

Nonadiabatic Quantum Molecular Dynamics

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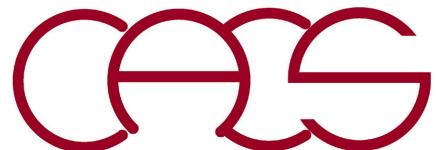
Department of Computer Science

Department of Physics & Astronomy

Department of Quantitative & Computational Biology

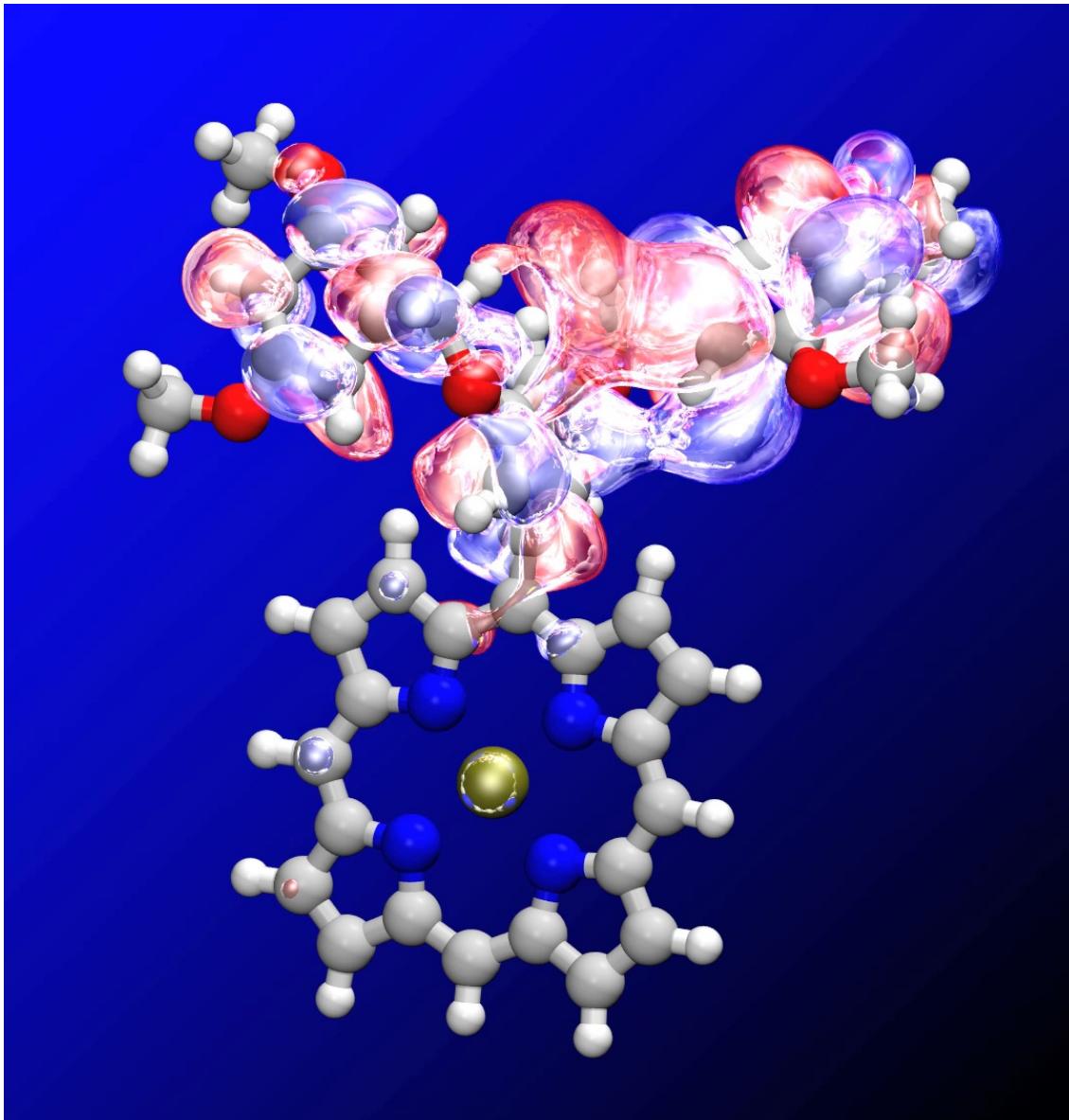
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I. NAQMD Basics

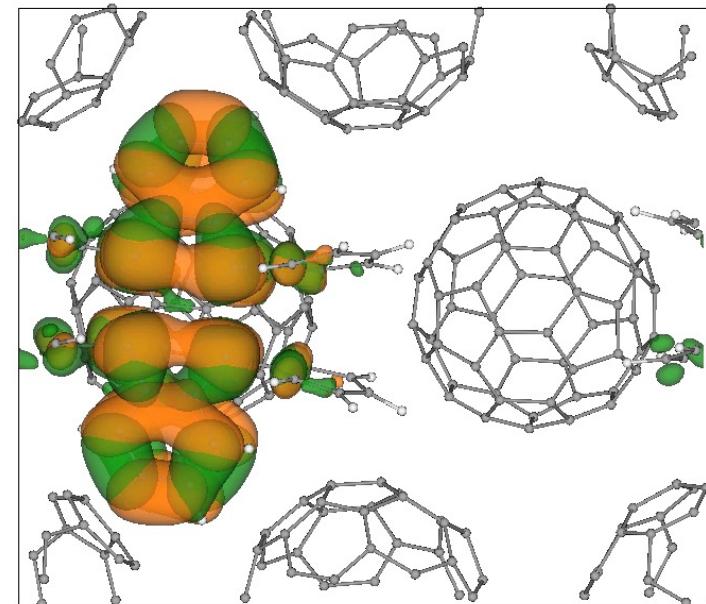
Nonadiabatic Quantum Molecular Dynamics



Appl. Phys. Lett. **98**, 113302 ('11); *ibid.* **100**, 203306 ('12); *ibid.* **102**, 173301 ('13); *Comput. Phys. Commun.* **184**, 1 ('13); *J. Chem. Phys.* **140**, 18A529 ('14); *IEEE Computer* **48**(11), 33 ('15); *Sci. Rep.* **5**, 19599 ('16); *Nature Commun.* **8**, 1745 ('17); *Nano Lett.* **18**, 4653 ('18); *Nature Photon.* **13**, 425 ('19); *Sci Adv.* **8**, eabk2625 ('22)

Zn porphyrin

Rubrene/C₆₀



quasi-electron; quasi-hole

- **Excited states:** Linear-response time-dependent density functional theory [Casida, '95]
- **Interstate transitions:** Surface hopping [Tully, '90; Jaeger, Fisher & Prezhdo, '12]

Time-Dependent Density Functional Theory

- **Invertibility theorem**

The mapping $G: \{v(\mathbf{r}, t) + c(t)\} \mapsto n(\mathbf{r}, t)$ is one-to-one & therefore is invertible

external
potential

time-dependent
constant

electron
density

- **Time-dependent density-functional theory (TDDFT) theorem:**

Every physical quantity is a functional of $n(\mathbf{r}, t)$

- **Action principle:**

mapping

Action integral is stationary at the exact density:

$$\delta A_v / \delta n(\mathbf{r}, t) = 0 \text{ at } n(\mathbf{r}, t) = G[v(\mathbf{r}, t)], \text{ where}$$

$$A_v[n(\mathbf{r}, t)] = \int dt \langle \psi(t) | i\hbar \partial / \partial t - T - U | \psi(t) \rangle - \int dt \int d\mathbf{r} n(\mathbf{r}, t) v(\mathbf{r}, t)$$

kinetic energy
operator

electron-electron
interaction

Time-Dependent Kohn-Sham Scheme

- Time-dependent many-body problem is equivalent to solving time-dependent Kohn-Sham (TDKS) equations

Hartree (mean-field) potential

$$\left\{ \begin{array}{l} \left[i\hbar \partial / \partial t + \hbar^2 \nabla^2 / 2m - v(\mathbf{r}, t) - \int d\mathbf{r}' \frac{e^2 n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} - v_{xc}(\mathbf{r}, t) \right] \psi_i(\mathbf{r}, t) = 0 \\ n(\mathbf{r}, t) = \sum_{i=1}^N |\psi_i(\mathbf{r}, t)|^2 \end{array} \right.$$

where the exchange-correlation (xc) potential is given by

$$v_{xc}(\mathbf{r}, t) = \delta A_{xc} / \delta n(\mathbf{r}, t)$$

$$A_{xc}[n(\mathbf{r}, t)] = - \int dt \langle \psi(t) | i\hbar \partial / \partial t - T - U | \psi(t) \rangle$$

non-interacting electrons action

$$+ \int dt \langle \psi(t) | i\hbar \partial / \partial t - T | \psi(t) \rangle_{e=0}$$

$$- \frac{1}{2} \int dt \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}, t) n(\mathbf{r}', t)$$

Hartree (mean-field) action

Runge & Gross, *Phys. Rev. Lett.* **52**, 997 ('84)

See notes on (1) [TDDFT summary](#), (2) [TDDFT fundamentals](#)

TDDFT & Many-Body Theory

- TDKS orbitals are used as a basis set to calculate physical properties with the help of many-body theory, e.g., GW approximation for one-body [Hybertsen & Louie, *Phys. Rev. Lett.* **55**, 1418 ('85)] & Bethe-Salpeter equation (BSE) [Rohlfing & Louie, *Phys. Rev. Lett.* **81**, 2312 ('98)] for two-body properties
- Many-body theory provides a systematic way to approximate TDKS exchange-correlation (xc) potential ($1 = (\mathbf{r}_1, t_1)$, etc.):

$$v_{\text{xc}}(1) = -2i \int d2 \int d3 \int d4 \pi^{-1}(1,2) G_0(2,3) \Sigma_{\text{xc}}(3,4) G(4,2)$$

where (p denotes a closed-time path & $\bar{\int}$ denotes integration over 1)

$$G(1,1') = -(i/2) \sum_{\sigma} \langle T_p [\psi_{\sigma}(1) \psi_{\sigma}^{\dagger}(1')] \rangle$$

$$\Sigma_{\text{xc}}(1,1') = -2^{-1} U(1, \bar{2}) \chi^{(2)}(\bar{3}, 1'; \bar{2}^+, \bar{2}) G^{-1}(\bar{3}, 1')$$

