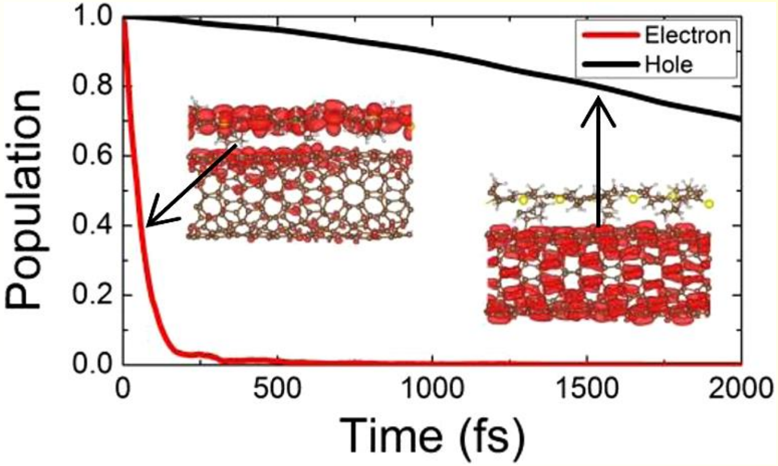


Much slower charge separation after CNT excitation: smaller acceptor DOS

CNT/Polymer Asymmetry

Long, Prezhdo *Nano Lett*, **14**, 3335 (2014)





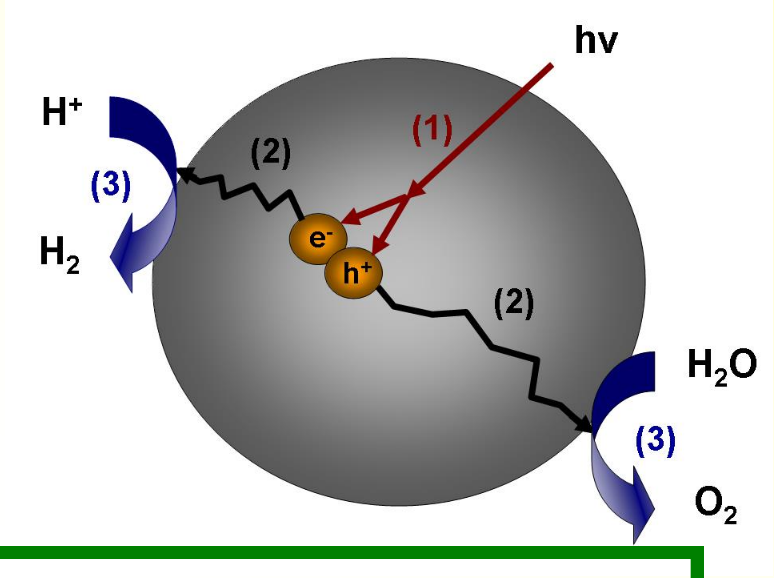
More CNT: harvest broader light spectrum; reduce energy/voltage losses
More P3HT: better charge separation and higher current

Photocatalytic water splitting

Akimov, Muckerman, Prezhdo *JACS*, **2013**, 135, 8682

Solar (renewable) fuel – photocatalytic water splitting:

$$2H_2O \rightarrow 2H_2 + O_2$$

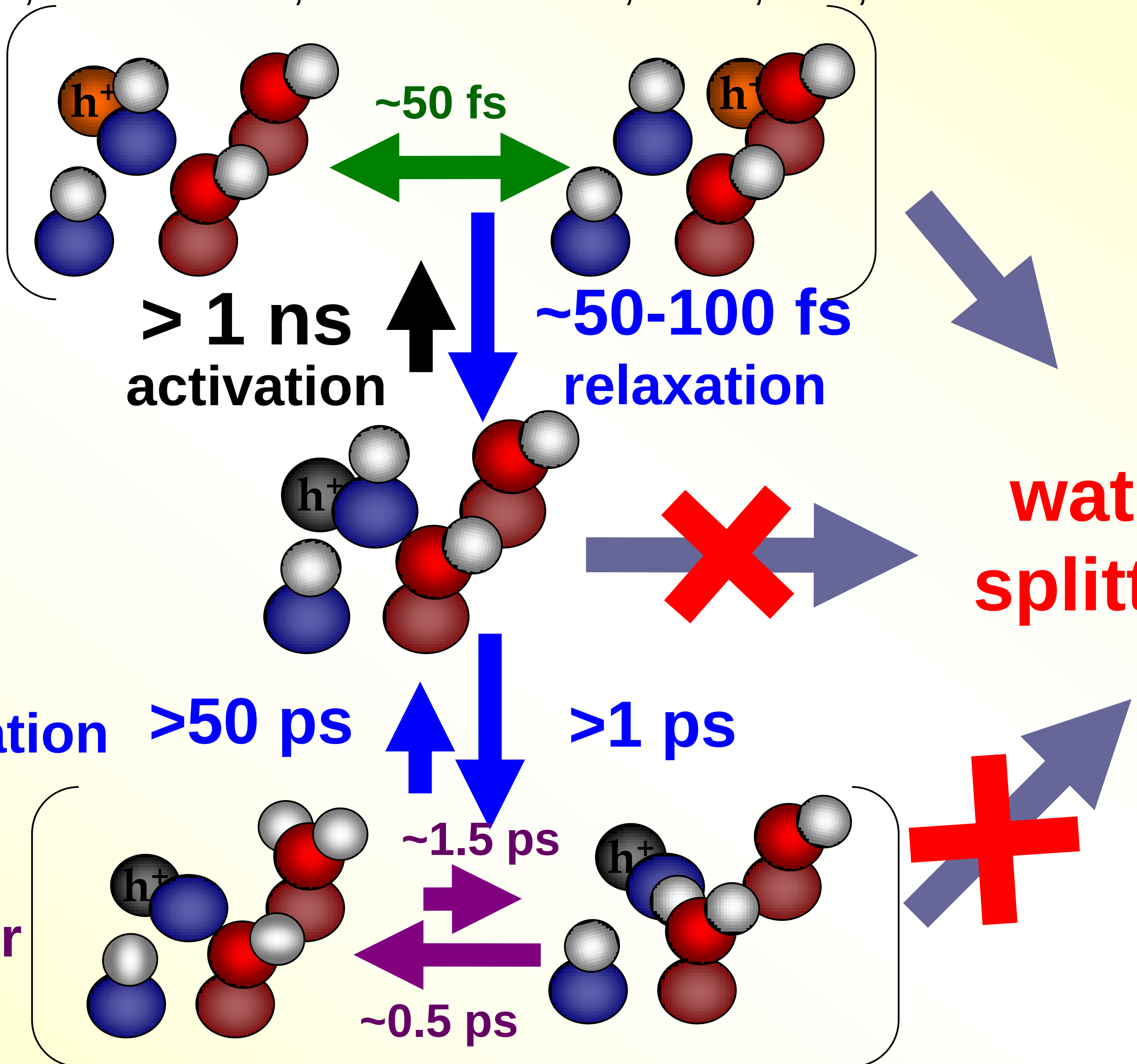


Materials: GaN (UV), GaN:ZnO (visible light); still not optimal

- what is the ***dynamics of the photohole*** in GaN/water?
- how does it affect the ***efficiency*** of the photocatalytic water splitting?

