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1938-9

Workshop on Nanoscience for Solar Energy Conversion

27 - 29 October 2008

Dynamics on the Nanoscale: Time-domain ab initio studies of quantum dots and carbon nanotubes

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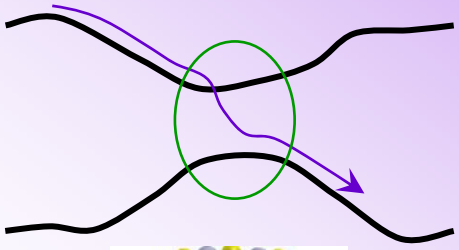
Excitation Dynamics in Novel Photovoltaic Materials

Oleg Prezhdo
U. Washington, Seattle, USA

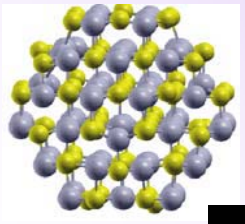
Trieste – Oct. 27, 2008

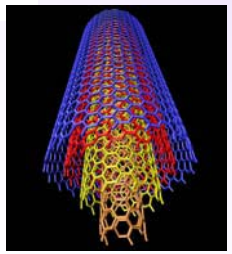
Outline

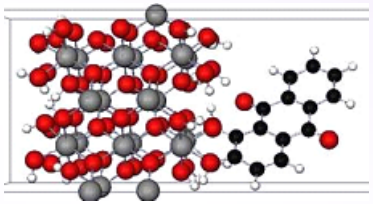
- Time-Domain DFT / Nonadiabatic Molecular Dynamics



- Excitation Dynamics in Nanoscale Materials
  - Quantum Dots
    Phonon bottleneck, Multiple excitons
  - Carbon Nanotubes
    Intraband relaxation, Fluorescence quenching, Defects
  - Chromophore-Semiconductor Interface
    Injection, Relaxation, Delocalization, Recombination

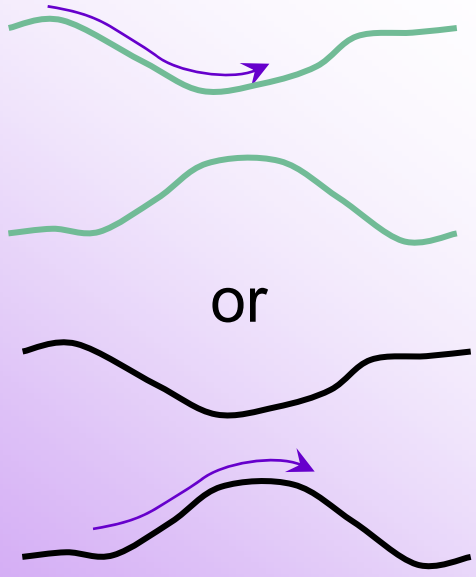


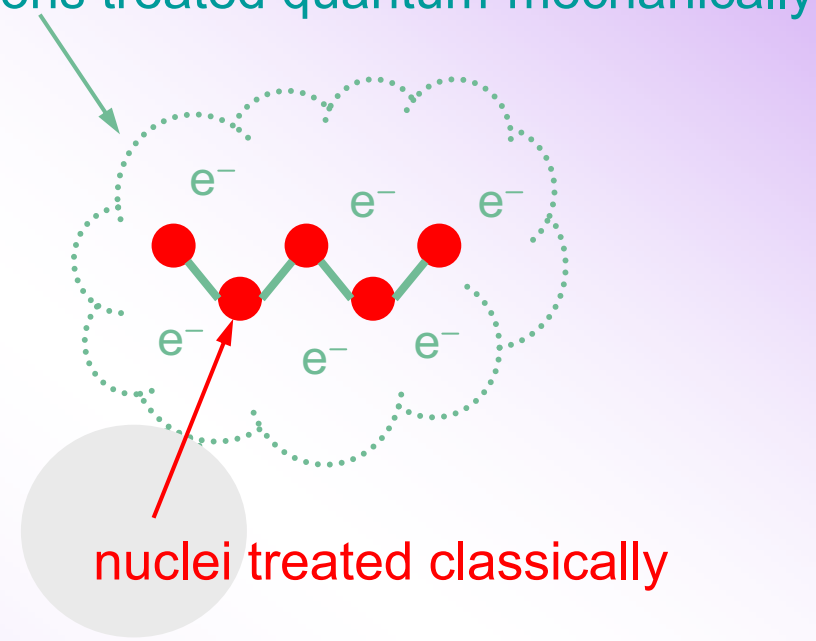




Adiabatic vs. Nonadiabatic MD

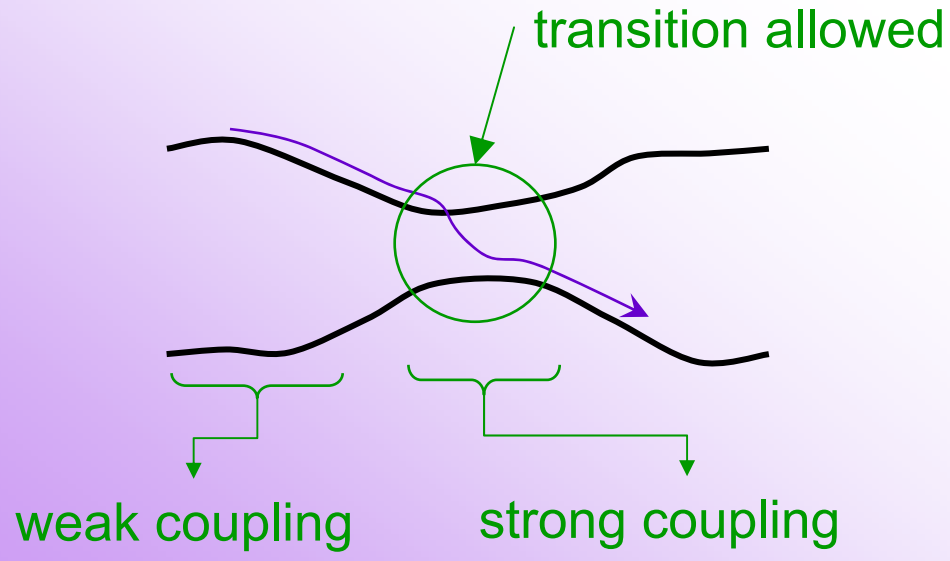
Adiabatic MD: Evolution on one potential energy surface; system remains in the same electronic state forever.

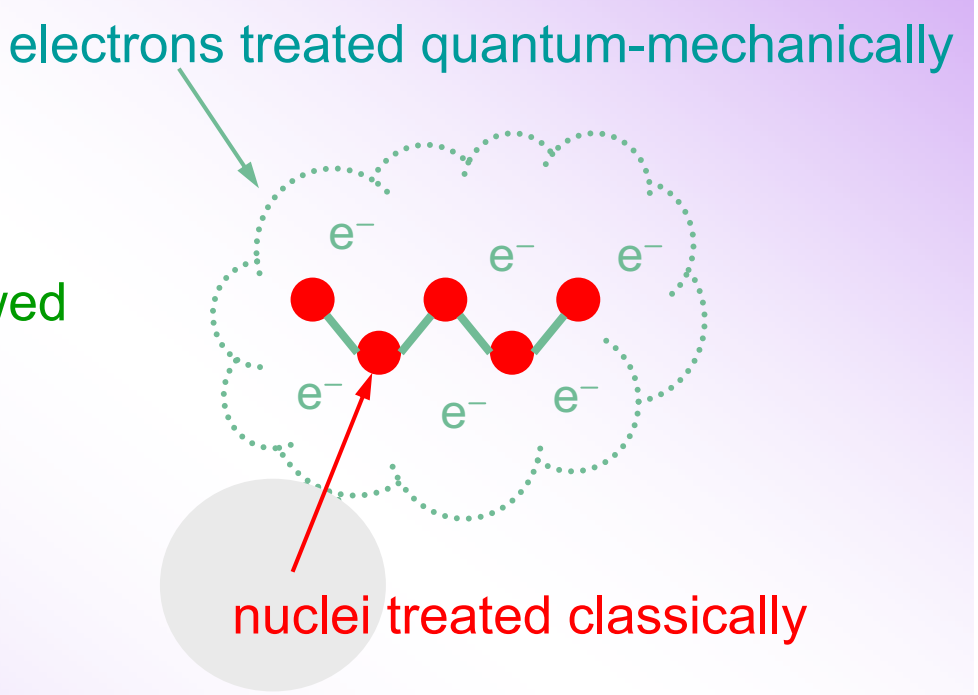




Adiabatic vs. Nonadiabatic MD

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





Time-Domain DFT for Nonadiabatic Molecular Dynamics

Electron density derives from Kohn-Sham orbitals

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

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 $$\varphi_p(x,t) = \sum c_p^\alpha(t)\chi^\alpha(x)$$

$$H(x;R(t))\chi^\alpha(x;R(t)) = \varepsilon^\alpha(R(t))\chi^\alpha(x;R(t))$$

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

Nuclear Evolution: Ehrenfest

Stier, Prezhdo *JPC* ***B*** **106** 8047 (2002)

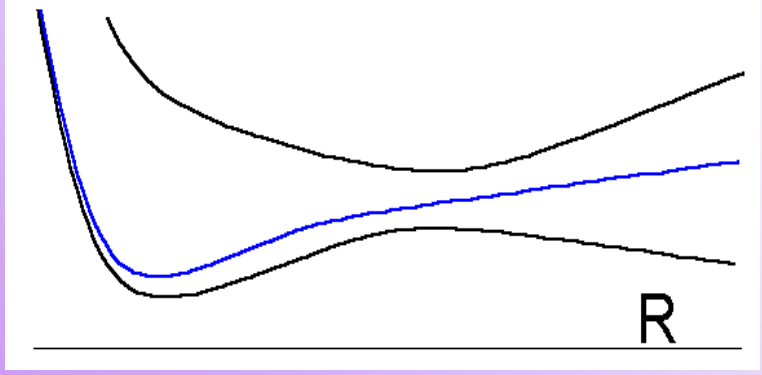
Total energy of electrons and nuclei

$$E_{tot} = \frac{M\dot{R}^2}{2} + V(R(t)) + Tr_x \rho(x) H(x; R(t))$$

is conserved

$$\frac{dE_{tot}}{dt} = 0$$

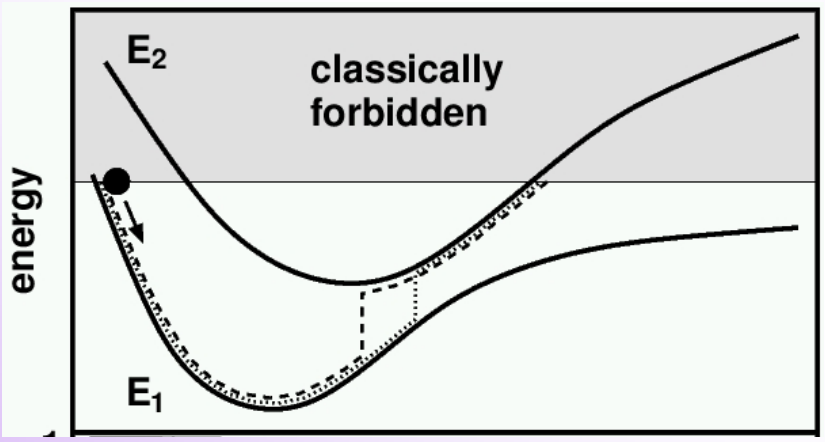
time-dependent Hellmann-Feynman theorem gives Newton equation



$$M\ddot{R} = -\vec{\nabla}_R V - Tr_x \rho(x) \vec{\nabla}_R H(x; R(t))$$

quantum force

Nuclear Evolution: Surface Hopping



a.k.a., quantum-master equation
with time-dependent transition rates:
- non-perturbative
- correct short time dynamics

Trajectory branching:
Tully, *JCP* **93**, 1061 (1990);

Within TDDFT:
Craig, Duncan, Prezhdo *PRL* **95,** 163001 (2005)

Detailed balance:
Parahdekar, Tully JCP **122**, 094102 (2005)

General Questions

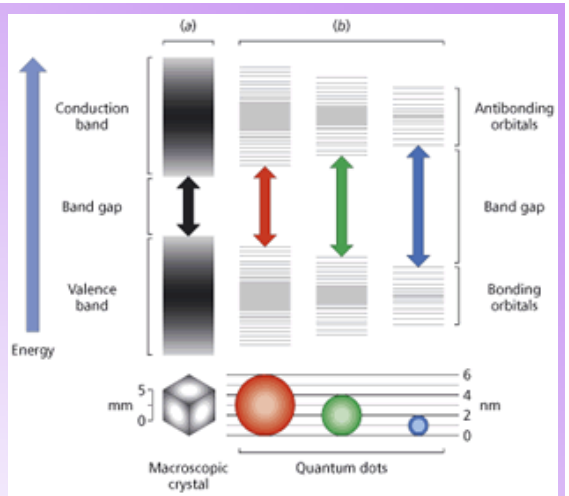
- ✓ How to think of bulk-molecule interface:
  "One big molecule" or MO's weakly coupled to bands?

- ✓ Quantum confinement effects on excitation dynamics:
  To what extent are there bottlenecks?

- ✓ Electron-vibrational relaxation (heating):
  Which phonons are involved and why?

"I'm on the verge of a major breakthrough, but I'm also at that point where chemistry leaves off and physics begins, so I'll have to drop the whole thing."

Publications



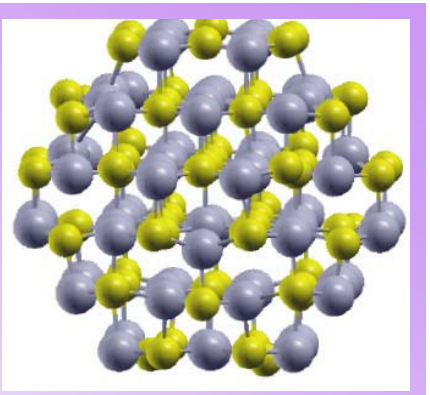
Papers

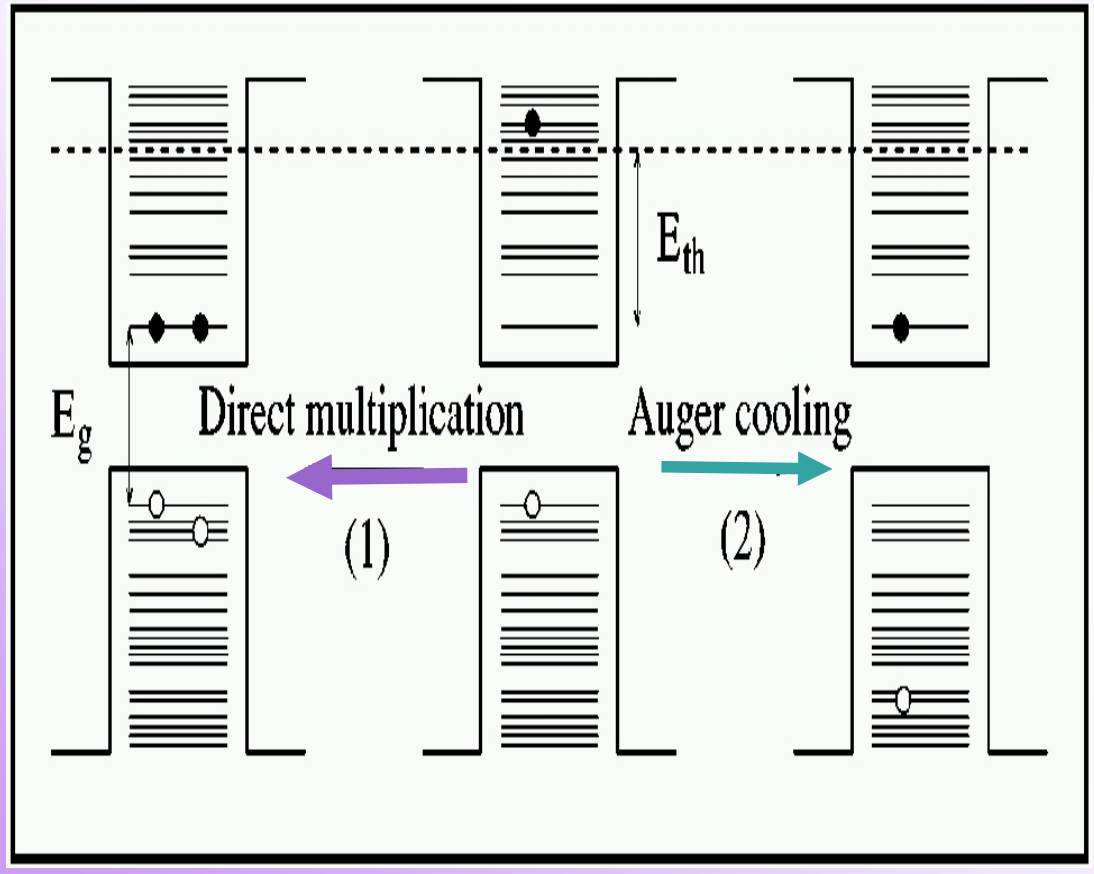
Nano Lett. **6** 2295 (2006)
J.Phys.Chem.C **111**, 4871 (2007)
J.Phys.Chem.C **112,** 7800 (2008)
Chem.Phys. Lett. **458** 113 (2008)
J.Photochem.-Photobiol.A **190**, 342 (2008)
Pure&Appl. Chem. in press
ACS-Nano submitted
J. Phys. Chem. C submitted
Chem.Phys. Lett. FRONTIER **460** 1 (2008)

