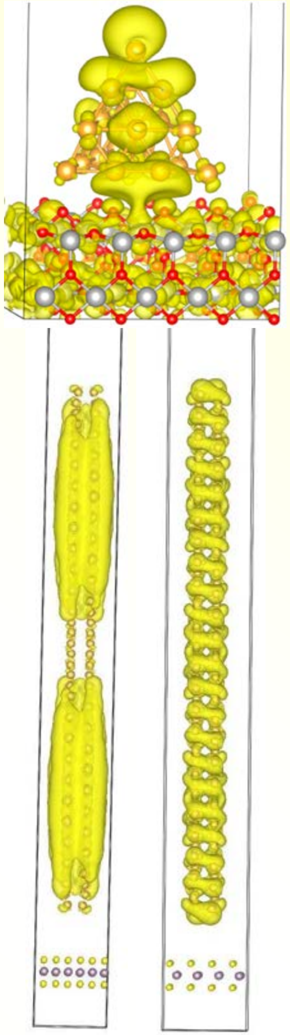
Nonadiabatic Dynamics in Nanoscale Materials with Time-Domain DFT

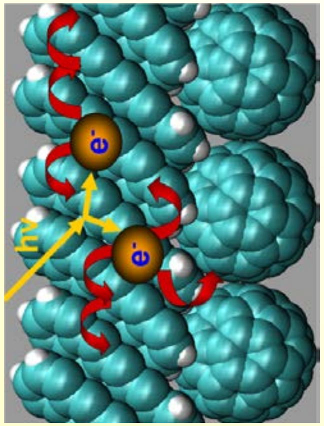


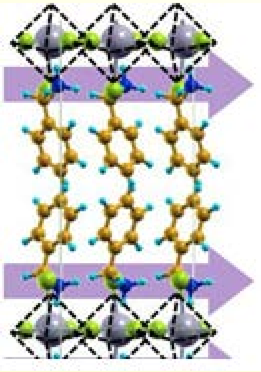
Oleg Prezhdo

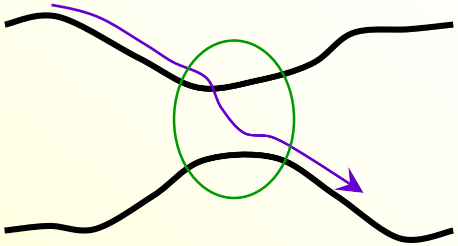
U. Southern California

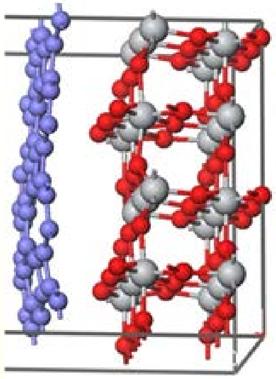
Trieste

May 9, 2017



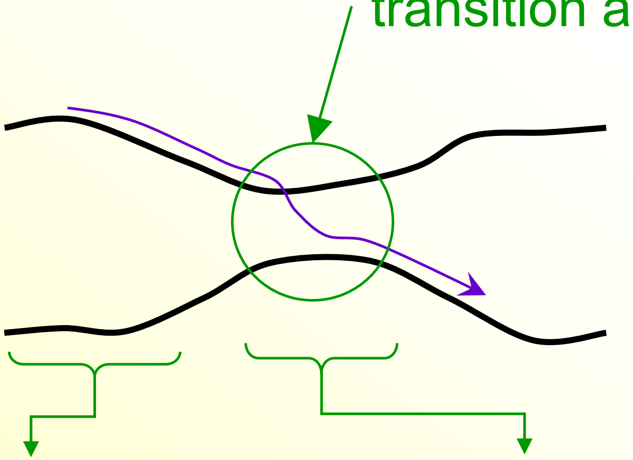






Nonadiabatic Molecular Dynamics

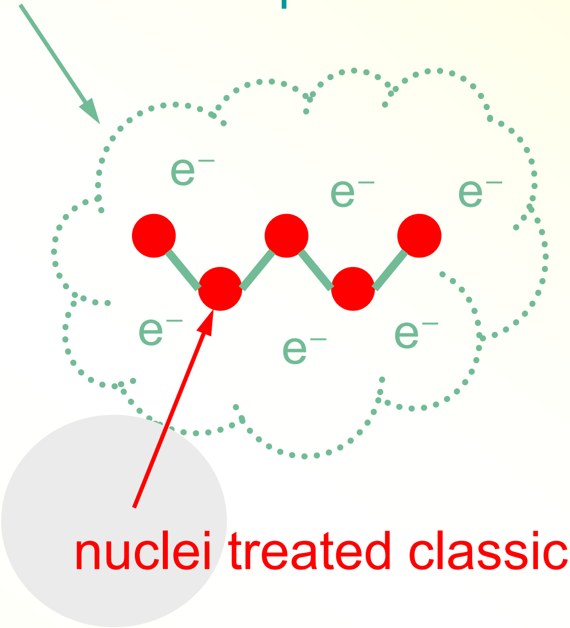
Nonadiabatic coupling between potential energy surfaces opens channels for system to change electronic states.



transition allowed

weak coupling

strong coupling



electrons treated quantum-mechanically

nuclei treated classically

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

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 electron-phonon coupling

Theoretical Questions

Perspective: *JPC Lett.* **7** 2100 (2016)

- ✓ 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

Decoherence induced surface hopping (DISH) *JCP* **137**, 22A545 (2012)
Coherence penalty functional (CPF) *JCP* **140**, 194107 (2014)

Self-consistent FSSH (SC-FSSH) *JPC-L* **5**, 713 (2014)

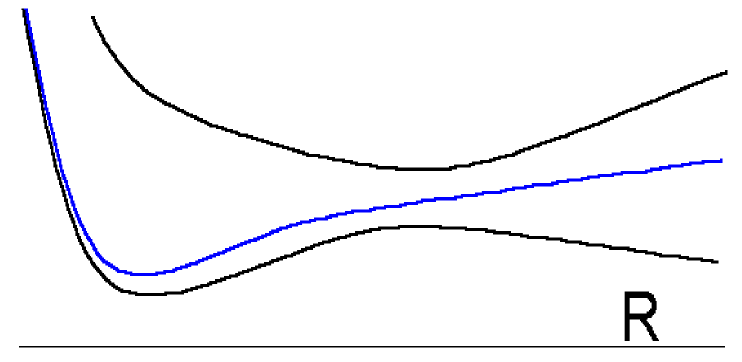
Global flux surface hopping (GFSH) *JCTC* **10**, 3598 (2014)
Second quantized surface hopping (SQUASH) *PRL* **113**, 153003 (2014)
FSSH in Liouville space *JPCL* **6**, 3827 (2015)
GFSH in Liouville space, *JCP-Rapid* **143**, 191102 (2015)

Ehrenfest Dynamics

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

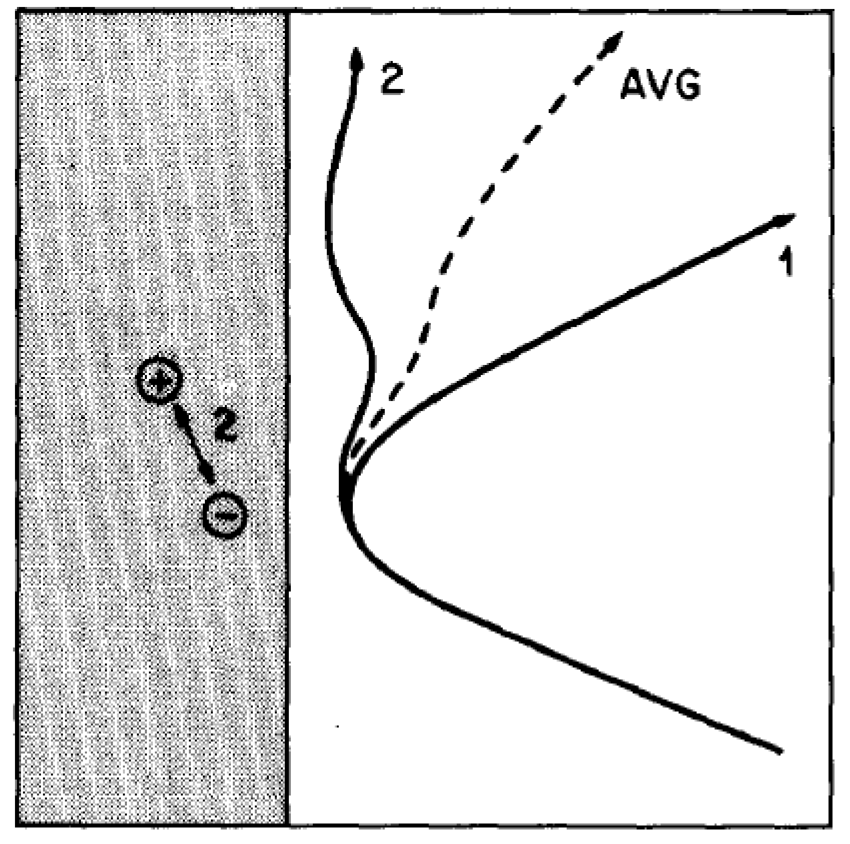
time-dependent Hellmann-Feynman theorem gives Newton equation



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

quantum force
(time-dependent Hellmann-Feynman theorem)

Why Surface Hopping Needed?



Average surface is not physical

Fewest Switches Surface Hopping

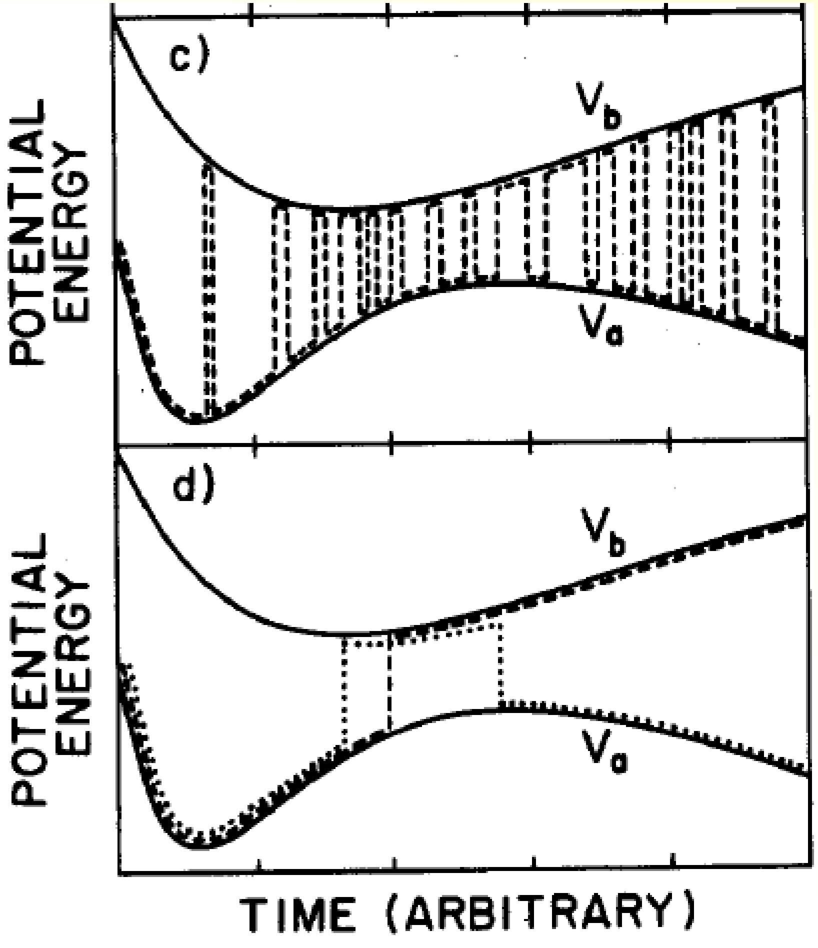
Tully, *JCP* **93**, 1061 (1990)

Based on probability $|c_i|^2$

(becomes effectively Ehrenfest)

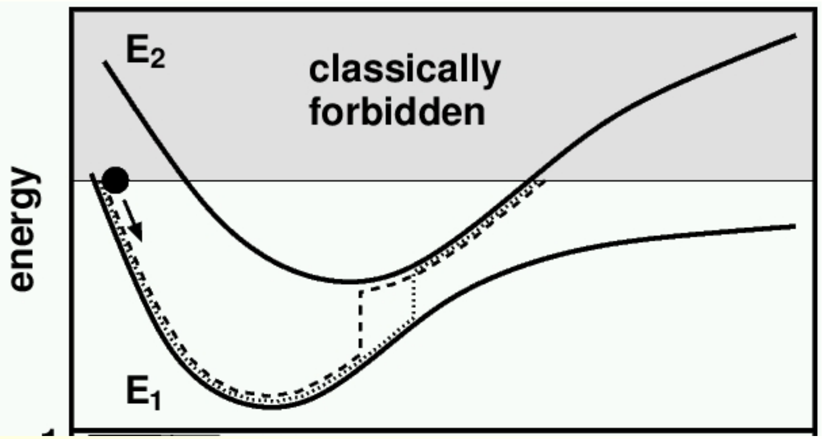
Fewest Switches

based on flux, $d\,|c_i|^2/dt$



Fewest Switches Surface Hopping

Tully, *JCP* **93**, 1061 (1990)



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, due to hop rejection,
needed for thermodynamic equilibrium:
Parahdekar, Tully *JCP* **122**, 094102 (2005)

Super-Exchange Problem

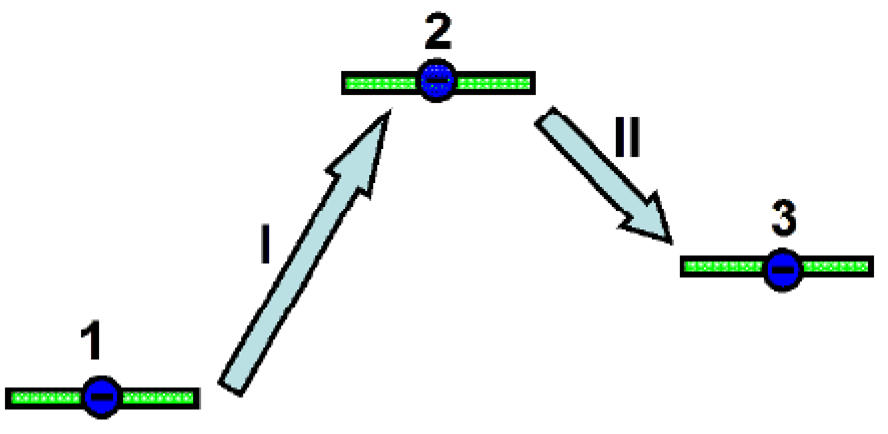
in Tully's surface hopping *J. Chem. Phys.* **93**, 1061 (1990)

Transition probability *i*→*j* is proportional to coupling V_{ij}, d_{ij}.

This excludes super-exchange: *Kramers 1934, Anderson 1950*

$$g_{ij} = \max\left\{\frac{-dt \cdot b_{ij}}{a_{ii}}, 0\right\}$$

$$b_{ij} = 2\hbar^{-1}\,\mathrm{Im}\left(a_{ij}^{*}V_{ij}\right) - 2\,\mathrm{Re}\left(a_{ij}^{*}\dot{\mathbf{R}}\cdot\mathbf{d}_{ij}\right)$$



If state 2 is higher than 1 by more than a few *kT* and 1 and 3 are not coupled *1->3* is forbidden

Global Flux Surface Hopping

Wang, Trivedi, Prezhdo, *J.Theor.Comp.Chem.* **10**, 3598 (2014)

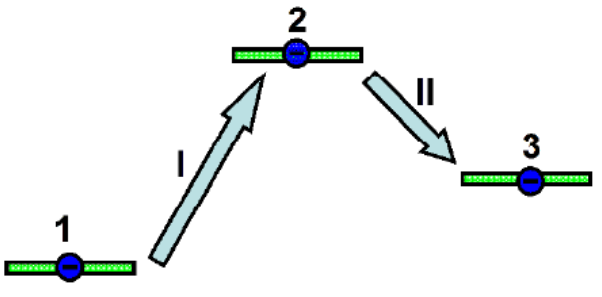
Superexchange model

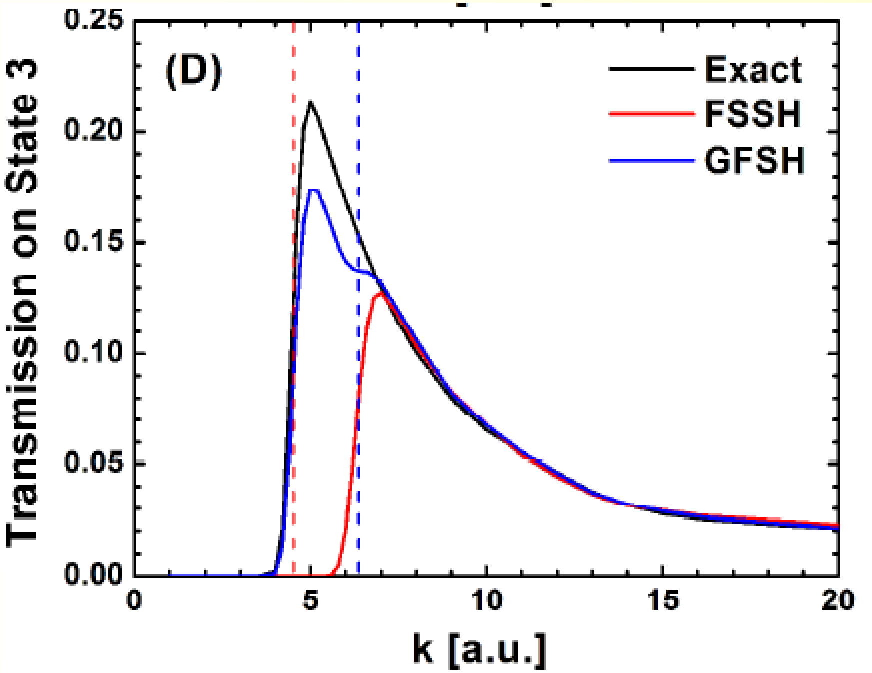
$V_{11}(x) = 0\,, \quad V_{22}(x) = 0.01\,, \; V_{33}(x) = 0.005$

$V_{12}(x) = V_{21}(x) = 0.001e^{-x^2/2}$

$V_{23}(x) = V_{32}(x) = 0.01e^{-x^2/2}$

$V_{13}(x) = V_{31}(x) = 0$





k=4-7 superexchange regime

FSSH in Liouville Space

L. Wang, A.E. Sifain, O.V.P. *J Phys Chem Lett* **6**, 3827 (2015)

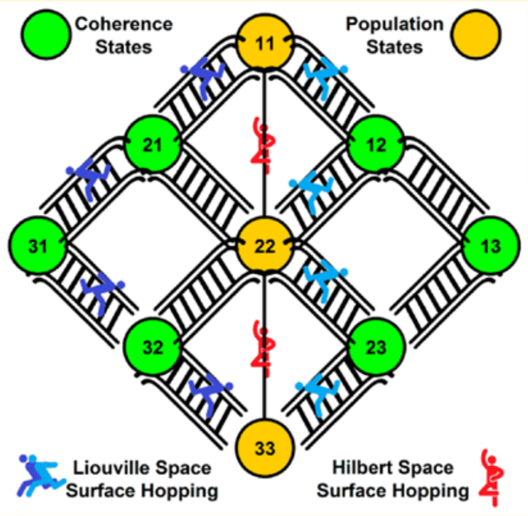
$$\frac{d|\psi(t)\rangle}{dt} = \frac{1}{i\hbar}\hat{H}|\psi(t)\rangle \qquad \hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|$$

$$\frac{d\hat{\rho}(t)}{dt} = \frac{1}{i\hbar}[\hat{H}, \hat{\rho}] \qquad |\rho\rangle\rangle = \sum_{ij} \rho_{ij}|ij\rangle\rangle$$

$$\frac{d}{dt}|\rho\rangle\rangle = \frac{1}{i\hbar}\hat{\hat{L}}|\rho\rangle\rangle$$

One trajectory at a time

Normal FSSH



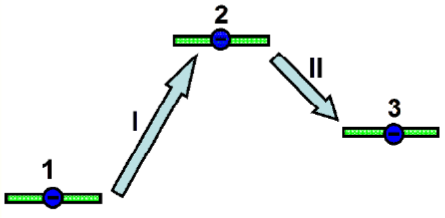
<u>Questions for coherence states, $i \neq j$</u>

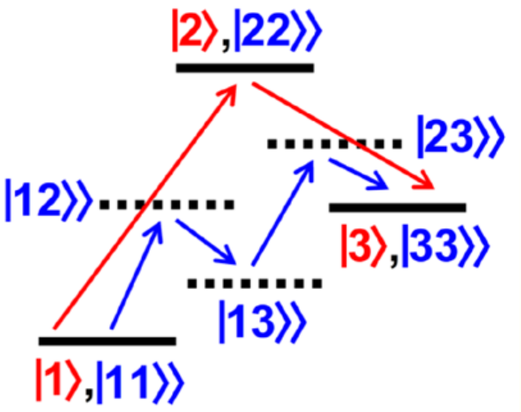
- Energy: $E_{ij}=(E_{ii}+E_{jj})/2$, similar to quantum-classical Liouville
- Interpretation of trajectories on *ij*: assign half to *ii*, half to *jj*
- Direction of velocity rescaling for transition *ij*→*kl*:

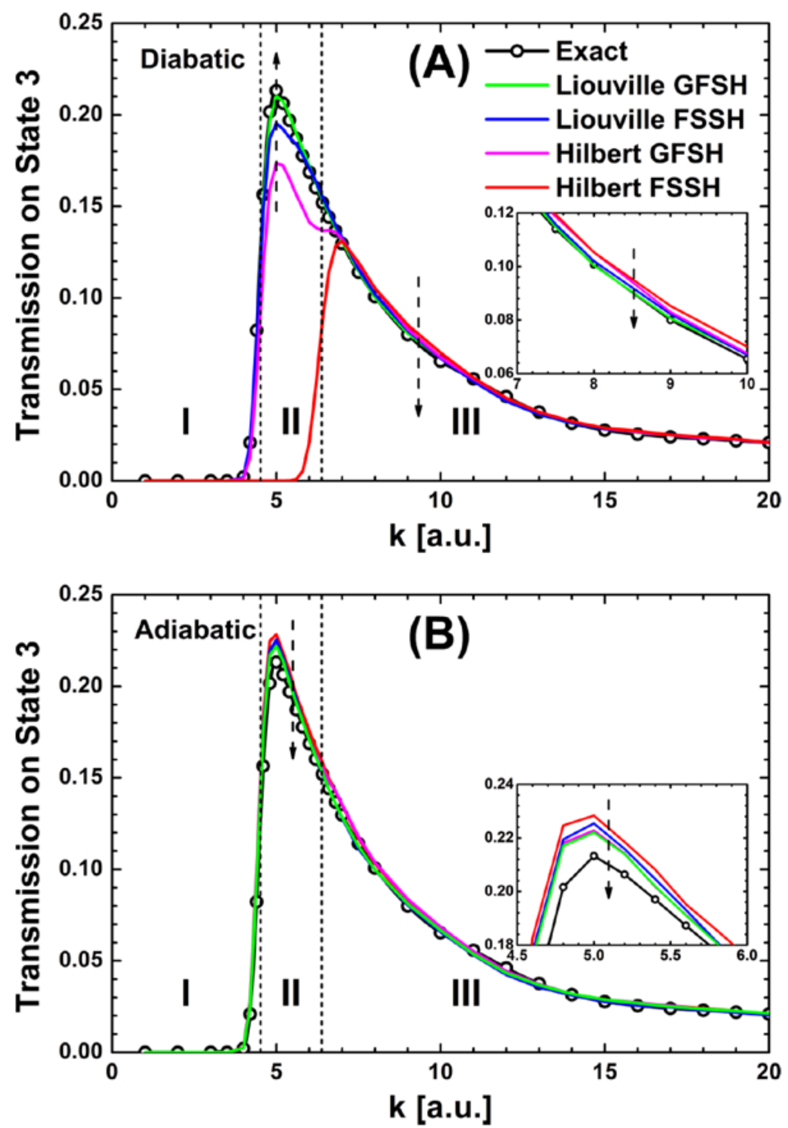
  add NA coupling vectors $NA_{ik}+NA_{jl}$

FSSH & GFSH in Liouville Space

L. Wang, A.E. Sifain, O.V.P. *JCP-Rapid* **143**, 191102 (2015)



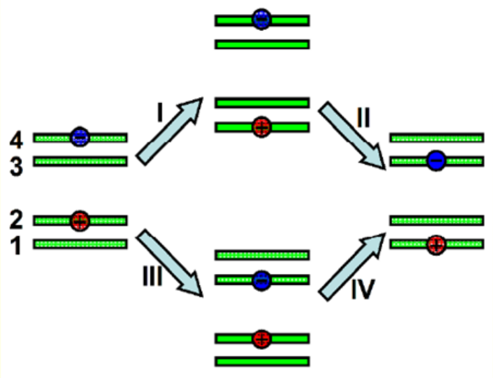


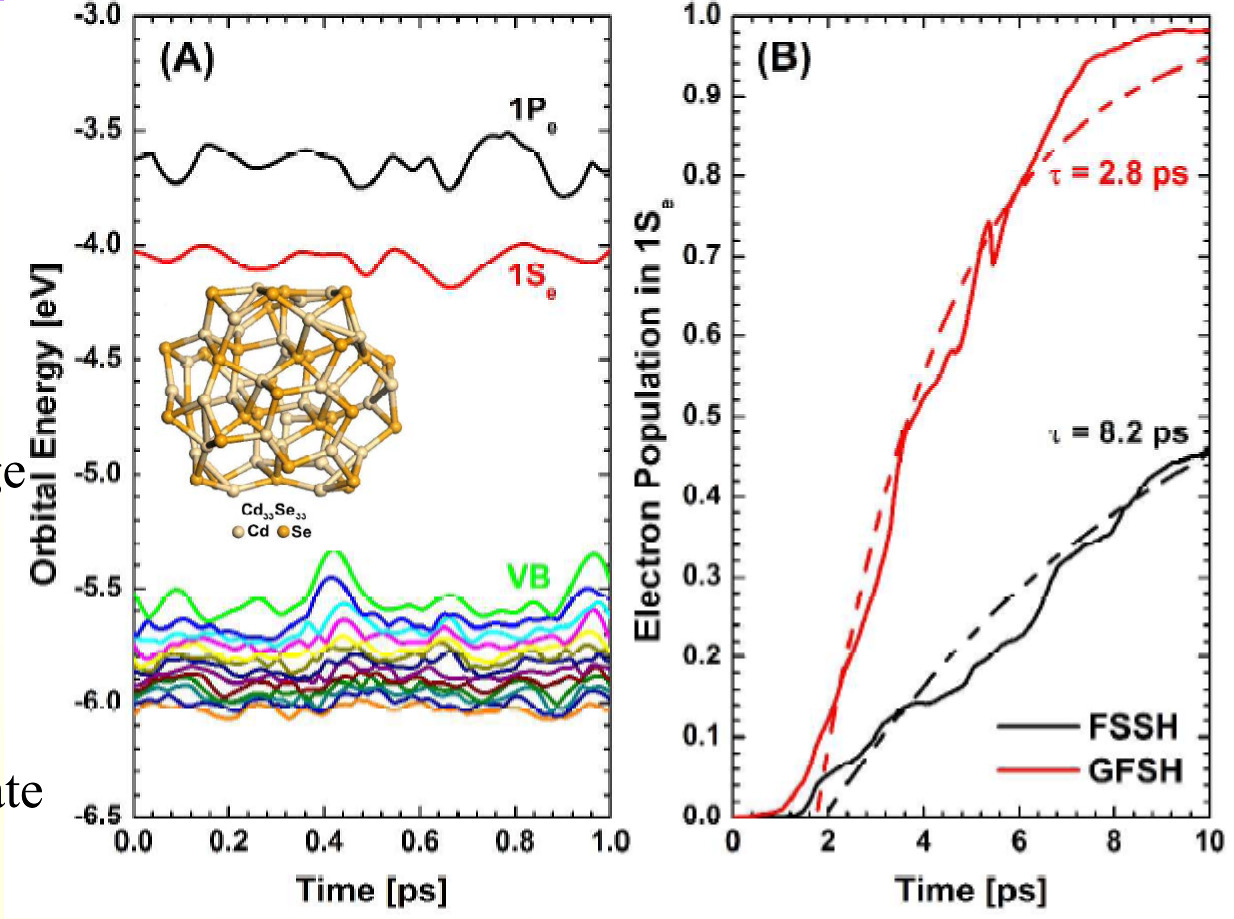


Super-exchange is obtained

Global Flux Surface Hopping

Wang, Trivedi, Prezhdo, *J.Theor.Comp.Chem.* **10**, 3598 (2014)
Trivedi, Wang, Prezhdo, *Nano Lett.* **15**, 2086 (2015)





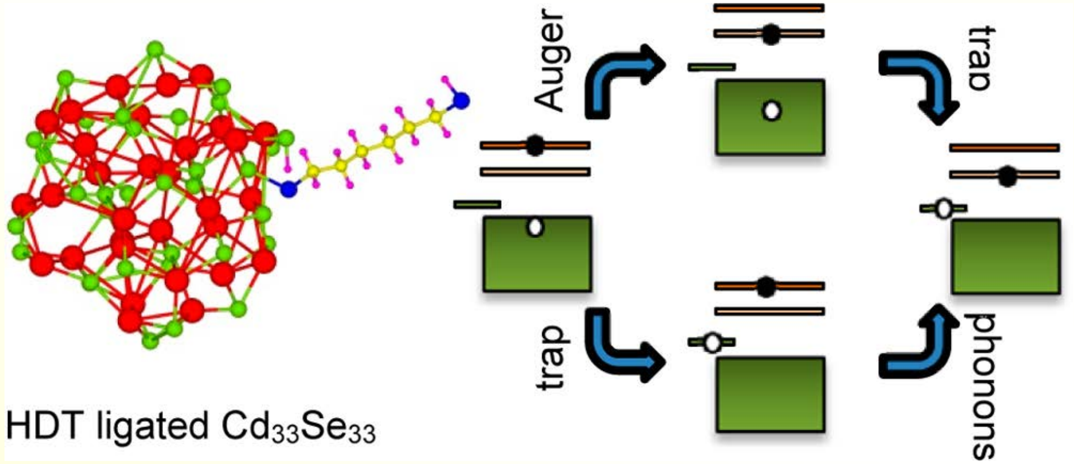
Electron-hole energy exchange

Multiple-exciton generation
and recombination

Singlet fission (via intermediate
charge transfer states)

Auger Electron-Hole Relaxation and Hole Trapping in CdSe QD

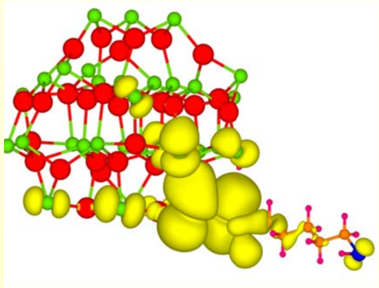
Trivedi, Wang, Prezhdo, *Nano Lett.* **15**, 2086 (2015)



HDT ligated $Cd_{33}Se_{33}$

<u>Electron Relaxation</u>
without trap 1.3 ps
with trap 1.8 ps

<u>Hole trapping</u> 1.2 ps



- Hole is localized on surface, ligand tail not important
- Bottleneck not achieved because hole trapping is too slow, not because hole still couples to electron

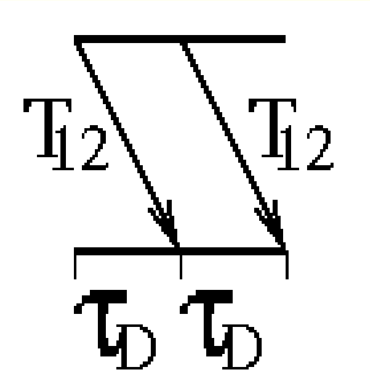
Experiment: Sippel et al. *Nano Lett.* **13** 1655 (2013)

Decoherence & Quantum Zeno Effect

O. V. Prezhdo, P. J. Rossky, *Phys. Rev. Lett.* **81**, 5294 (1998)
O. V. Prezhdo, *Phys. Rev. Lett.* **85**, 4413 (2000)

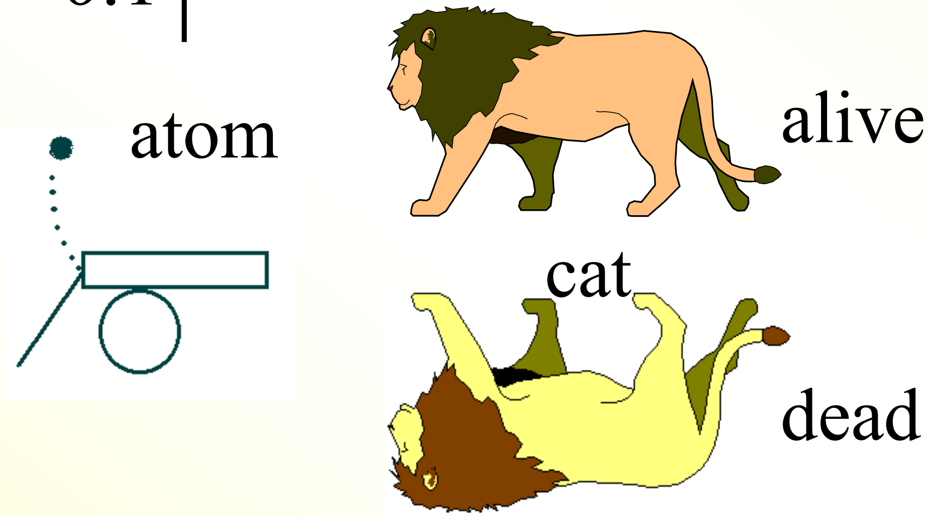
With decoherence: $P_{12} = |T_{12}|^2 + |T_{12}|^2 + \ldots$

Without decoherence $P_{12} = |T_{12} + T_{12} + \ldots|^2$



Decoherence makes transitions less likely

$$|0.1|^2 + |0.1|^2 < |0.1 + 0.1|^2$$

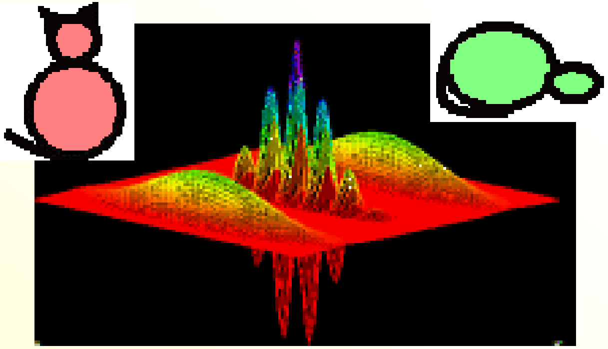


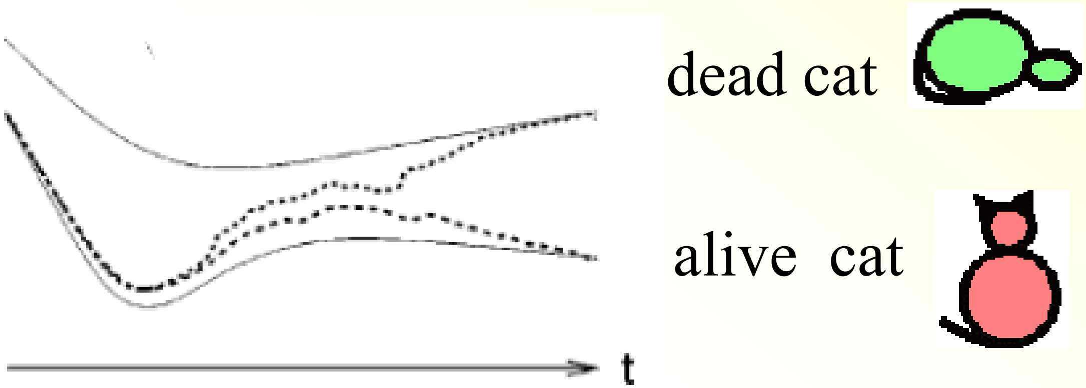
Stochastic Mean-Field (decoherence gives branching)

Prezhdo *J. Chem. Phys.* **111**, 8366 (1999)

No ad hoc expressions for hopping probability

Cat Density





quantum Brownian motion

$$|d\Psi\rangle = -iH|\Psi\rangle dt - {}^{\gamma}\!/_{2}\, L^{+}L|\Psi\rangle dt + \sqrt{\gamma}\, L|\Psi\rangle dW$$

friction noise

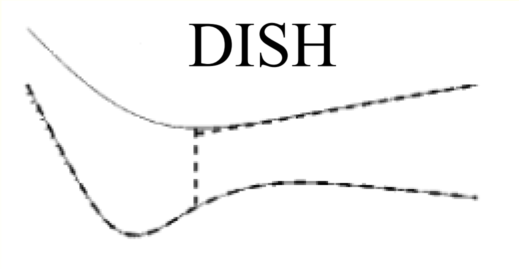
Decoherence Induced Surface Hopping (DISH)

Jaeger, Fisher, Prezhdo *J. Chem. Phys.* **137**, 22A545 (2012)

Evolve in an adiabatic state.

Hop when a decoherence event occurs.

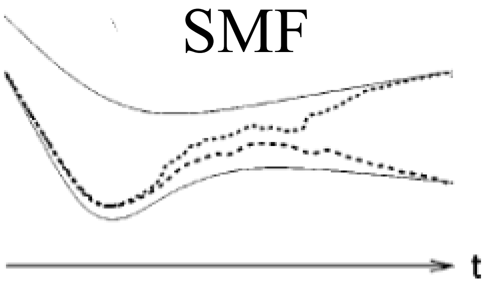
Rescale velocity as before in SH.



DISH

Advantages

1. Includes decoherence
2. Gives branching
3. Nuclear evolution in pure states



SMF

Corresponds to a piece-wise continuous stochastic Schrodinger equation

Coherence Penalty Functional

Akimov, Long, Prezhdo, *J. Chem. Phys.* **140**, 194107 (2014)

- Retain computational efficiency of Ehrenfest – no stochastic sampling: 1 trajectory, ordinary differential equations
- Penalize development of coherence

$$i\hbar\frac{\partial c_i(t)}{\partial t} = \sum_i \left[E_i(R(t))\,\delta_{i,j} - i\hbar\frac{P}{M}d_{ij}\right]c_j(t) \qquad \begin{aligned} q_i &= \mathrm{Re}(c_i) \\ p_i &= \mathrm{Im}(c_i) \end{aligned}$$

$$H = \sum_i \frac{E_i}{2\hbar}\left(q_i^2 + p_i^2\right) - \frac{P}{M}\sum_{i,j} d_{ij}\,p_i q_j \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \dot{q}_i = -\frac{\partial H}{\partial p_i}$$

Coherence Penalty Functional

Akimov, Long, Prezhdo, *J. Chem. Phys.* **140**, 194107 (2014)

- Retain computational efficiency of Ehrenfest – no stochastic sampling: 1 trajectory, ordinary differential equations
- Penalize development of coherence

$$i\hbar\frac{\partial c_i(t)}{\partial t} = \sum_i \left[E_i(R(t))\delta_{i,j} - i\hbar\frac{P}{M}d_{ij}\right]c_j(t)$$

$$q_i = \mathrm{Re}(c_i)$$
$$p_i = \mathrm{Im}(c_i)$$

$$H = \sum_i \frac{E_i}{2\hbar}\left(q_i^2 + p_i^2\right) - \frac{P}{M}\sum_{i,j} d_{ij}p_iq_j \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \dot{q}_i = -\frac{\partial H}{\partial p_i}$$

$$\tilde{H} = H + \sum_{\substack{i,j\\ i\neq j}} \lambda_{ij}\left(q_i^2 + p_i^2\right)\left(q_j^2 + p_j^2\right)$$

states with large coherence are energy maxima

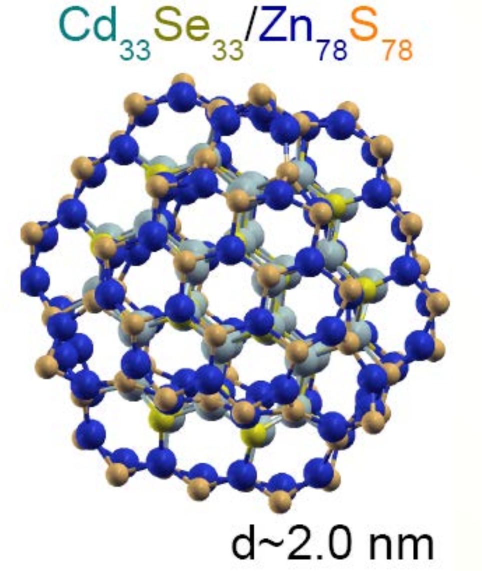
$$(q_i^2 + p_i^2)(q_j^2 + p_j^2) = |c_i^* c_j|^2$$