Comprehensive Kinetics

Akimov, Muckerman, Prezhdo *JACS*, **2013**, 135, 8682



Hole generation/ migration

~50 fs

> 1 ns
activation

~50-100 fs
relaxation

water splitting

N-H deprotonation

>50 ps

>1 ps

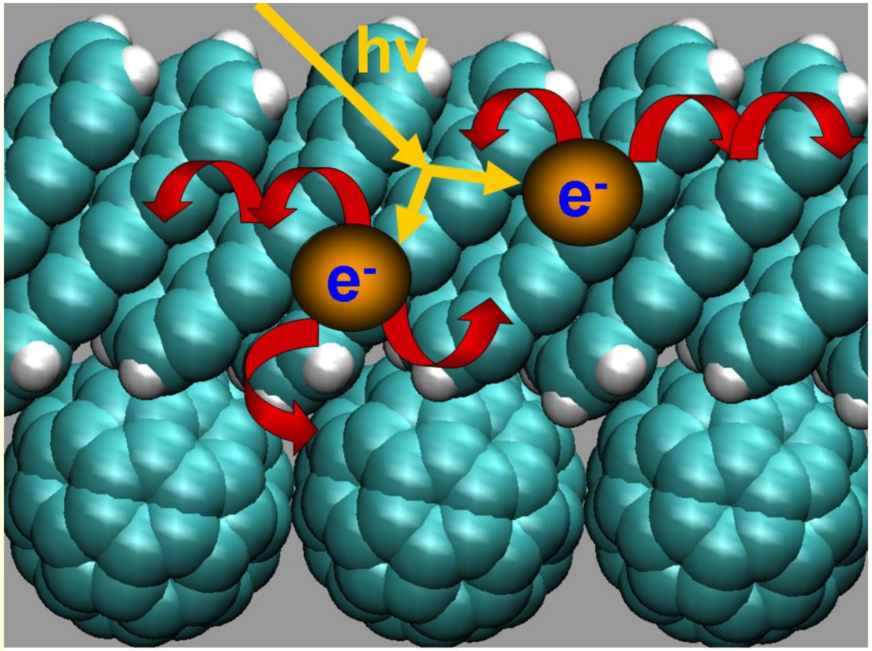
~1.5 ps

Proton transfer

~0.5 ps

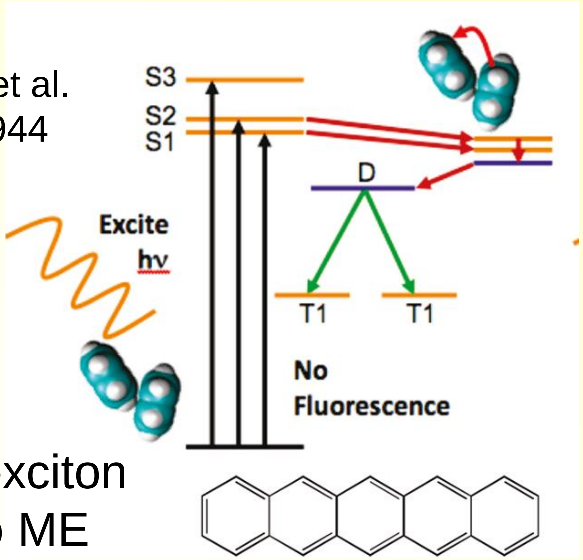
Singlet fission

Akimov, Prezhdo
JACS, **2014**, 136, 1599



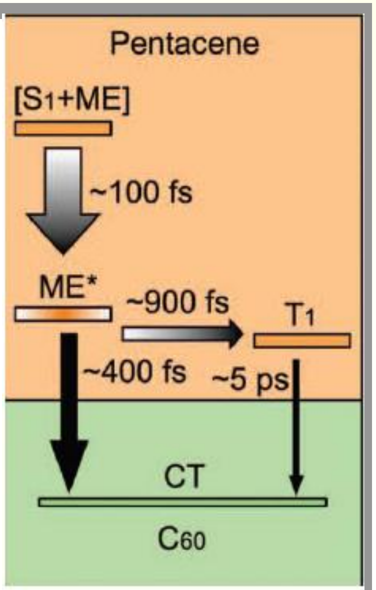
1 photon = 2 electrons:
max ~44%

Theory: Zimmerman et al.
JACS **2011**, 133, 19944



spontaneous S_1 exciton localization into ME

Experiment: Chan et al.
Science **2011**, 334, 1541



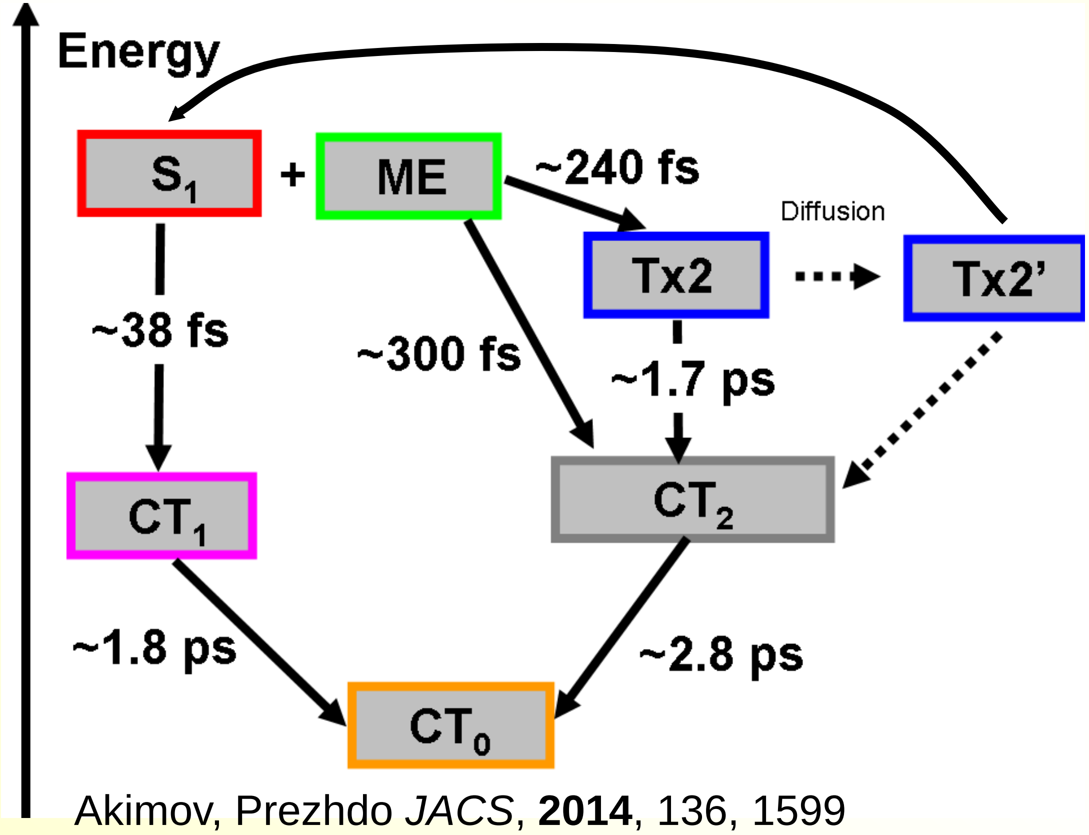
observation of ME

ME does not originate from S1

initial state is a superposition of S1 and ME

Comprehensive Kinetics

Akimov, Prezhdo *JACS*, **2014**, 136, 1599



Akimov, Prezhdo *JACS*, **2014**, 136, 1599

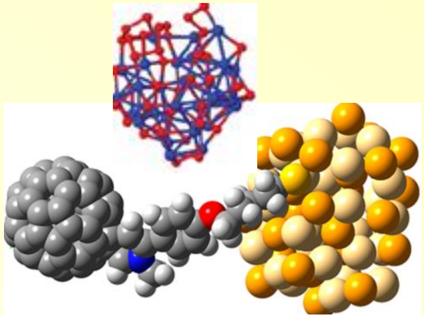
1) Reproduce experimental timescales
2) CT competes with SF, reducing efficiency
3) Intermediate ME and CT states are important
4) S_1 to ME transition is slow
5) Resolved inconsistency in energy alignment, CT_0

SF photovoltaic design principles

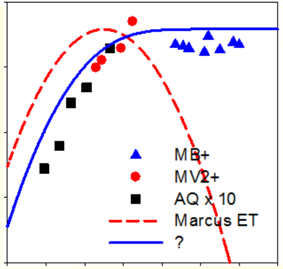
S_1 and ME should be coupled during photoexcitation

Thick pentacene layer slows down CT, allowing SF to happen

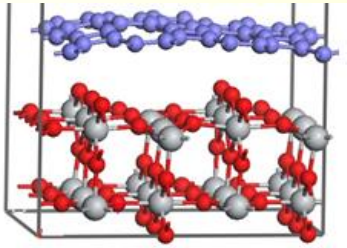
In Lieu of Conclusions

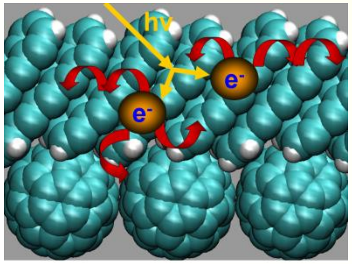


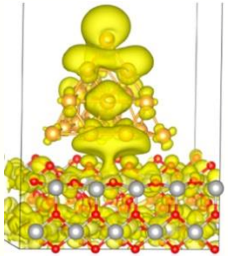
- Nonadiabatic Molecular Dynamics & Time-Dependent Density Functional Theory

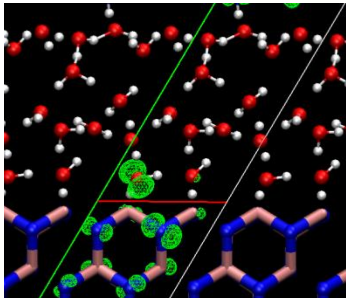


- Applications
  - Are defects good or bad for QD applications?
  - Why long bridge accelerates ET from QD to C_{60}?
  - Lack of Marcus inverted regime – Auger assisted ET
  - Why graphene (metal!) can be used as light-harvester?
  - Instantaneous plasmon-driven ET
  - Dimensionality and ET mechanism
  - Exploiting asymmetry of ET in CNT/polymer systems
  - Why H_2O splitting is not efficient on GaN?
  - Singlet fission vs. charge transfer?