Book Chapters

Springer (2006)

Competing Relaxation Mechanisms





1. Direct multiplication

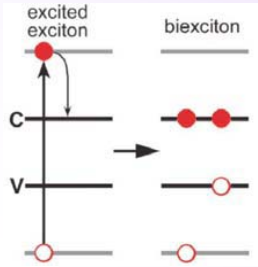
   must be faster than

2. Auger,
3. Electron-phonon,
4. Radiative processes

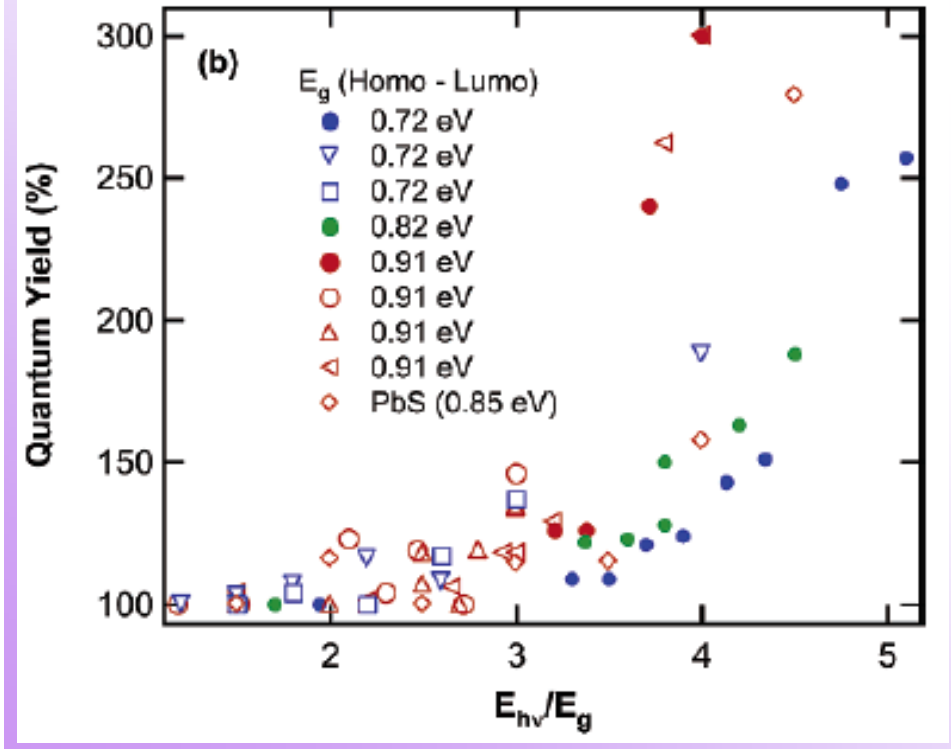
Biexcitons in PbSe Quantum Dots

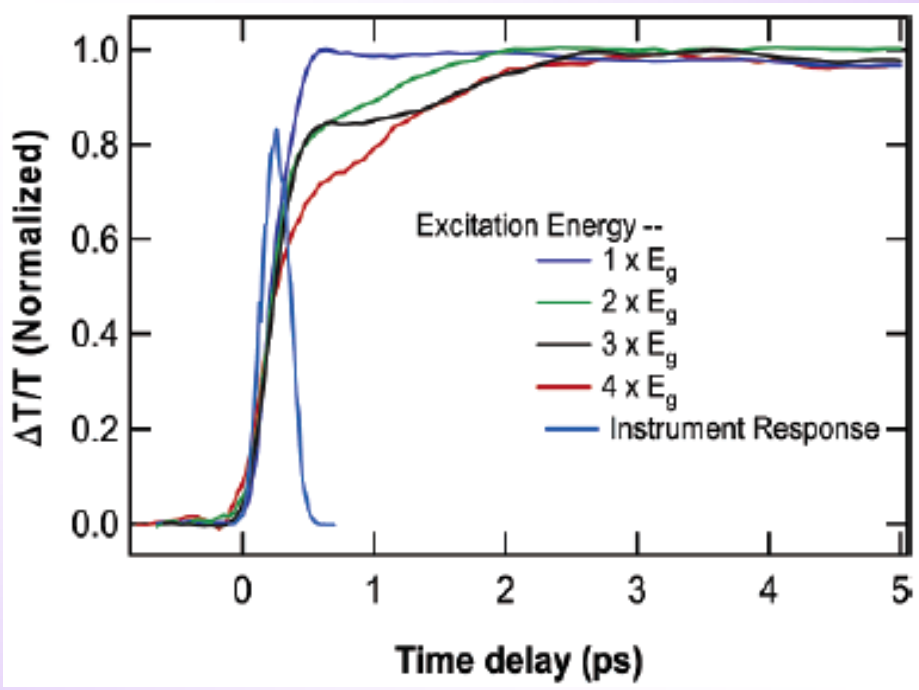
Shaller, Klimov *PRL* **92** 186601 (2004); Ellingson, Beard, Johnson, Yu, Micic, Nozik, Shabaev, Efros, *NanoLett* **5** 865 (2005)

Biexciton creation yield



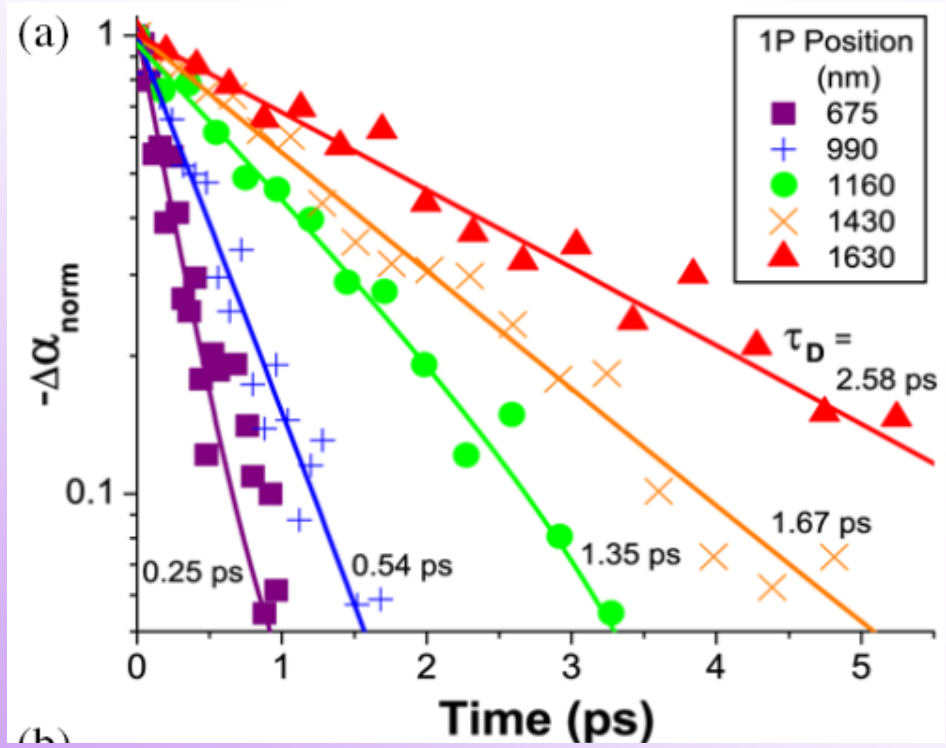
Exciton to biexciton time under 0.25ps





Electron-Phonon Relaxation in PbSe Quantum Dots

Schaller, Pietryga, Goupalov, Petruska, Ivanov, Klimov *PRL* **95** 196401 (2005)



No phonon bottleneck.

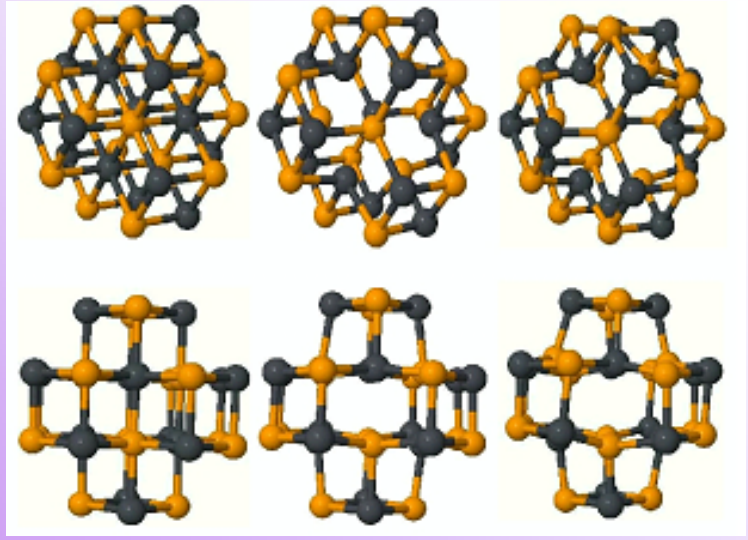
Times are similar to biexciton creation times

Larger dots relax slower ?!

Structural relaxation of PbSe Quantum Dots

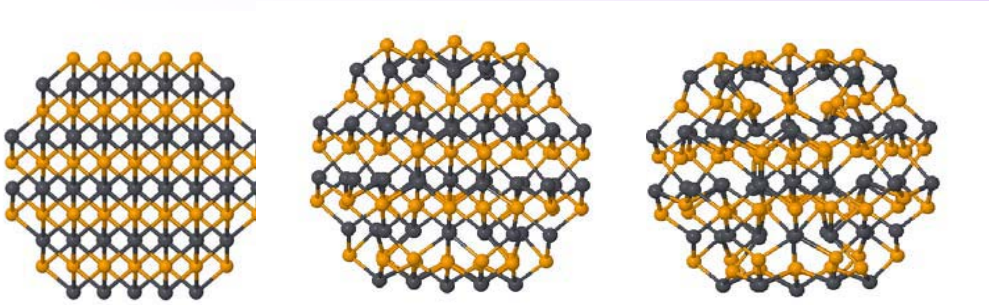
32 atoms $Pb_{16}Se_{16}$ d=0.9nm

Bulk, T=0 K | Relaxed, T=0 K | Heated, T=300 K



136 atoms $Pb_{68}Se_{68}$ d=1.3nm

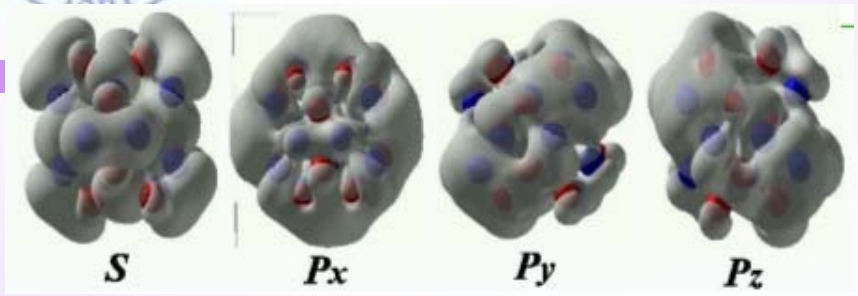
Bulk, T=0 K | Relaxed, T=0 K | Heated, T=300 K



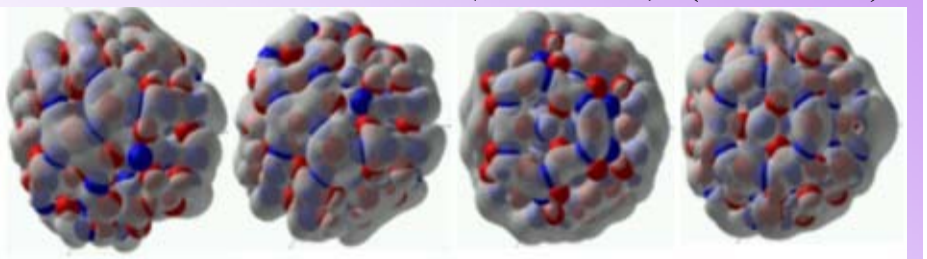
Even a very small PbSe quantum dot preserves its bulk topology

Orbitals and Density of States

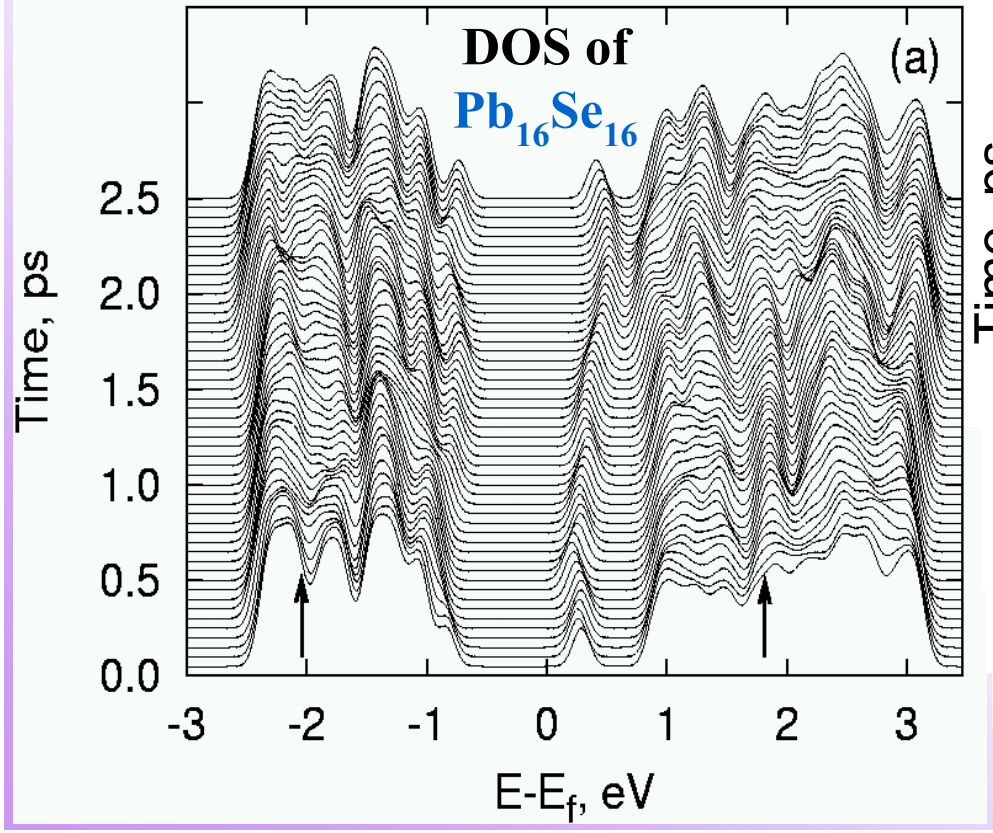
(LUMO) (LUMO+1) (LUMO+2) (LUMO+3)