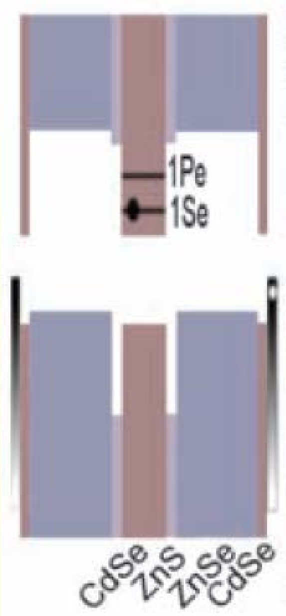
coherence measure

λ_{ij} - decoherence rate

Phonon Bottleneck in CdSe QD

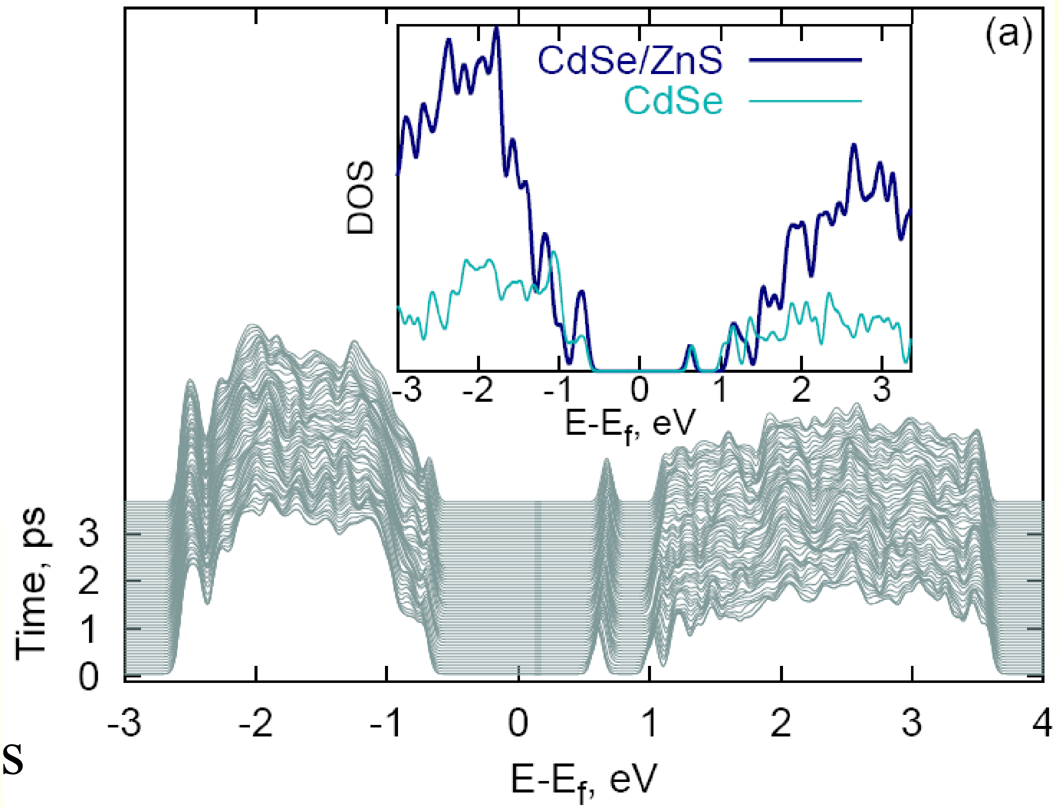
Kilina, Neukirch, Habenicht. Kilin, Prezhdo, *PRL* **110**, 180404 (2013)





Experiment: 1ns

Pandey, Guyot-Sionnest
Science **322** 929 (2008)



Calculation: 0.7ns
without decoherence: 0.003ns

PYXAID: PYthon eXtension of Ab Initio Dynamics

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

Python interfaced with Quantum Espresso, VASP

In DFTB+: Pal, Trivedi, Akimov, Aradi, Frauenheim, Prezhdo
JCTC **12** 1436 (2016)

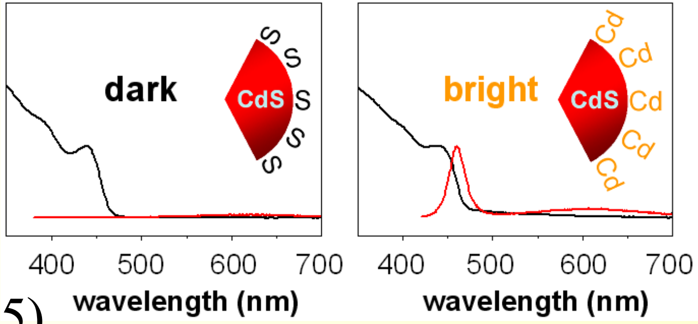
Fragment approach in Gamess: Negben, Prezhdo
JPC A **120** 7205 (2016)

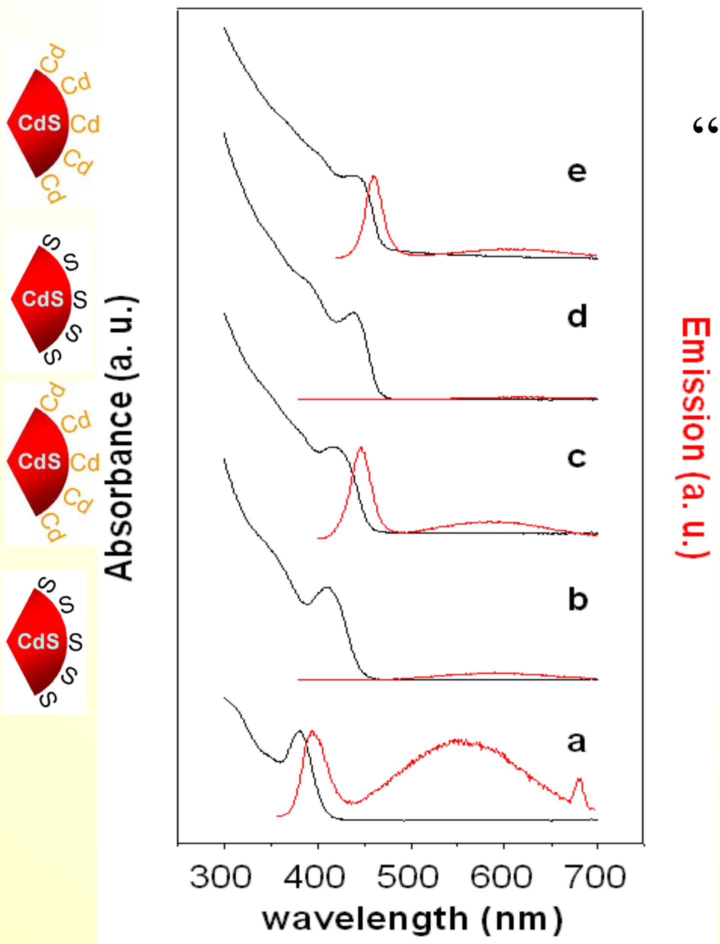
Overview of new methods
Perspective Article in
JPC Lett. **7** 2100 (2016)

Surface Chemistry Controls Relaxation

Krauss, Prezhdo, et al.

Nano Lett **12** 4465 (2012); *Chem Phys* (2015)

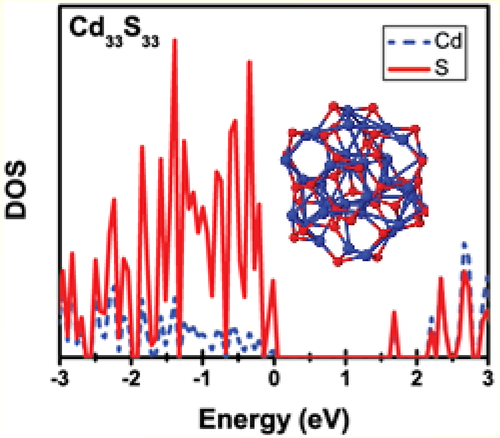


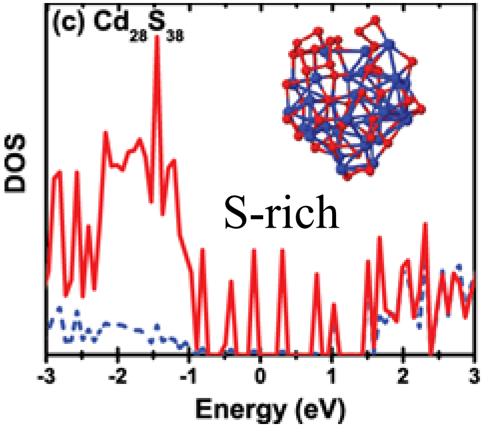


Metallic Cd

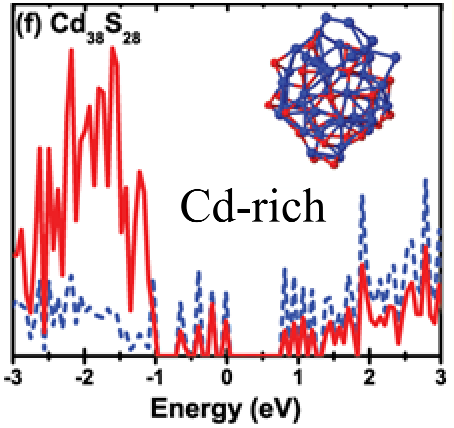
“heals” dangling bonds

Covalent S does not





S-rich

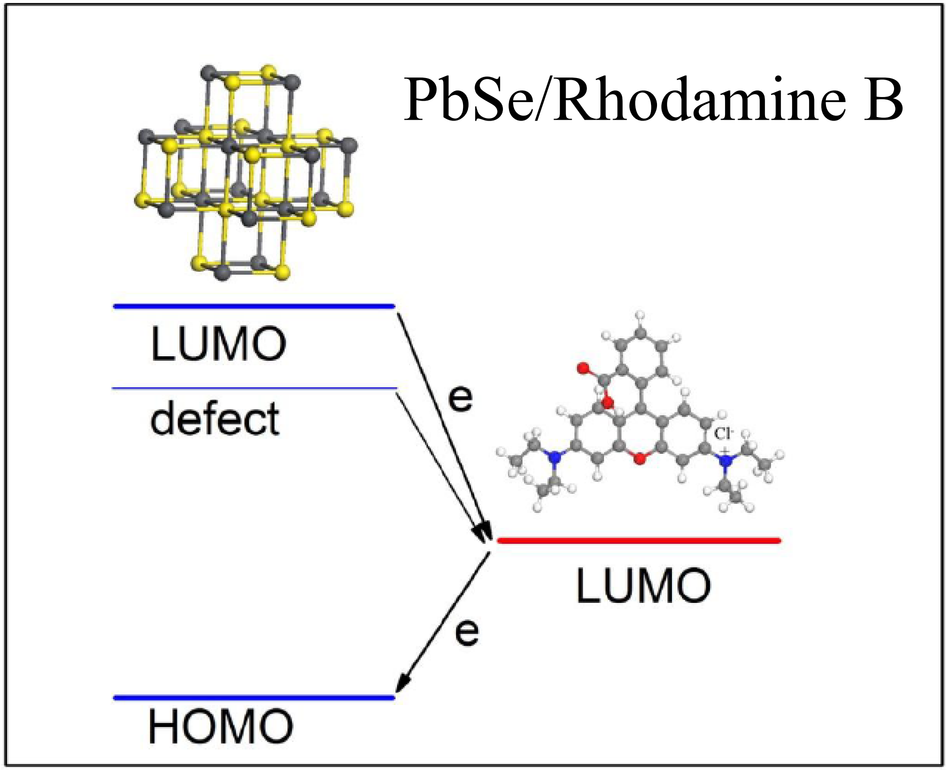


Cd-rich

Surface states facilitate non-radiative relaxation

Defects Help Charge Separation

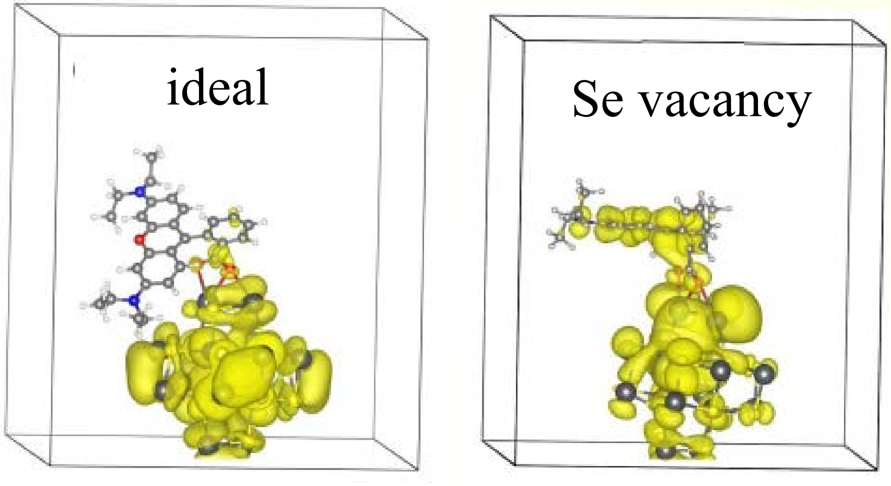
L. Run, N. English, O. V. Prezhdo *J. Am. Chem. Soc.* **135**, 18892 (2013)



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
T.Lian *JACS* 133, 9246 (2011)		
Ideal:	3.4	10
Defect:	1.0	

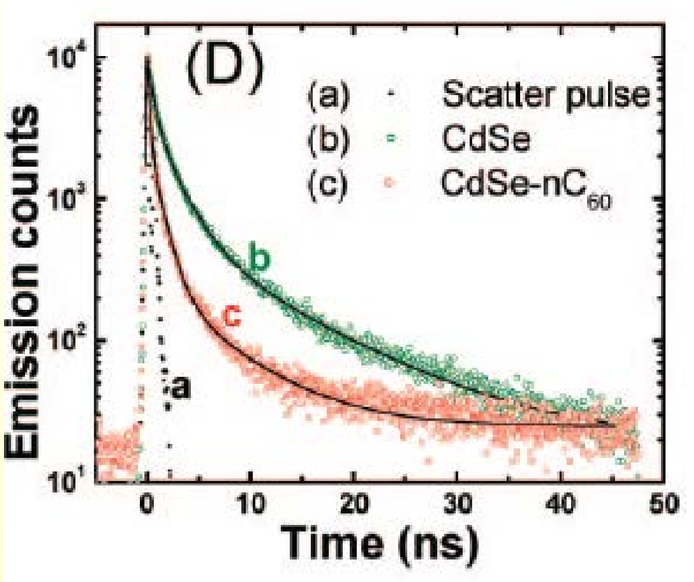


QD LUMO

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

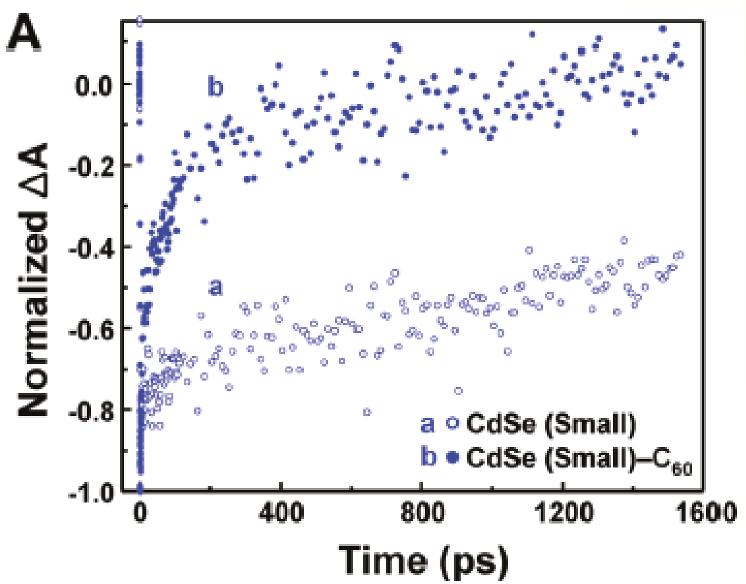
Chaban & Prezhdo, *J. Phys. Chem. Lett* **4**, 1 (2013)

Mechanical mixture: 10ns

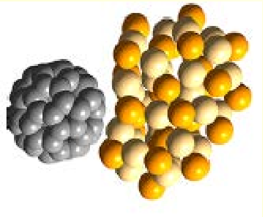


Brown & Kamat, *JACS* **130**, 8891 (2008)

Bridged: 10-100ps

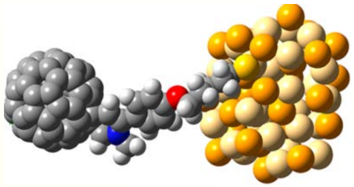


Bang & Kamat, *ACS Nano* **12**, 9421 (2011)



<= closer contact

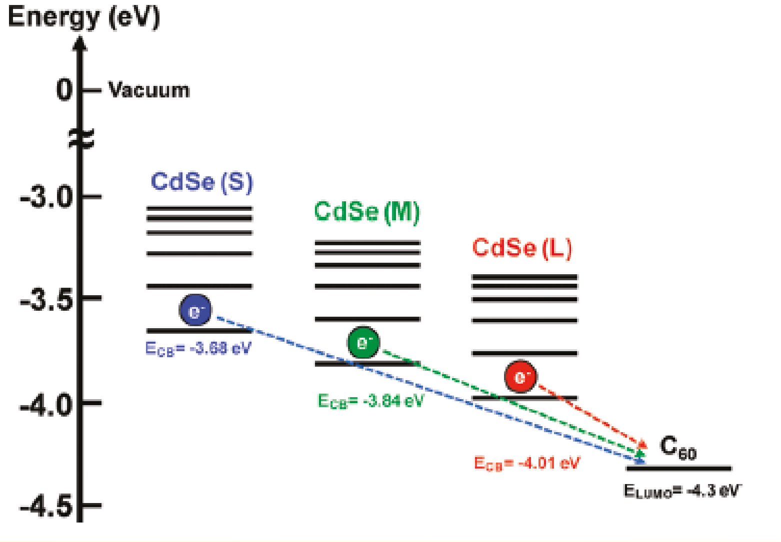
faster dynamics =>



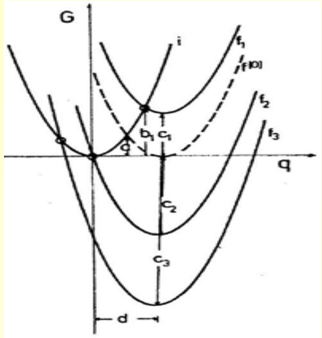
ET between CdSe QD and C_{60}

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

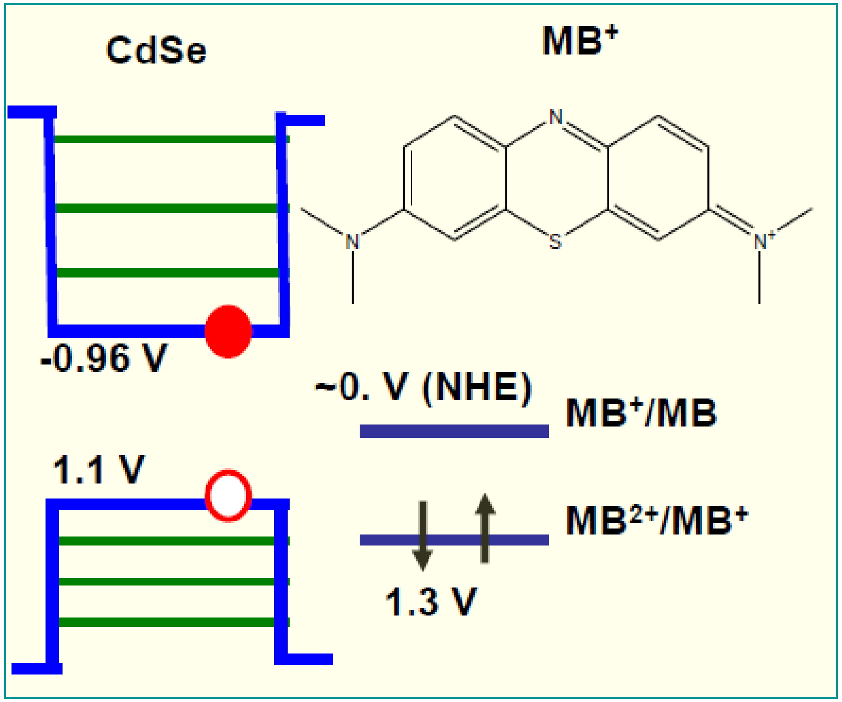


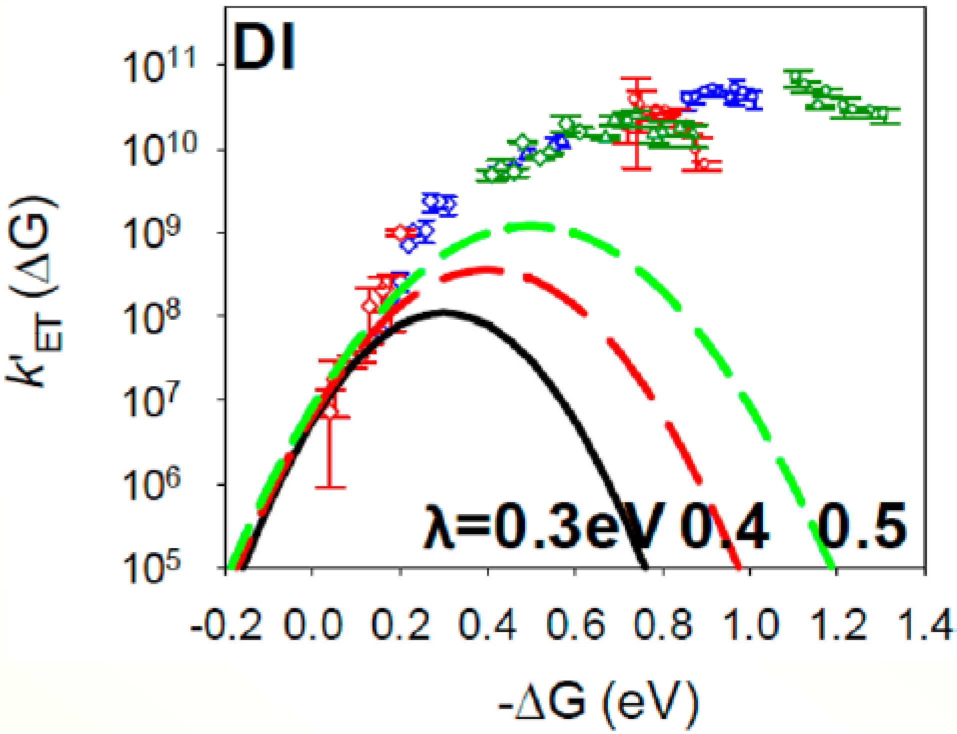
Bridge provides strong NA electron-phonon coupling needed to remove excess electron energy