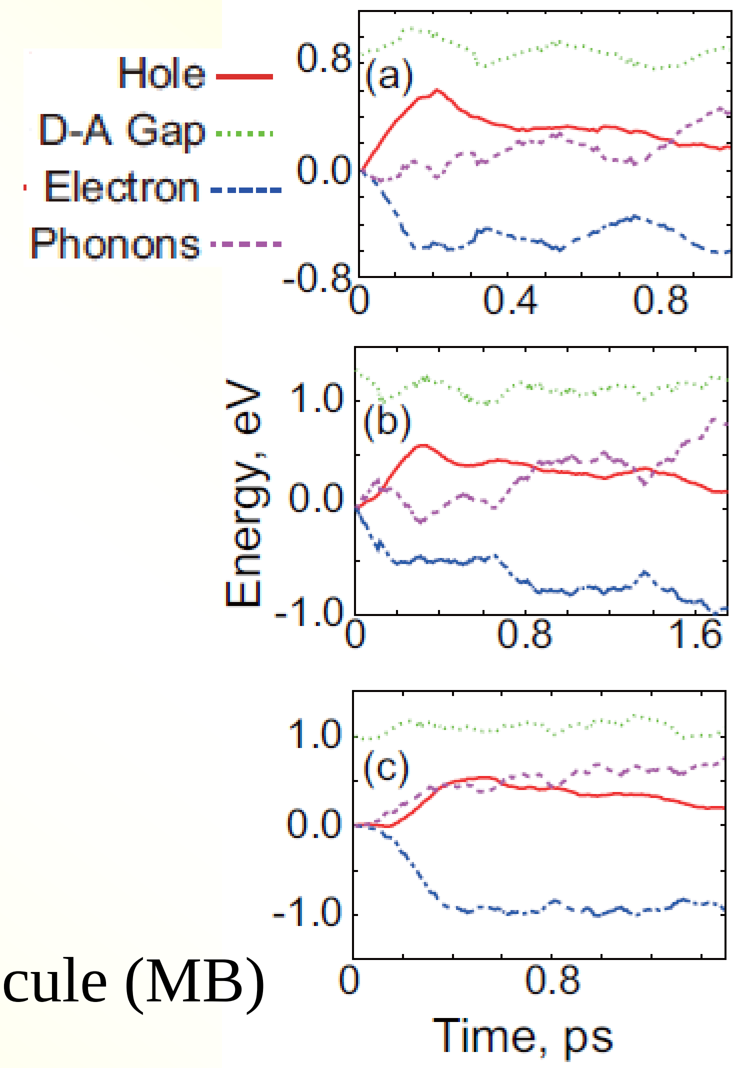


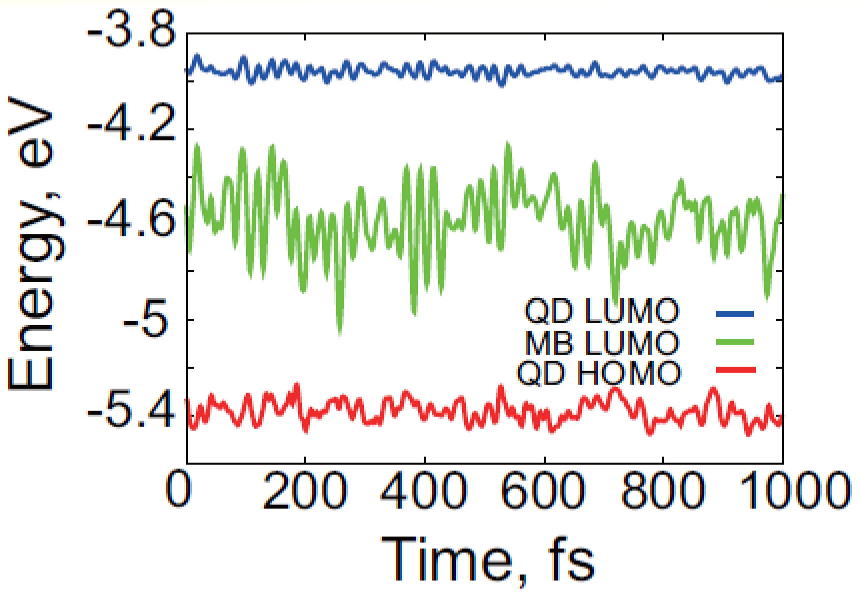

USC

Auger-assisted ET

Zhu, Yang, Hyeon-Deuk, Califano, Song, Wang,
Zhang, Prezhdo, Lian, *Nano Lett.* **14**, 1263 (2014)

(a) Electron-hole, then phonons
(b) Phonons important initially
(c) Hole and phonons equally important

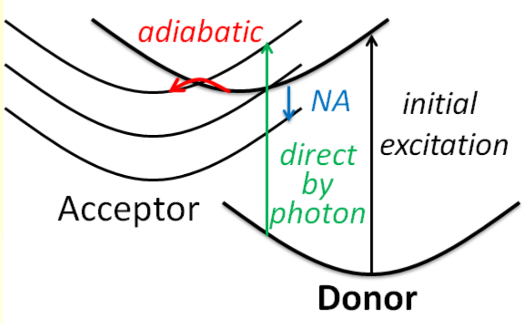


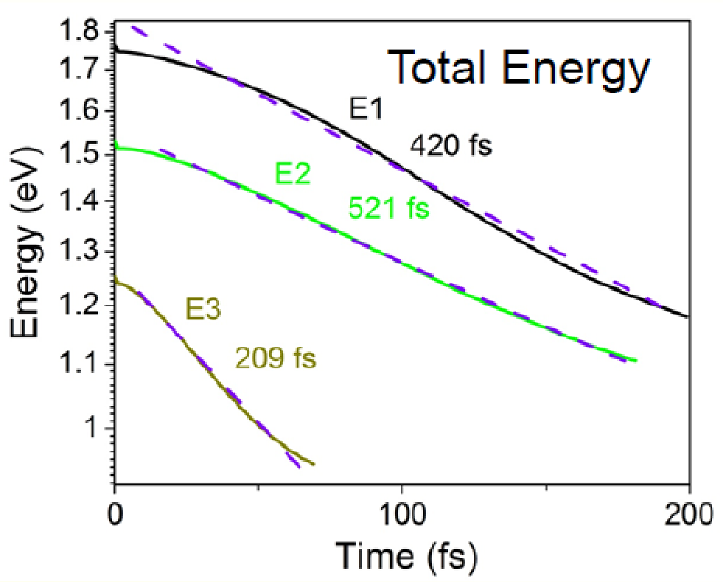


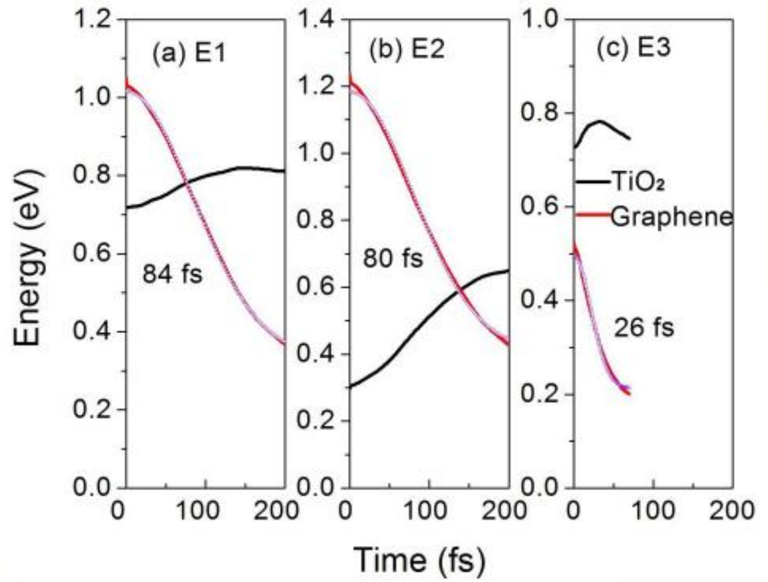
Strong electron-phonon coupling in molecule (MB)