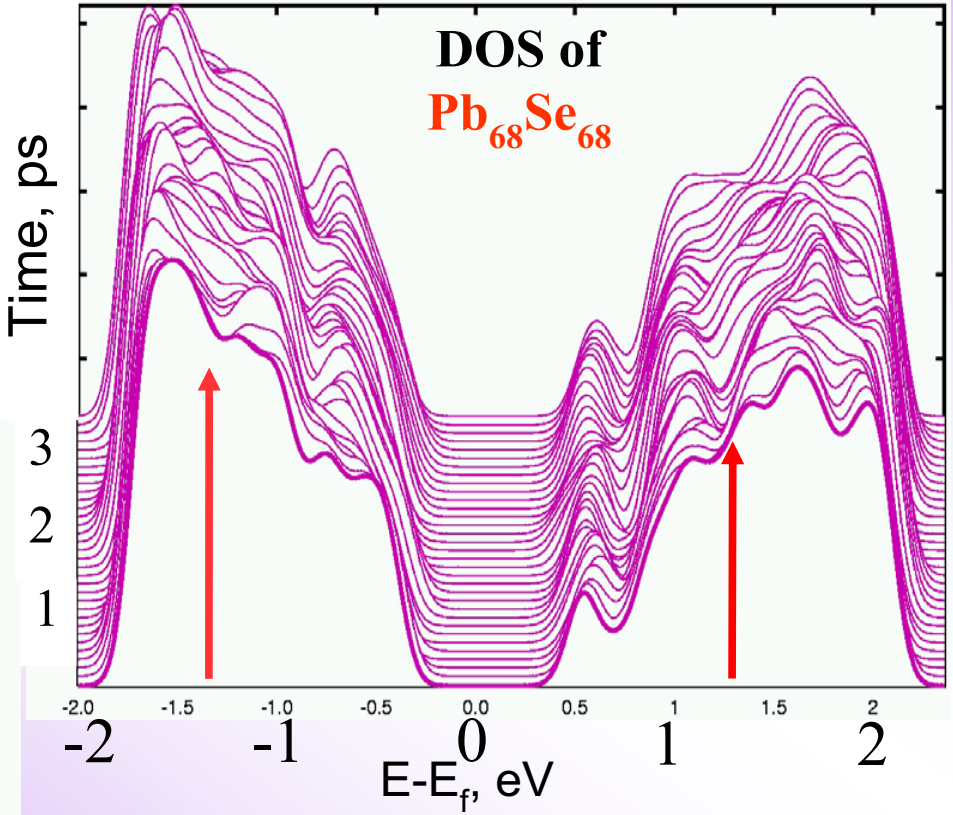


(LUMO) (LUMO+1) (LUMO+2) (LUMO+3)

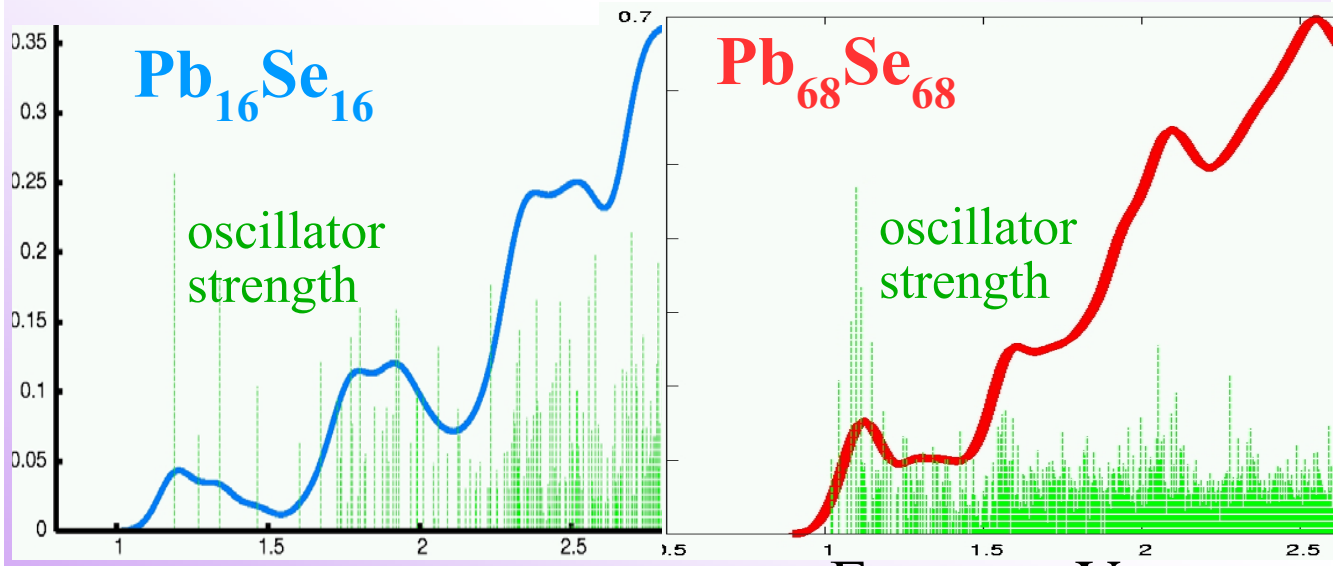


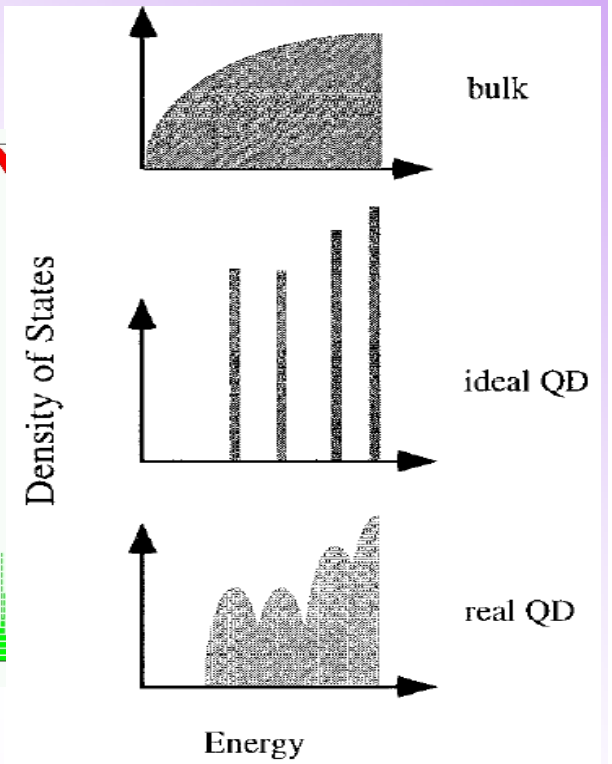
states mix; sp^3 hybridization (?)



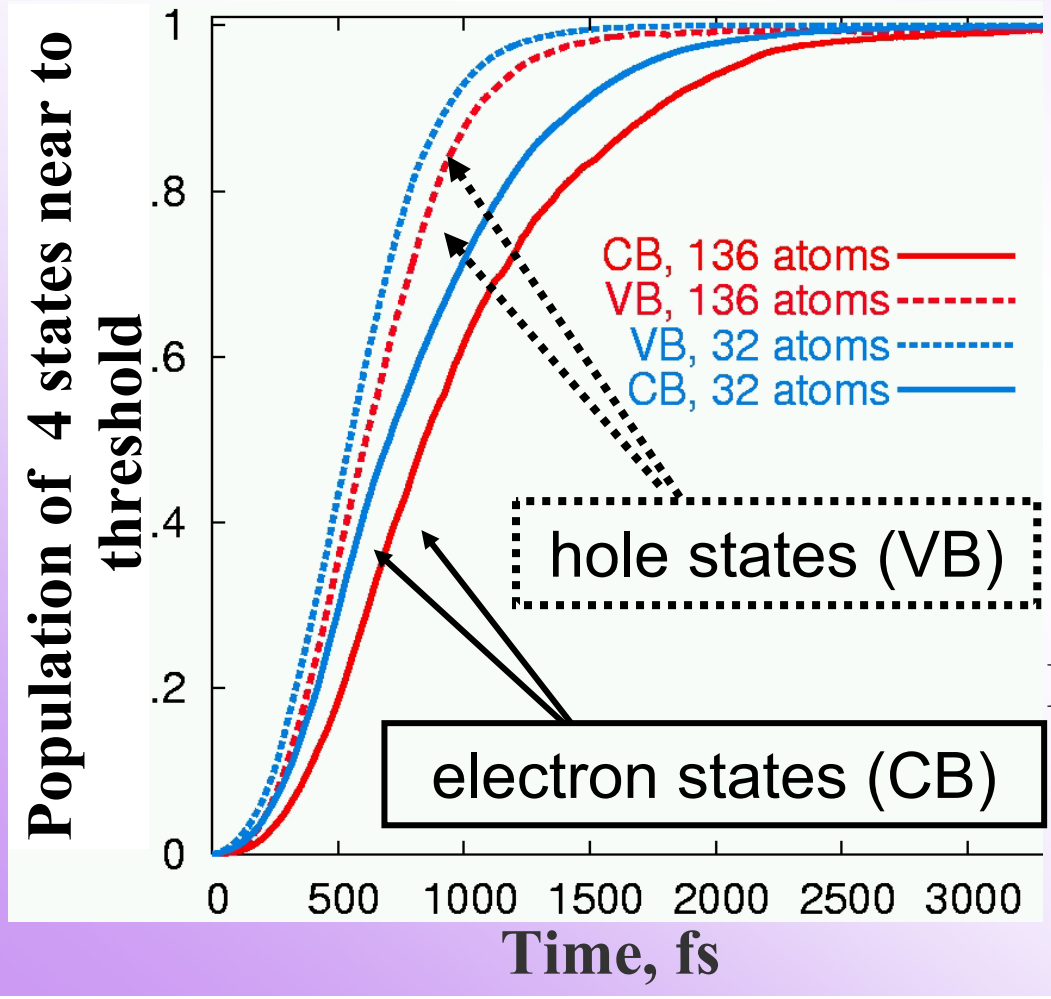


Absorption Spectra





Comparison of Relaxation



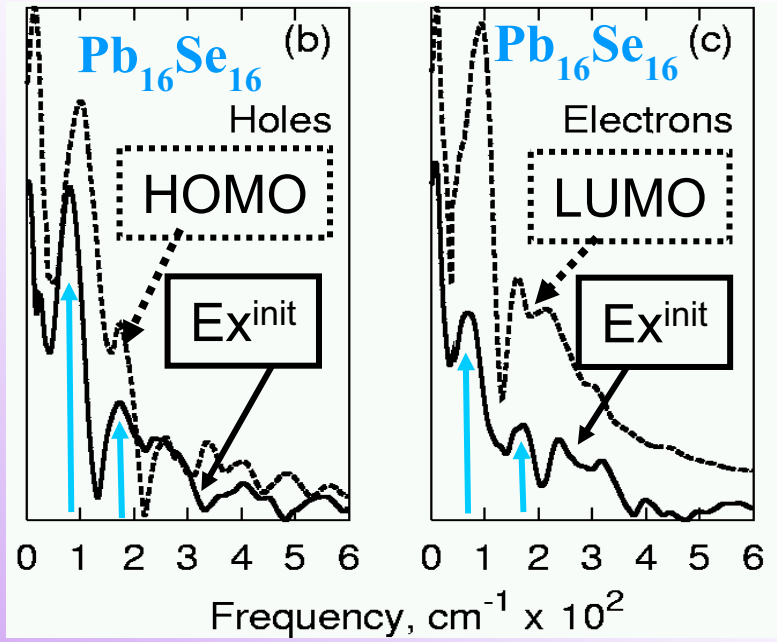
Times agree with experiment

Similar relaxation times for electrons and holes

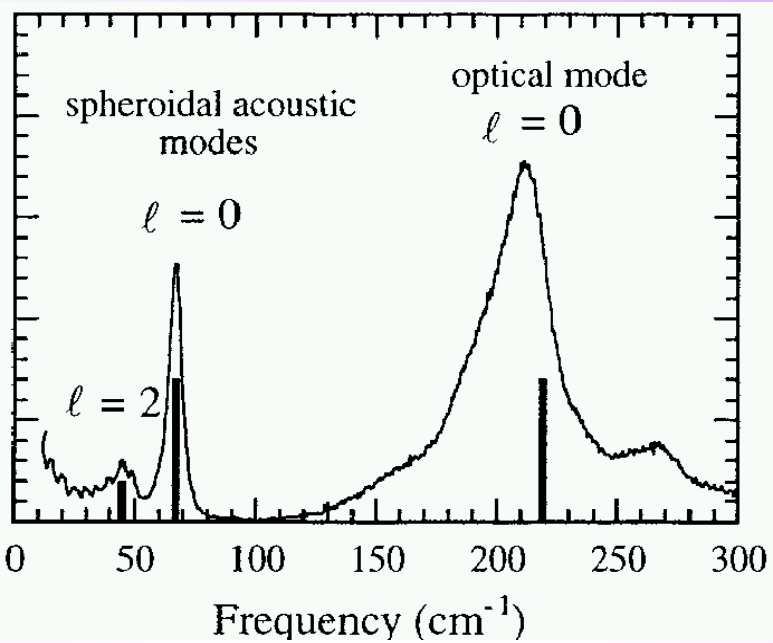
Biexciton creation is faster than relaxation

Larger dot relaxes more slowly due to weaker NA coupling

Active Phonon Modes



Lower frequency acoustic modes are more active than optical modes



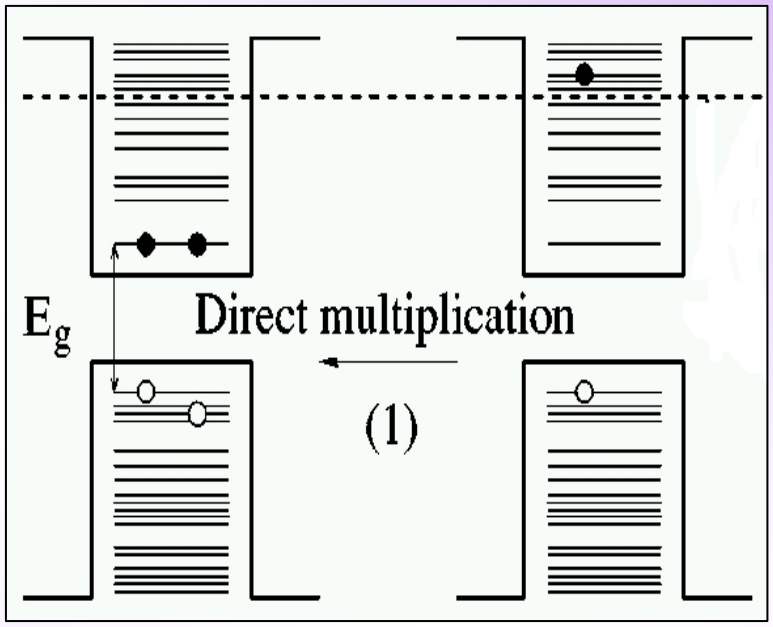
Raman Spectrum of 3-nm PbS QD
[Acc Chem. Res. 2000, 33, 773-780]