$$U(1,2) = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta_p(t_1 - t_2)$$

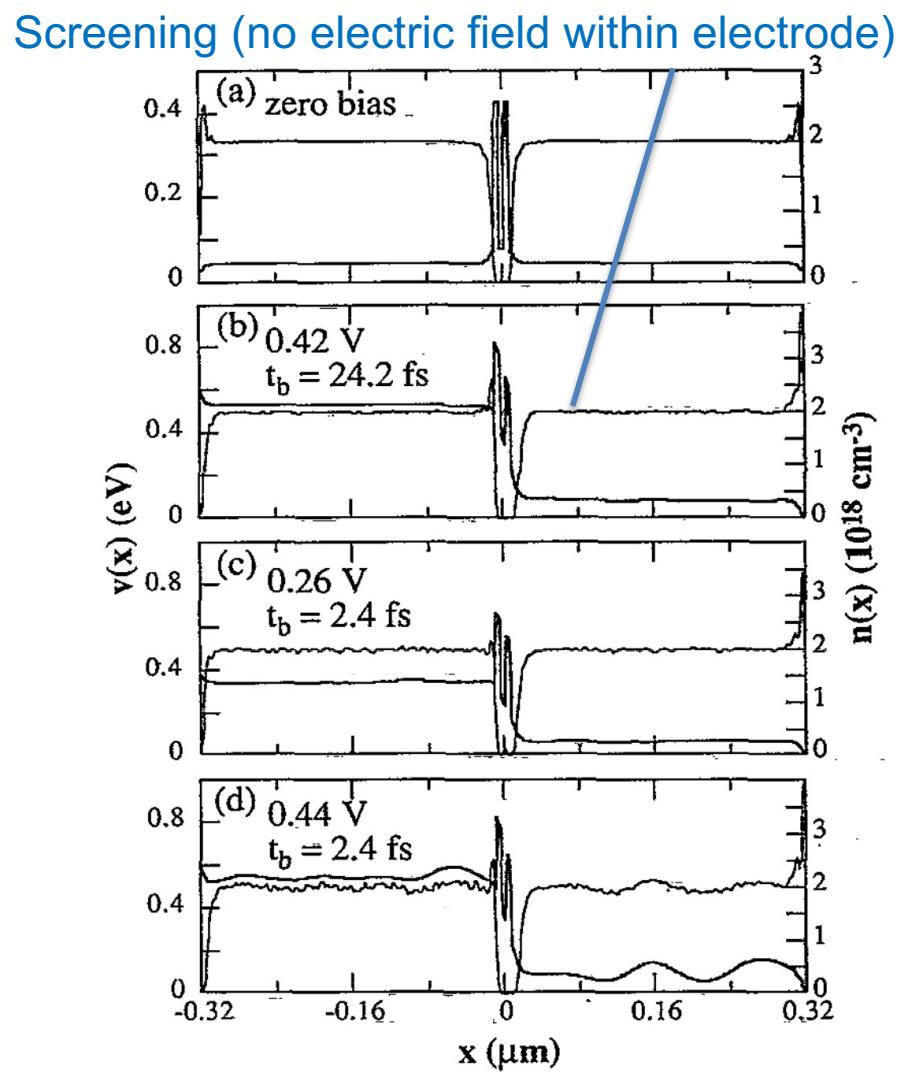
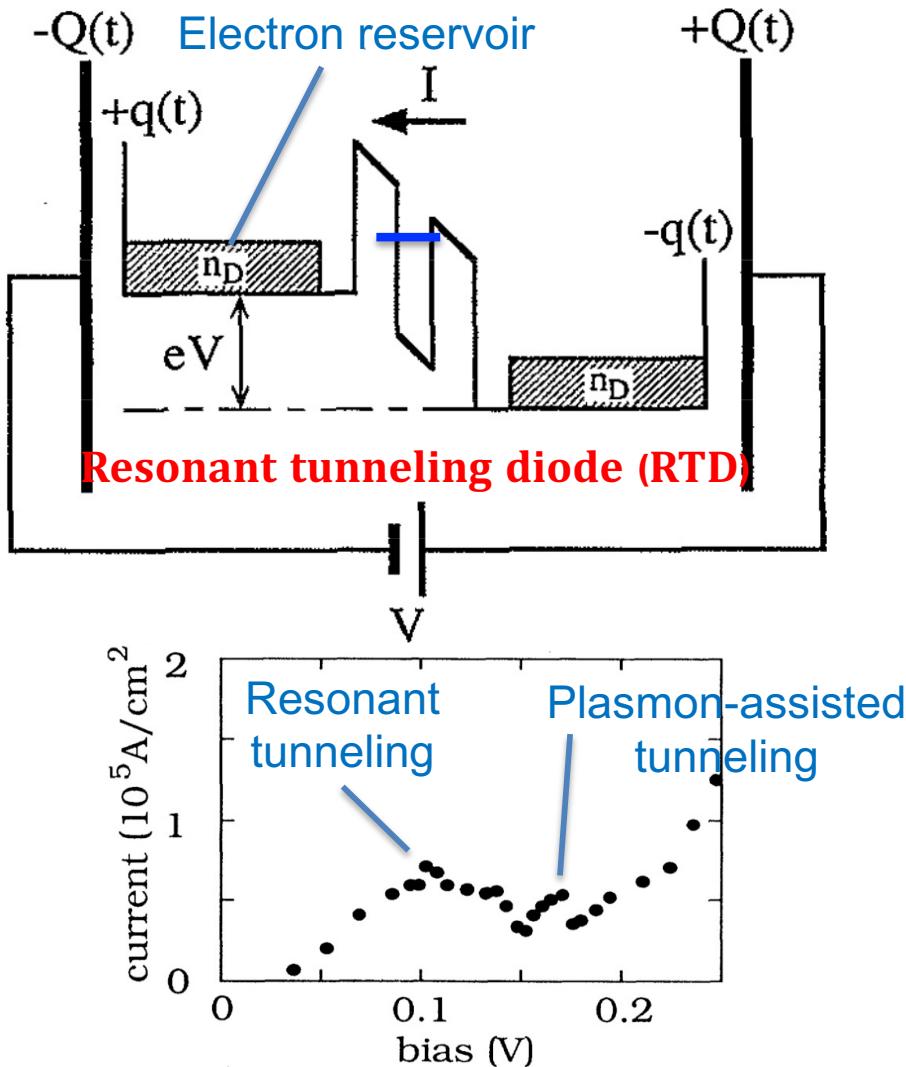
$$\chi^{(\nu)}(1, 1'; \dots; \nu, \nu') = \frac{\delta^{\nu-1}}{\delta \phi(1, 1') \dots \delta \phi(\nu, \nu')} \sum_{\sigma} \langle T_p [\psi_{\sigma}(1) \psi_{\sigma}^{\dagger}(1')] \rangle$$

$$G_0^{\text{r|a}}(1,1') = \mp i[\theta(t_1 - t'_1)|\theta(t'_1 - t_1)] \sum_i \psi_i(1) \psi_i^*(1') ; G_0^{\text{c}}(1,1') = -i \sum_i \psi_i(1) \psi_i^*(1') \\ \pi_{\text{r}}(1,2) = -2i\hbar^{-1}[G_0^{\text{r}}(1,2)G^{\text{c}}(2,1) + G_0^{\text{c}}(1,2)G^{\text{a}}(2,1)]$$

See note on field-theory of xc potential

TDDFT & Physics

- TDKS equations, even within the random phase approximation (RPA, $v_{xc} = 0$) or static v_{xc} , describe collective effects like screening & plasma oscillation



Nakano et al., Phys. Rev. B 43, 9066 ('91); Appl. Phys. Lett. 64, 2569 ('94)

Collective Effects

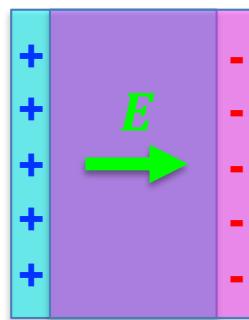
- **Screening:** In electrons with average number density n , along with uniform positive charge that neutralizes the total electronic charge, the electrostatic potential $\phi(\mathbf{r})$ due to an external point charge Q is obtained (within large n & linearized approximations) as

$$\phi(\mathbf{r}) = \frac{Q}{r} \exp(-k_{\text{TF}} r); k_{\text{TF}} = \left(\frac{6\pi n e^2}{E_F} \right)^{1/2}; E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

Fermi energy
Thomas-Fermi wave number

- **Plasma oscillation:** A slab of uniform electron/positive-background can sustain an oscillation with plasma frequency

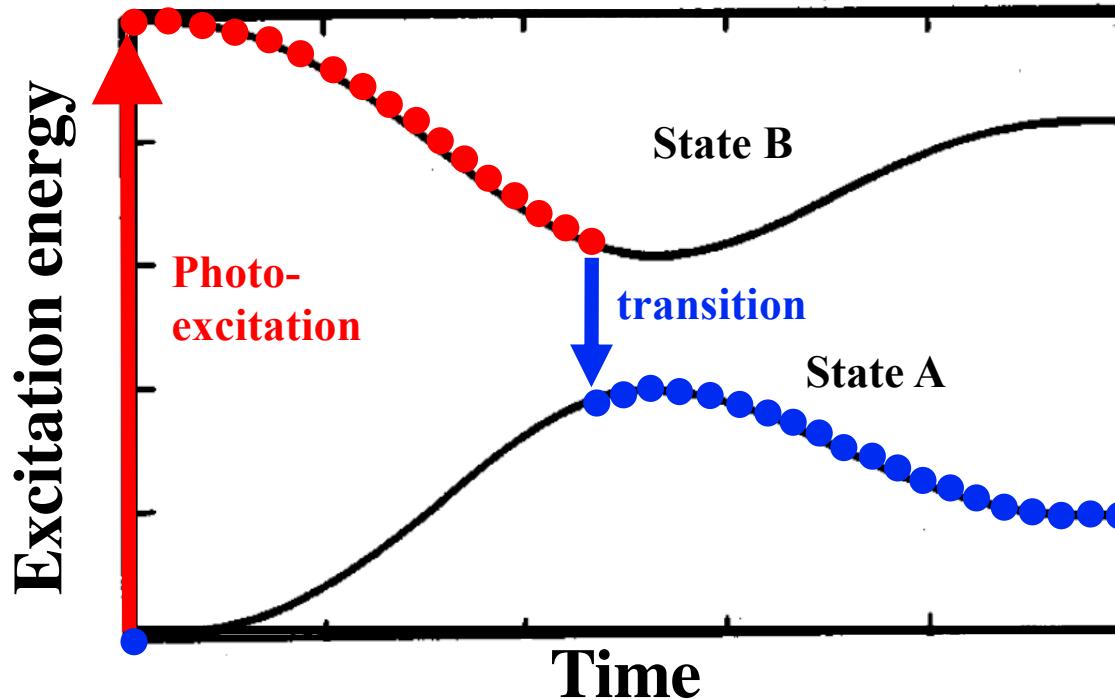
$$\omega_p = \left(\frac{4\pi n e^2}{m} \right)^{1/2}$$



Surface-Hopping NAQMD

- Incorporate electron transitions with the time-dependent density-functional theory (TDDFT) & surface-hopping method