Graphene-TiO_2

Long, English, Prezhdo *JACS* **134**, 14238 (2012)
chosen for *JACS* Spotlight



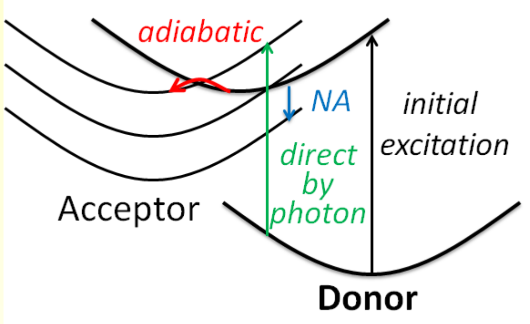


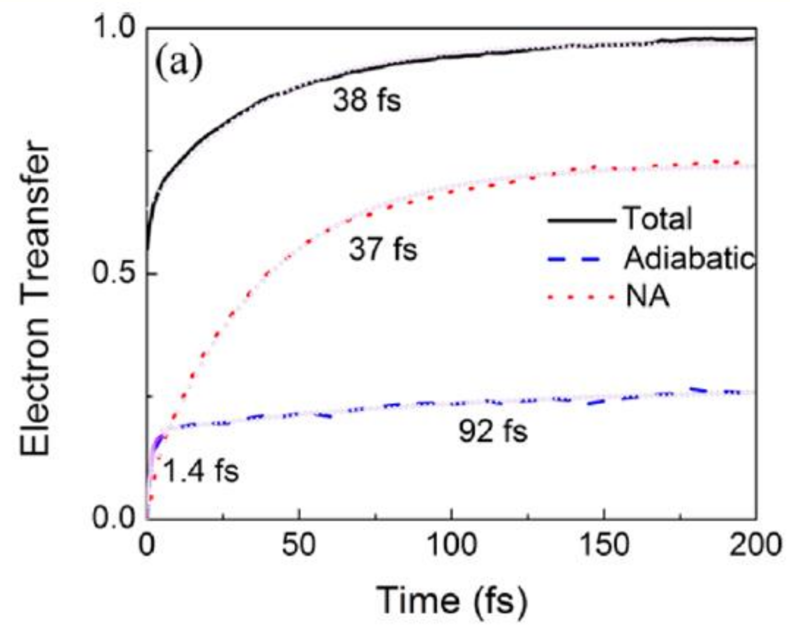


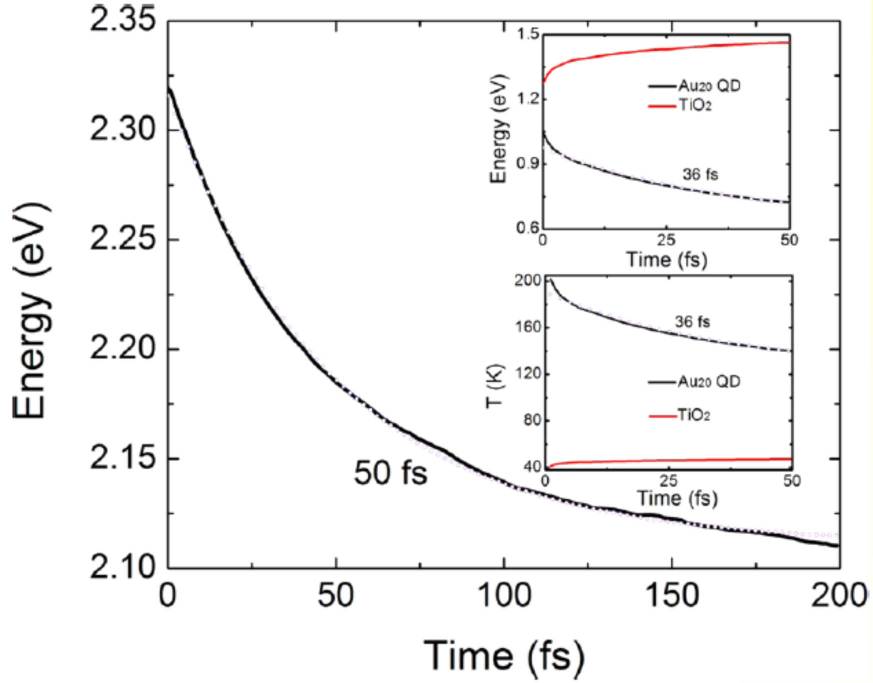
- TiO_2 heats up transiently
- Sub-100fs relaxation in graphene

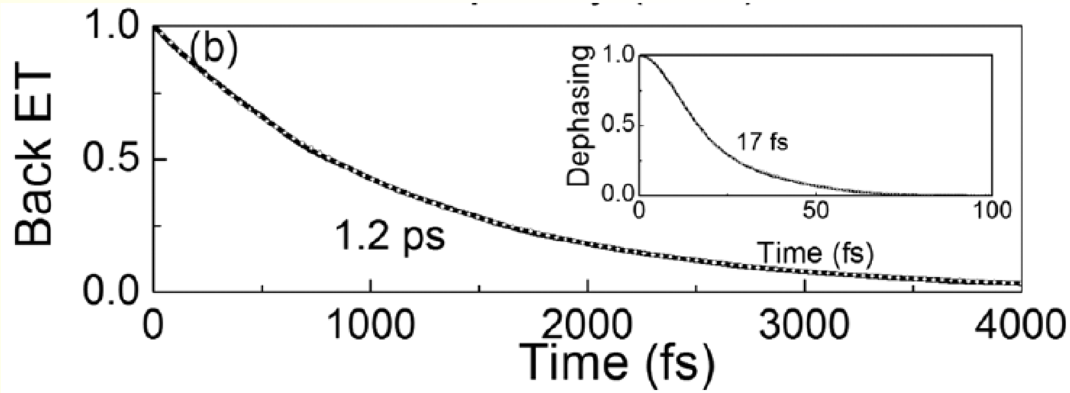
Plasmon-driven ET

Long, English, Prezhdo *JACS* **136**, 4343 (2014)



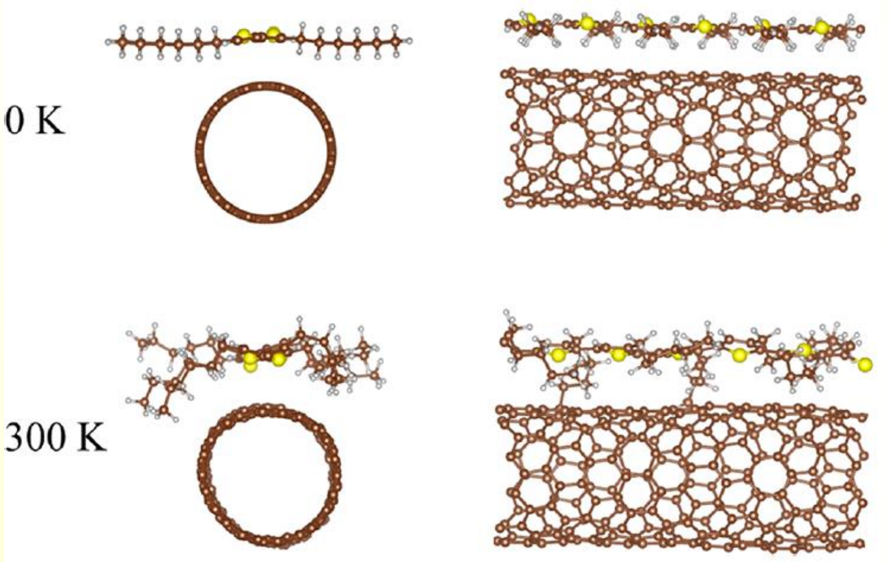


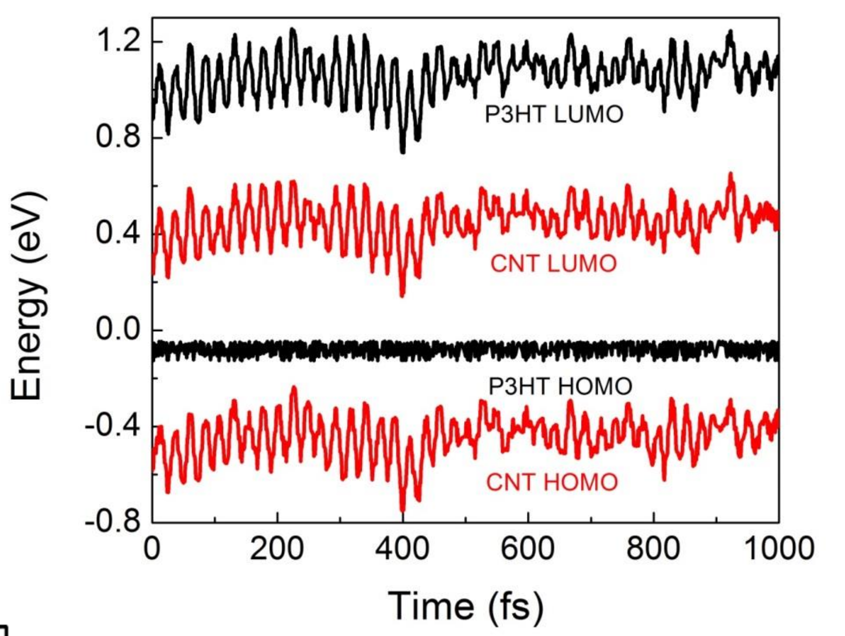


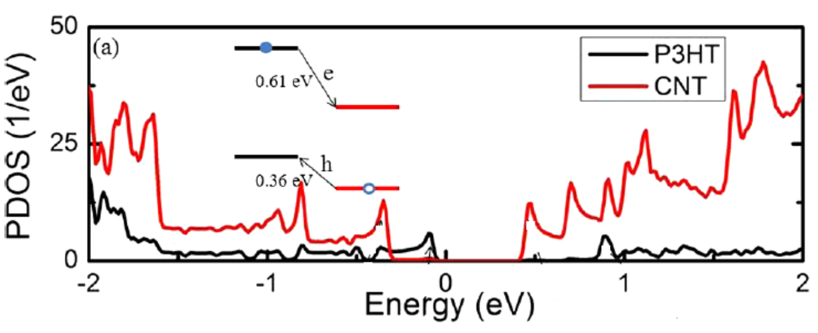


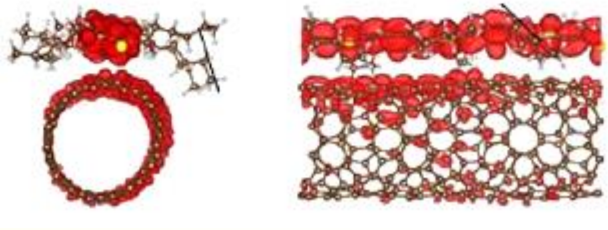
CNT/Polymer Asymmetry

Long, Prezhdo *Nano Lett*, in press









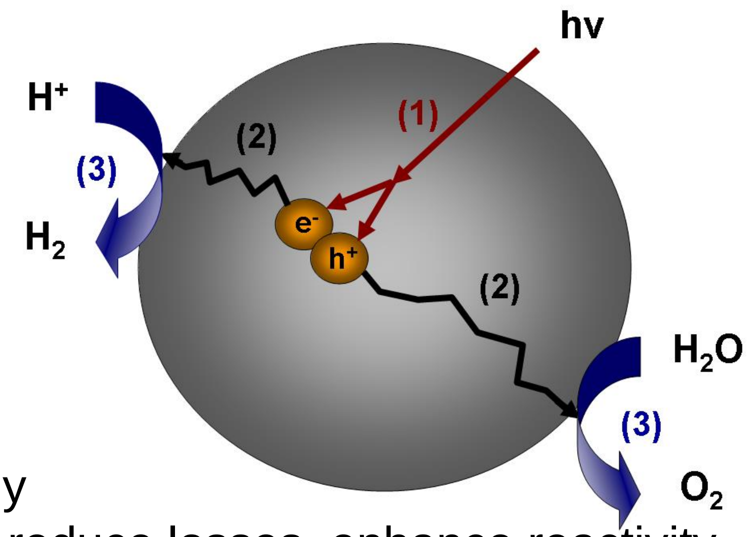
P3HT HOMO

Photocatalytic water splitting

Solar (renewable) fuel – photocatalytic water splitting:

$$2H_2O \rightarrow 2H_2 + O_2$$

Materials: GaN (UV), GaN:ZnO (visible light); still not optimal



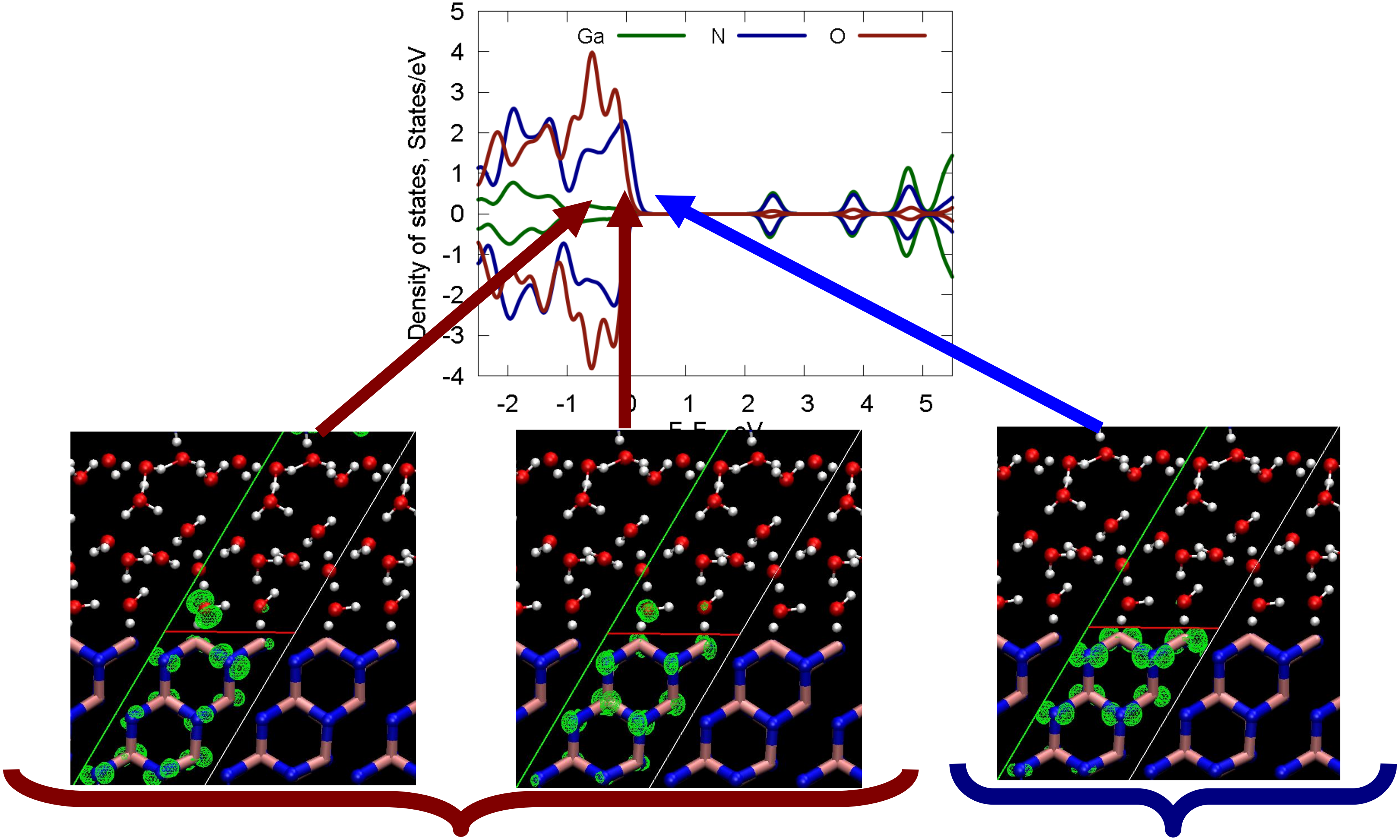
Principles for material search/optimization:

- Light absorption – ability to absorb max energy
- Material properties (surface, purity, defects) – reduce losses, enhance reactivity
- Band edge position – proper Red/Ox potential
- Nanotechnology (core/shell) – reduce products recombination

- what is the ***dynamics of the photohole*** in GaN/water?
- how does it affect the ***efficiency*** of the photocatalytic water splitting?

Hole states

fixed geometry, but different energy levels

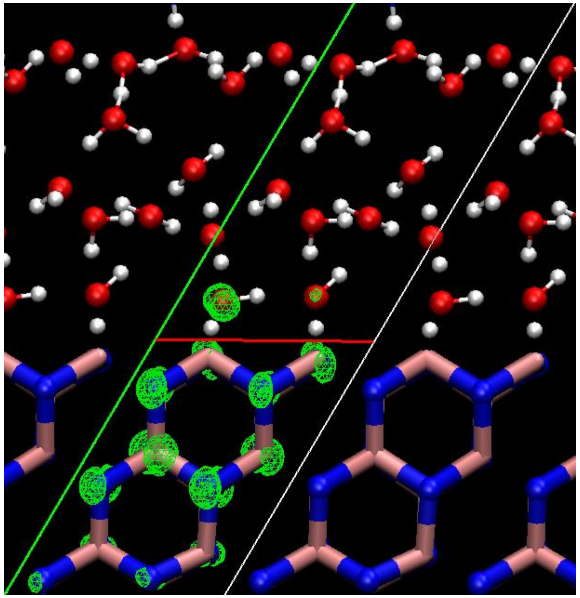


$E_h > 0$: hole on N and O

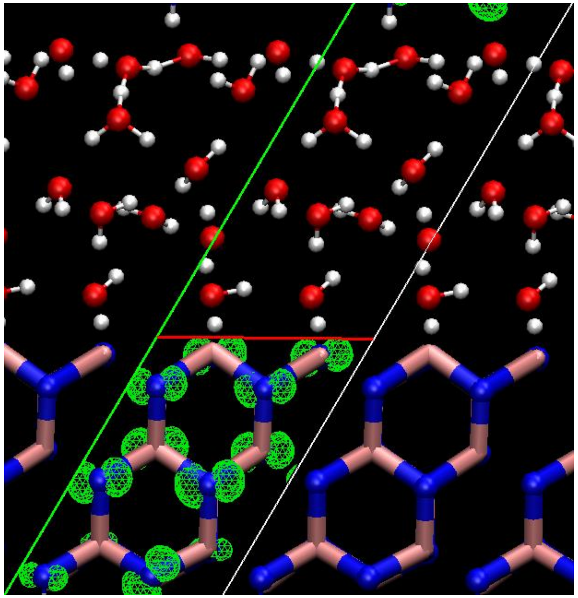
$E_h = 0$: hole only on N

Hole diffusion

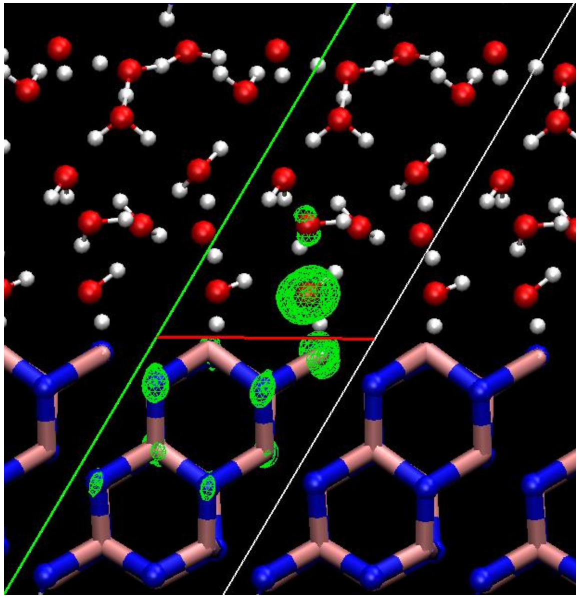
fixed energy level, but different geometries