Proposed Multiplication Mechanisms

Inverse Auger

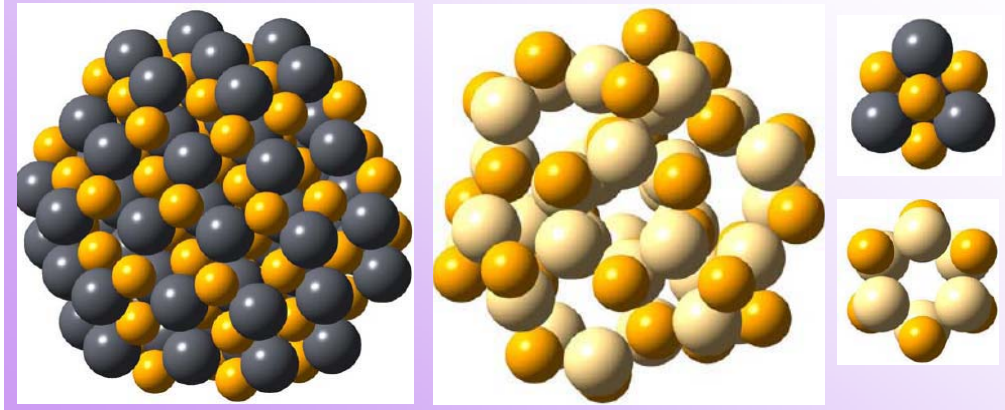
Dephasing

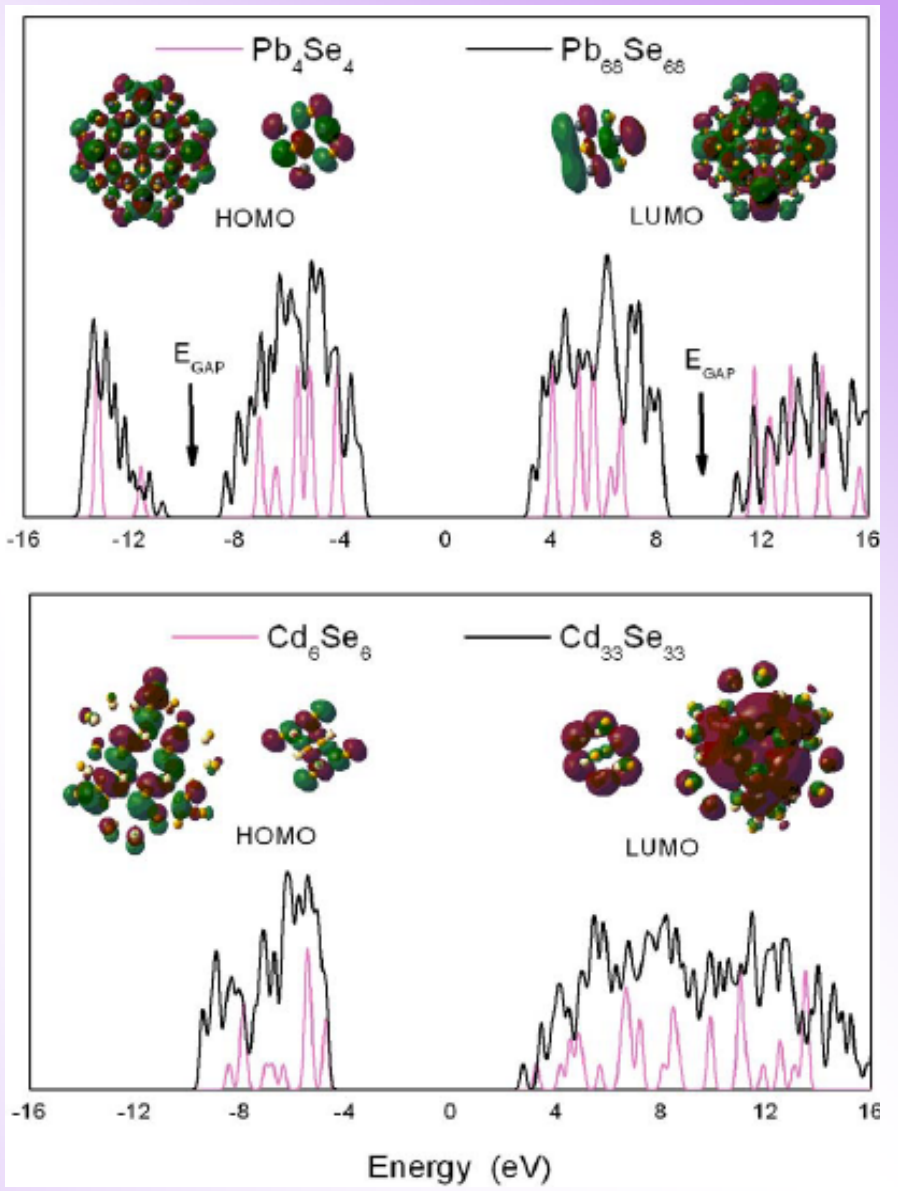
Direct Excitation



Hartree-Fock Band Structure

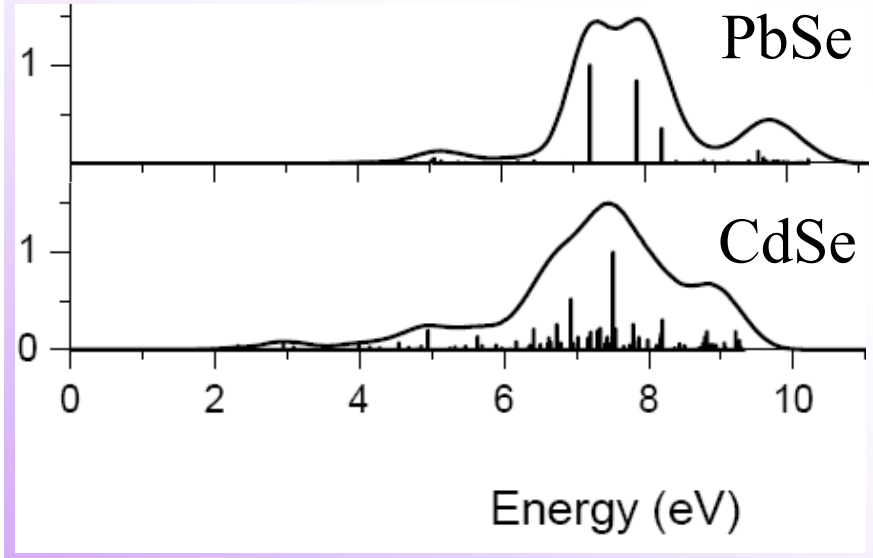
1. Small dots represent large dot DOS
2. Huge one-electron gap
3. Symmetric vs. asymmetric DOS
4. Secondary gaps in PbSe DOS



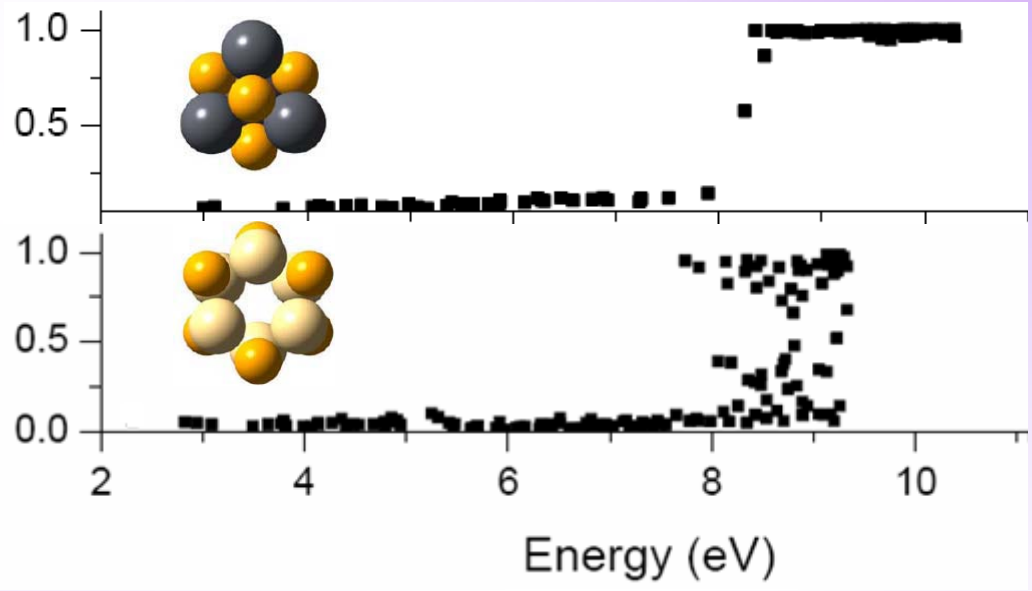


SAC-CI Spectra and Fraction of Multiple Excitons

spectra



fraction of multiple excitons



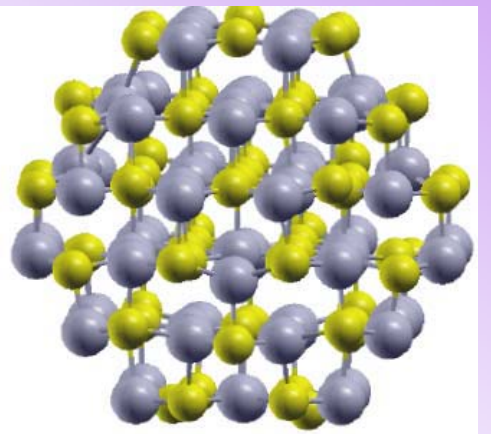
CdSe spectra agree with experiment *JACS* **128**, 629 (2006)

1. Sharp onset of multiple excitons
2. Above threshold: double excitons in PbSe; single, double and superpositions in CdSe

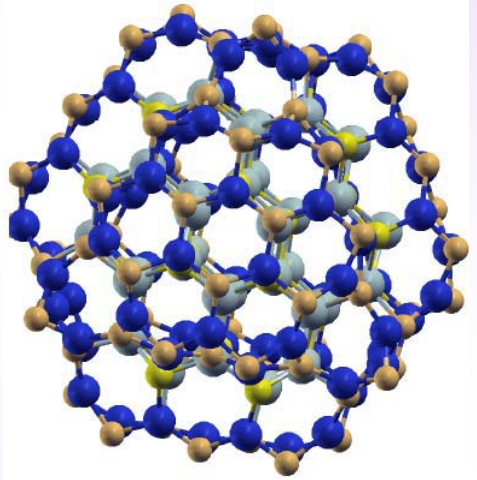
Summary

- ✓ Absence of relaxation bottleneck due to small gaps between states
- ✓ Smaller dots relax faster, coupling wins over density of states
- ✓ Electron-phonon relaxation is still slower than exciton multiplication
- ✓ Acoustic, not optical modes are active
- ✓ All three MEG mechanisms can be important: inverse Auger, dephasing and direct, direct especially in PbSe

PbSe

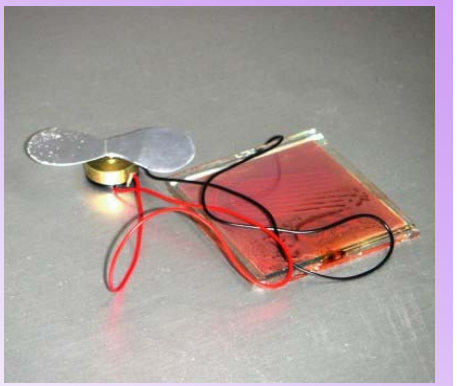


CdSe/ZnS

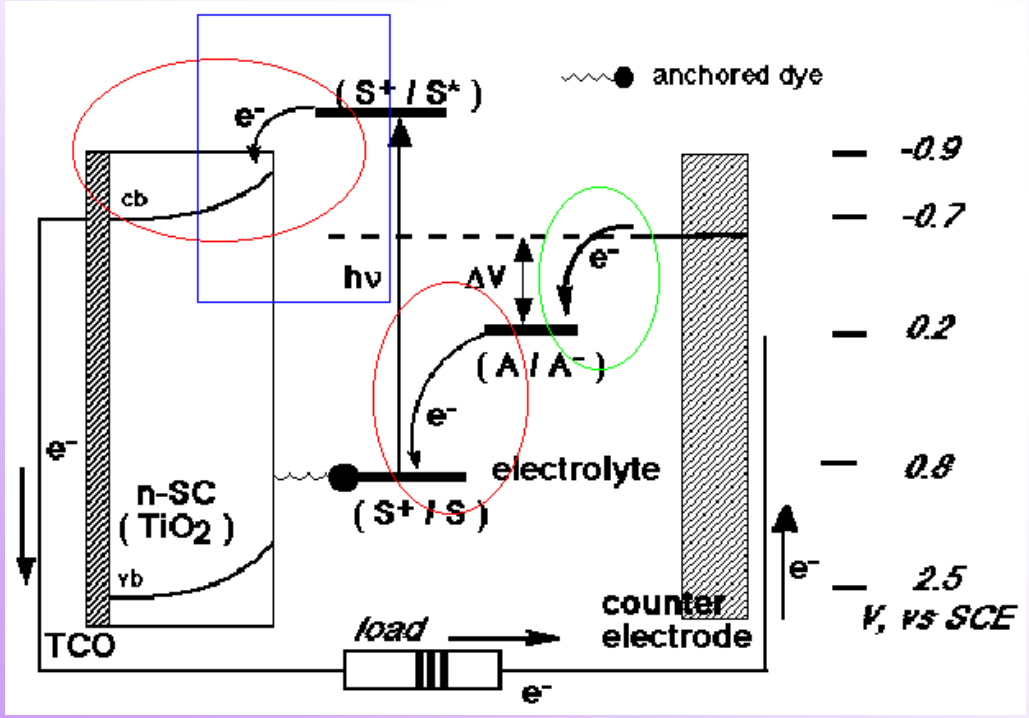


"Bunsen, I must tell you how excellent your study of chemical spectroscopy is, as is your pioneer work in photochemistry — but what really impresses me is that cute little burner you've come up with."

Dye-Sensitized Semiconductor Solar Cell



Oregan, Gratzel *Nature* **353** 6346 (1991)



Photovoltaics:

optimize voltage, current, photo yield

electron transfer mechanism and its properties

Molecule-bulk interface:

least understood in molecular-electronics

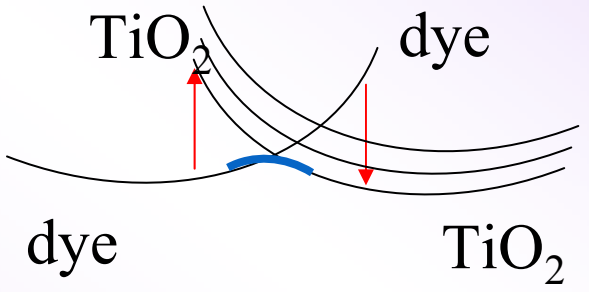
Reaction Mechanism ?

- A new mechanism, not Marcus-Levich-Jortner-Gerischer ?

"The electron transfer did not involve redistribution of vibrational excitation energy and was completely different from the well known Marcus-Levich-Jortner-Gersicher mechanism."

Burfeindt, Hannappel, Storck, Willig *JPC* **101** 6799 (1997)

- Adiabatic or Non-adiabatic ?

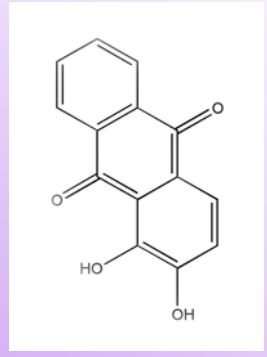


"One possibility for the observed fast injection is a strong coupling of the dcbpy π* orbital with TiO_2, leading to an adiabatic electron transfer from dcbpy to TiO_2."