Tully, J. Chem. Phys. 93, 1061 ('90), *ibid.* 129, 044104 ('08); Duncan et al., J. Am. Chem. Soc. 129, 8528 ('07)



- Electronic transitions from the current state to another occur stochastically based on the switching probability obtained by solving TDDFT equations

K-th excitation frequency

$$\Psi(\mathbf{r}, t) = \sum_J C_J^{(I)}(t) \Phi_J(\mathbf{r}; \mathbf{R}(t)) \quad C_I^{(I)}(0) = \delta_{I,J}$$
$$\frac{d}{dt} C_J^{(I)}(t) = - \sum_k C_k^{(I)}(t) \left(i\omega_K \delta_{JK} + \langle \Phi_J | \frac{\partial}{\partial t} | \Phi_K \rangle \right)$$

J-th adiabatic excited state

Electronic transition assisted by nuclei motion

Surface-Hopping Procedure

- **Density matrix** $a_{kl}(t)$ & **state probability** $p_k(t)$

$$a_{kl}(t) \equiv c_k(t)c_l^*(t); p_k(t) \equiv a_{kk}(t) = |c_k(t)|^2$$

- **Probability dynamics**

$$\frac{d}{dt}p_k(t) = \sum_{k'(\neq k)} b_{kk'} \quad \text{Nonadiabatic coupling}$$
$$b_{kk'} = 2 \frac{d\mathbf{R}}{dt} \bullet \text{Re}(\mathbf{d}_{kk'} \bullet a_{k'k}); \mathbf{d}_{kk'} = \left\langle \psi_k \left| \frac{\partial}{\partial \mathbf{R}} \right| \psi_l \right\rangle$$

- **Fewest-switches surface hopping (FSSH) algorithm**

During one NAQMD step (Δt), stochastically choose a state transition according to the transition probability matrix

$$\pi_{k' \leftarrow k} = \frac{\Delta t b_{k'k}}{p_k} = 2\Delta t \frac{d\mathbf{R}}{dt} \bullet \frac{\text{Re}(\mathbf{d}_{kk'} \bullet a_{k'k})}{a_{kk}}$$

- **From a swarm of independent classical trajectories toward a quantum-mechanical description of nuclei motion**

DISH: Jaeger *et al.*, *J. Chem. Phys.* **137**, 22A545 ('12) — implemented in QXMD; SQUASH: Akimov & Prezhdo, *Phys. Rev. Lett.* **113**, 153003 ('14); Liouville space hopping: Wang *et al.*, *J. Phys. Chem. Lett.* **6**, 3827 ('15)

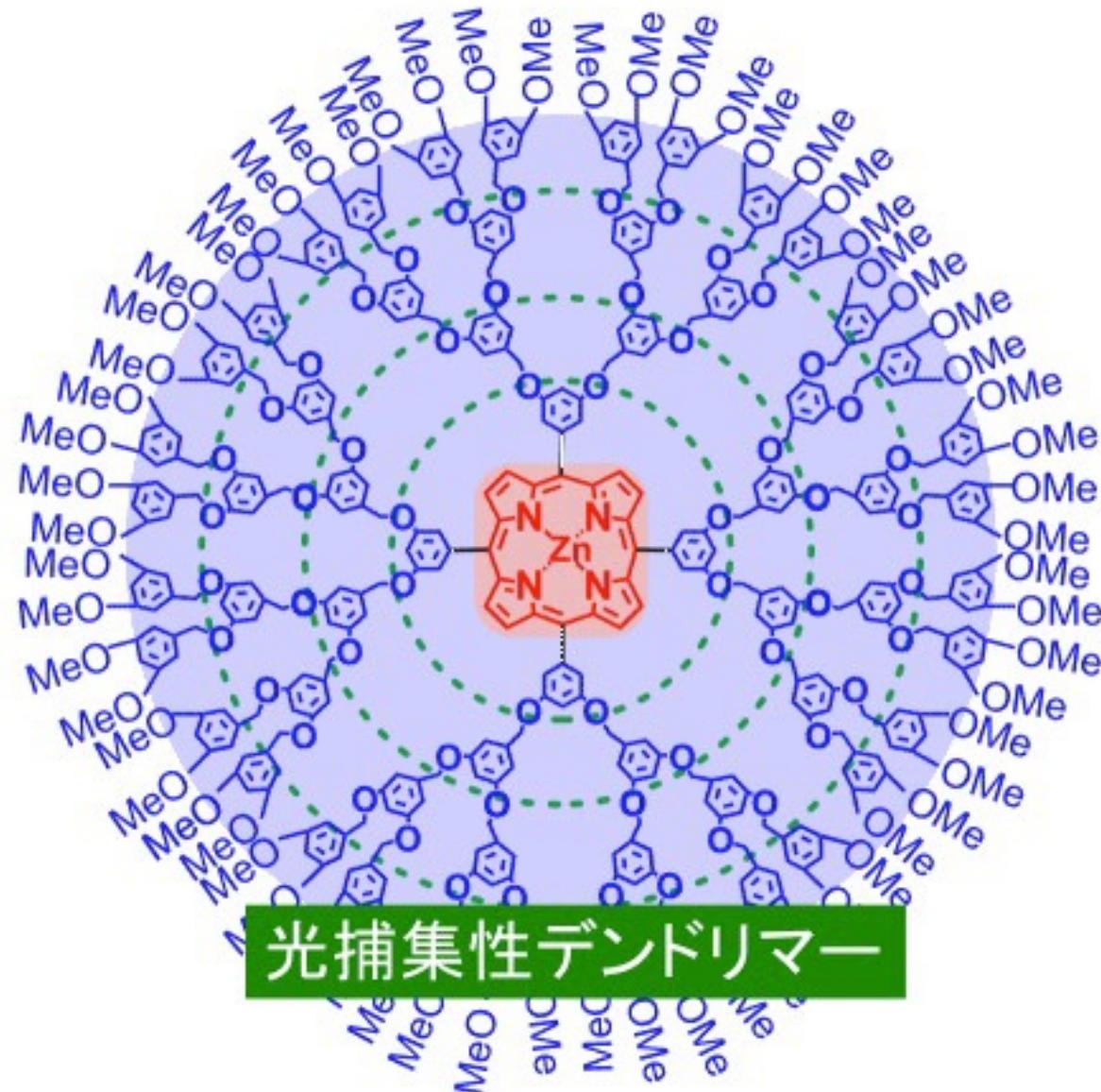
See note on fewest-switch surface hopping

II. NAQMD Applications

- Photovoltaics: photocarrier, charge transfer, charge recombination, singlet fission
- Dielectric breakdown of polymers: hot-carrier dynamics & chemistry
- Photoinduced phase transition & quantum matter
- Optoelectronics
- Laser-driven photochemistry

Example: Light Harvesting Dendrimers

Electron-hole pairs photoexcited at peripheral antennas travel to the core

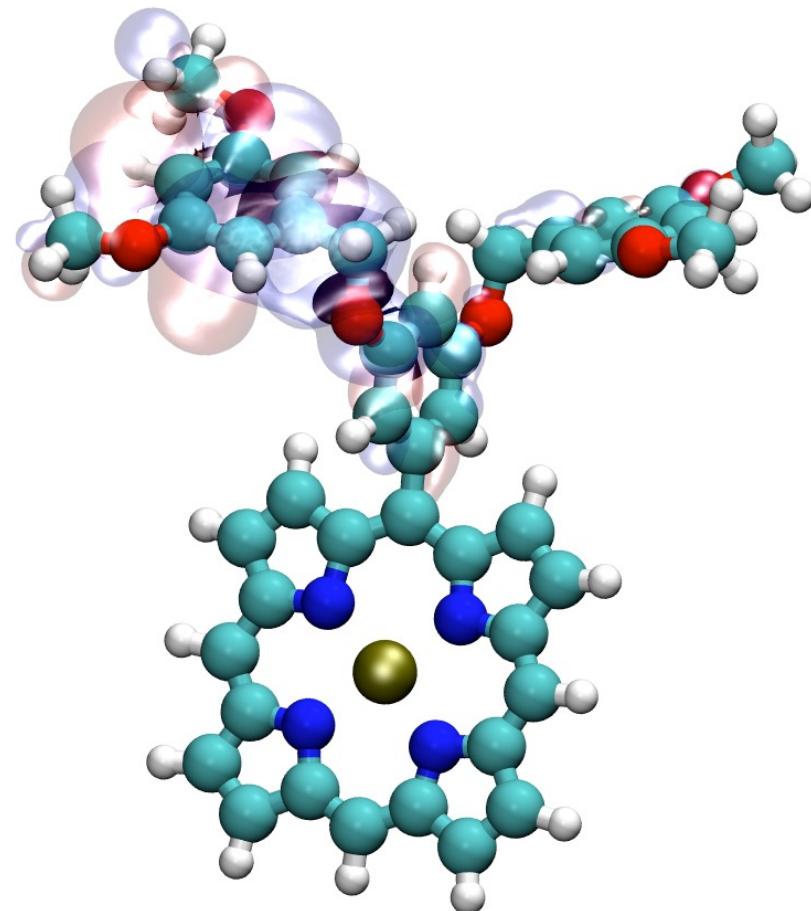
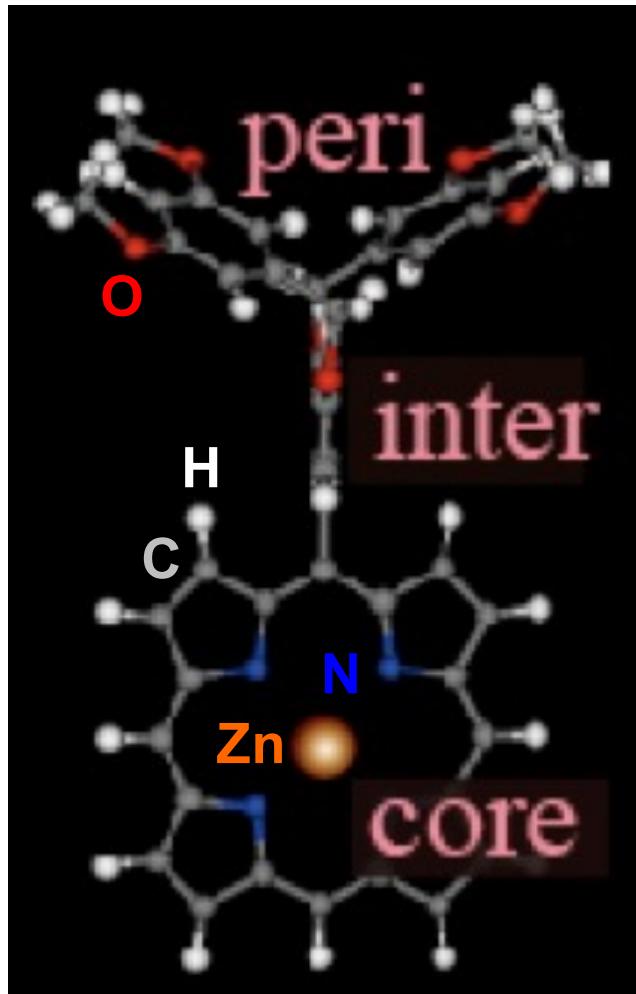


Prof. I. Akai
Kumamoto Univ.