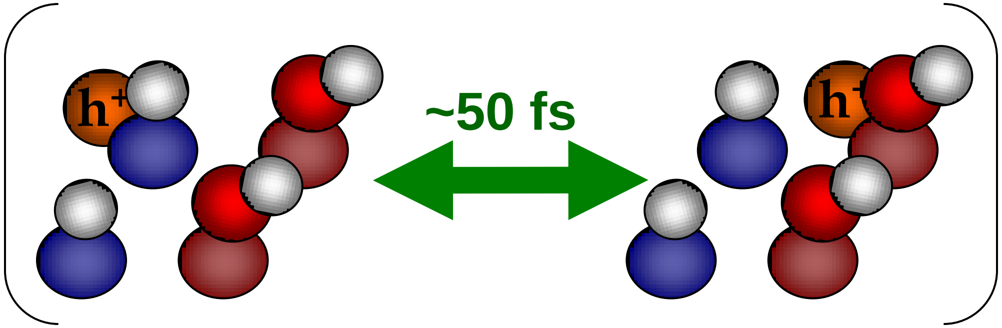
t = 0 fs



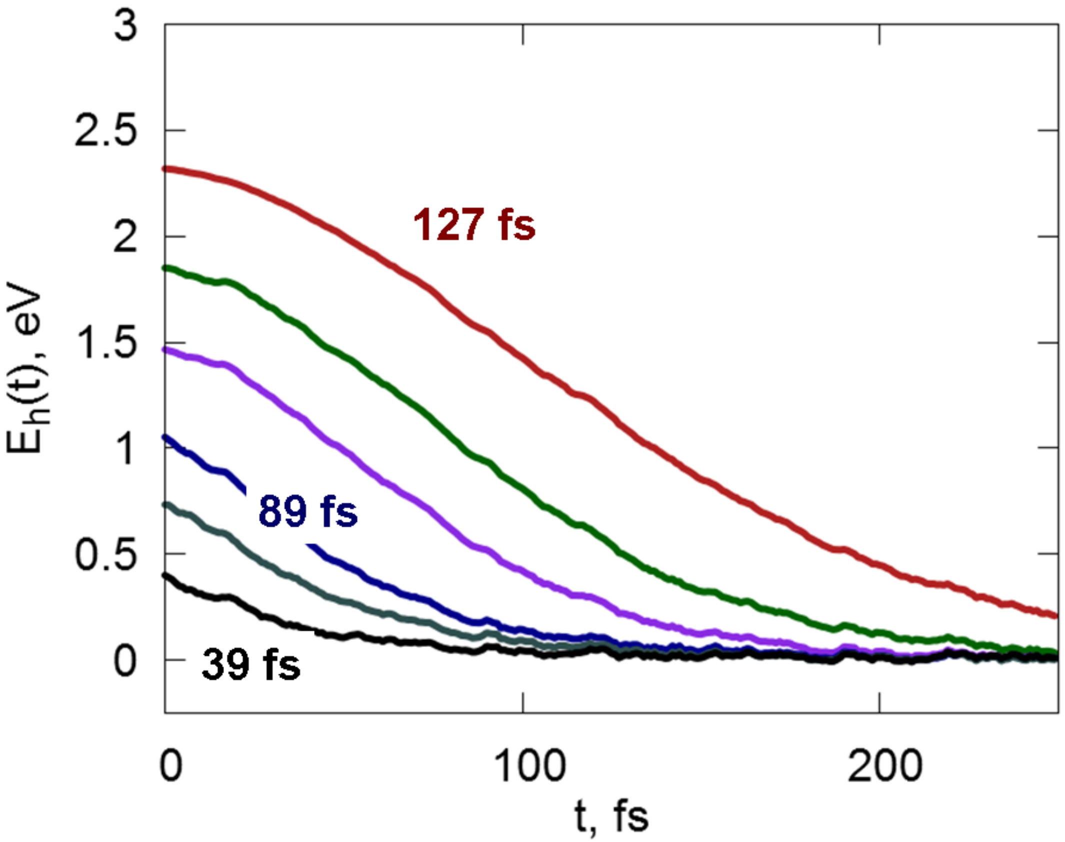
t = 50 fs



t = 100 fs



Hole energy relaxation



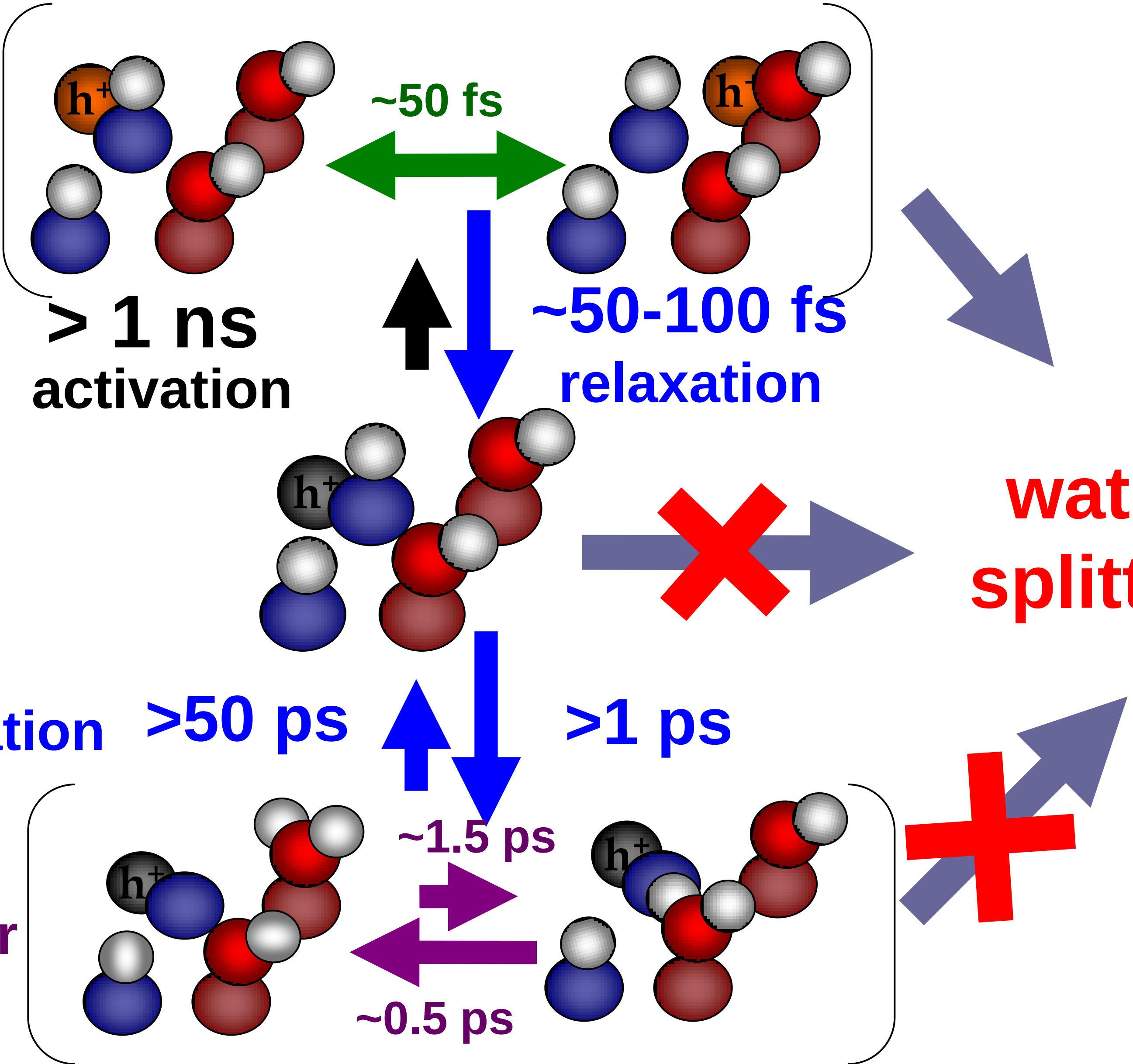
$$E_h(t) = \sum_i \varepsilon_i(t) \left| c_i(t) \right|^2$$

1. Relaxation on the ~50-100 fs time scale
2. Hole only transiently populates O-containing species
3. Eventually ends up on N

What is next?

Summary

Akimov, Muckerman, Prezhdo *JACS*, **2013**, 135, 8682



Hole generation/ migration

~50 fs

> 1 ns activation

~50-100 fs relaxation

water splitting

N-H deprotonation

>50 ps

>1 ps

~1.5 ps

Proton transfer

~0.5 ps

Photocatalyst design

Material should:

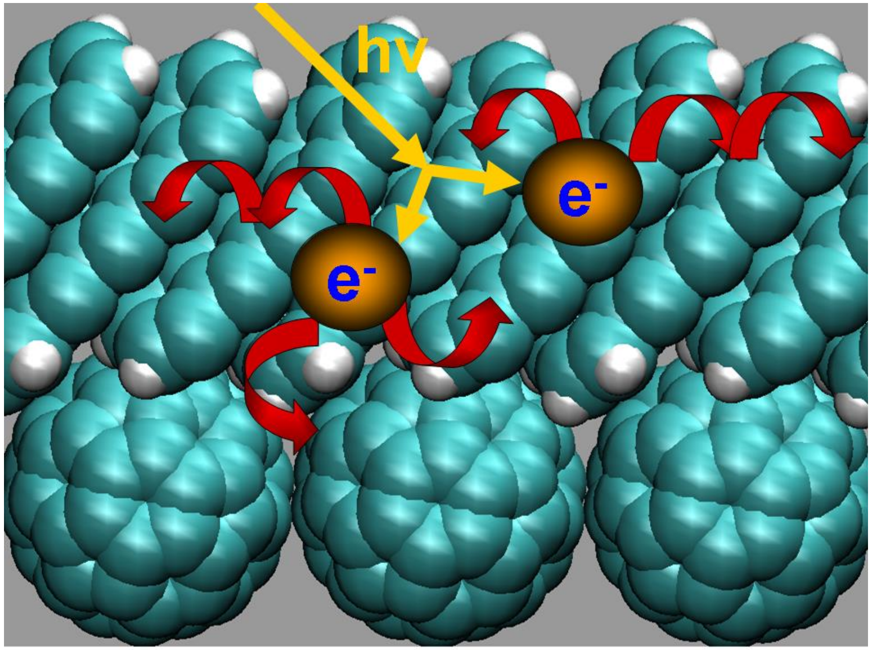
- Favor hole **localization on** interfacial **O**-containing species
- Favor **easy thermal activation** of hole onto O-states
- Favor **slow** hole **relaxation**