Auger-assisted ET

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

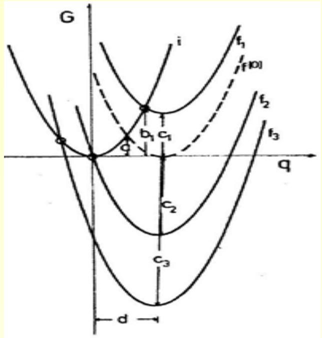


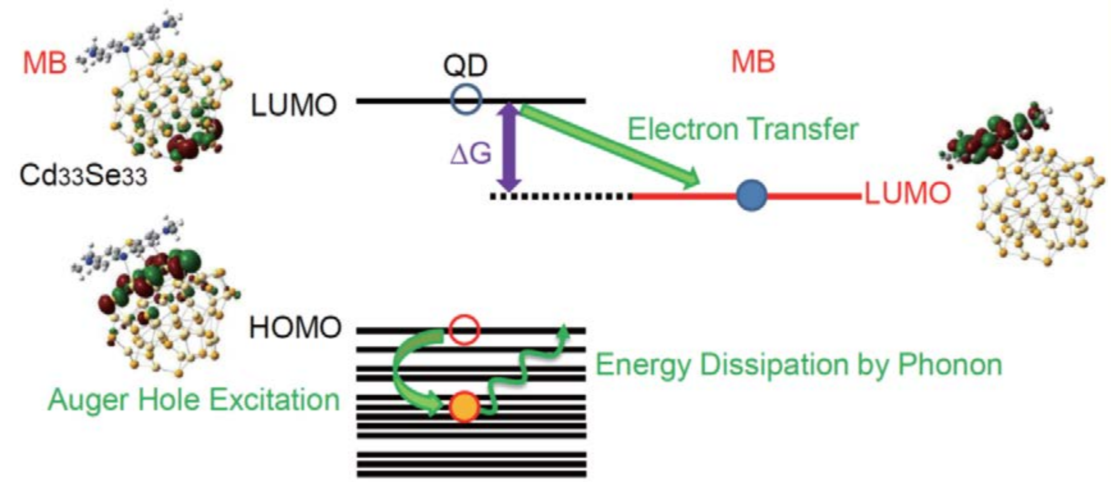


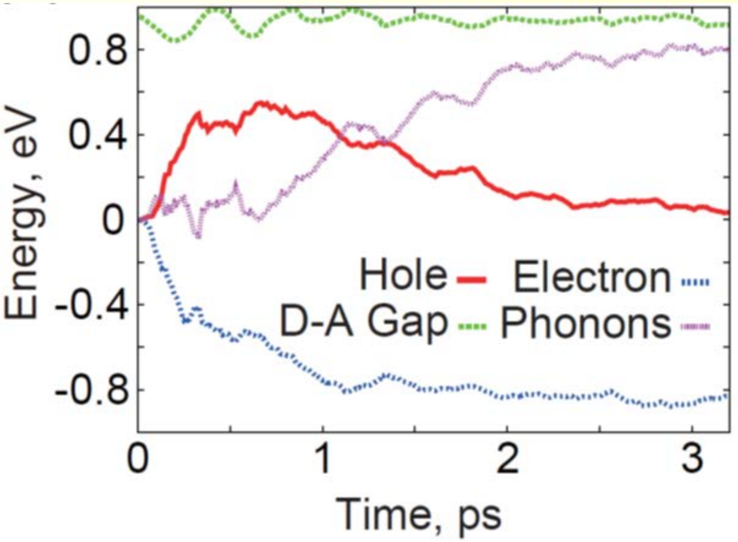
Why is there no Marcus inverted region? $k(r) \propto e^{-\frac{[\Delta G(r)+\lambda]^2}{4\lambda RT}}$

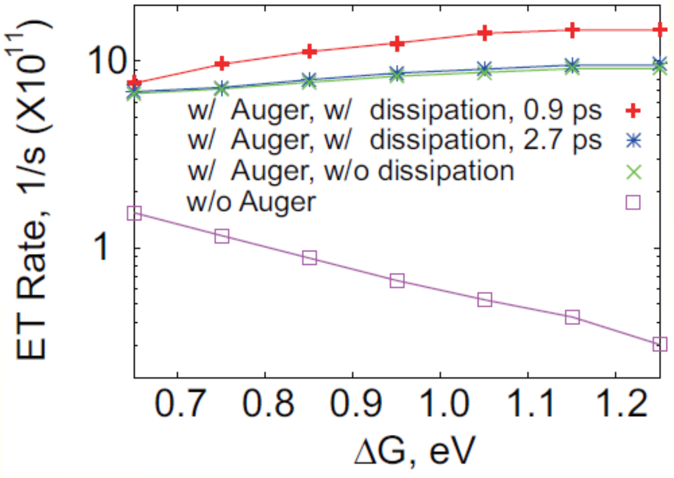
Auger-assisted ET

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





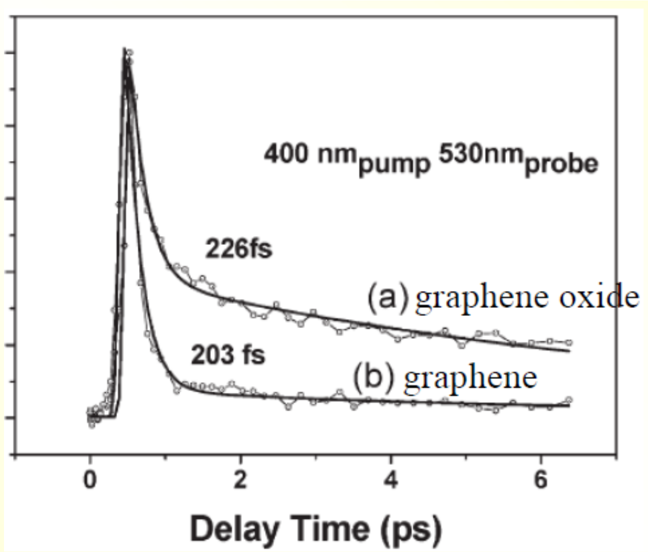




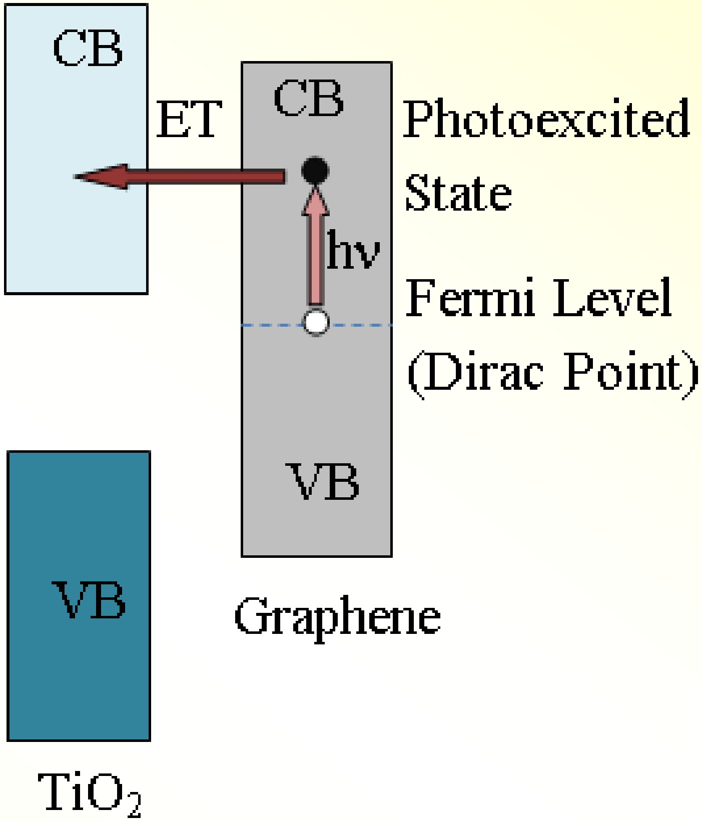
- Normally, excess energy goes to phonons
- In QDs, hole excitation accompanies ET
- Then, hole transfers energy to phonons

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)

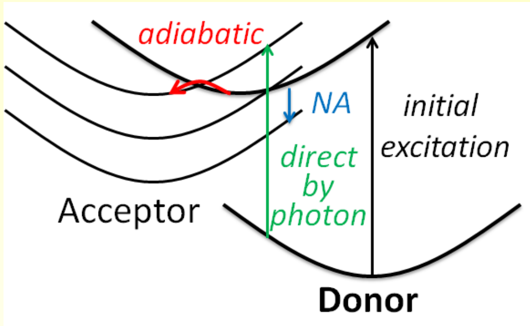


Graphene is a metal: electrons and holes can annihilate, not separate

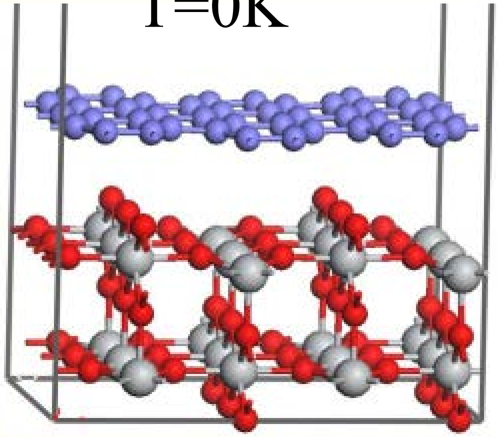
Can electrons transfer into TiO_2 before they relax?

Graphene-TiO$_2$

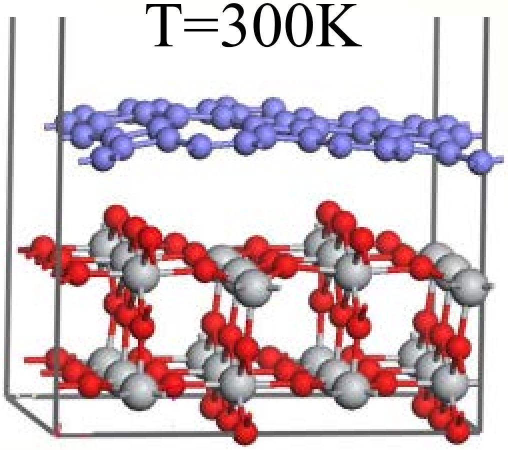
Long, English, Prezhdo *JACS* **134**, 14238 (2012)
chosen for *JACS* Spotlight



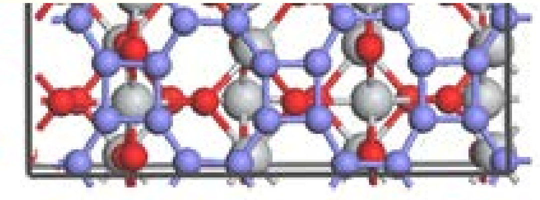
T=0K

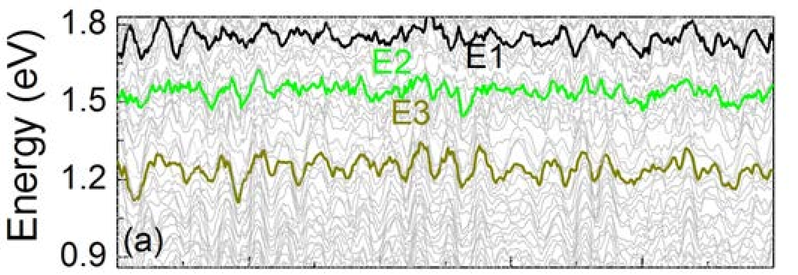


T=300K

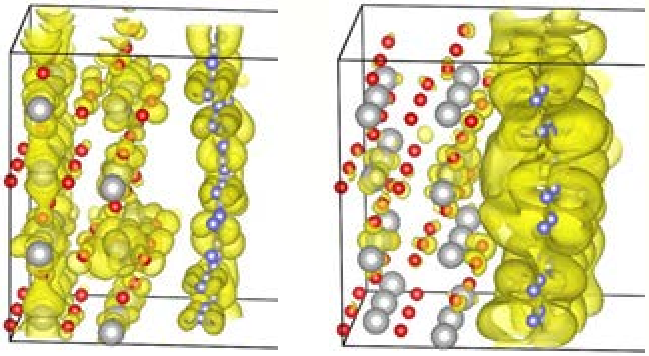


Chemisorption
at room T





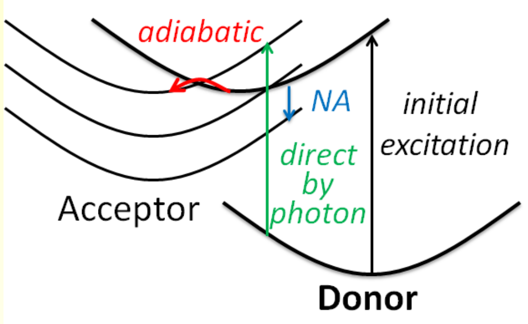
Photoexcited states

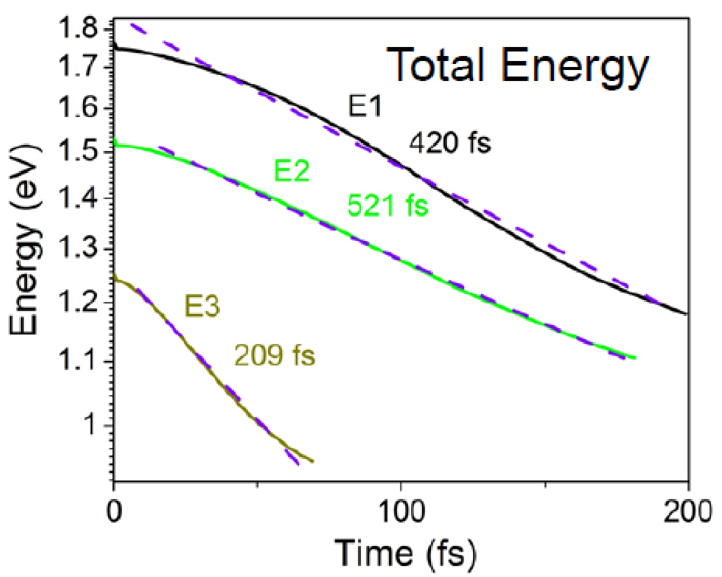


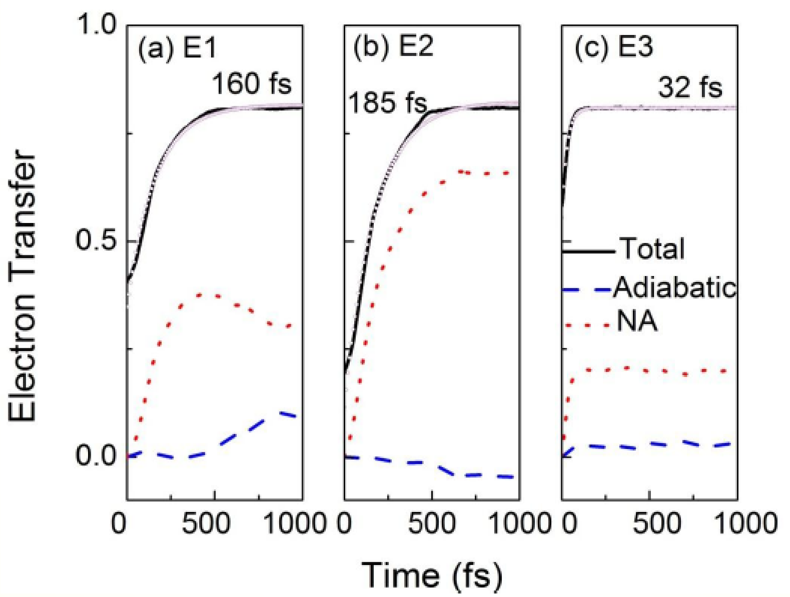
“Direct” ET

Graphene-TiO$_2$

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



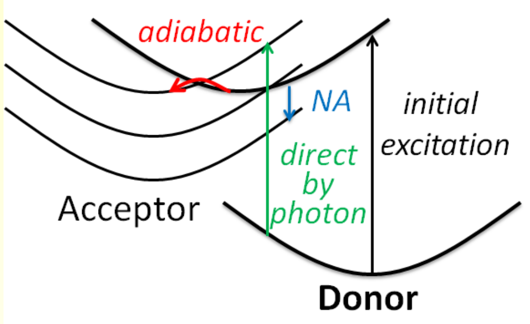


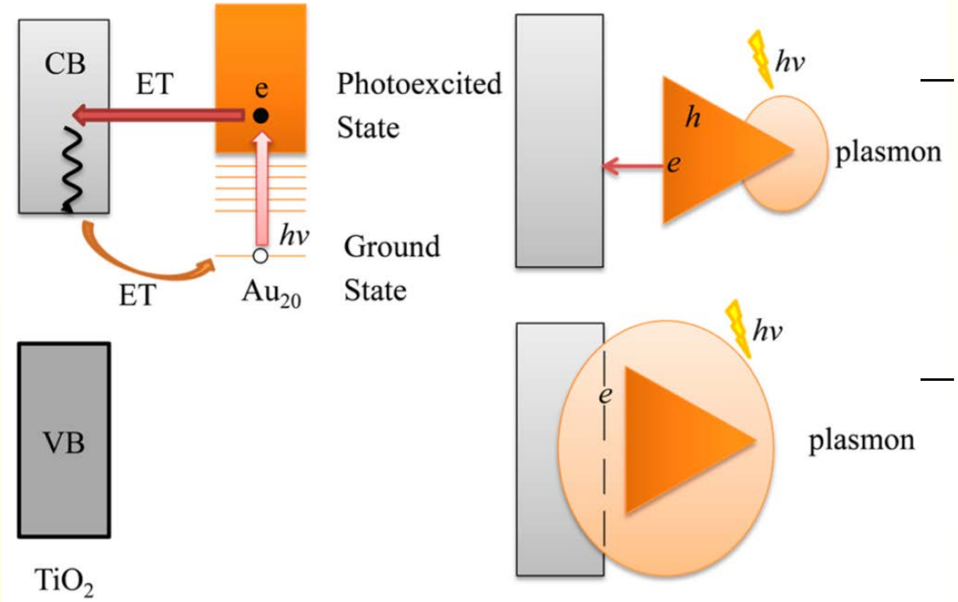


- ET consistently faster than energy loss
- Fast ET due to strong donor-acceptor coupling
- NA ET, though coupling is strong; dense state manifold
- 30-60% of direct ET, delocalized excited state

Plasmon-driven ET

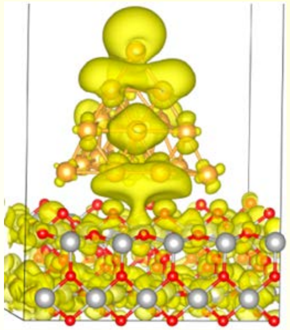
Long, English, Prezhdo *JACS* **136**, 4343 (2014)

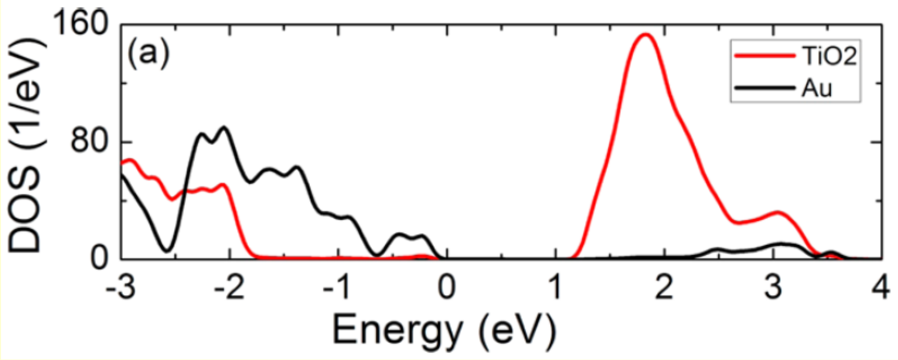


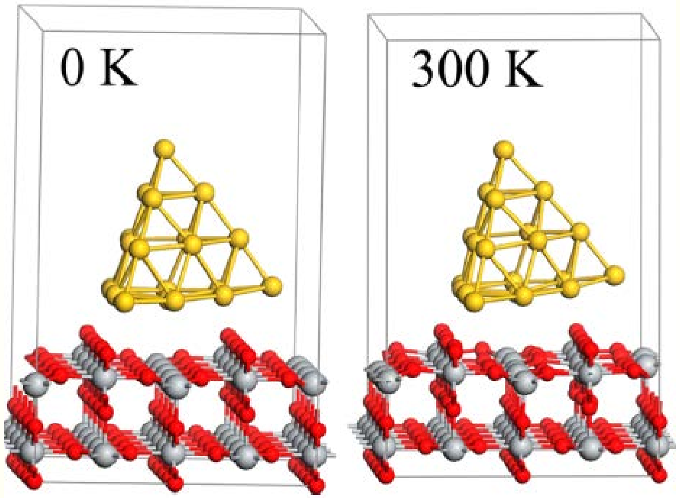


– traditional view

– our calculation

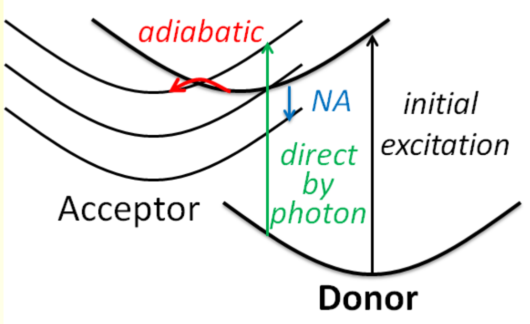


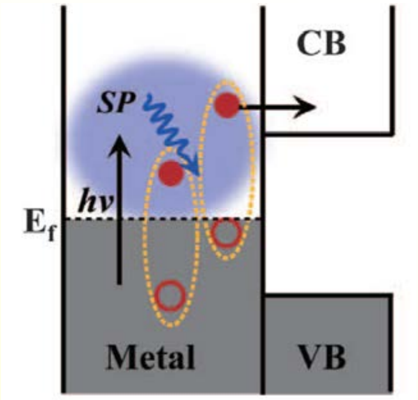




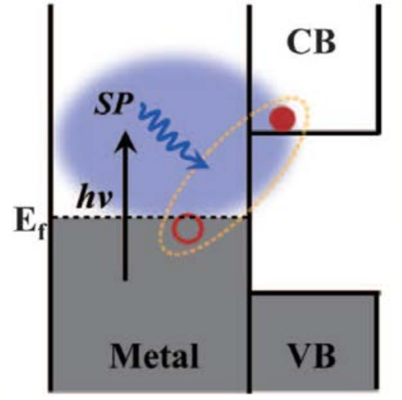
Experimental Evidence

Lian et al, *Science* **349** 632 (2015)