Key: Rapid electron transfer for solar-energy applications

Electron Transfer in a Dendrimer

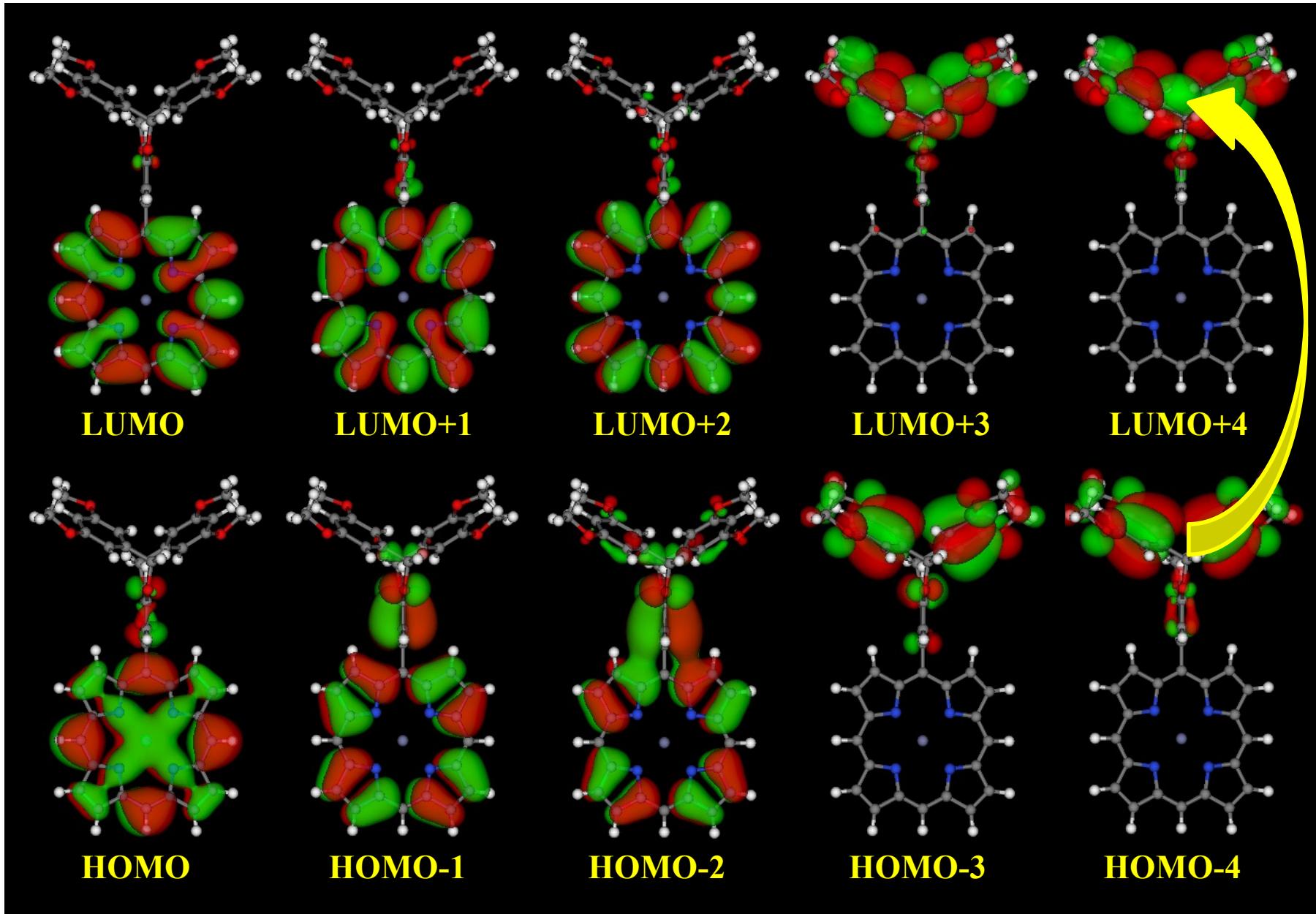
Nonadiabatic quantum molecular dynamics simulation with fewest-switches surface hopping [Tully, '90] & time-dependent density functional theory



Ohmura *et al.*, *Appl. Phys. Lett.* **98**, 113302 ('11)

Photoexcitation Simulation

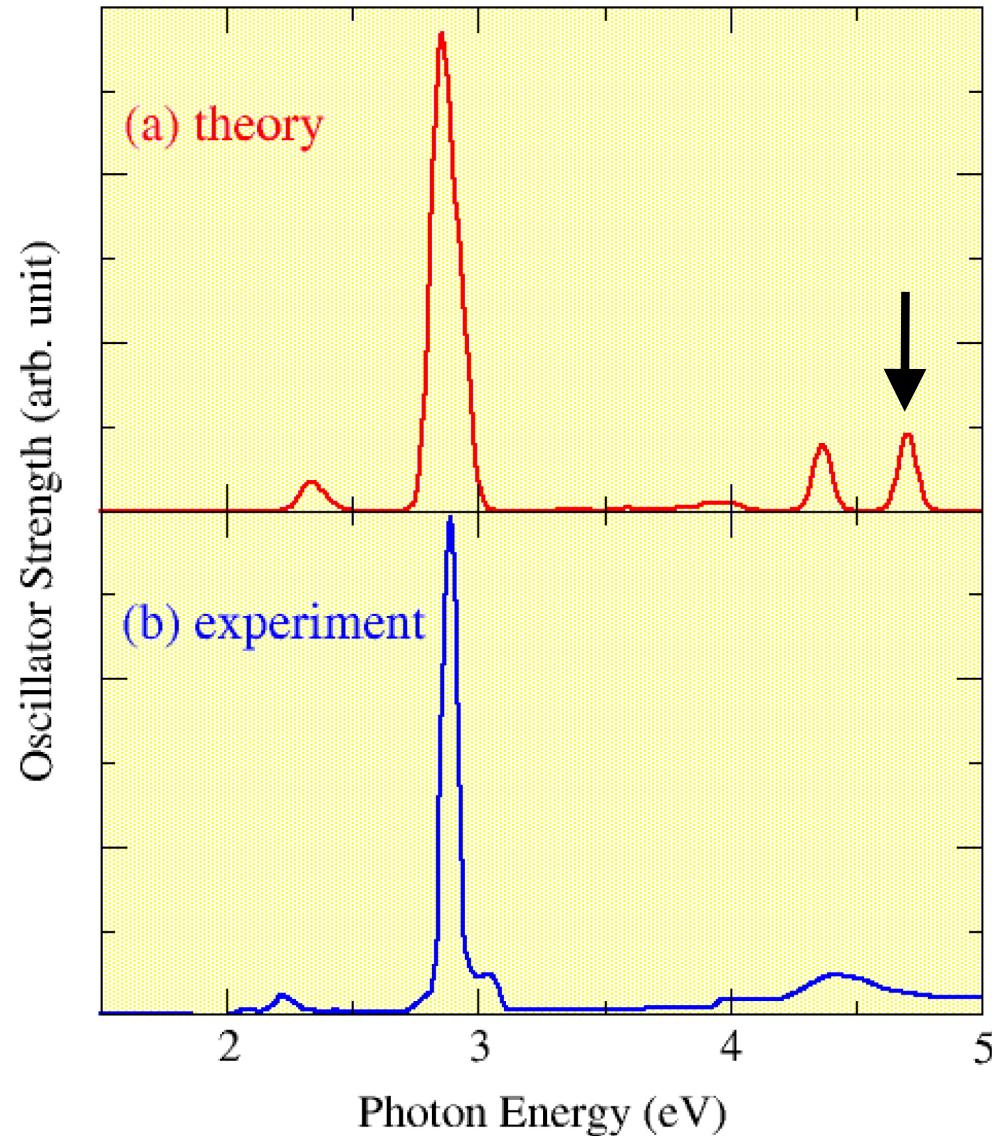
Unoccupied



An electron in HOMO-4 is excited to LUMO+4

Optical Absorption Spectrum

- Oscillator strength calculated by the linear-response TDDFT



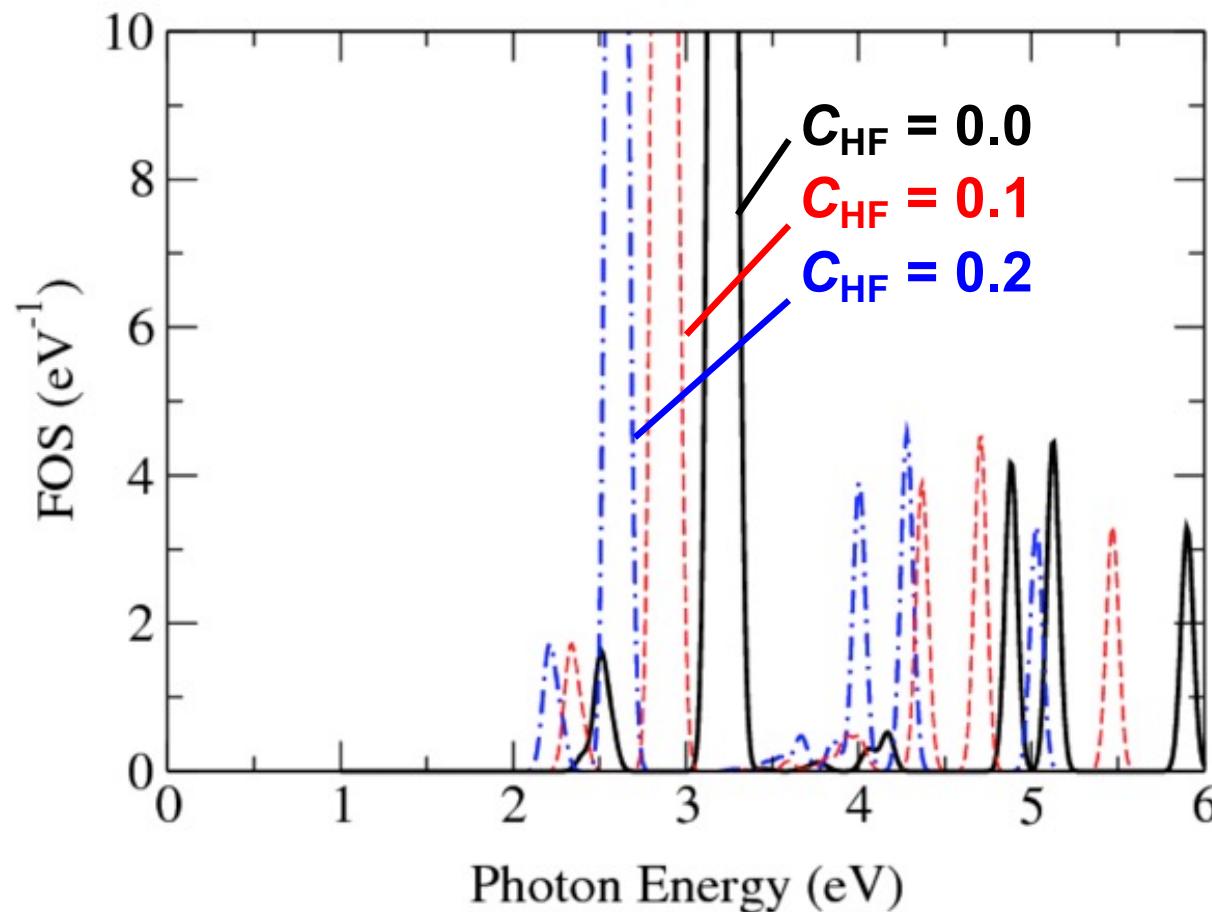
- Excellent agreement with experimental data [Akai *et al.*, '06]