Ways:

- Dopants
- Oxides
- Surface modification

Singlet fission

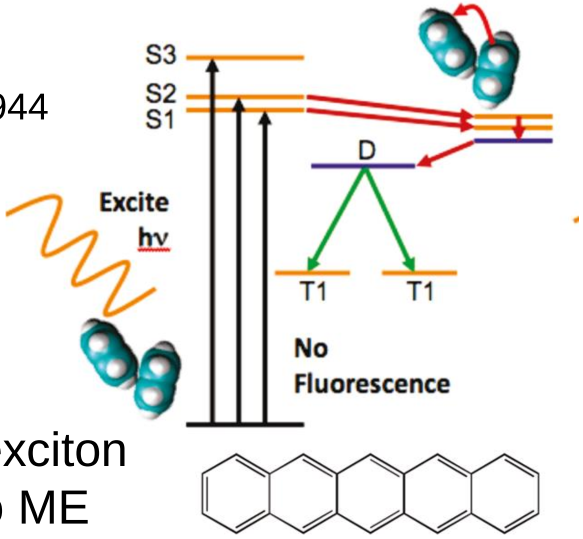
Singlet Fission (a.k.a. multiple exciton generation)



1 photon = 2 electrons:

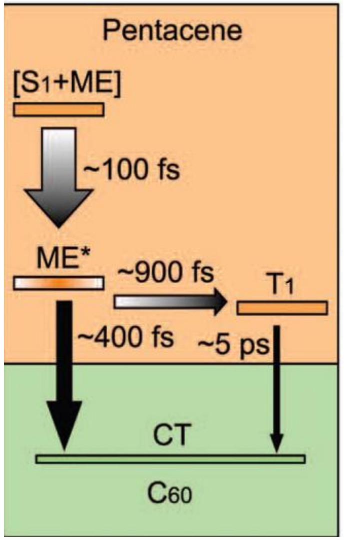
max ~44%

Zimmerman et al.
JACS **2011**, 133, 19944



spontaneous S_1 exciton localization into ME

Chan et al.
Science **2011**, 334, 1541

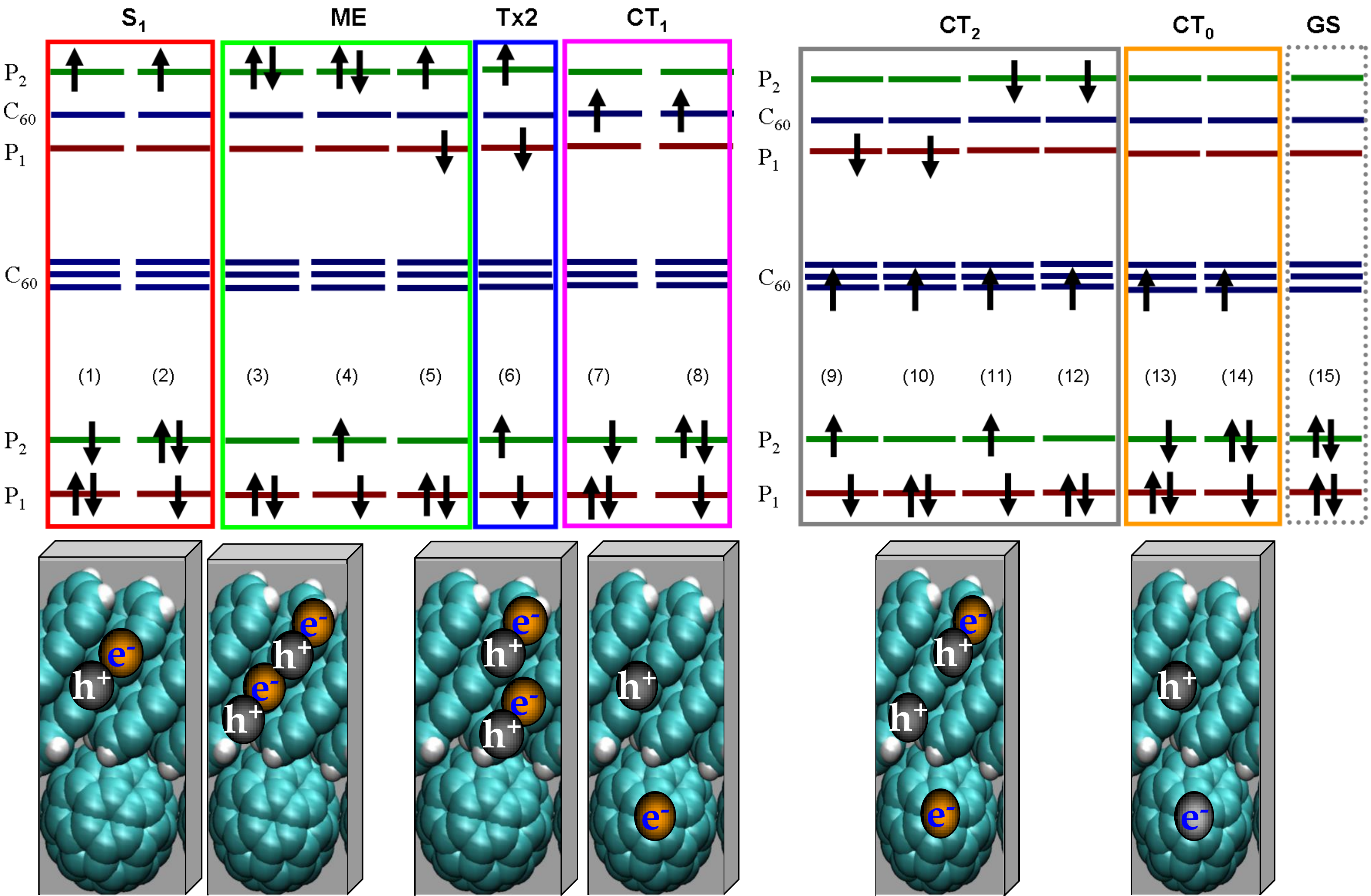


observation of ME

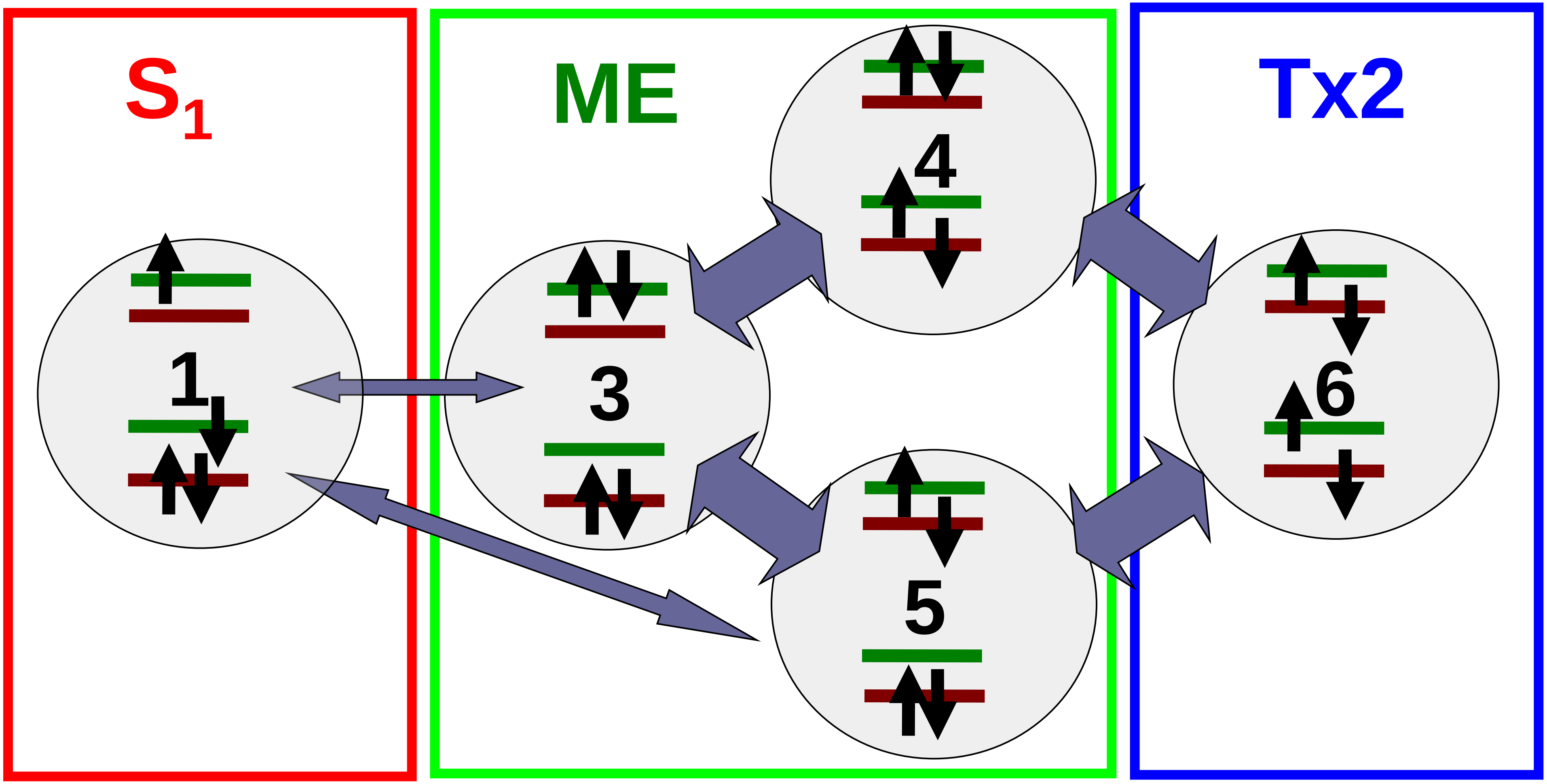
ME does not originate from S1

initial state is a superposition of S1 and ME

Minimal basis: Multielectron states



Importance of intermediates



Energy levels alignment