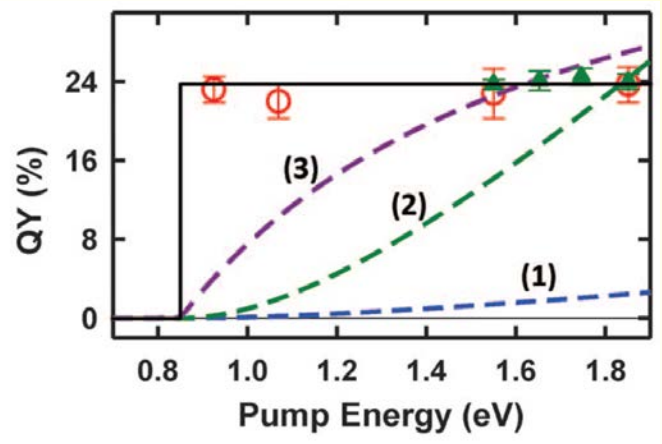




traditional view



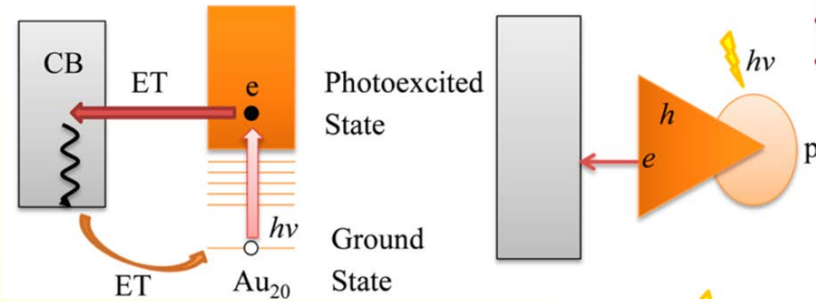
this experiment

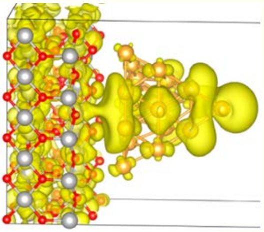


Quantum yield is independent of excitation energy, in contrast to traditional model

$$QY(\omega) = (\hbar\omega - E_{\mathrm{B}})^2/(4E_{\mathrm{F}}\hbar\omega)$$

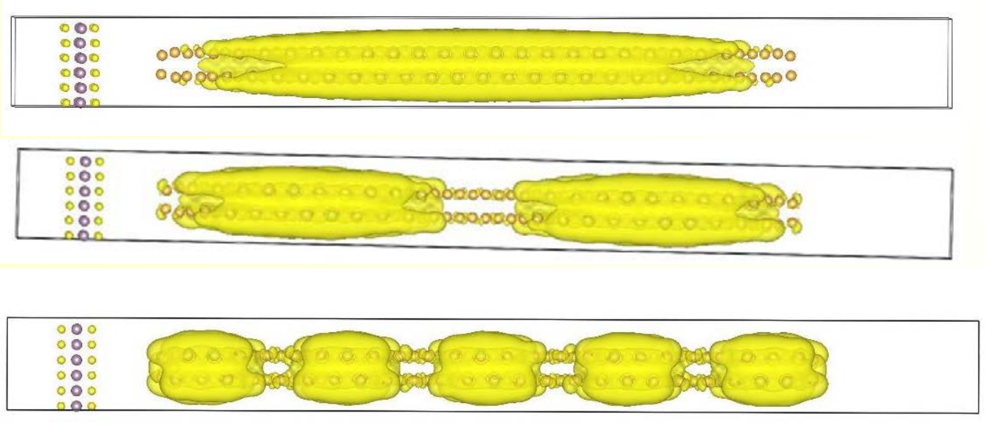
Plasmon-driven ET; gold on MoS_2



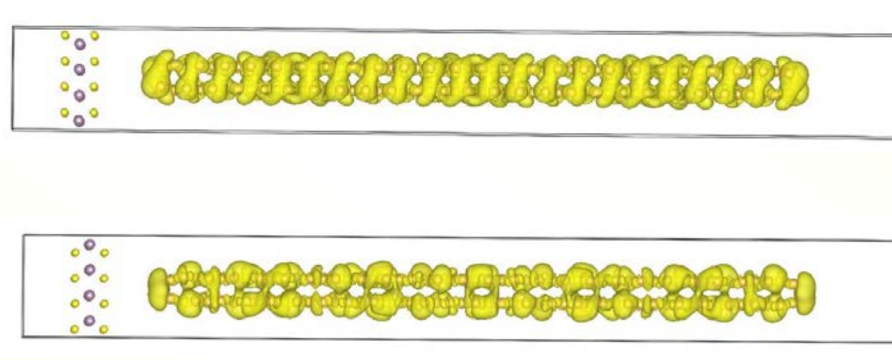


– traditional view holds, because coupling is weak

Plasmon-like excitations have no density on MoS_2



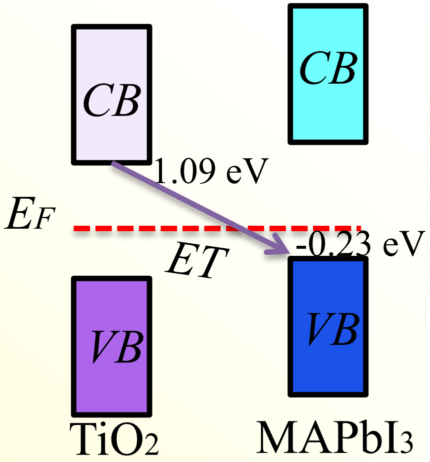
plasmons

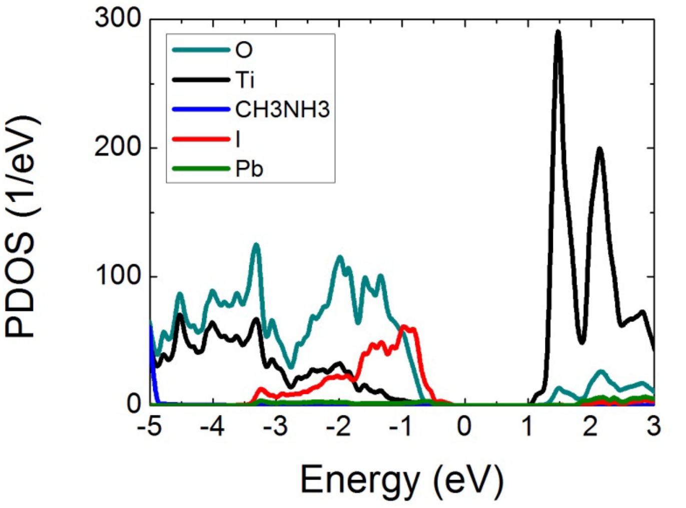


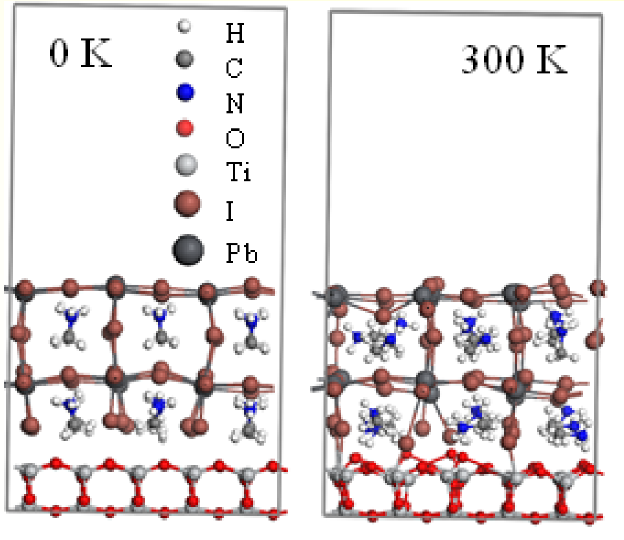
bulk states

Perovskite/TiO_2 and Doping

Long, Prezhdo *ACS Nano* **9**, 11143 (2015)
Liu, Prezhdo *JPC Lett* **6**, 4463 (2015)



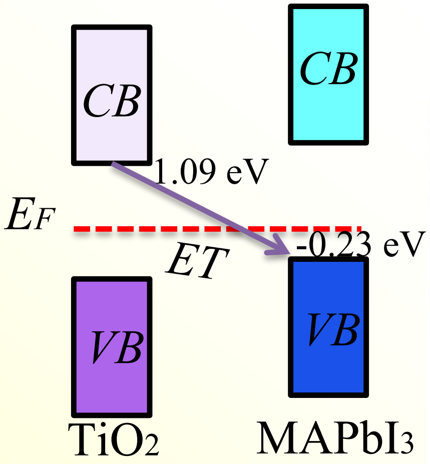


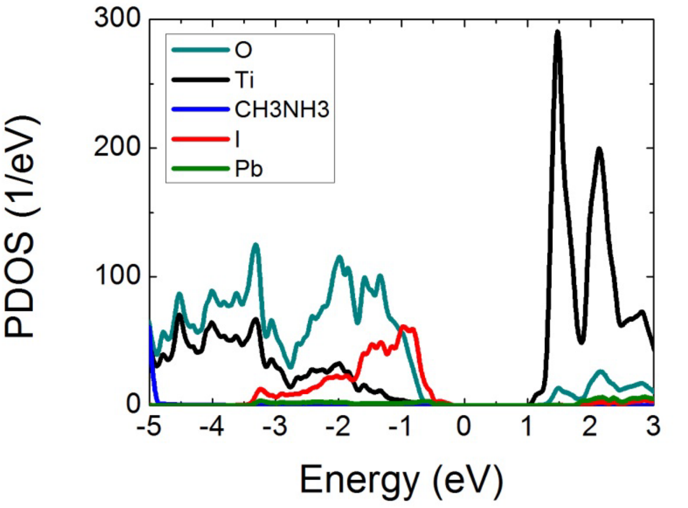


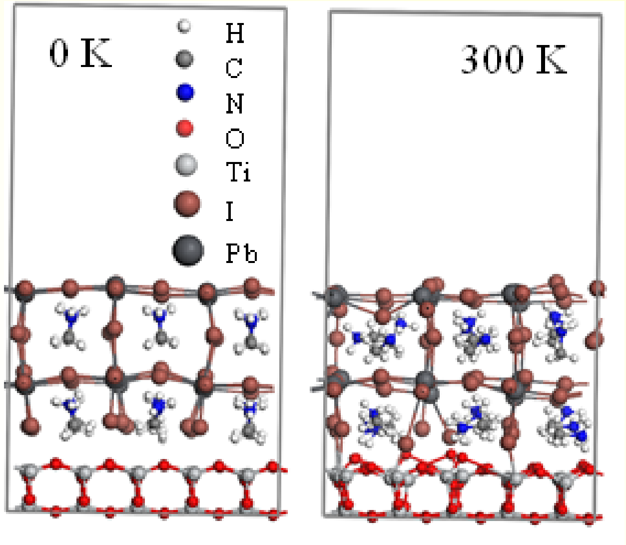
- Electron-hole recombination limits photovoltaic efficiency
- Cl and Br doping increase efficiency: *Nano Lett.* **13**, 1764 (2013); *Science* **345**, 542 (2014)
- Sn doping decreases efficiency: *J. Phys. Chem. Lett.* **5**, 1004 (2014)

Perovskite/TiO_2 and Doping

Long, Prezhdo *ACS Nano* **9**, 11143 (2015)
Liu, Prezhdo *JPC Lett* **6**, 4463 (2015)



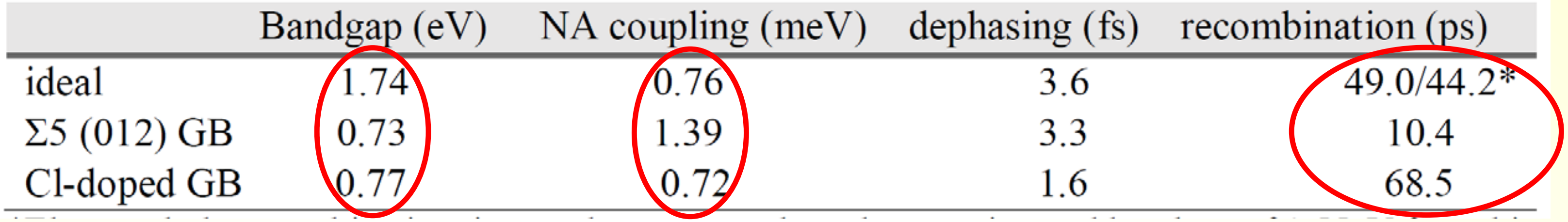




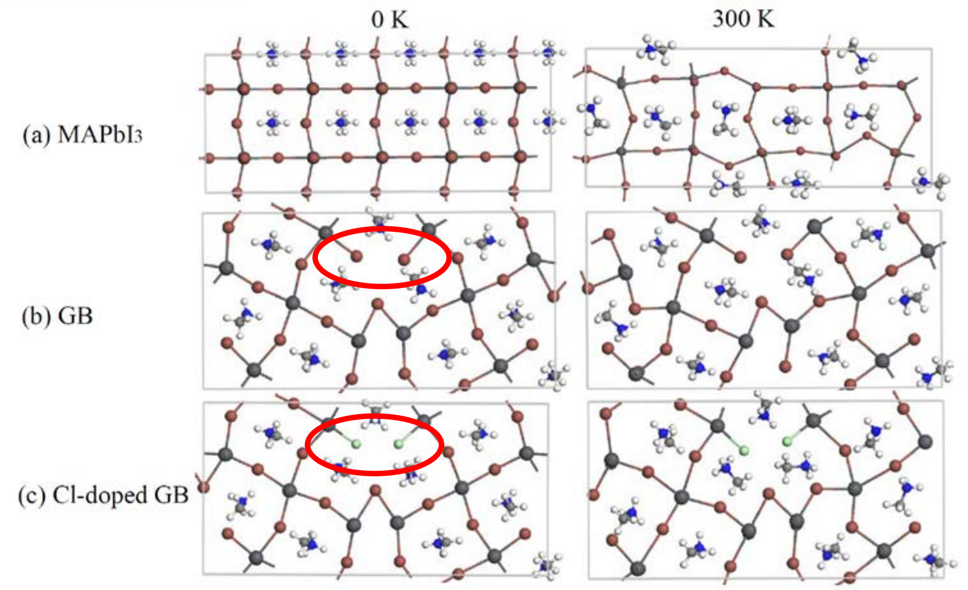
- Cl, Br are smaller than I; poorer contact with TiO_2
- Cl, Br do not contribute to HOMO; NA coupling decreases
- Sn contributes to HOMO, is lighter than Pb; NA coupling increases
- Lighter Cl, Br shorten quantum coherence; reduce rate

Perovskite Grain Boundary

Long, Liu, Prezhdo, *JACS* **138** 3884 (2016); *JACS* spotlight



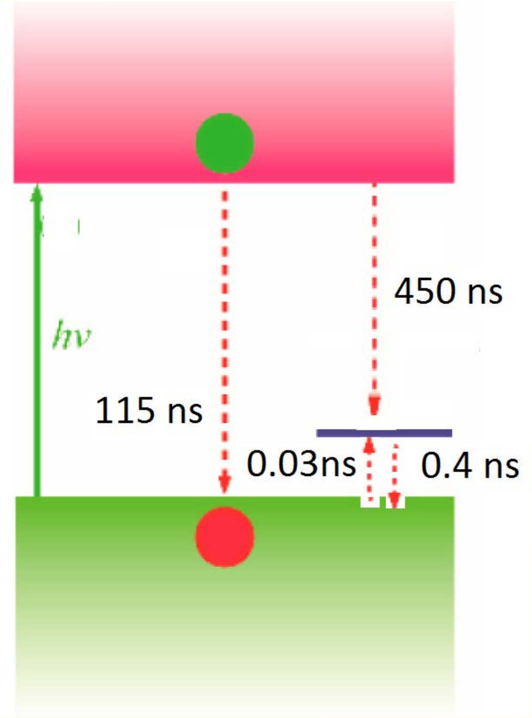
	Bandgap (eV)	NA coupling (meV)	dephasing (fs)	recombination (ps)
ideal	1.74	0.76	3.6	49.0/44.2*
Σ5 (012) GB	0.73	1.39	3.3	10.4
Cl-doped GB	0.77	0.72	1.6	68.5



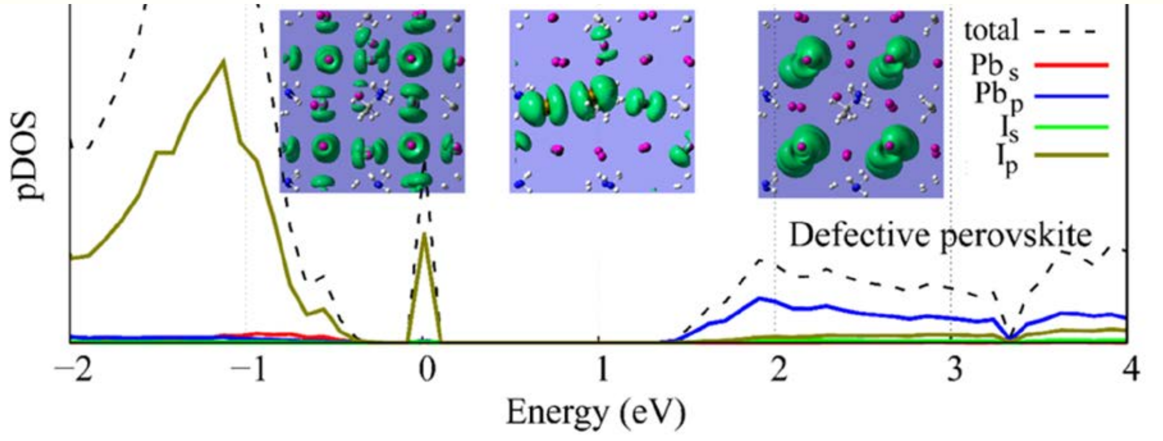
- By creating localized states, grain boundary decreases gap and increases coupling
- Cl-doping pushes e-h states away from boundary, reduces coupling

Perovskite Iodine Interstitial Defect

Li, Liu, Bai, Zhang, Prezhdo, *ACS Energ. Lett.* in press

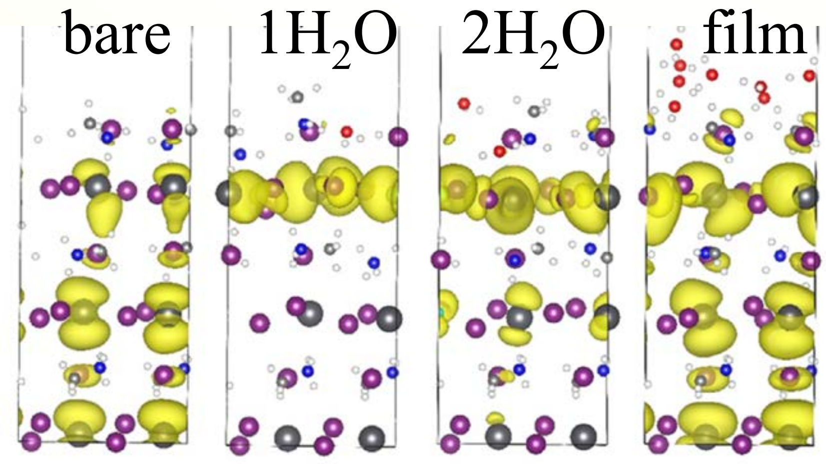


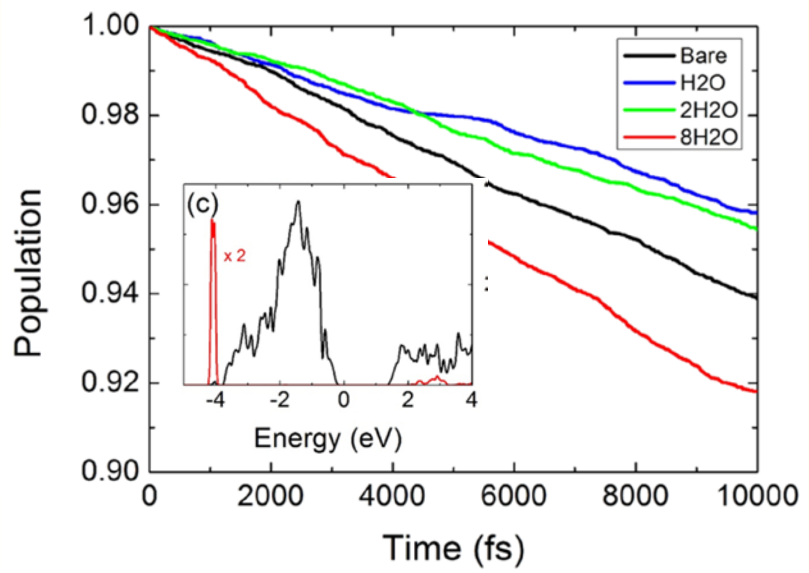
- Hole trapping is fast, but recombination of trapped hole with electron is very slow because electron and hole are separated
- Hole can be trapped and de-trapped multiple times before recombining, increasing free carrier lifetimes