Effect of Exchange-Correlation Functional

- Oscillator strength calculated by the linear-response TDDFT

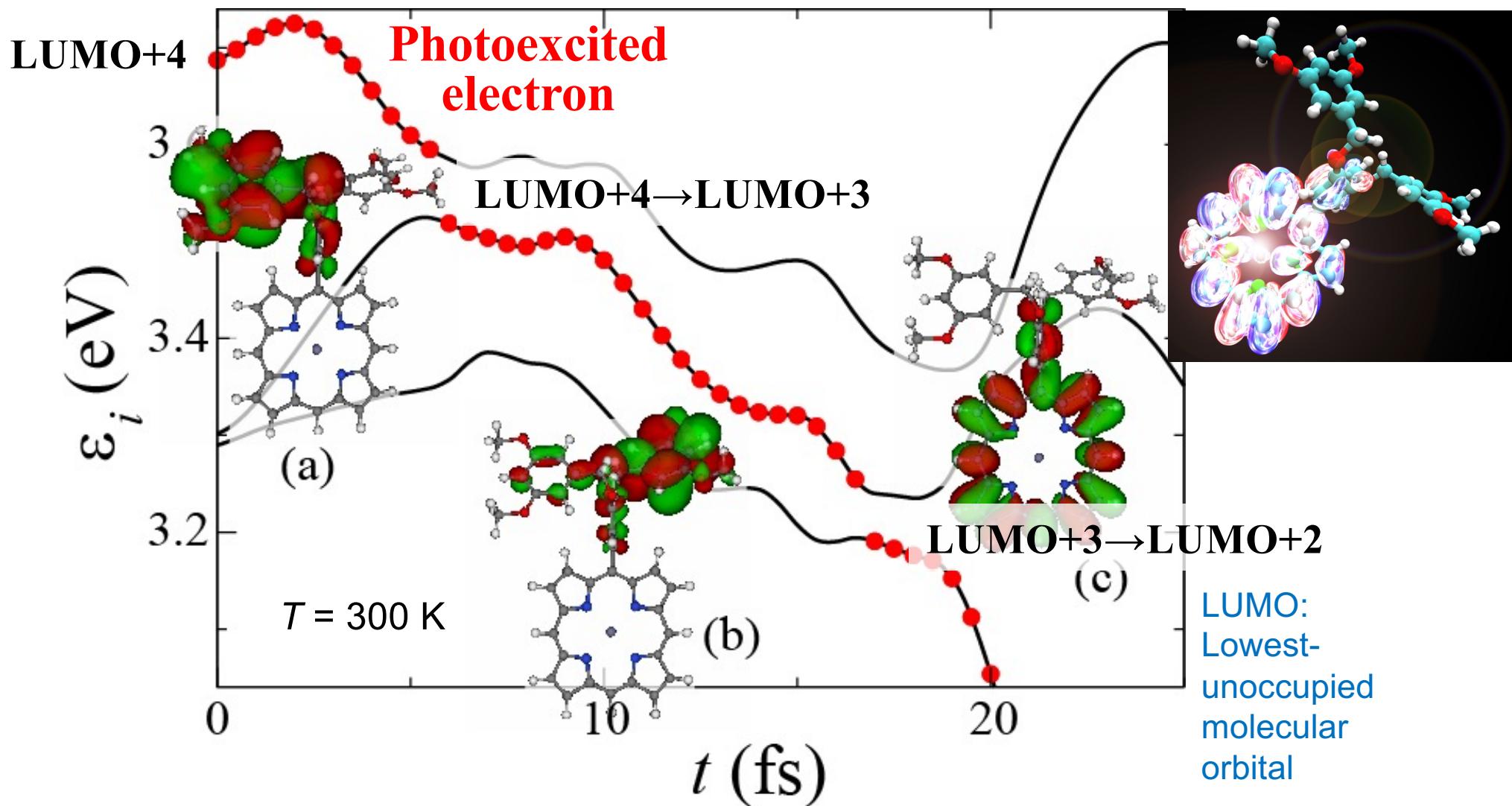
$$K_{ia\sigma,jb\tau} = \left[\psi_{i\sigma} \psi_{a\sigma}^* \left| \psi_{j\tau} \psi_{b\tau}^* \right. \right] - C_{\text{HF}} \delta_{\sigma\tau} \left[\psi_{i\sigma} \psi_{j\sigma}^* \left| \psi_{a\tau} \psi_{b\tau}^* \right. \right] + (1 - C_{\text{HF}}) f_{ia\sigma,jb\tau}^x + f_{ia\sigma,jb\tau}^c$$

$$[g|h] = \int d\mathbf{r} \int d\mathbf{r}' \frac{g(\mathbf{r})h(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$



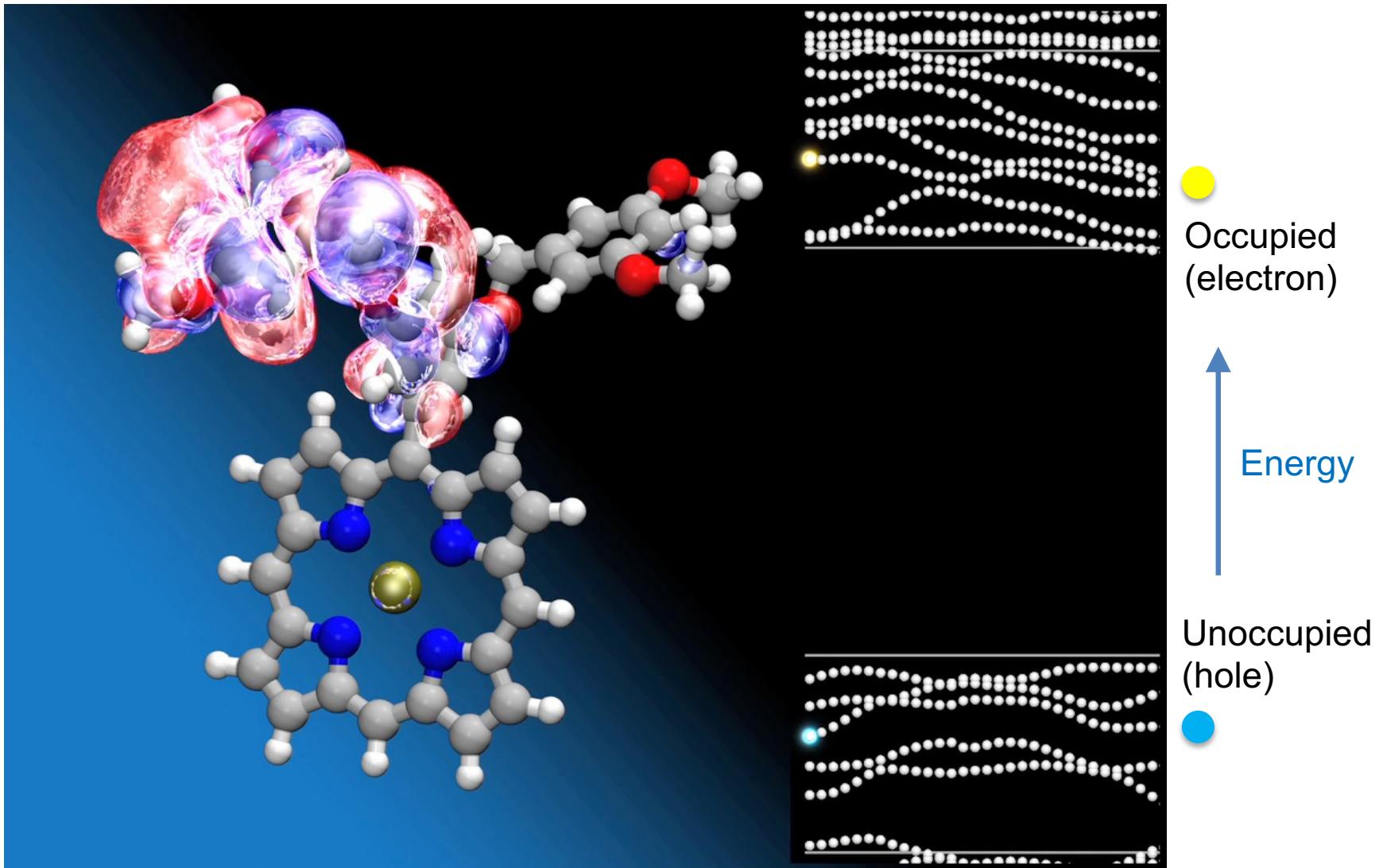
- At most 20% difference in excitation energies by different approximations

Electron Transfer in a Dendrimer



- The photoexcited electron at the peripheral antenna is transferred to the core due to the energy-crossing & overlapping of orbitals assisted by thermal molecular motions