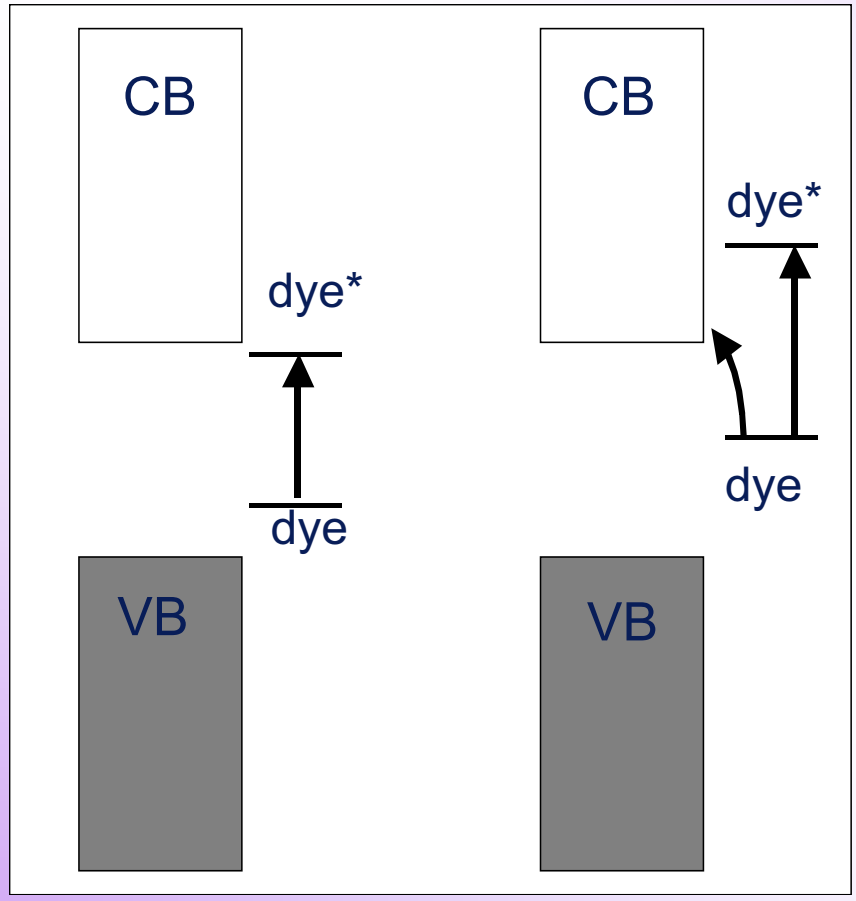
"However, it is unclear whether strong coupling is necessary… a large accepting state density in TiO_2 would also give rise to an ultrafast injection time even when the coupling … is weak."

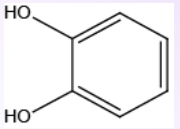
Asbury, Ellingson, Ghosh, Ferrere, Nozik, Lian *JPC* **103** 3110 (1999)

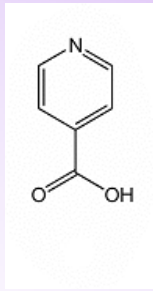
Types of Photoexcitation

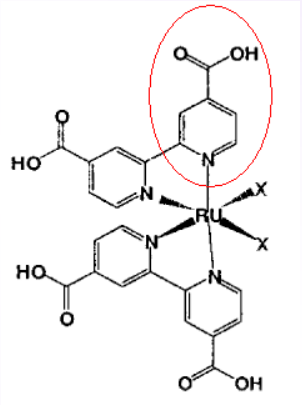


TiO_2-Alizarin TiO_2-Catechol, Ru-dyes



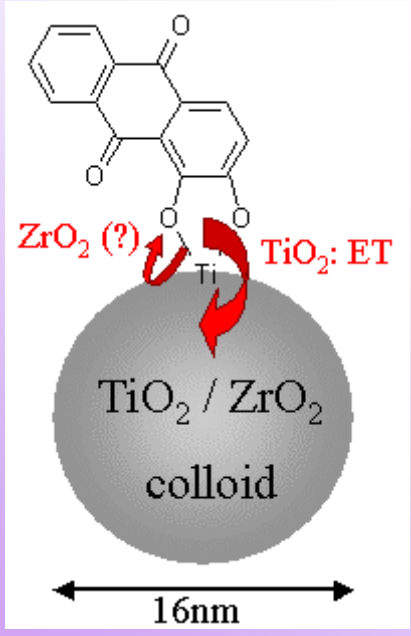






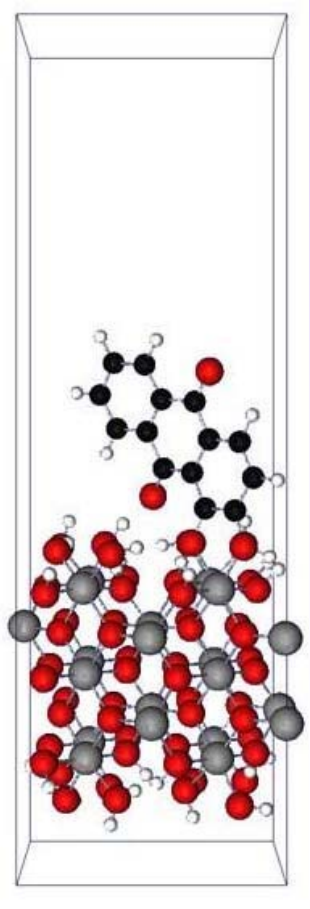
Electron Injection in Alizarin/TiO_2

Colloid, 298K
6 fs transfer



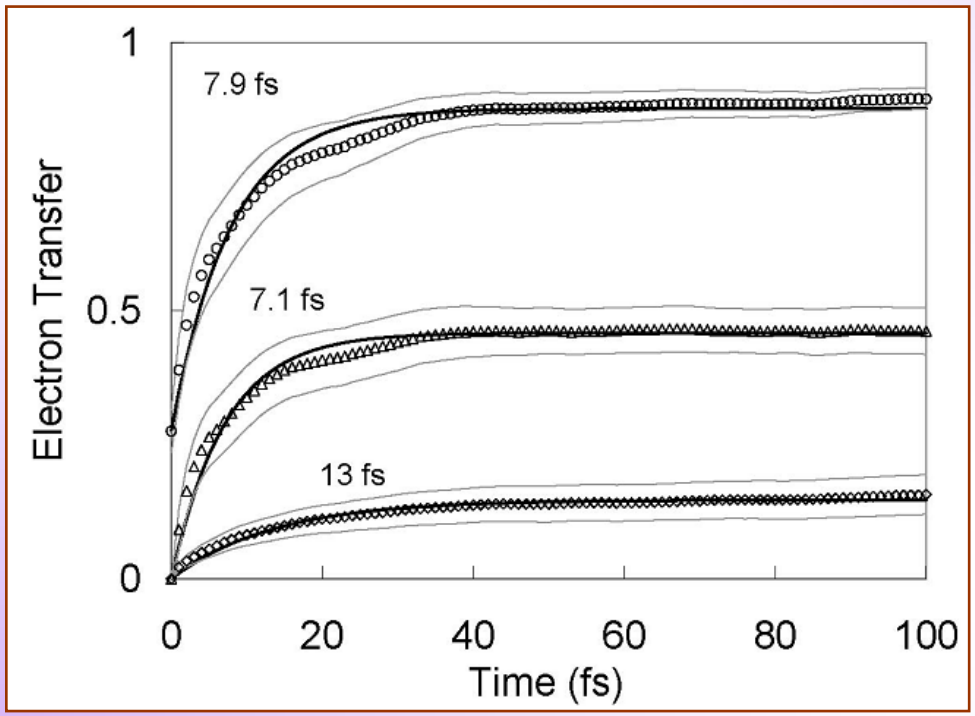
Experiment:
Huber, Moser, Grätzel, Wachtveitl
*JPC-**B*** **106** 6494 (2002)

Theory:
Duncan, Stier, Prezhdo
Adv. Mater. **16** 240 (2004)
JACS **127** 7941 (2005)



Alizarin ET, simulation

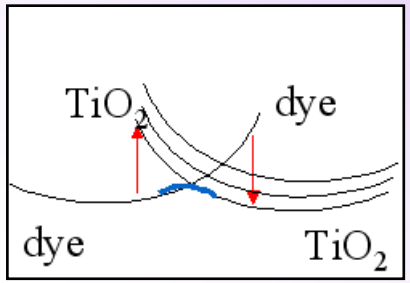
Duncan, Stier, Prezhdo *Adv. Mater.* **16** 240 (2004)
JACS **127** 7941 (2005)



total

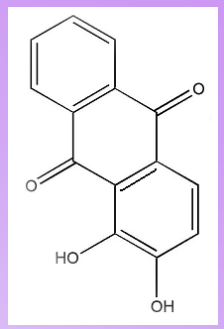
adiab.

NA

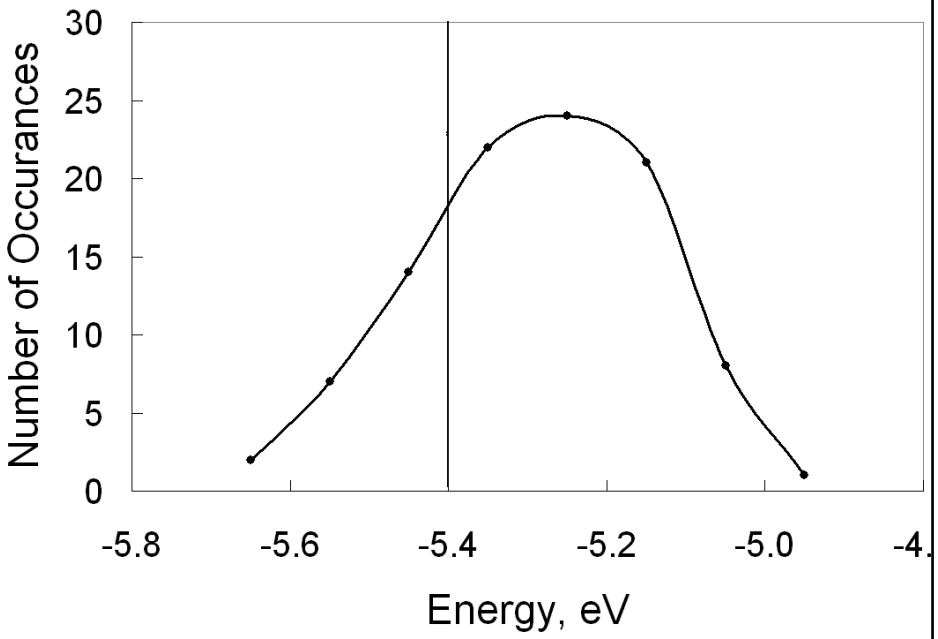


Experiment 6 fs, theory 8 fs
Adiabatic ET dominates over non-adiabatic ET
Photoexcited state is 30% delocalized onto TiO_2

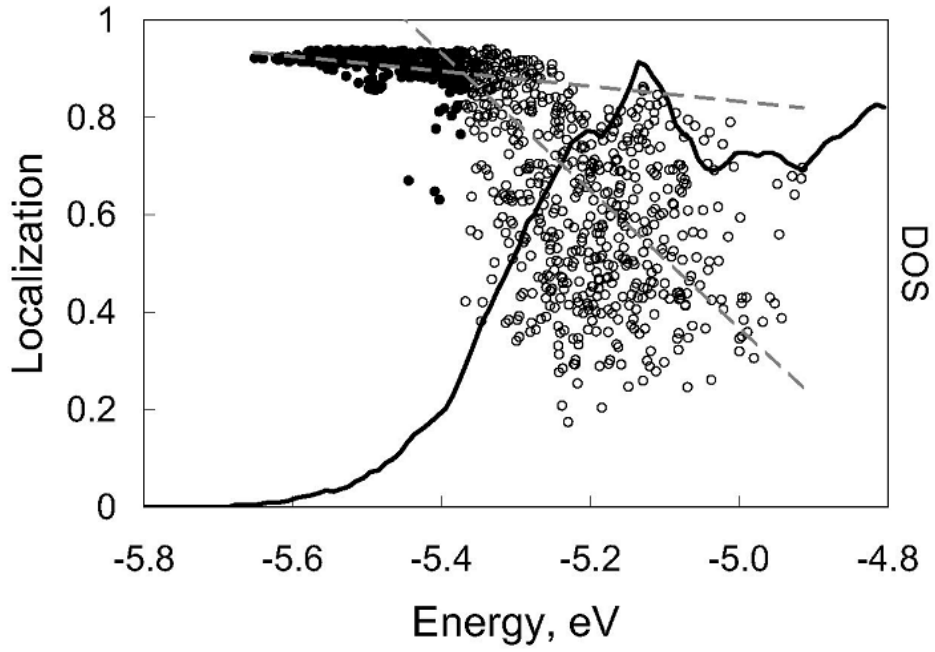
Photoexcited State Energy and Localization



Distribution of Excite State Energies

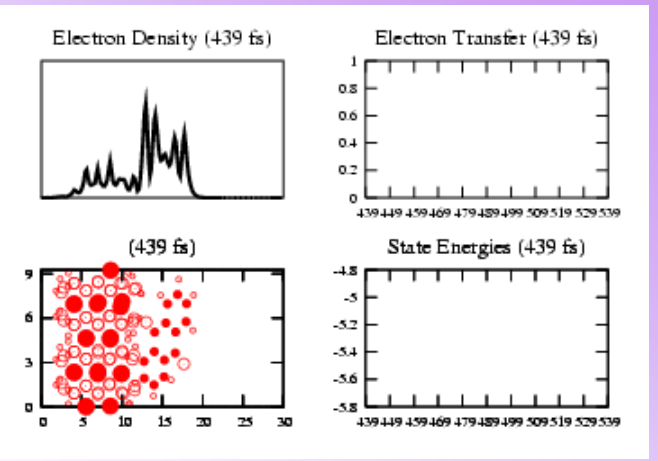


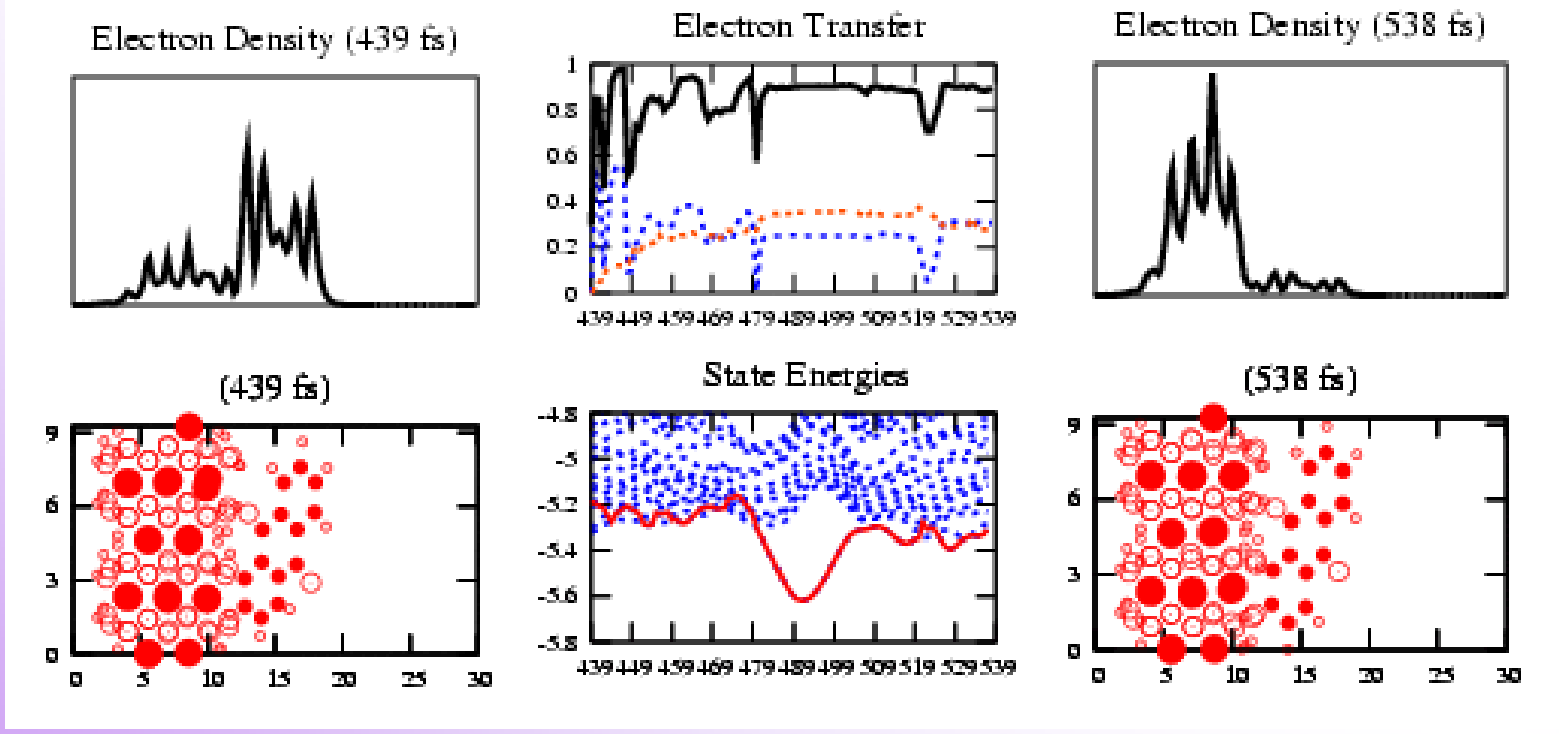
Localization of Photoexcited State on Alizarin