Moisture and e-h Recombination

Long, Fang, Prezhdo, *J Phys Chem Lett* **7** 3215 (2016)



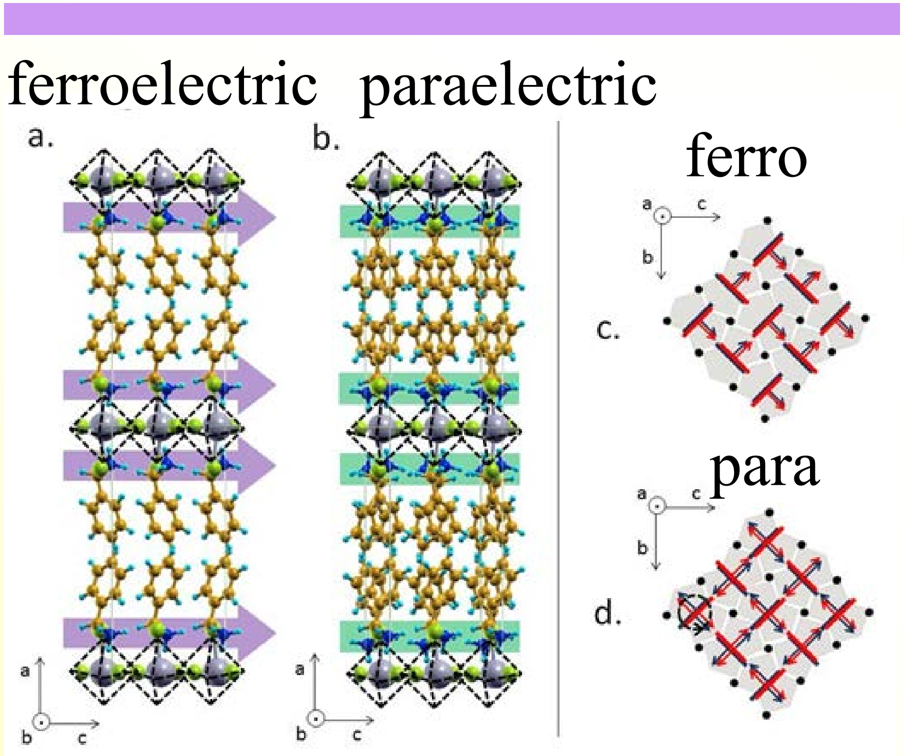


- Small amount of water localizes electron, distances it from hole
- Water film increases phonon coupling, accelerates e-h recombination
- Electron trap is not deep, next to conduction band edge

Some moisture is good: *Science* 542 **345** (2014); *ACS Nano* ***9*** 9380 (2015)
A lot of moisture is bad: *ACS Nano* ***9*** 9380 (2015); *J Am Chem Soc* **137** 1530 (2015)

Local Order in Perovskites

Jankowska, Prezhdo, *J. Phys. Chem. Lett.* **8**, 812 (2017)



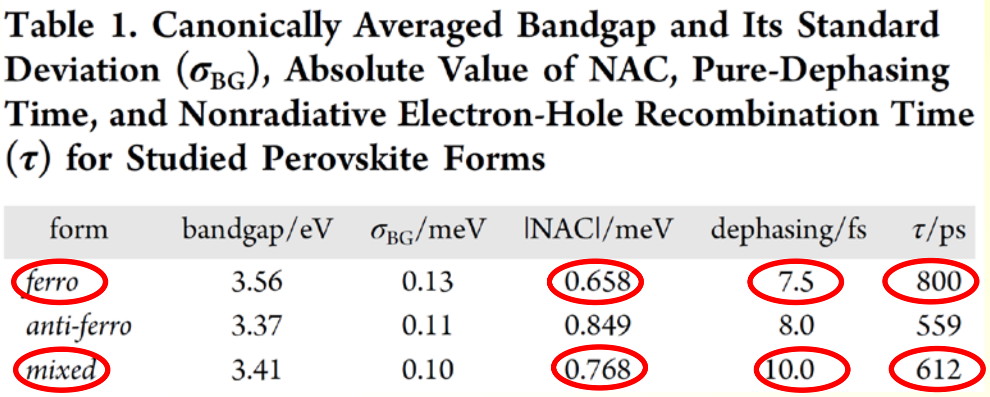
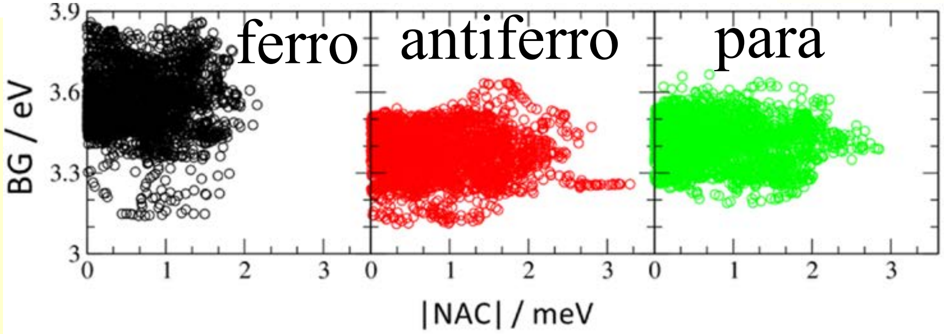


Table 1. Canonically Averaged Bandgap and Its Standard Deviation (σ_{BG}), Absolute Value of NAC, Pure-Dephasing Time, and Nonradiative Electron-Hole Recombination Time (τ) for Studied Perovskite Forms

form	bandgap/eV	σ_{BG}/meV	|NAC|/meV	dephasing/fs	τ/ps
ferro	3.56	0.13	0.658	7.5	800
anti-ferro	3.37	0.11	0.849	8.0	559
mixed	3.41	0.10	0.768	10.0	612

Ferro-electric order decreases NA coupling, shortens coherence, and hence, increases lifetime

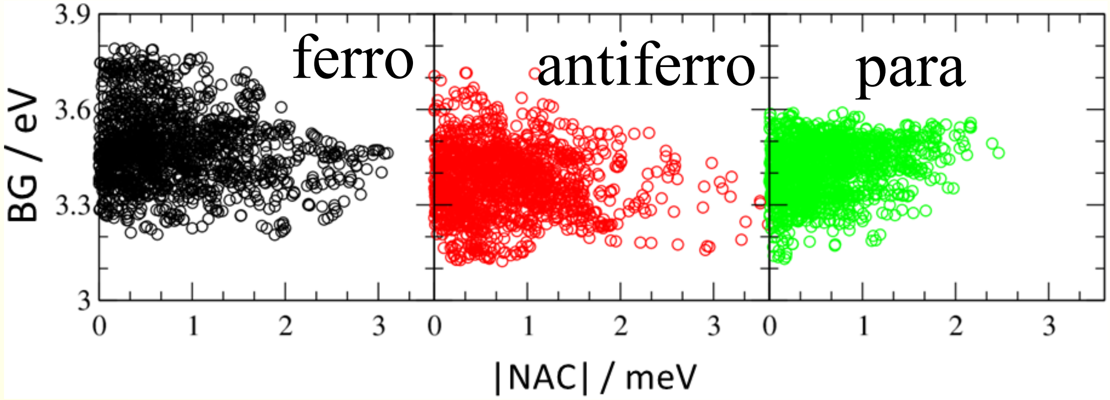


There is no NA coupling tail in ferro phase

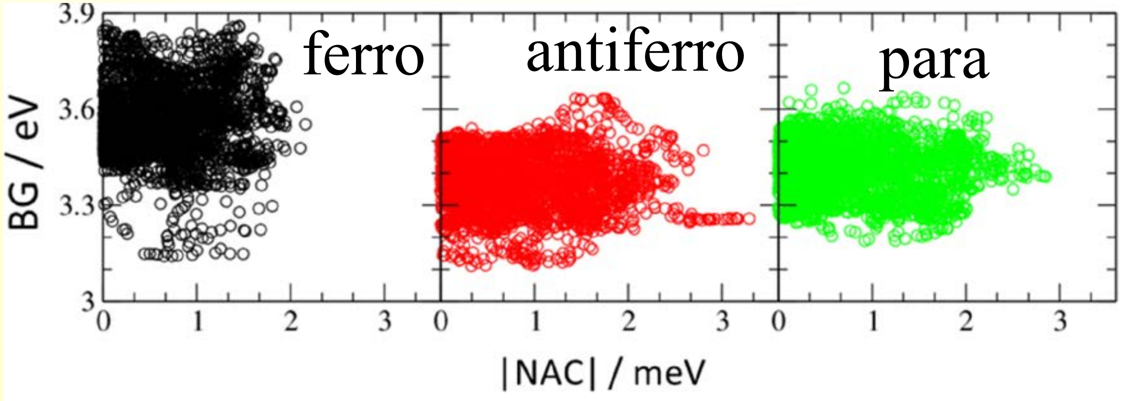
Local Order in Perovskites

Jankowska, Prezhdo, *J. Phys. Chem. Lett.* **8**, 812 (2017)

van der Waals interactions are very important



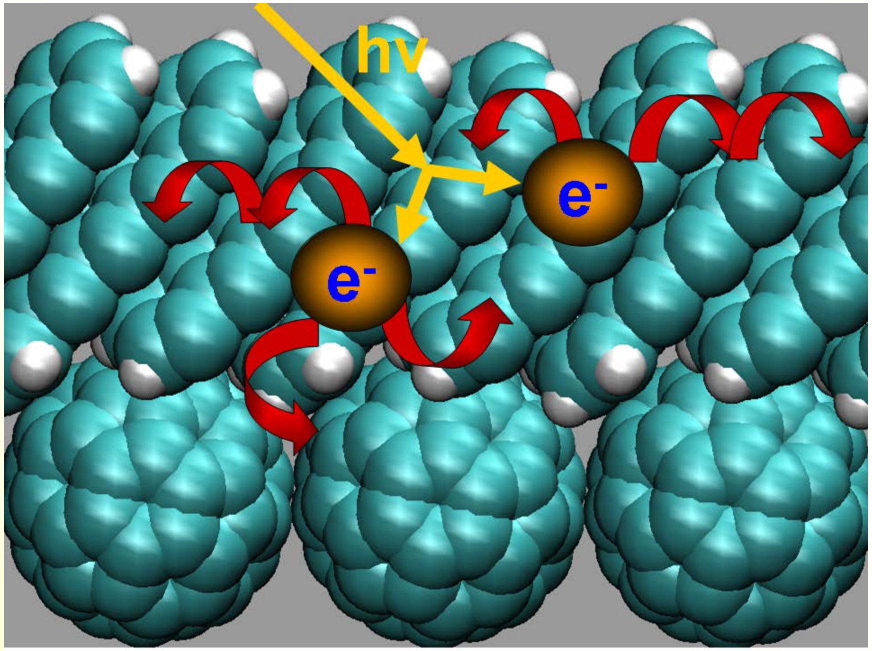
no van der Waals



with van der Waals
tail in ferro disappears

Singlet Fission

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

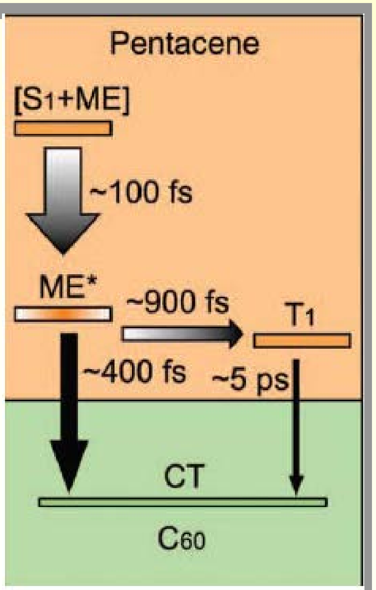


Experiment: Chan et al.
Science **2011**, 334, 1541

observation of ME

ME does not originate from S1

initial state is a superposition of S1 and ME

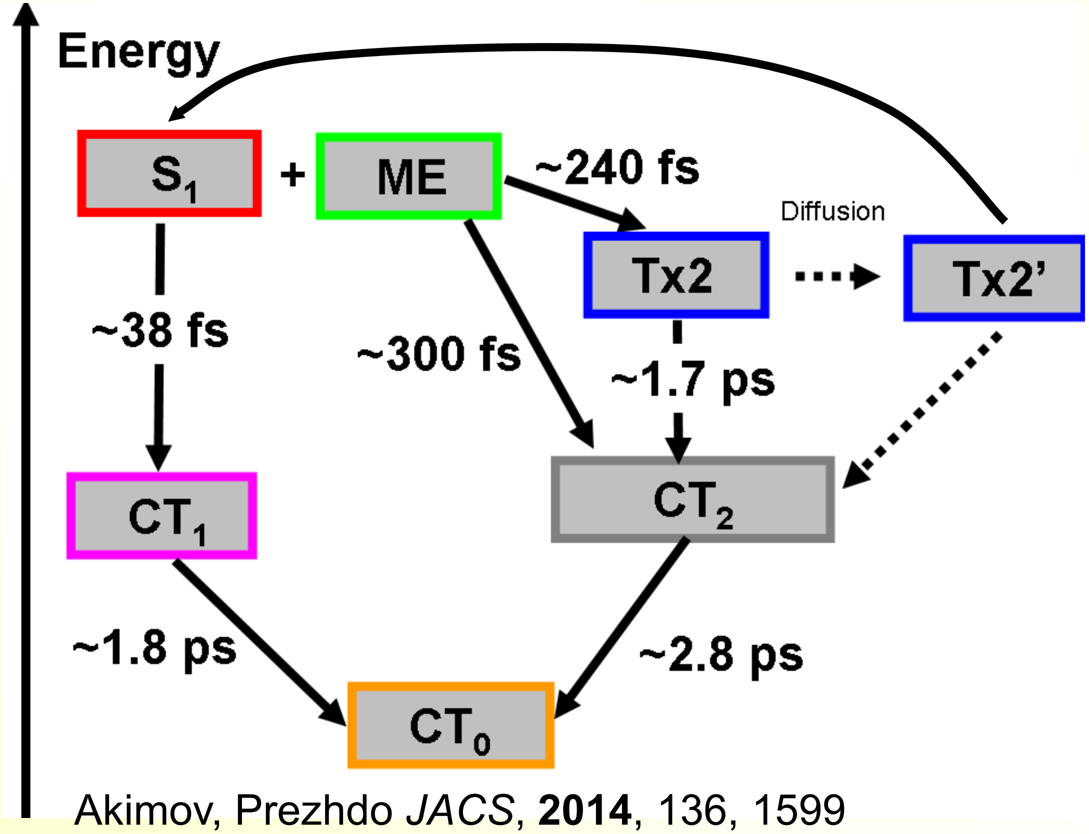


1 photon = 2 electrons:

max ~44%

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

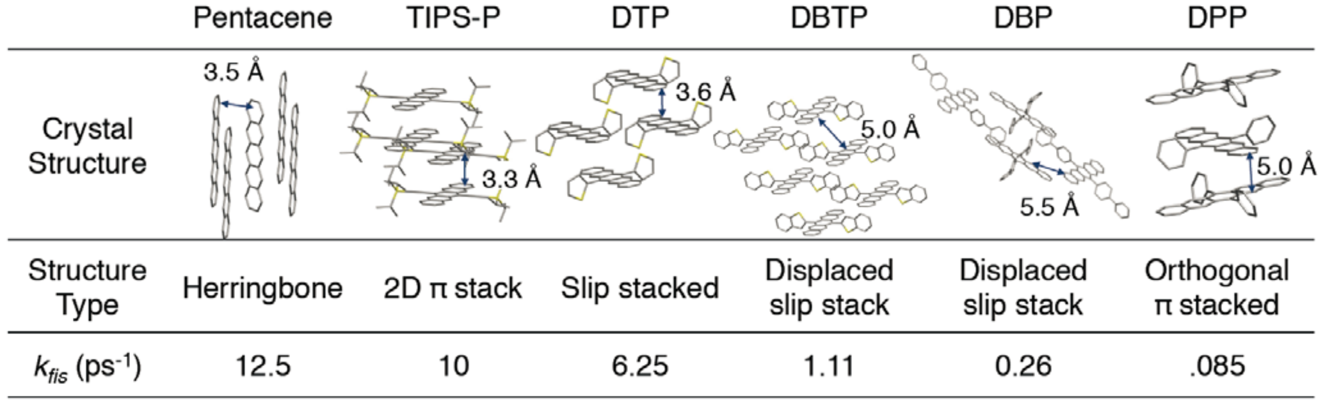
SF photovoltaic design principles

S_1 and ME should be coupled during photoexcitation

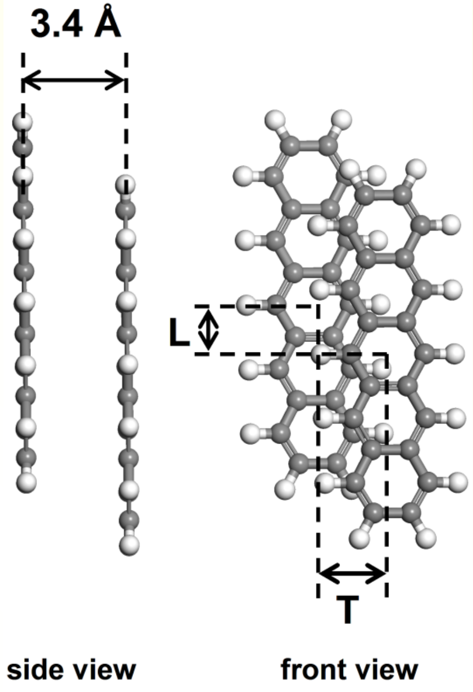
Thick pentacene layer slows down CT, allowing SF to happen

2D Mapping of Pentacene

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



	Pentacene	TIPS-P	DTP	DBTP	DBP	DPP
Crystal Structure	3.5 Å	3.3 Å	3.6 Å	5.0 Å	5.5 Å	5.0 Å
Structure Type	Herringbone	2D π stack	Slip stacked	Displaced slip stack	Displaced slip stack	Orthogonal π stacked
k_{fis} (ps^{-1})	12.5	10	6.25	1.11	0.26	.085