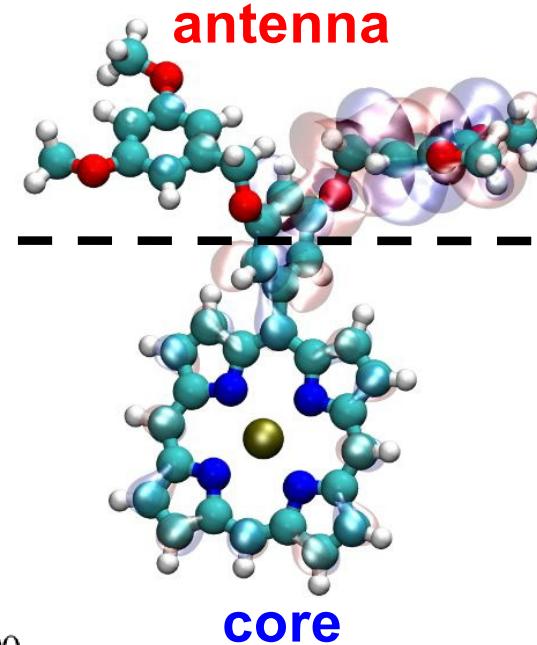
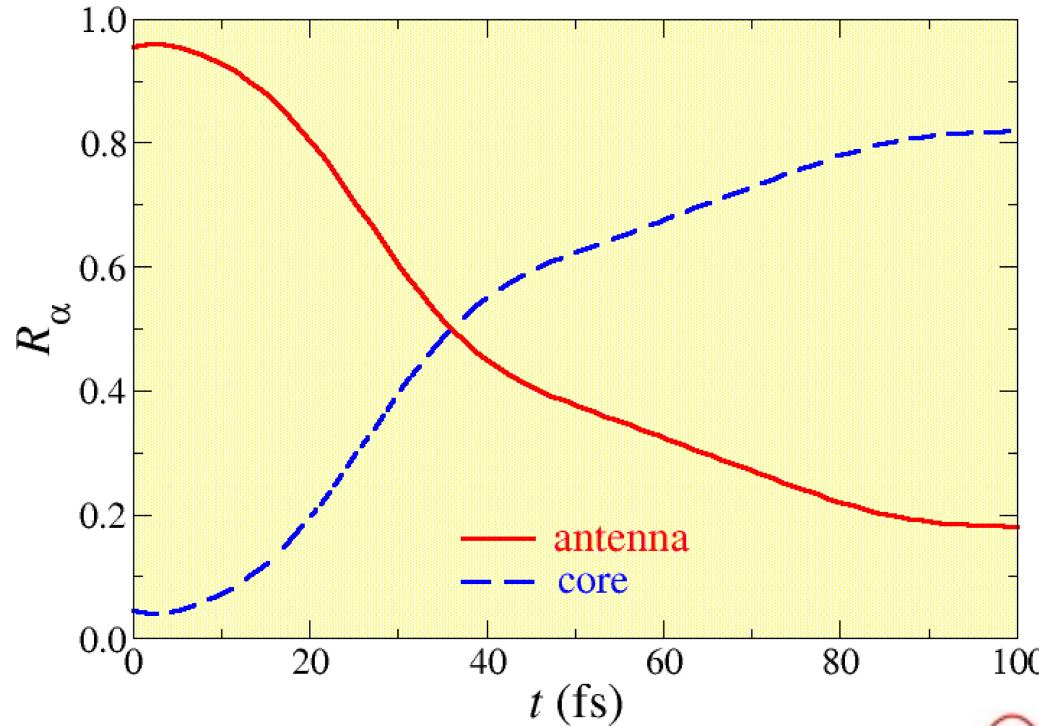
Electron Transfer in a Light-Harvesting Dendrimer



- The photoexcited electron at the peripheral antenna is transferred to the core due to the energy-crossing & overlapping of orbitals assisted by thermal molecular motions

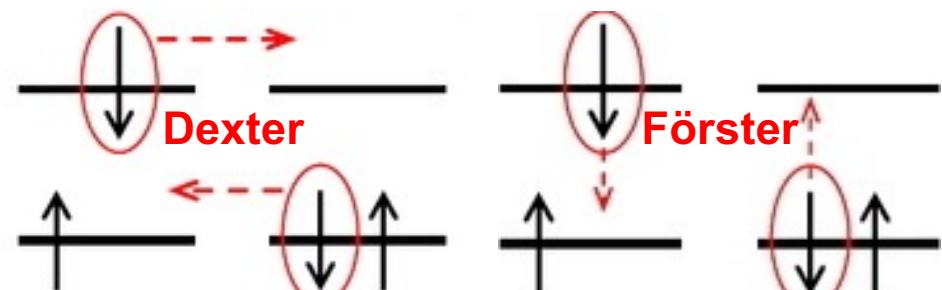
Electron Transfer Mechanism

- Probability in the antenna & core regions (averaged over 15 trajectories)



- The resulting electron transfer rate due to the *Dexter* mechanism is much larger than that due to the *Förster* mechanism

$$k_{\text{Dexter}}^{-1} = \boxed{40 \text{ fs}}$$

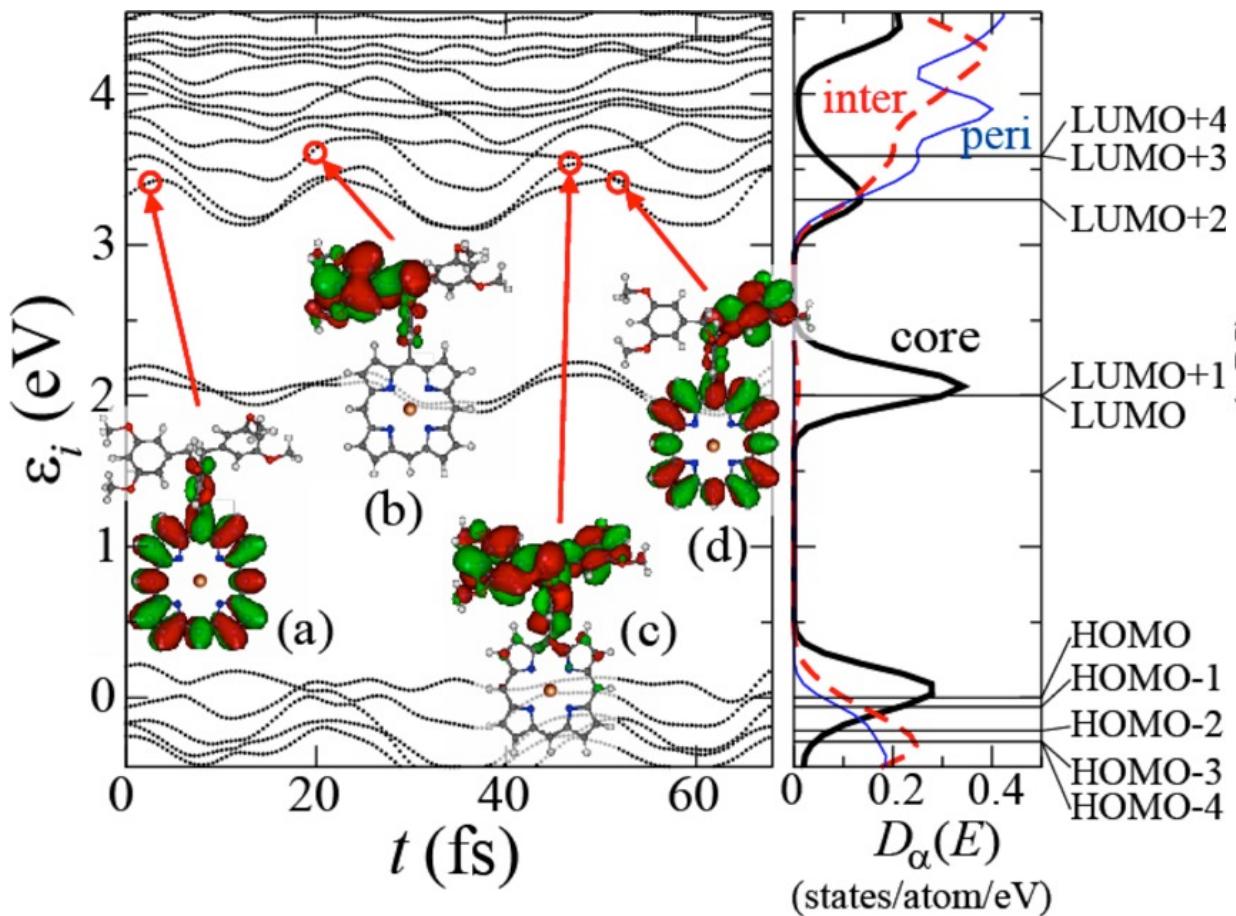


$$\ll k_{\text{Forster}}^{-1} = \left[\frac{2\pi}{\hbar} \sum_{b \notin \{\text{occ}\}; j \in \{\text{occ}\}} \left| K_{ia\sigma, jb\sigma} \right|^2 \times \frac{1}{\sqrt{2\pi\alpha}} \exp\left(-\frac{(\omega_{ia\sigma} - \omega_{jb\sigma})^2}{2\alpha^2}\right) \right]^{-1} = \boxed{1 \text{ ps}}$$