~40 vibrations give Gaussian distribution of excited state energy
alizarin excited state delocalizes into CB at high energy

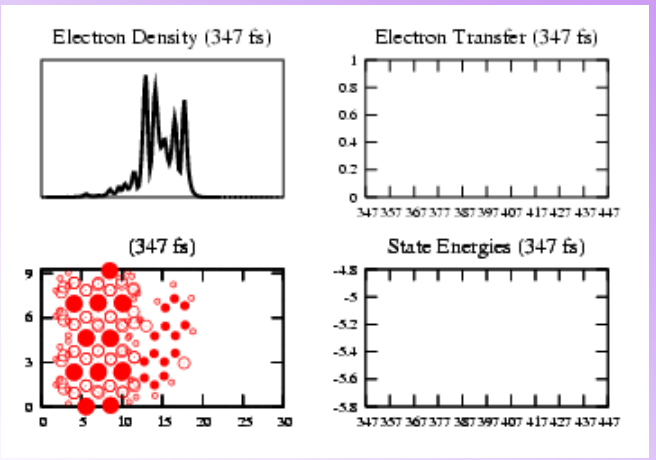
Inside conduction band

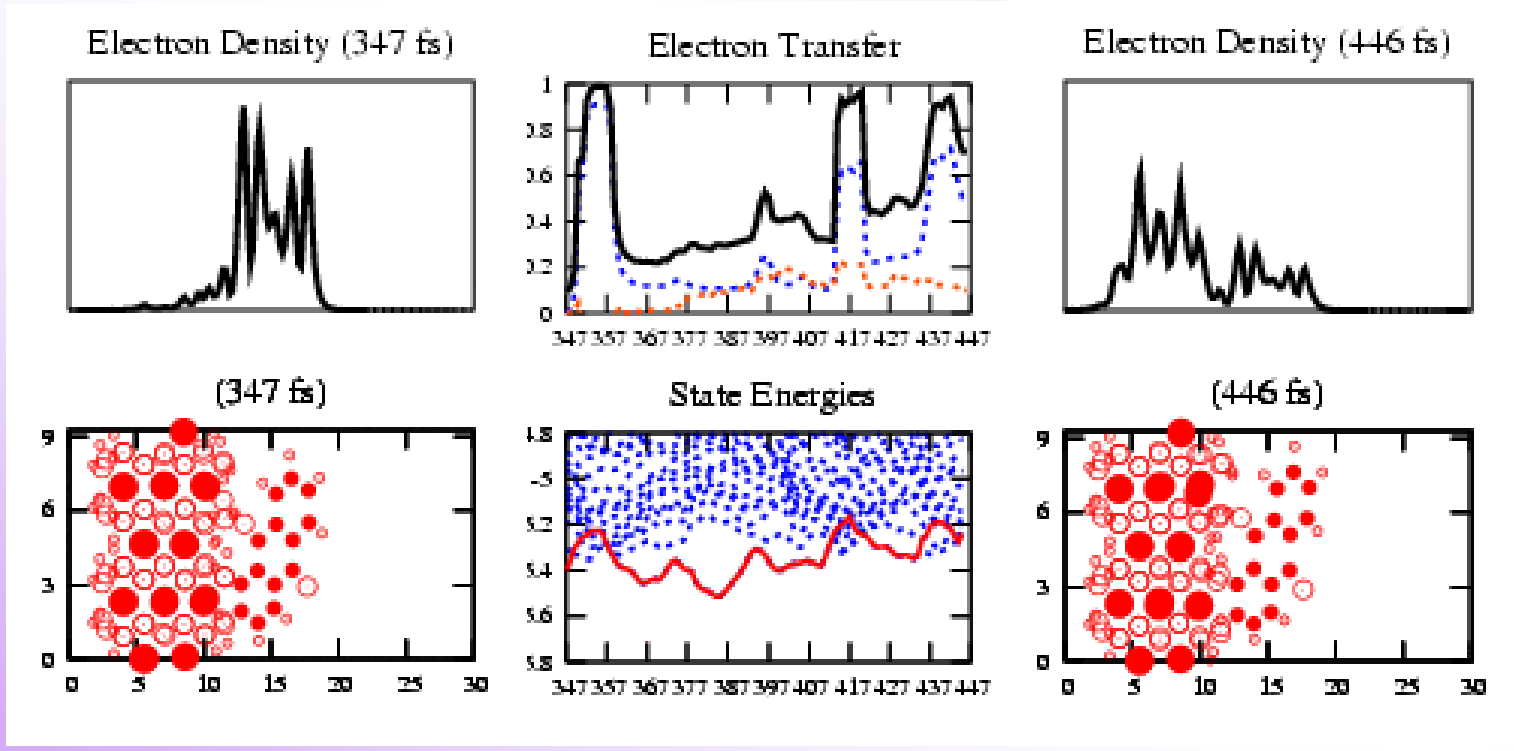




initial state dynamics final state

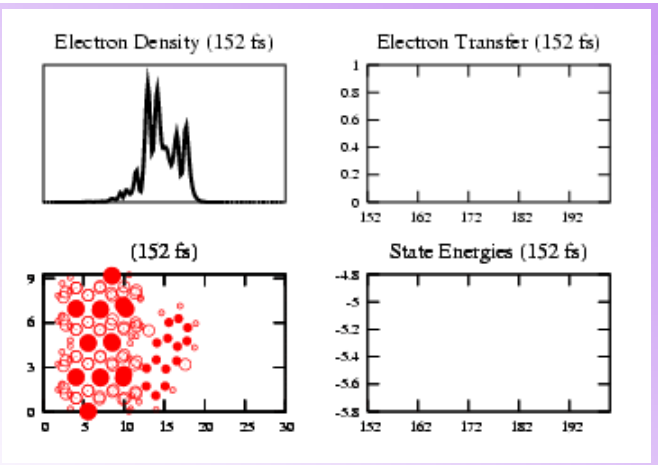
Multiple entrances into conduction band

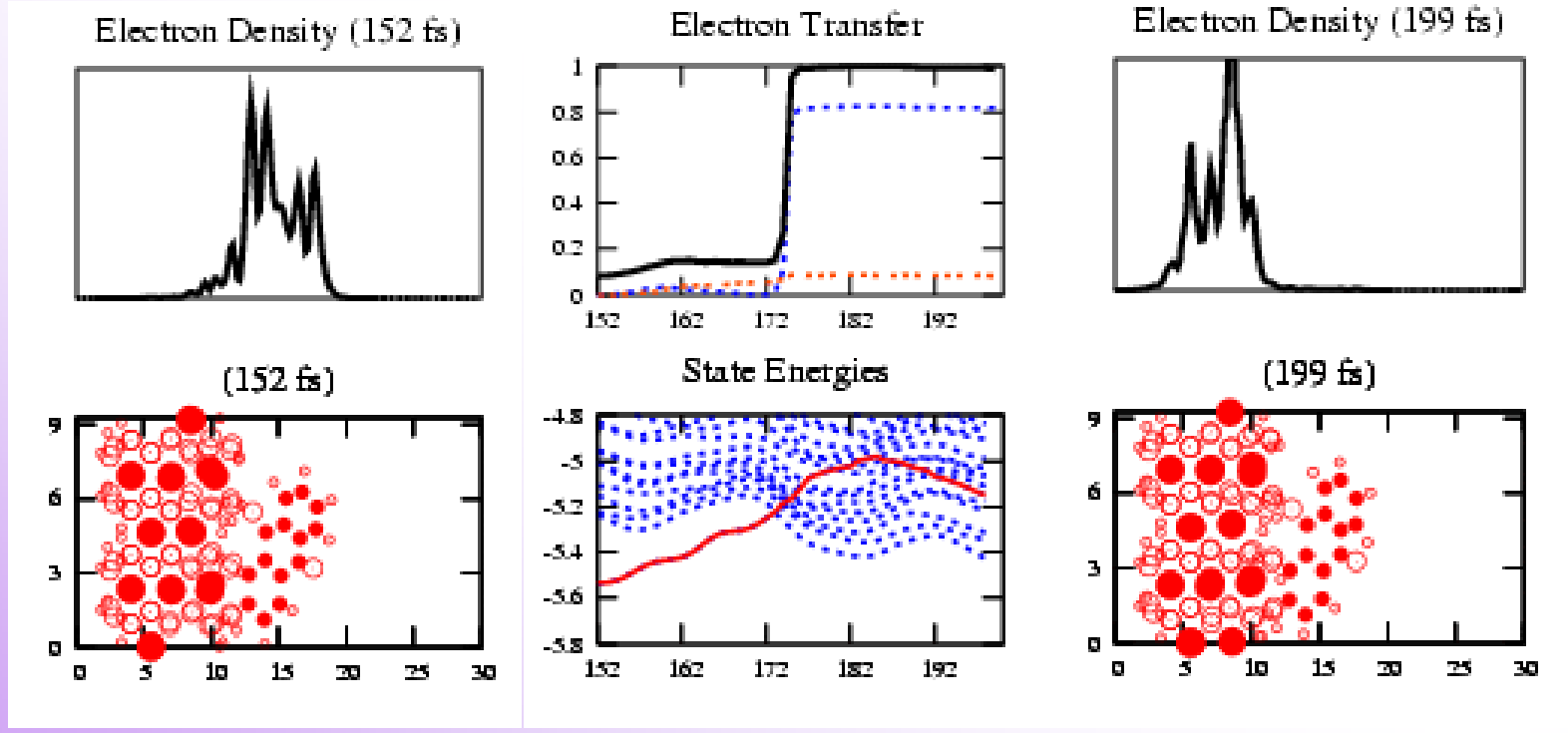




initial state dynamics final state

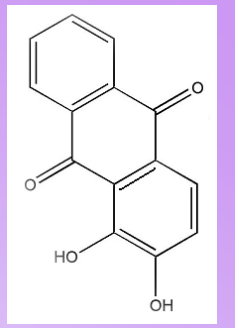
Single entrance into conduction band



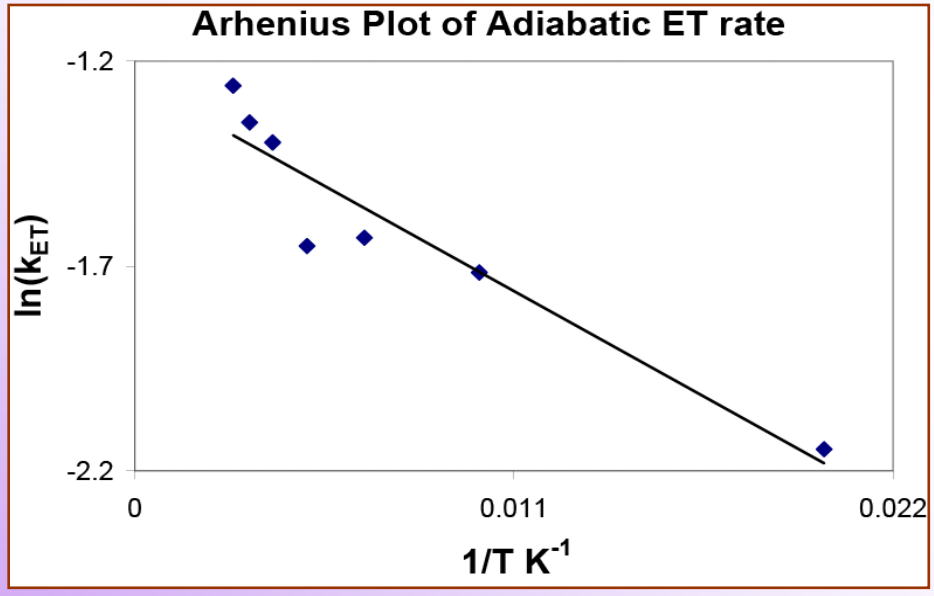


initial state dynamics final state

Adiabatic ET vs. Temperature



$$k_{ET} = \nu \exp(-\Delta G / kT)$$