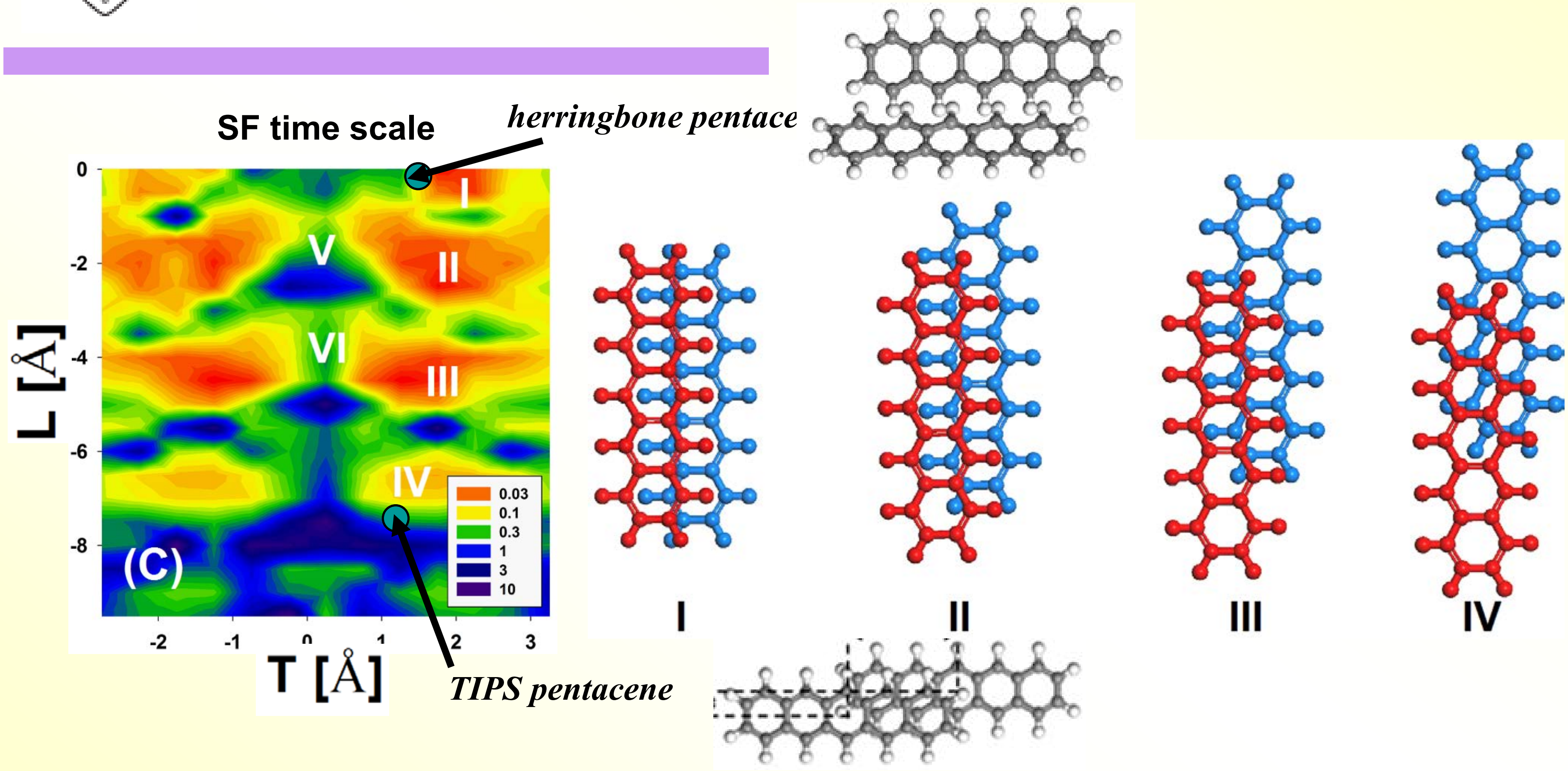


model dimer

2D mappings of inter-chromophore structure suggest how to maximize singlet fission through molecular packing

Optimal Packings for SF

Wang, Olivier, Prezhdo, Beljonne, *J. Phys. Chem. Lett.* **5**, 3345 (2014)



herringbone pentace

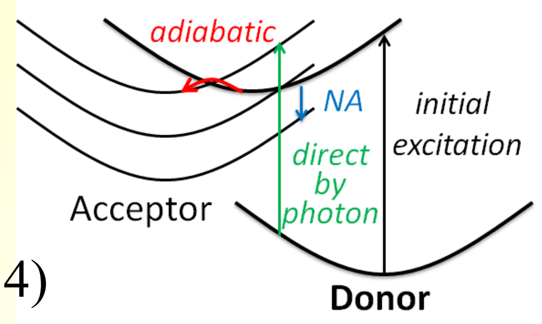
TIPS pentacene

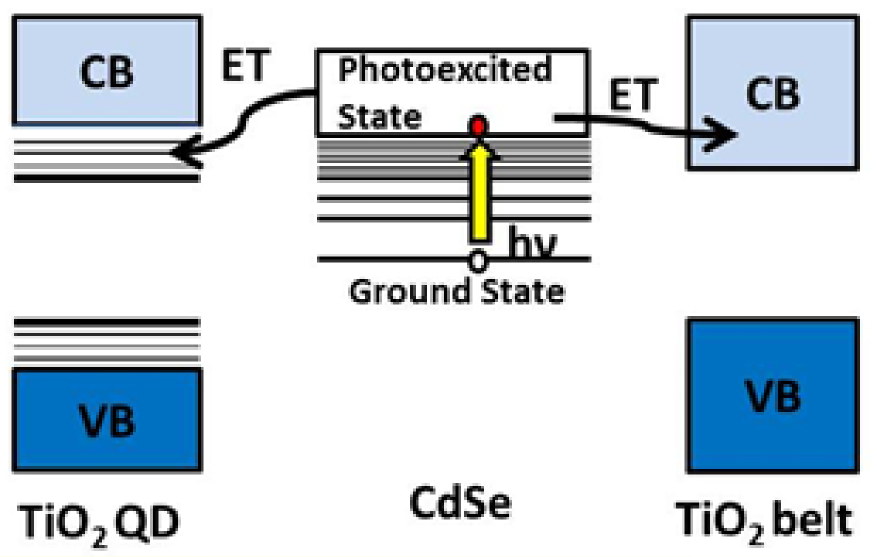
Standard structures are not optimal

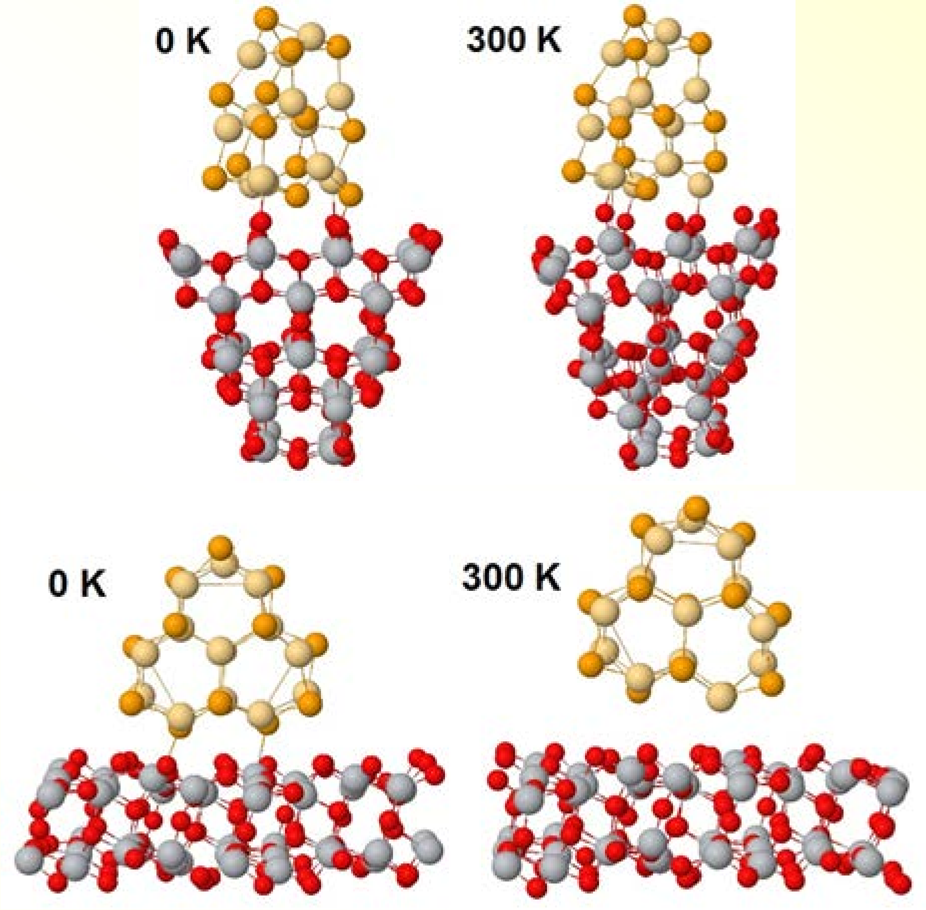
Optimal conformations are slipped in transverse direction by one ring

Dimensionality and ET Mechanism

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







adiabatic

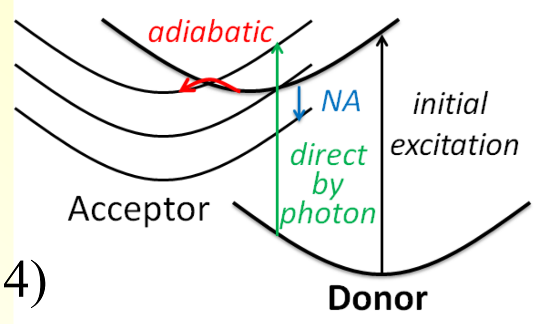
non-adiabatic

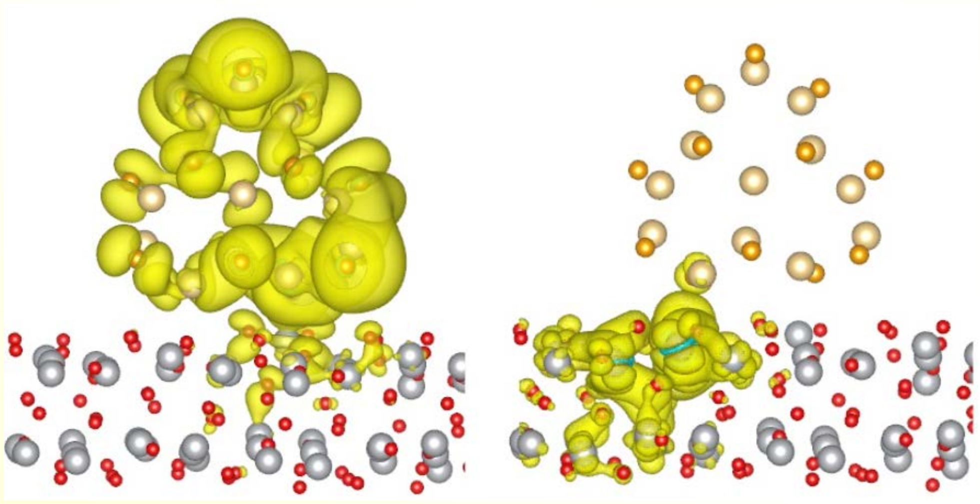
chemical bonding
low state density

weak coupling
high state density

Dimensionality and ET Mechanism

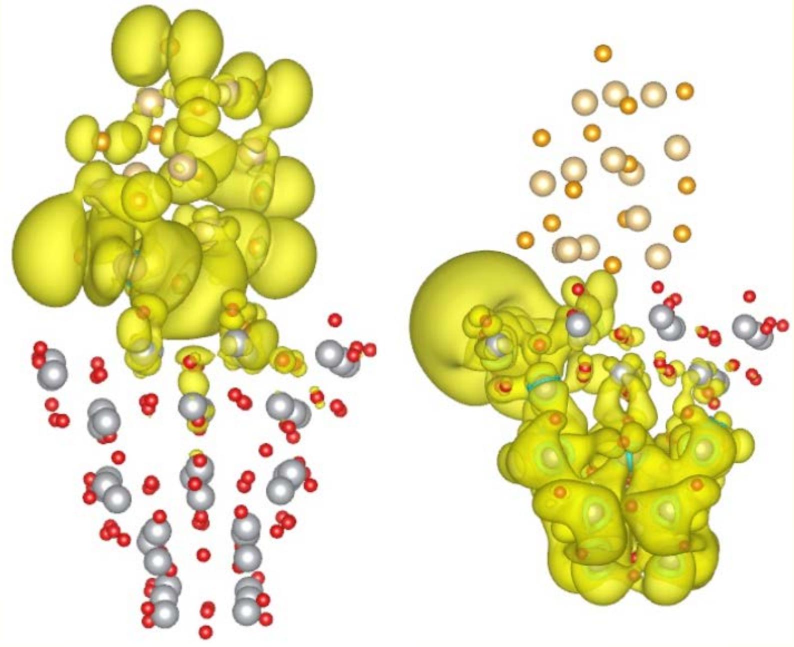
Tafen, Long, Prezhdo *Nano Lett.* **14**, 1790 (2014)





donor

acceptor



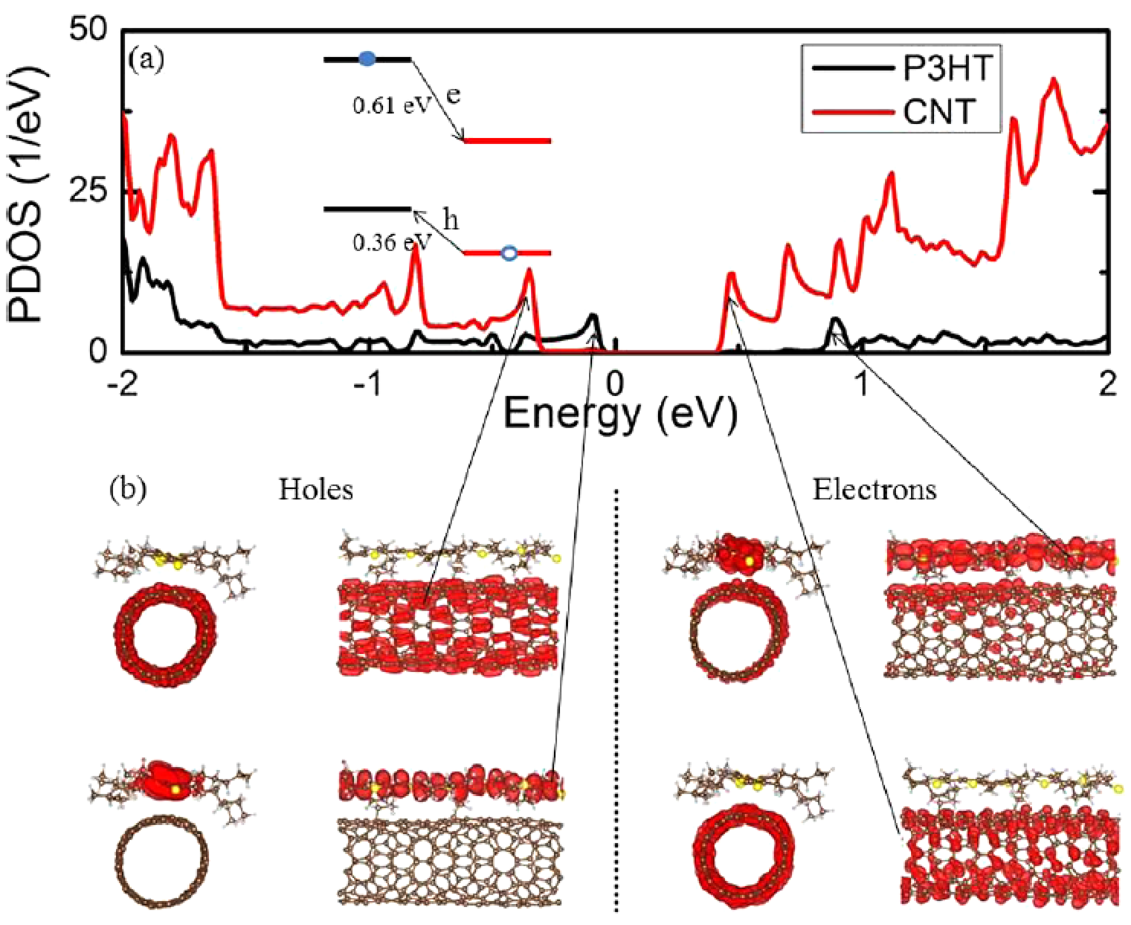
donor

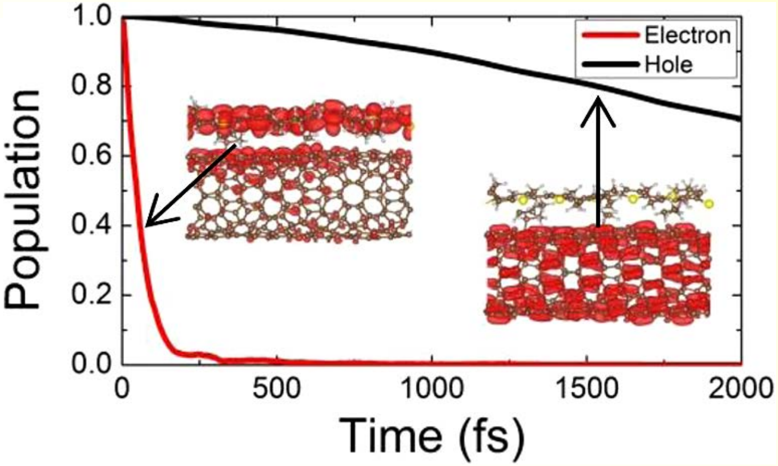
acceptor

acceptor state is localized even in belt

CNT/Polymer Asymmetry

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

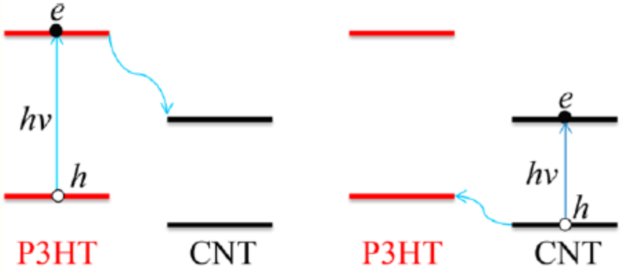


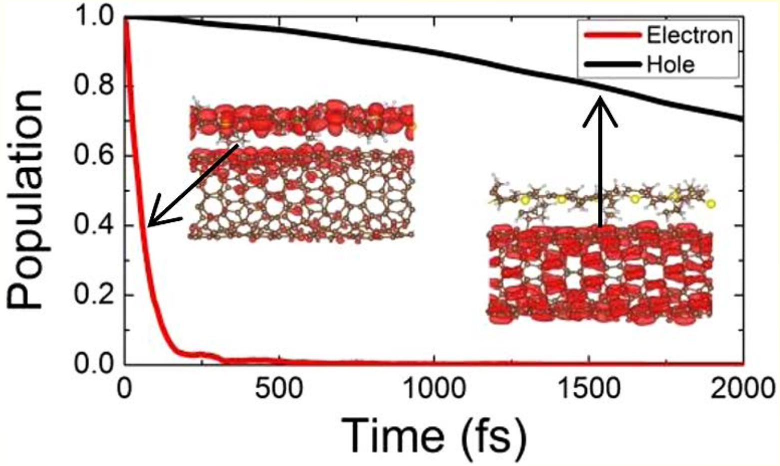


Much slower charge separation after CNT excitation: smaller acceptor DOS

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

Superconductors

Long, Prezhdo, *J. Phys. Chem. Lett.* **8**, 193 (2017)

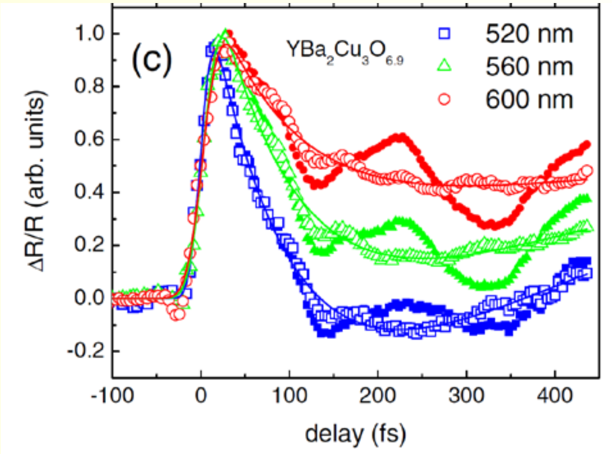
- Electron-phonon coupling leads to Cooper pairing
- Measuring electron-phonon relaxation time gives experimental estimate of coupling (earlier from Raman or neutron scattering)

$$\lambda\langle\omega^2\rangle = \frac{2\pi}{3}\frac{k_B T_l}{\hbar\tau_{e\text{-ph}}}$$

electron-phonon coupling (2nd moment of Eliashberg function)
Eliashberg theory generalizes Bardeen-Cooper-Schriffer theory

$$T_c = \omega_D \lambda/2$$

critical temperature for superconductivity in strong coupling limit

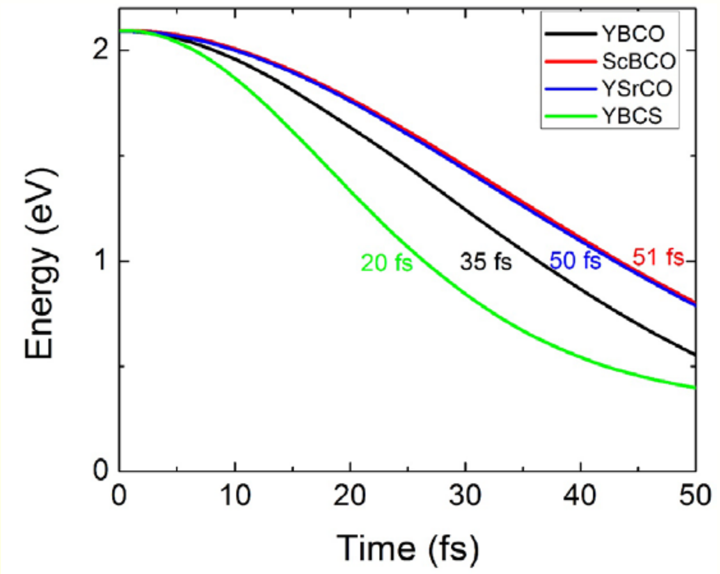


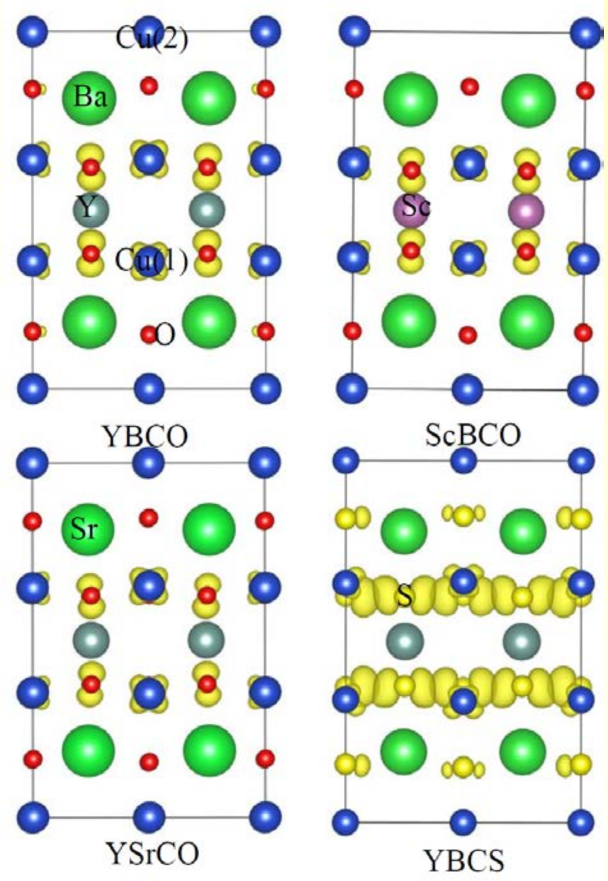
Faster, 100 fs component is associated with electron-phonon interactions