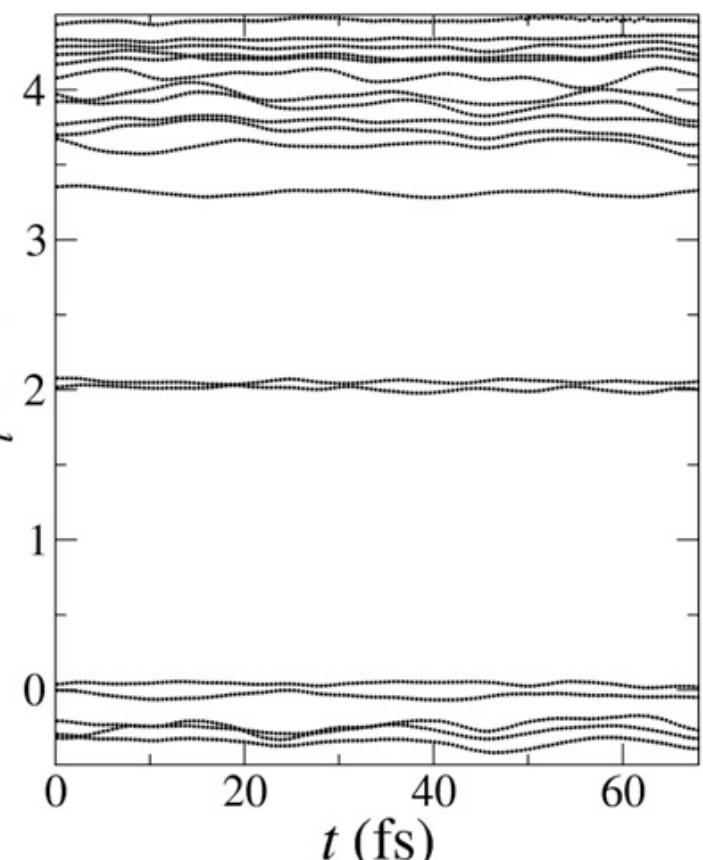
Effect of Temperature

Adiabatic MD simulation of a dendrimer at temperature 300 & 100 K

300 K



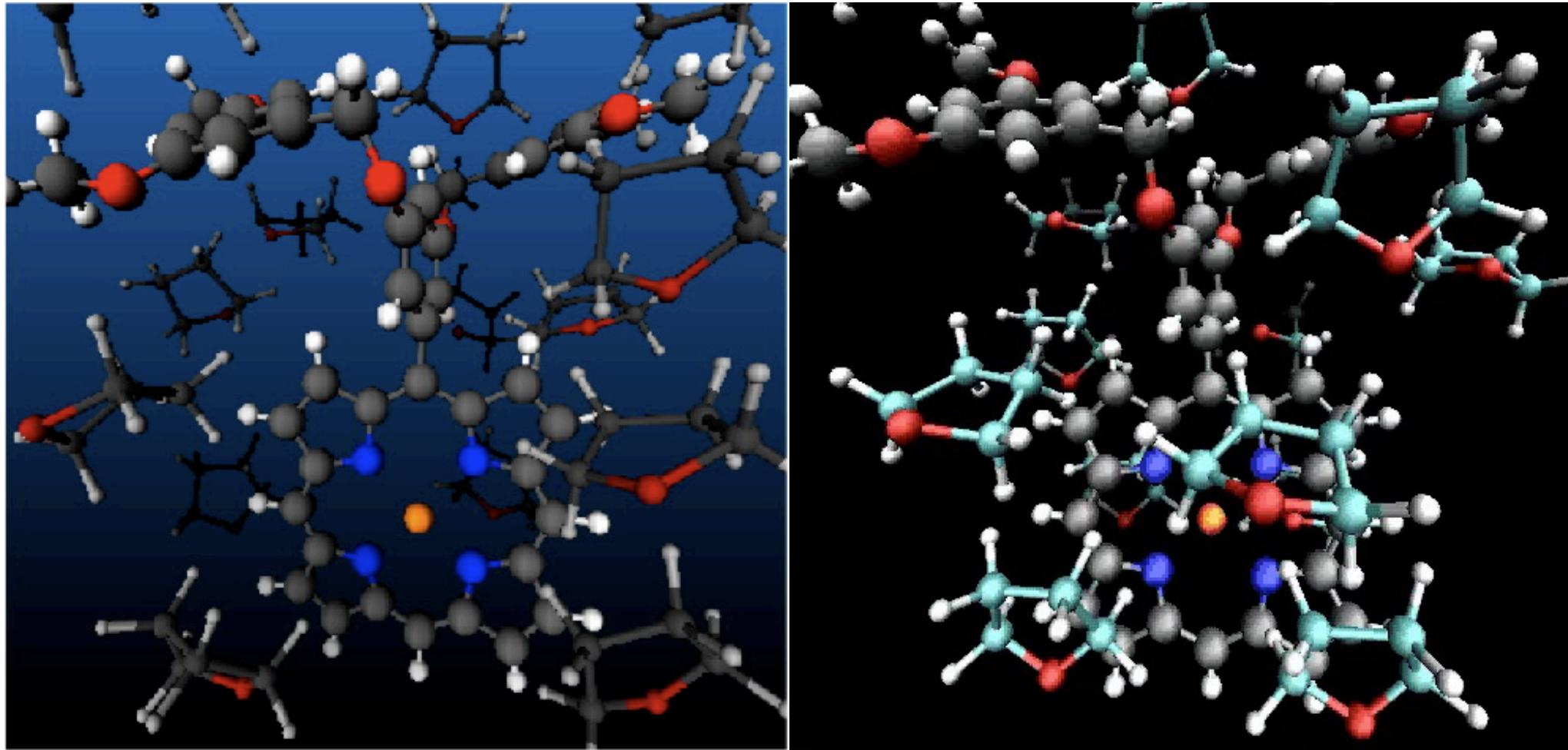
100 K



Electron transfer is suppressed at low temperatures

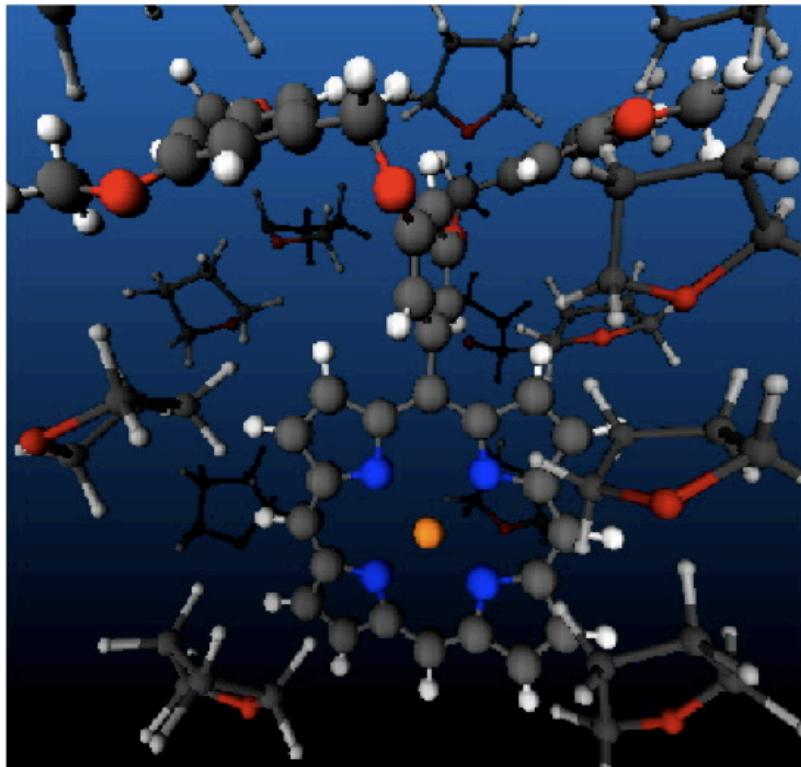
Effect of Solvent

Adiabatic QMD simulation of a dendrimer in solvent,
tetrahydrofuran (THF), $(\text{CH}_2)_4\text{O}$, at temperature 300 K
used in experiments [Akai et al., '06, '08]



Solvent suppresses orbital energy-crossing & consequently electron transfer

Key Molecular Mechanism

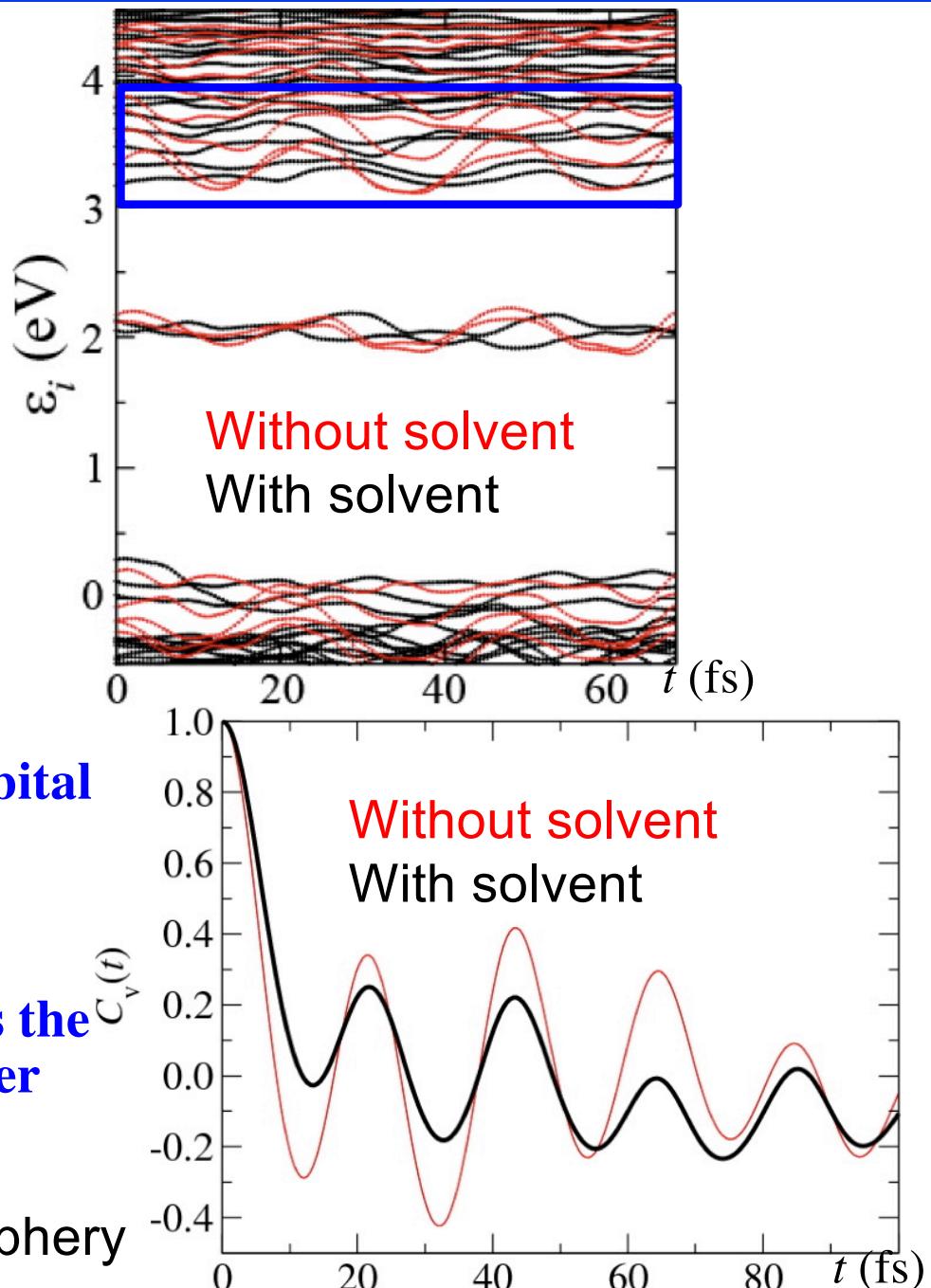


- Solvent (tetrahydrofuran) suppresses orbital energy-crossing & electron transfer

$$\sigma = \langle \varepsilon_i^2 \rangle - \langle \varepsilon_i \rangle^2 = 0.13\text{eV}(\text{vacuum}) \rightarrow 0.04\text{eV}(\text{THF})$$