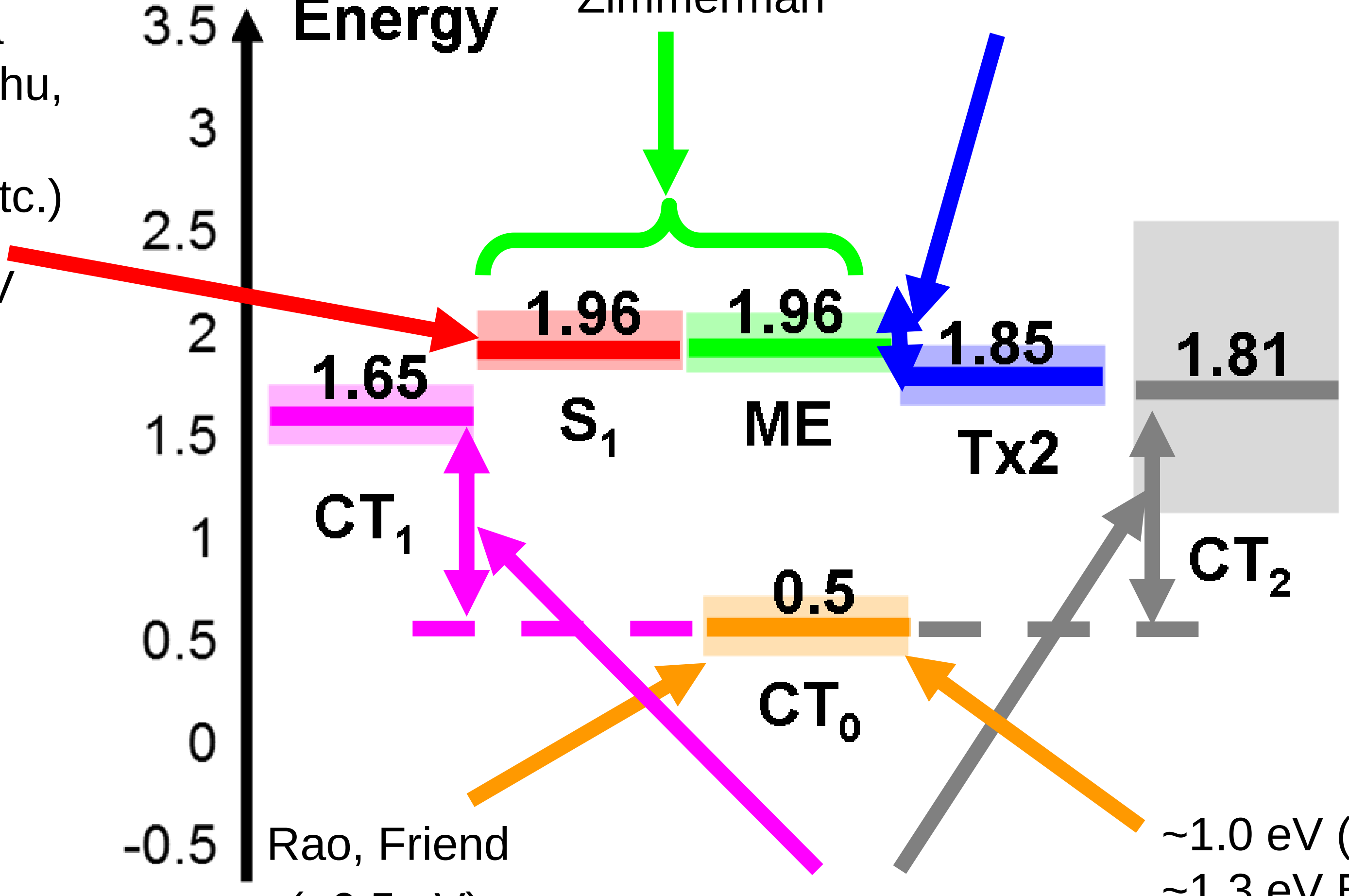
(~4.0 at SP)
correlation

Zhu
Zimmerman

Zhu, Thorsmolle (~0.11 eV)

Extensive data
(Rao/Friend, Zhu,
Thorsmolle,
Zimmerman, etc.)

PBE0: ~2.2 eV

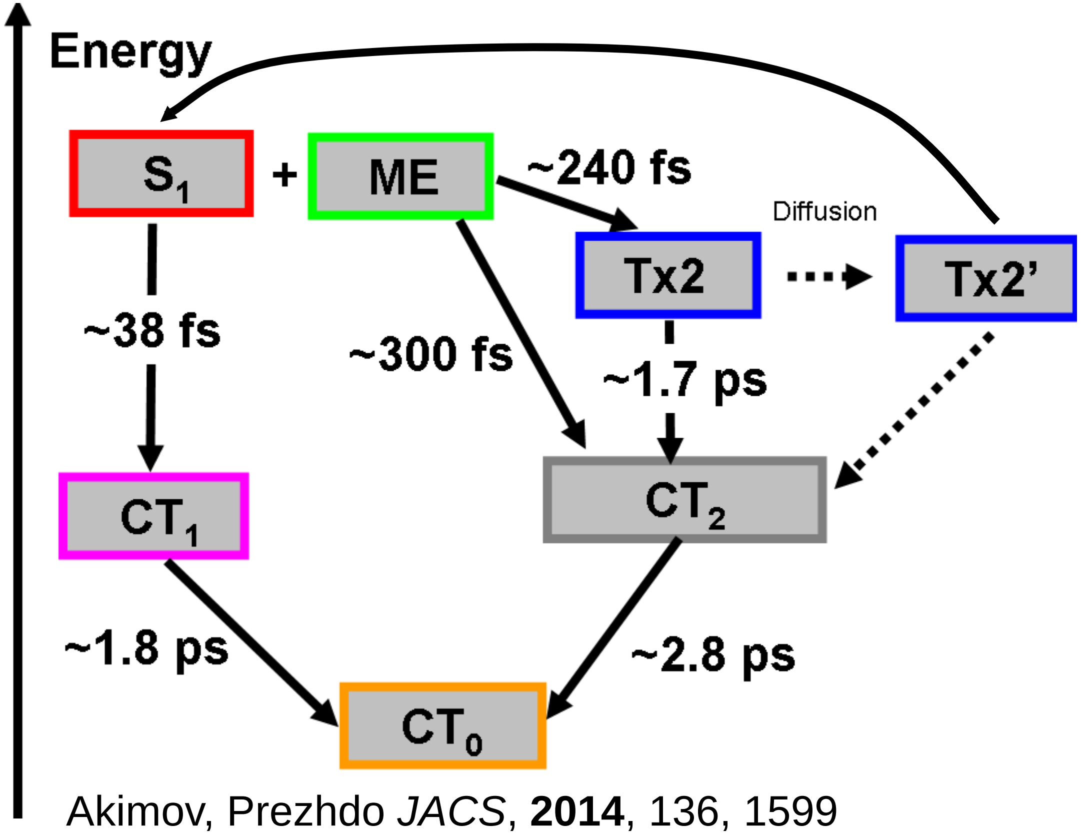


Rao, Friend
(~0.5 eV)

Expt.

~1.0 eV (PBE0)
~1.3 eV Bredas

Summary



Akimov, Prezhdo *JACS*, **2014**, 136, 1599

Findings

1) Intermediate states of CT character are important
2) No ME generation from S_1
3) Correlation is important
4) Energy alignment (CT_0) is important (revised)
5) Reproduce expt. timescales

SF photovoltaic design principles

S_1 and ME coupled during photoexcitation step:

? efficient quantum pump
? material with larger ME weight