PRL **105** 257001 (2010)

Superconductors

Long, Prezhdo, *JPC Lett.*
8, 193 (2017)



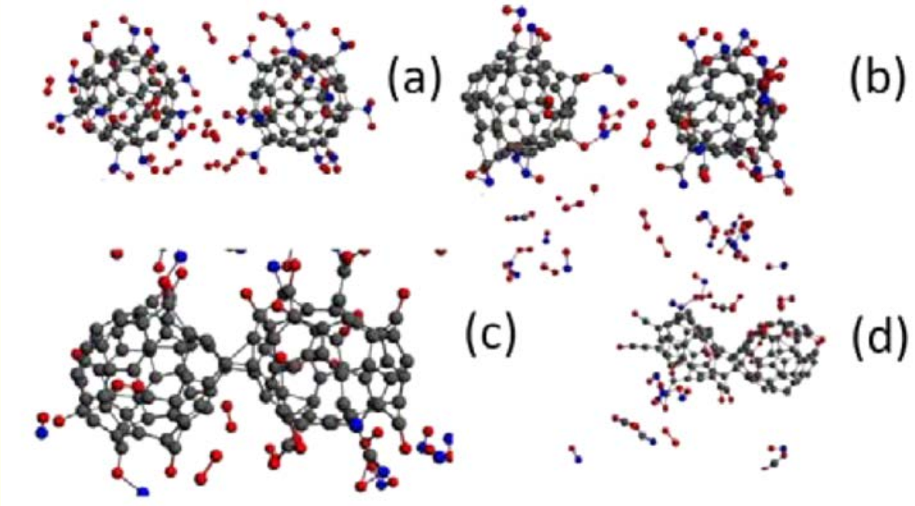


- Reproduced dynamics in YBCO; considered 3 derivatives
- YBCS shows stronger electron-phonon coupling, possibly higher T_c
- Though S is heavier that O, but stronger bonding interaction
- Higher valence band density of states

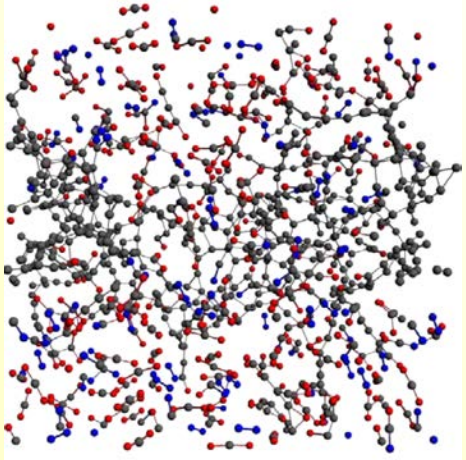
Decomposition of Nitro-Fullerene

Chaban, Prezhdo *J. Phys. Chem. Lett* **6** 913 (2015)

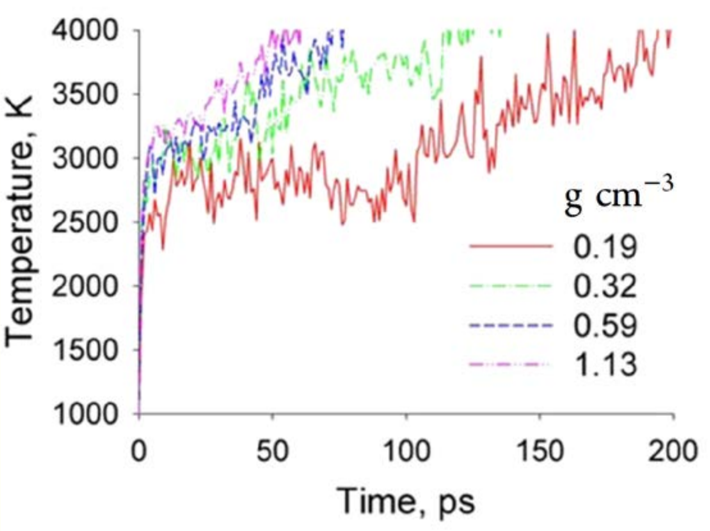
$C_{60}\,[NO_2]_{12}$



(a) Initial configuration
(b) $C\text{-}NO_2 \Rightarrow C\text{-}O\text{-}N\text{-}O$
(c) CO, NO on C_{60} surface
(d) Explosion, $CO \Rightarrow CO_2$
$NO \Rightarrow NO_2$



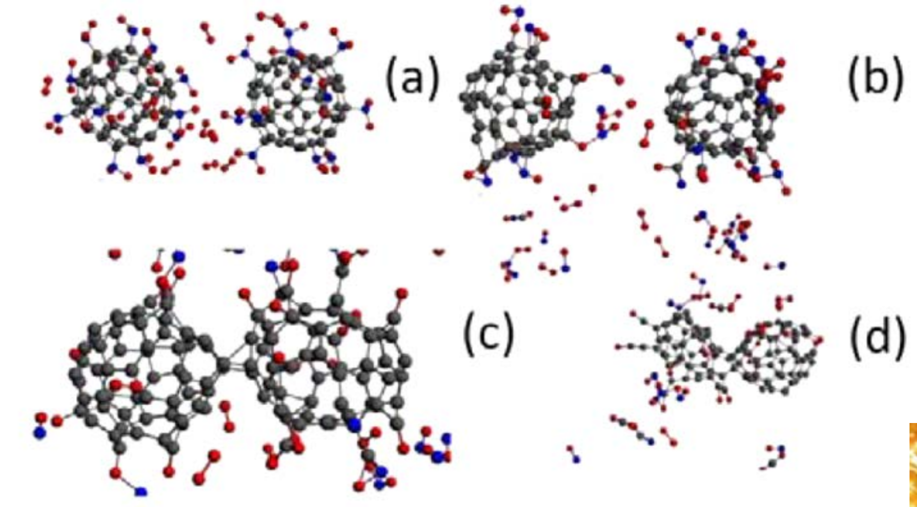
After
100 ps



Explosion of Nitro-Fullerene

Chaban, Prezhdo *JPC Lett* **6** 913 (2015)

$C_{60}\,[NO_2]_{12}$



(a) Initial configuration
(b) $C\text{-}NO_2 \Rightarrow C\text{-}O\text{-}N\text{-}O$
(c) CO, NO on C_{60} surface
(d) Explosion, $CO \Rightarrow CO_2$
$NO \Rightarrow NO_2$

NewScientist


Tiny buckybombs could make bacteria explode

03 September 2014

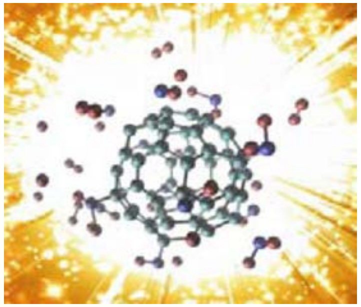
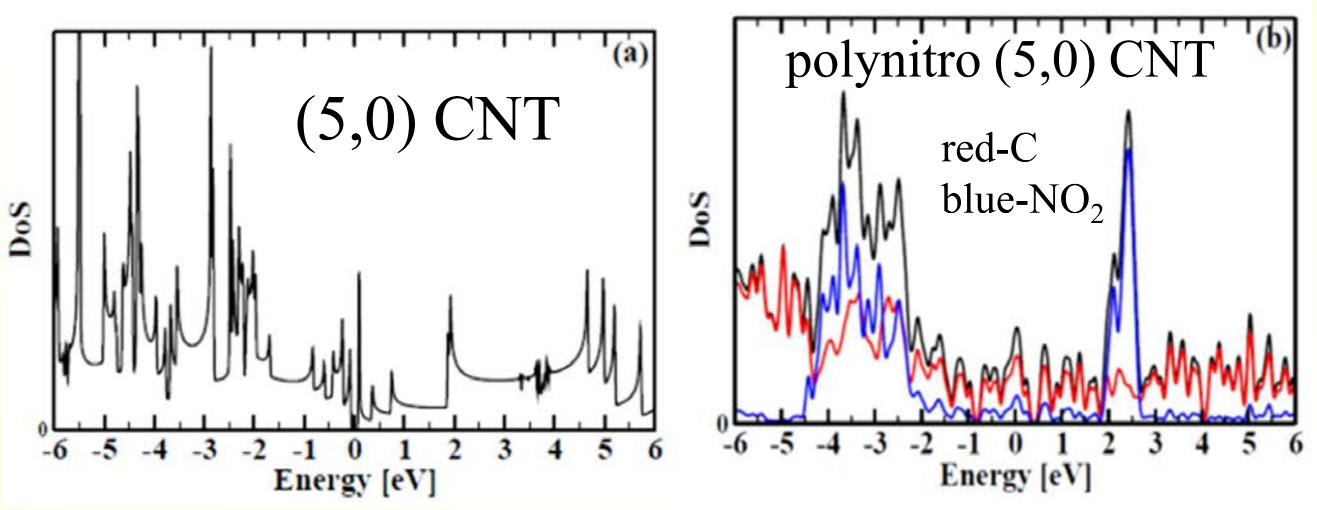
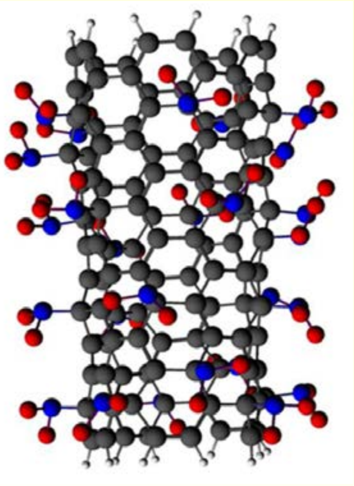


Photo-Initiated Explosion of Polynitro-CNT

Chaban, Pal, Prezhdo, *JACS* **138**, 15927 (2016)

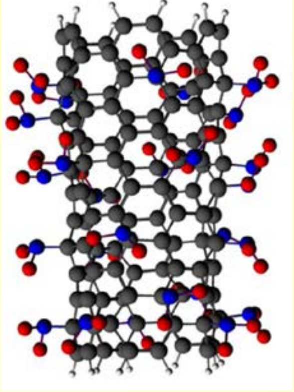


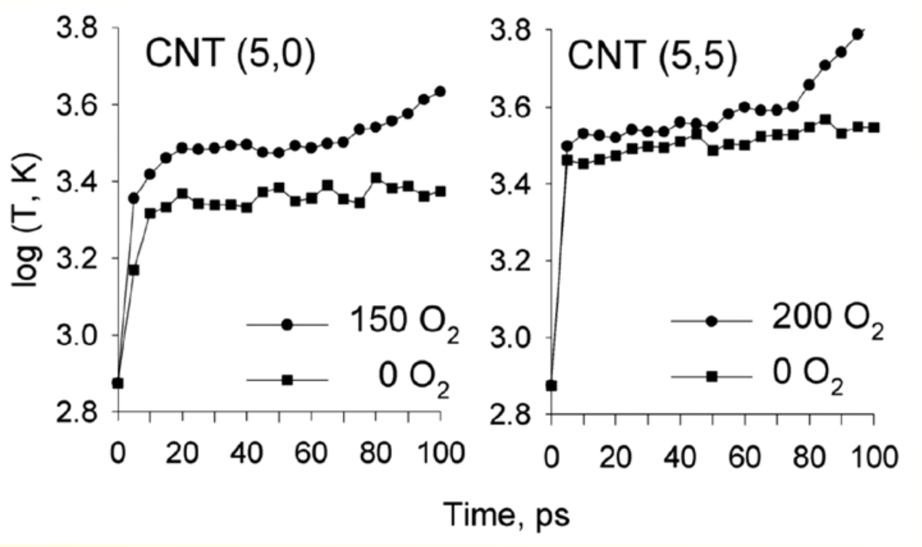


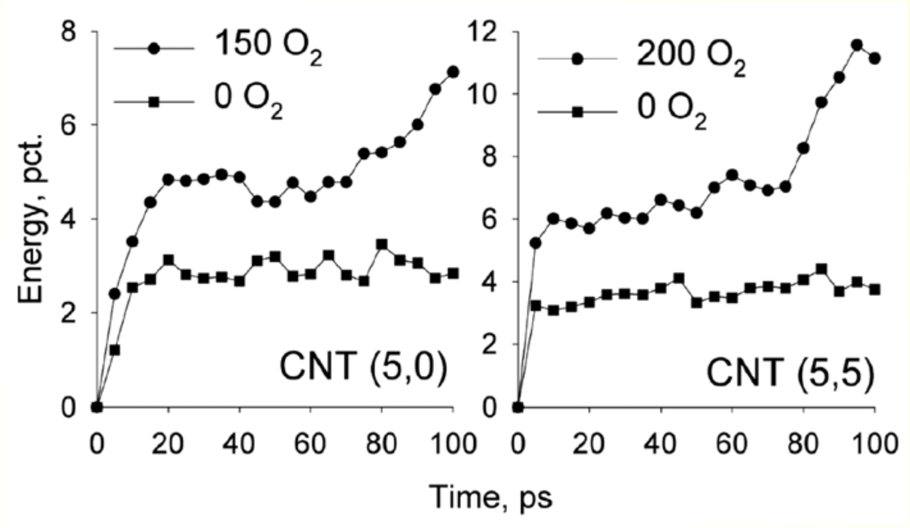
- NO_2 groups contribute to DOS at all energies; hence, immediately activated by electron-phonon relaxation after IR absorption
- Electron-phonon energy redistribution within 0.1-1ps
- Explosion within 10ps
- Chemistry continues past 100ps

Photo-Initiated Explosion of Polynitro-CNT

Chaban, Pal, Prezhdo, *JACS* **138**, 15927 (2016)

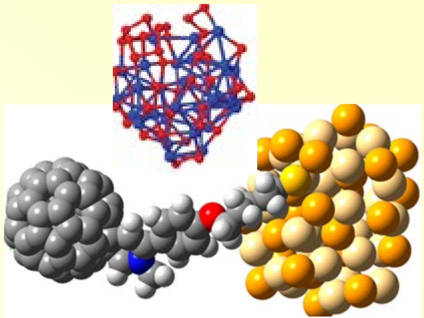


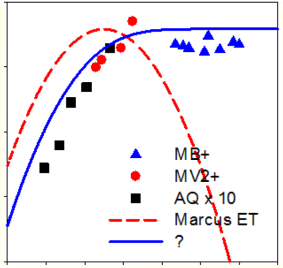




- Explosion is possible both with and without oxygen
- About twice more energy is released if oxygen is present

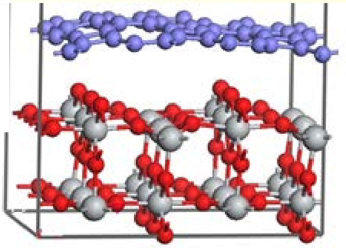
In Lieu of Conclusions

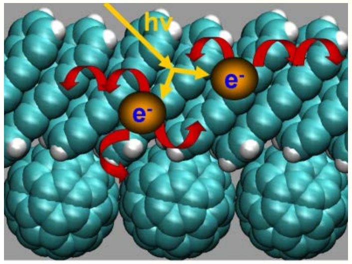


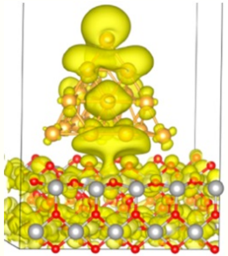


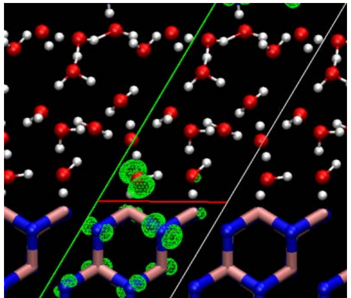
- Nonadiabatic Molecular Dynamics with Time-Dependent Density Functional Theory

- Applications
  - Auger assisted ET; lack of Marcus inverted regime –
  - Why graphene (metal!) can be used as light-harvester?
  - Instantaneous plasmon-driven ET
  - Perovskites, role of boundaries, dopants, humidity, order
  - Singlet fission vs. charge transfer?
  - Dimensionality and ET mechanism
  - Exploiting asymmetry of ET in CNT/polymer systems
  - Measure of el-ph coupling in superconductors
  - Photo-induced explosion of nitro-CNTs







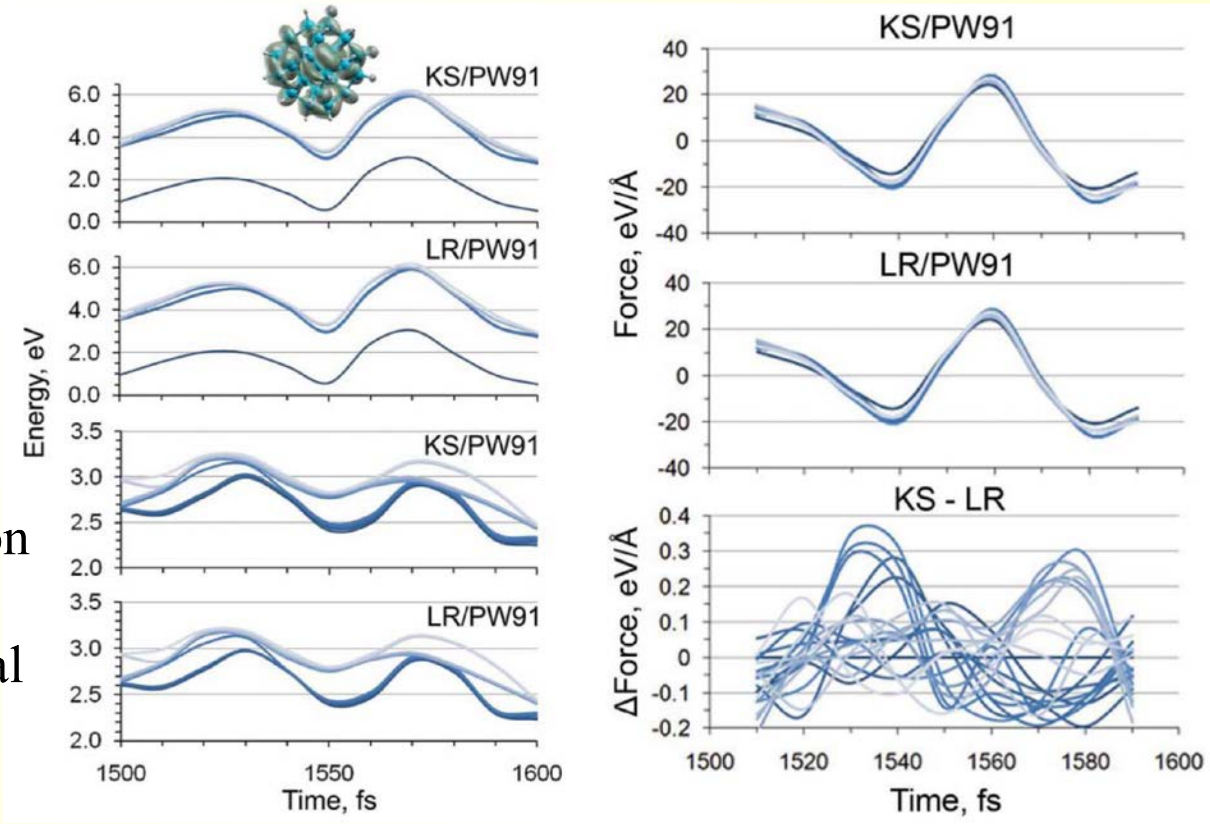



USC

Why Surface Hopping in Kohn-Sham Representation Works

S. Fischer, B. Habenicht, A. Madrid, W. Duncan,
O. V. Prezhdo, *J. Chem. Phys.* **134**, 024102 (2011)

- KS close to LR/TDDFT (in contrast to HF and CIS)
- No bond-breaking, conformational changes.
- Many-electrons, single excitation small perturbation
- Averaging over many initial conditions and pathways



Additional Approximations Useful for Nanoscale Systems

1. DFT functional (Hamiltonian) depends on ground state density, even though the true density does evolve
2. Ground and excited state nuclear trajectories are similar

Justification:

1. Excitation of 1 or 2 electrons out of hundreds does not change density and forces much
2. Thermal fluctuations are often larger than differences in the equilibrium geometries of ground and excited electronic states

Key Advantage – allows use of ground state trajectory, while still performing TDKS & SH for electronic state populations