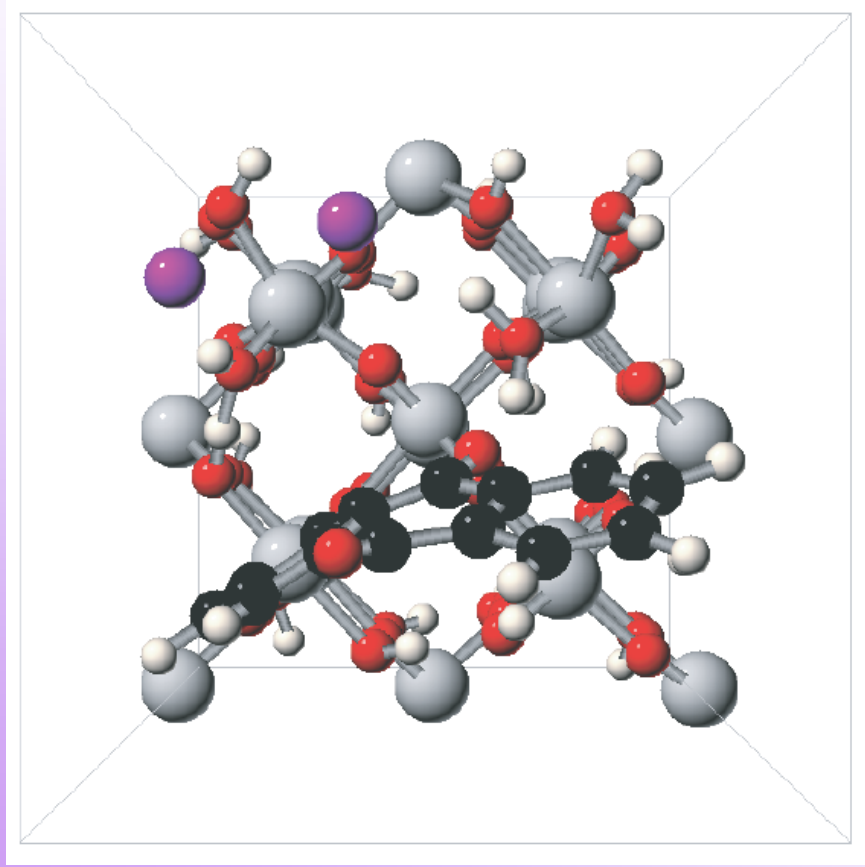
$$\Delta G \approx 50K$$

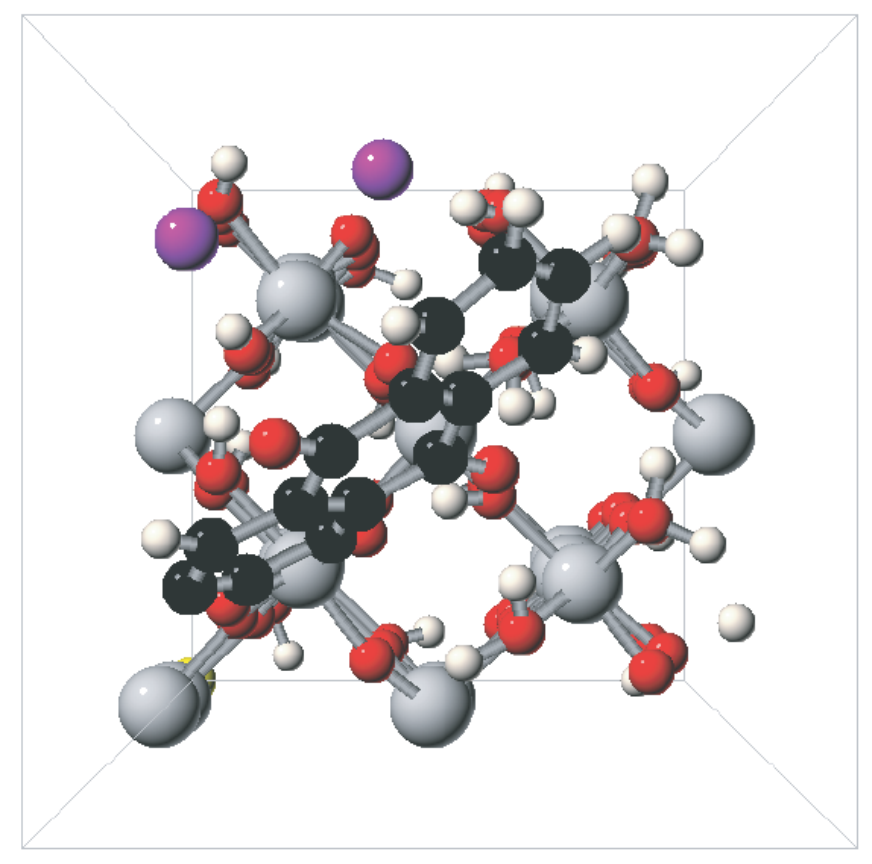
$$\nu = 2.8x10^{14}\, s^{-1}$$

$$\nu_{dye} = 2x10^{13}\, s^{-1}$$

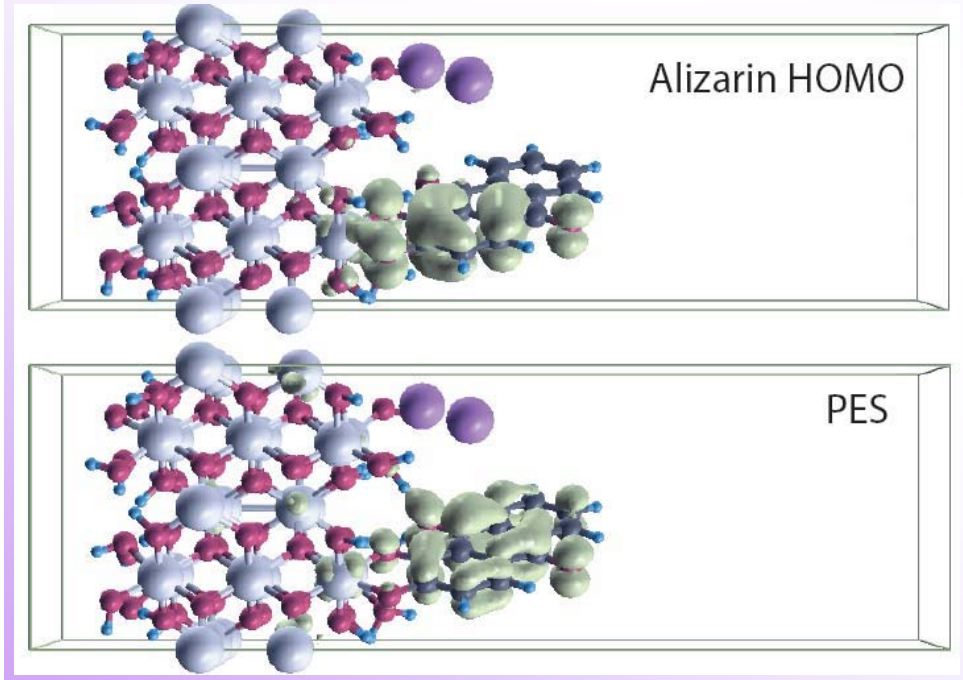
low barrier, hard to see T-dependence experimentally
multiple acceptor states speed up transfer

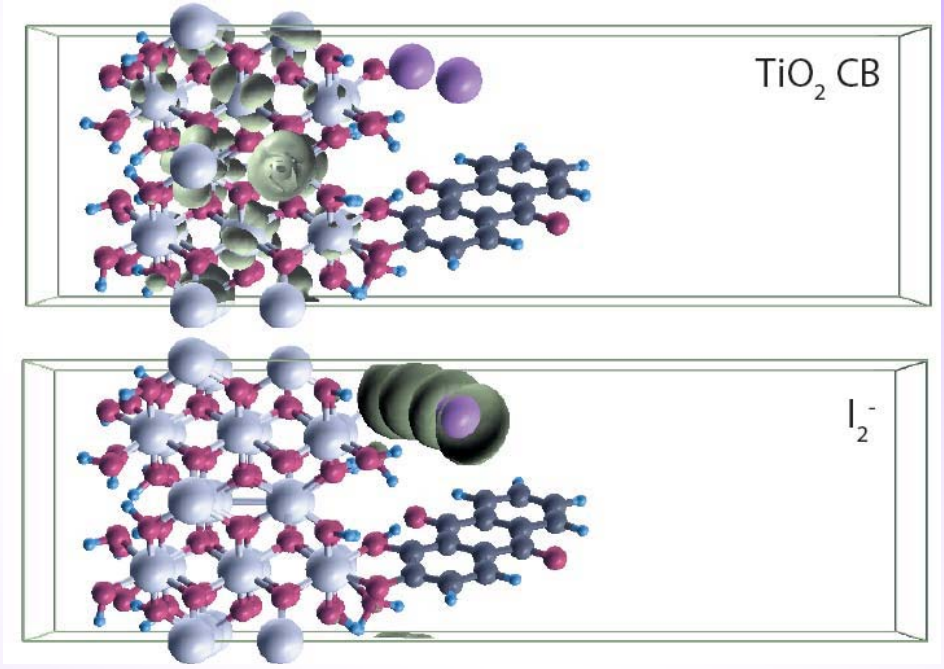
Alizarin Motion



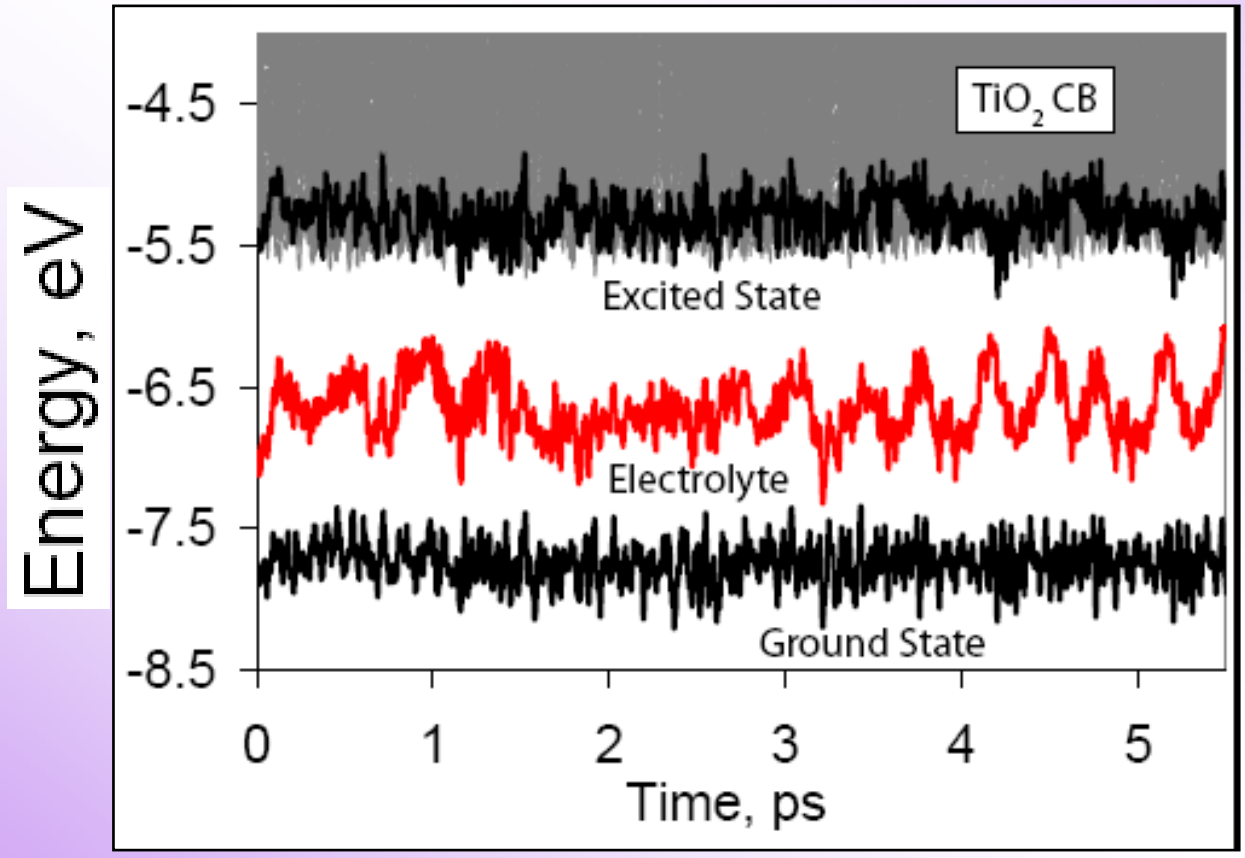


Electronic State Densities

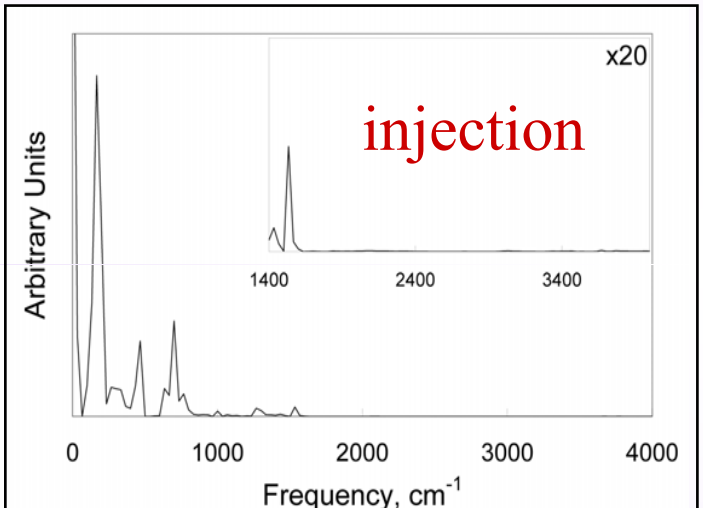


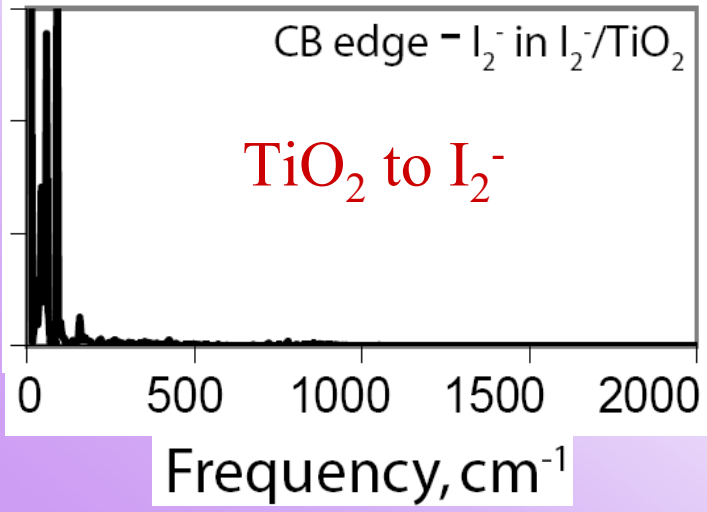


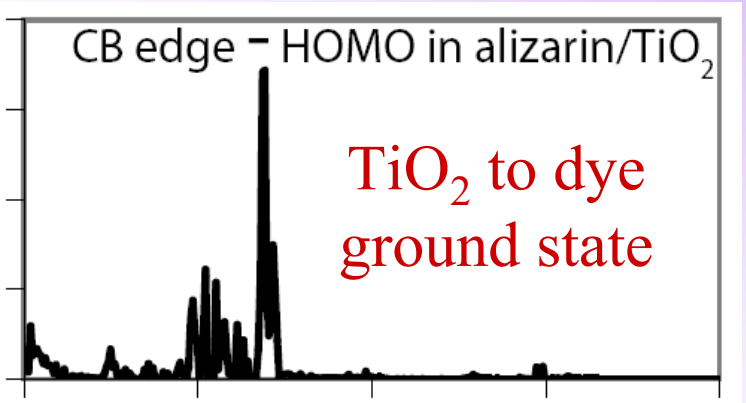
Vibrationally Induced Dynamics of Electronic Energy Levels

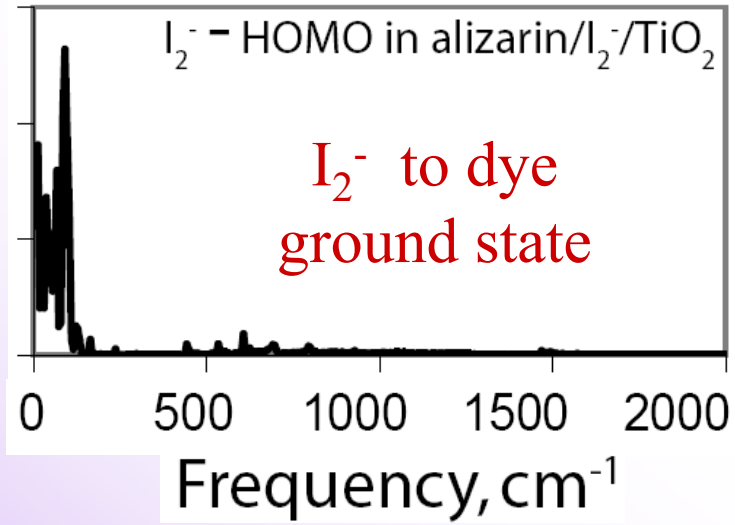


Active Vibrational Modes



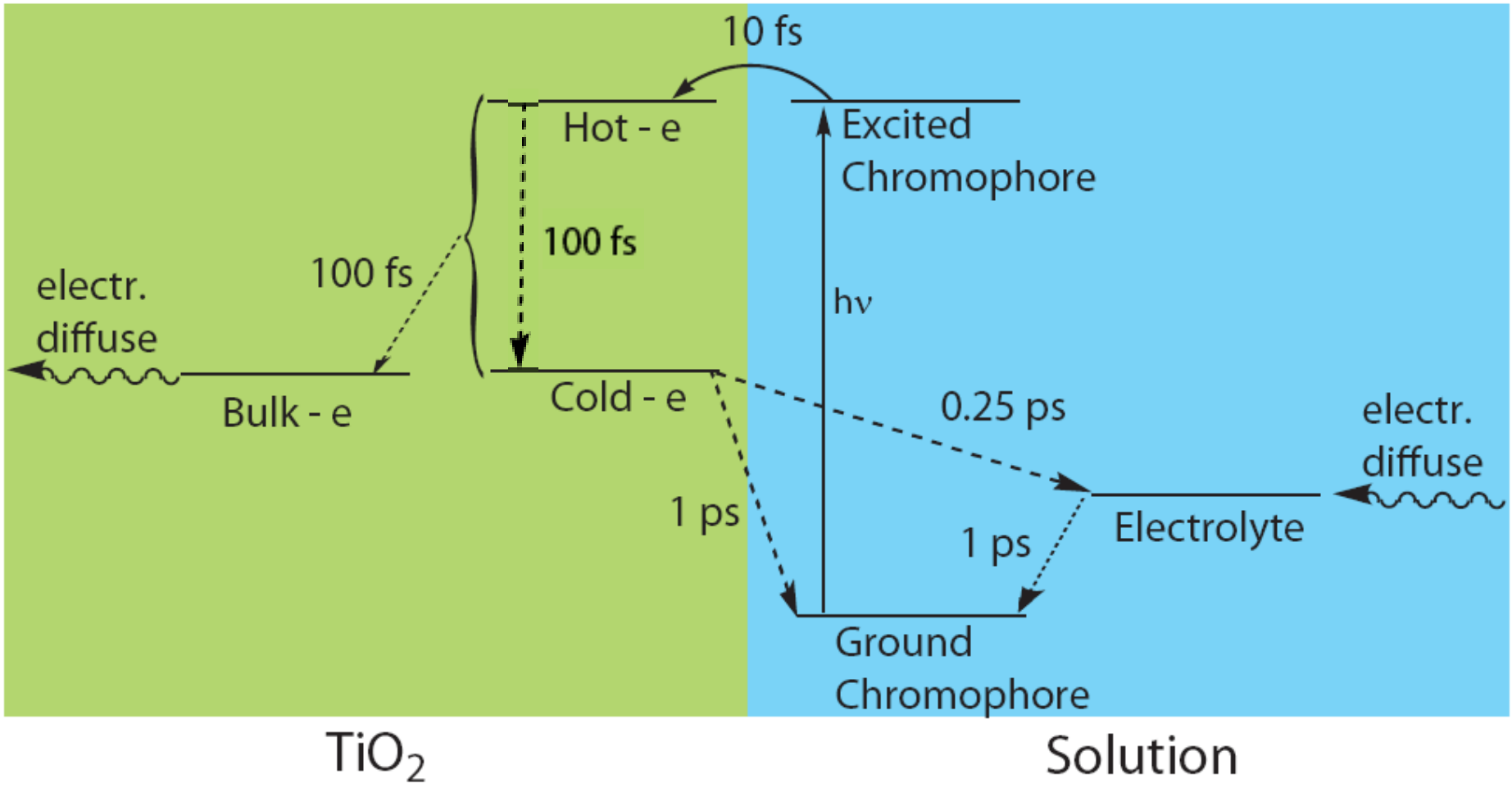






Complete Sequence of Events

(based on alizarin simulation)

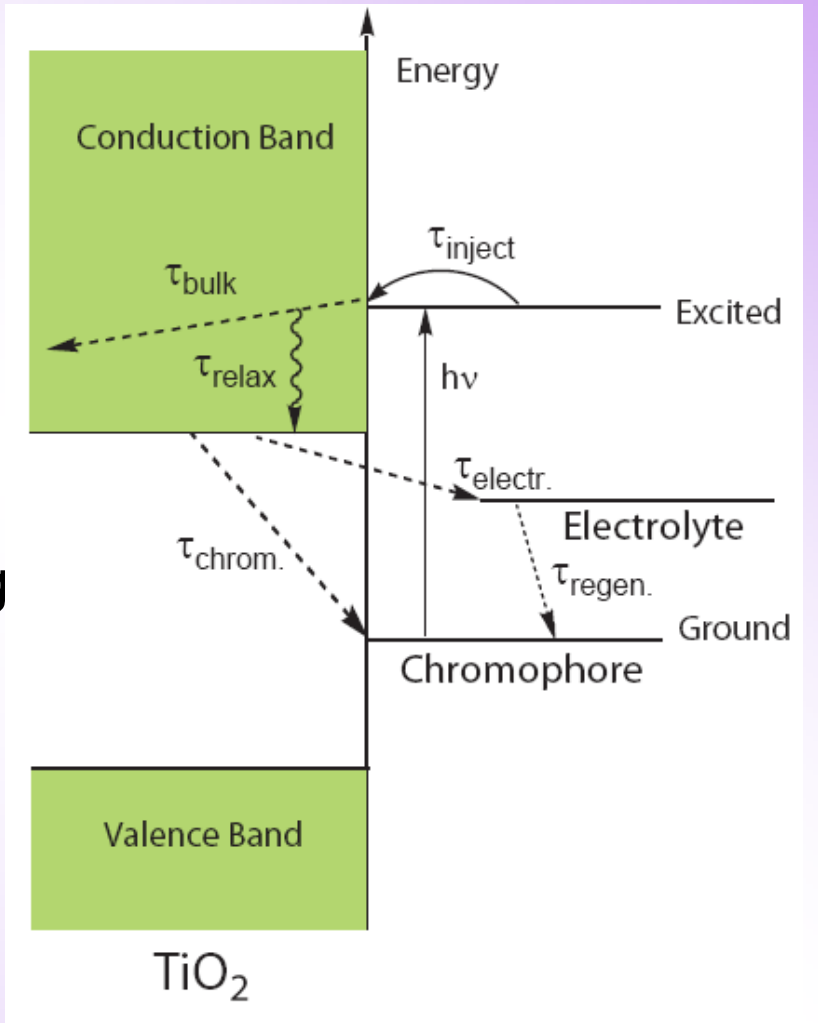


Summary: Injection

- ✓ 3 types of photoexcitation
- ✓ Strong/weak (adiabatic/NA) limits
- ✓ Variety of injection events

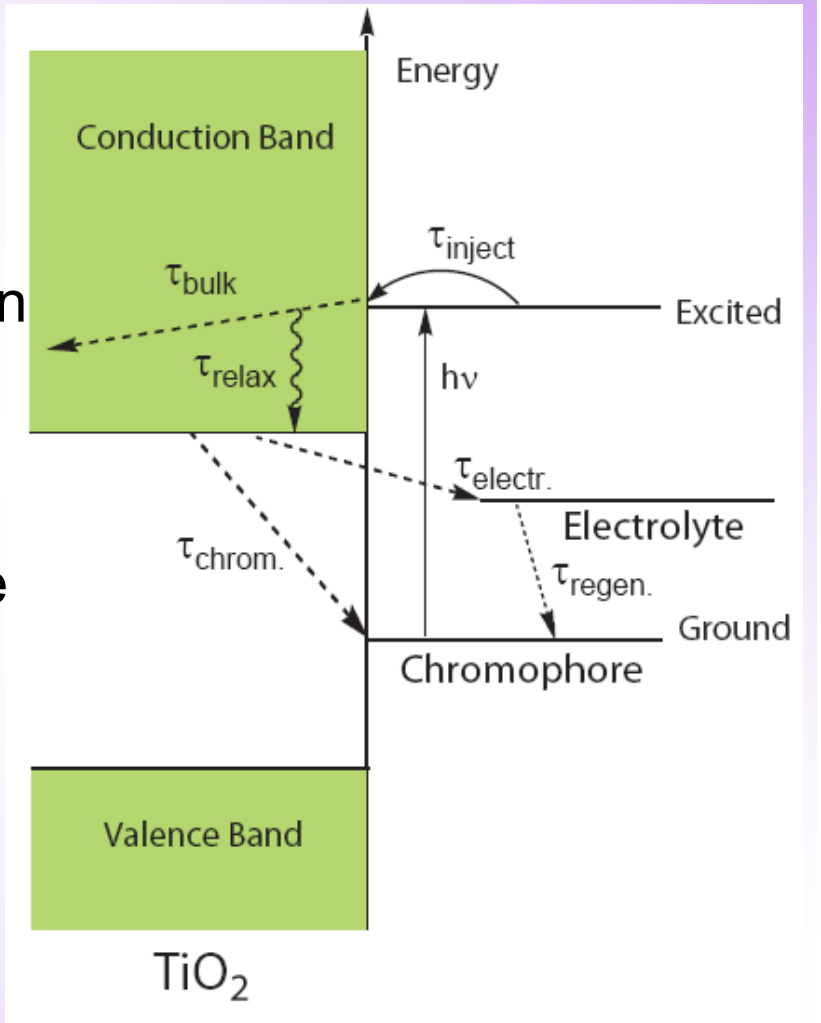
- ✓ Surface state acceptor
- ✓ Strong effect of vibrational motions
- ✓ Surface OH affect electronic coupling

- ✓ Weak temperature dependence
- ✓ TiO_2 surface vs. Ti^{4+} in solution

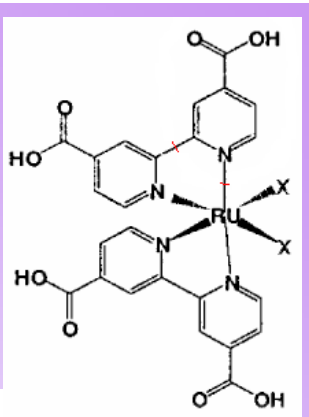


Summary: Relaxation and Recombination

- ✓ Relaxation – little energy dependence
- ✓ Delocalization – same time as relaxation
- ✓ Back-ET if electron is trapped
- ✓ Recombination to electrolyte on surface
- ✓ Electrolyte-dye ET varies with distance and orientation



Practical Considerations



VOLTAGE

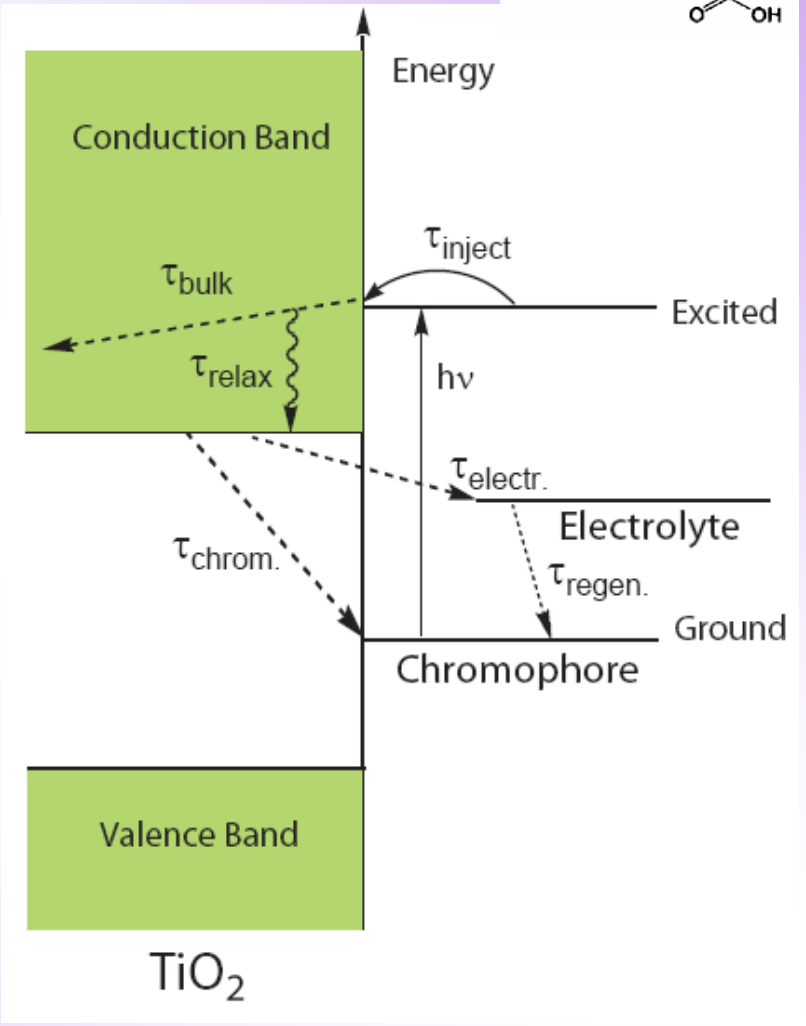
- ✓ Injection at CB edge

CURRENT

- ✓ Anneal surface traps
- ✓ Keep electrolyte away from surface

METAL vs. ORGANIC DYES

- ✓ Excited state towards surface
- ✓ Ground state away from surface
- ✓ Slower vibrational modes



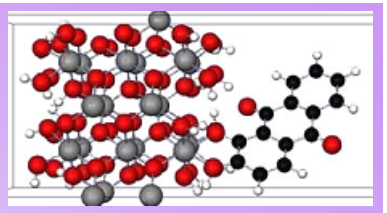
General Questions

- ✓ How to think of bulk-molecule interface:
  "One big molecule" or MO's weakly coupled to bands?

- ✓ Quantum confinement effects on excitation dynamics:
  To what extent are there bottlenecks?

- ✓ Electron-vibrational relaxation (heating):
  Which phonons are involved and why? $i\hbar\left\langle \chi^{\alpha} \left| \vec{\nabla}_R \right| \chi^{\beta} \right\rangle \cdot \dot{\vec{R}}$

Dr. Walter Duncan
currently faculty in Seattle U.



- Reviews

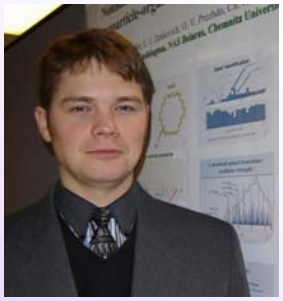
  Annu. Rev. Phys. Chem. **58** 143 (2007), *Acc. Chem. Res.* **41** 339 (2008)
- Papers

  J. Phys. Chem. ***B*** **106** 8047 (2002), *ibid.* **109** 365 (2005)**,** *ibid.* **109** 17998 (2005), *J. Mol. Struct* **630** 33-43 (2003), *Isr. J. Chem.* **42** 213-224 (2003), *Adv. Mater.* **16** 240 (2004), *J. Am. Chem. Soc.* **127** 7941 (2005), *Phys. Rev. Lett.* **95** 163001 (2005), *J. Am. Chem. Soc.* **129** 8528 (2007), *J. Am. Chem. Soc.* **130** 9756 (2008)
- Proceedings Papers

  Optical Soc. (*SPIE)* **5223** 132-146 (2003), *Electrochem. Soc.* (2004)
- Book Chapters

  Springer (2006), *Elsevier* (2006), *Springer* (2007)

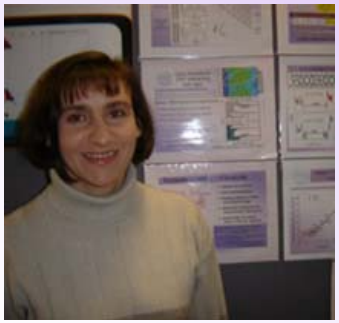
$$ NSF, DOE, ACS-PRF, UW-RRF



Dr. Dmitri Kilin
quantum dots
QHD

Dr.Walter Duncan
class.path TDDFT
alizarin/TiO_2

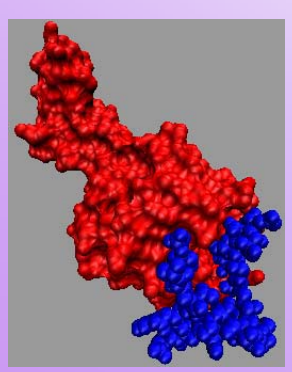
Dr.Colleen Craig
SH-TDDFT



Dr.Sveta Kilina
quantum dots

Brad Habenicht
carbon nanotubes

my daughter Eugenia
for "(n-m) mod 3= 0"



More group members

Dr. Yuriy Pereverzev (QHD, NLO polymers, bio-adhesion)

Kim Gunnerson (ozone chemistry, bio-adhesion)

Eric Heatwole (QHD)