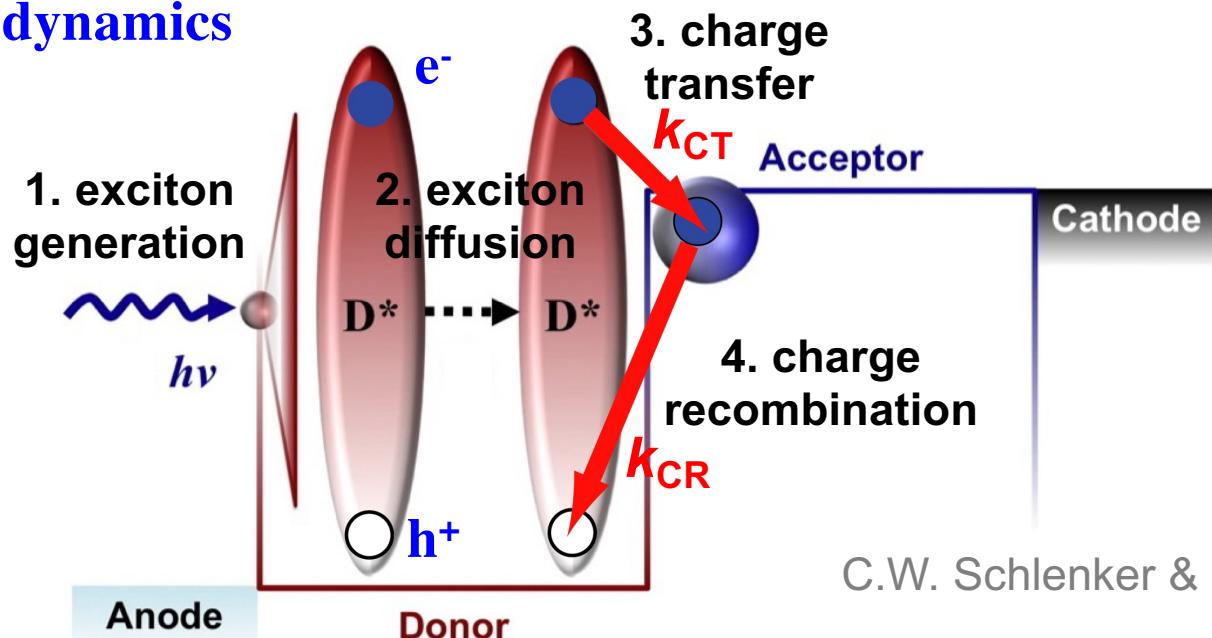
- Aromatic ring motion in the periphery is the key mechanism for rapid electron transfer

Velocity autocorrelation
in the aromatic rings in the periphery



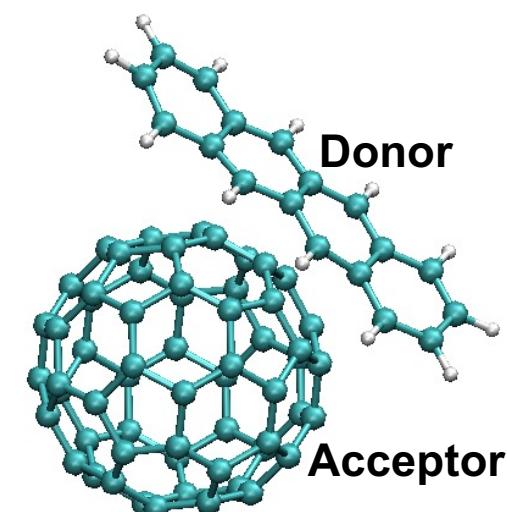
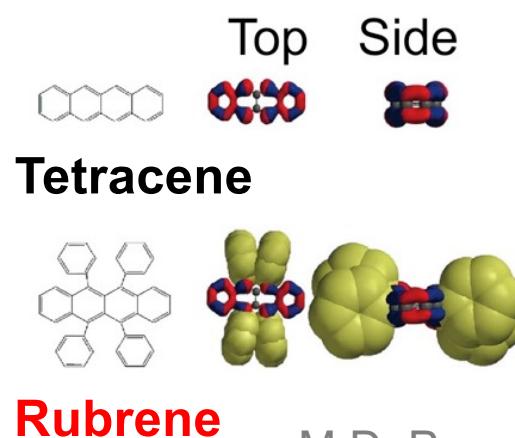
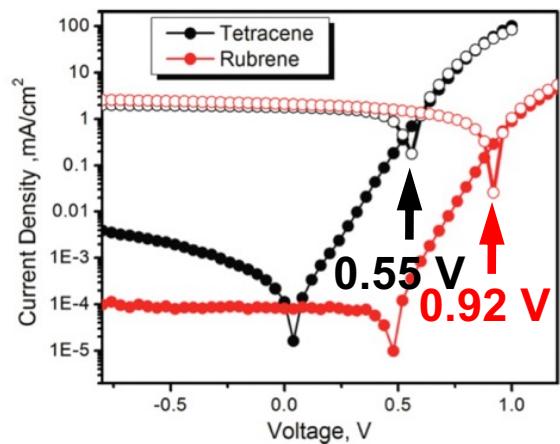
Organic Photovoltaics (OPV)

- Exciton dynamics



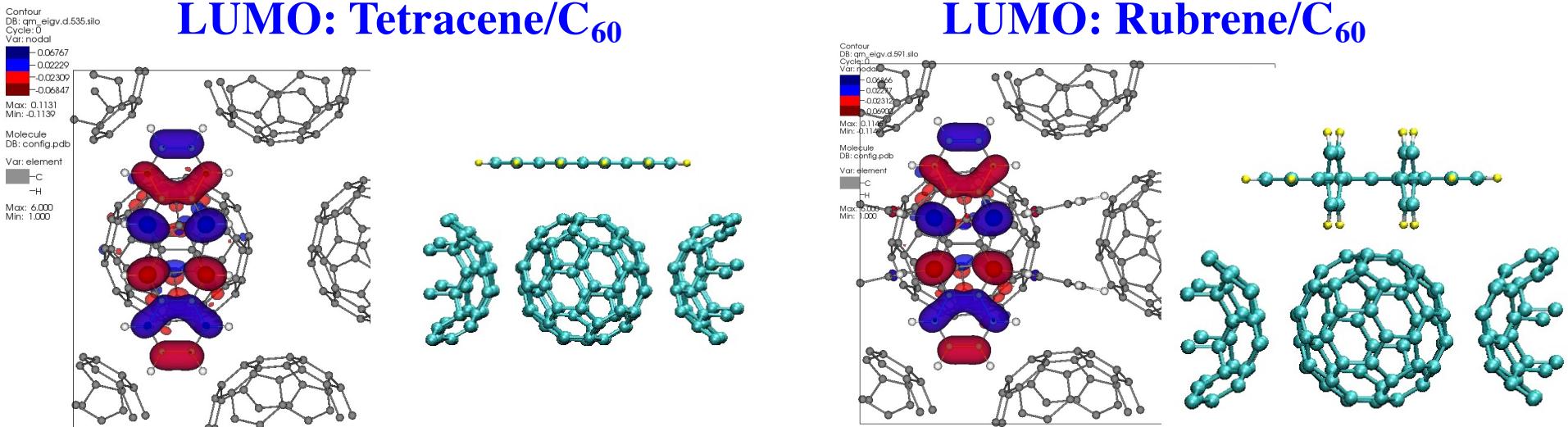
C.W. Schlenker & M. E. Thompson ('11)

- Open-circuit voltage is sensitive to the interfacial structure

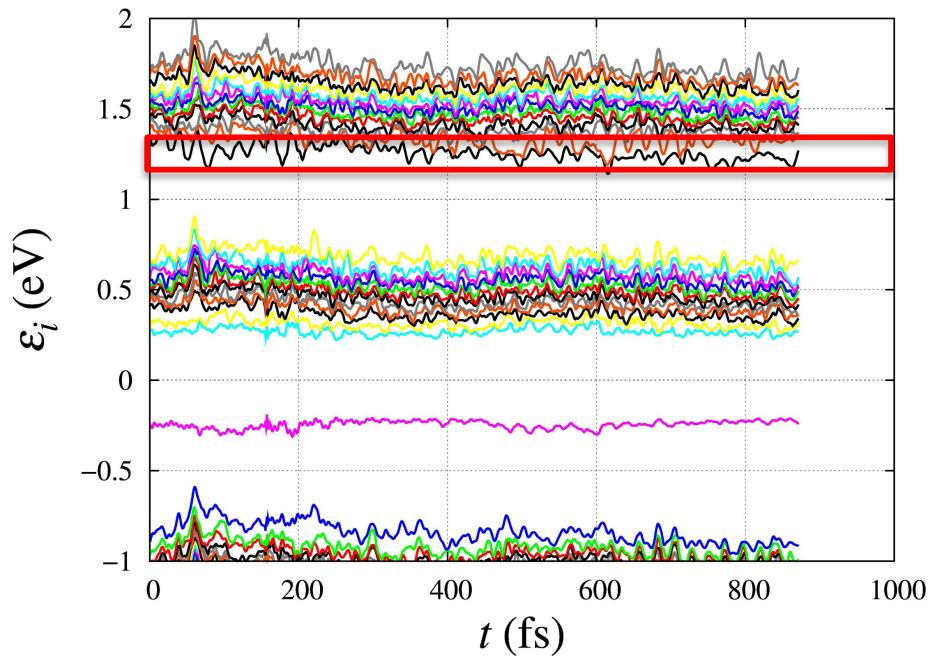


M.D. Perez *et al.*, JACS 131, 9281 ('09)

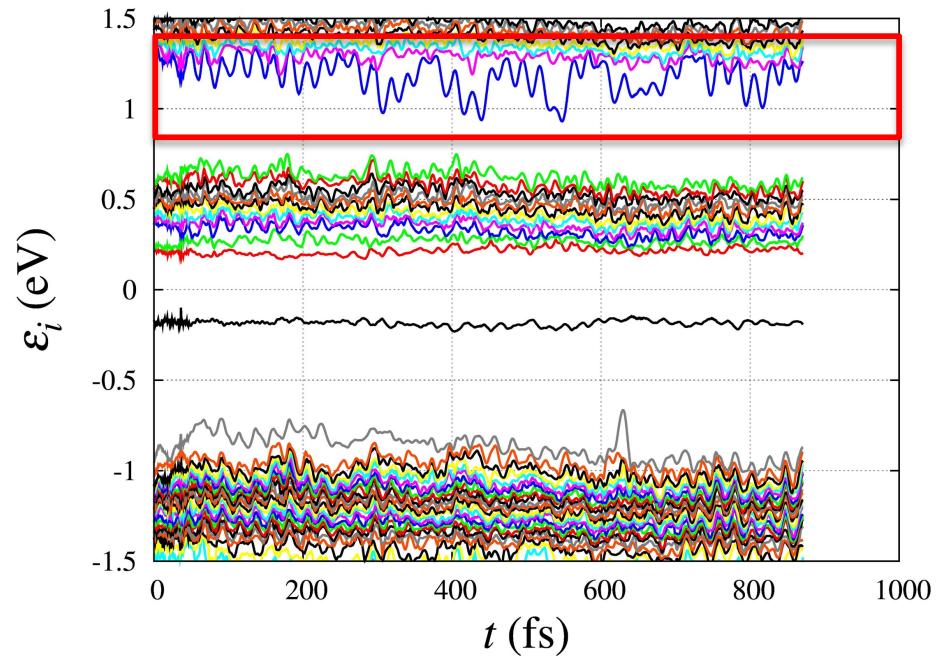
Tetracene or Rubrene/Fullerene



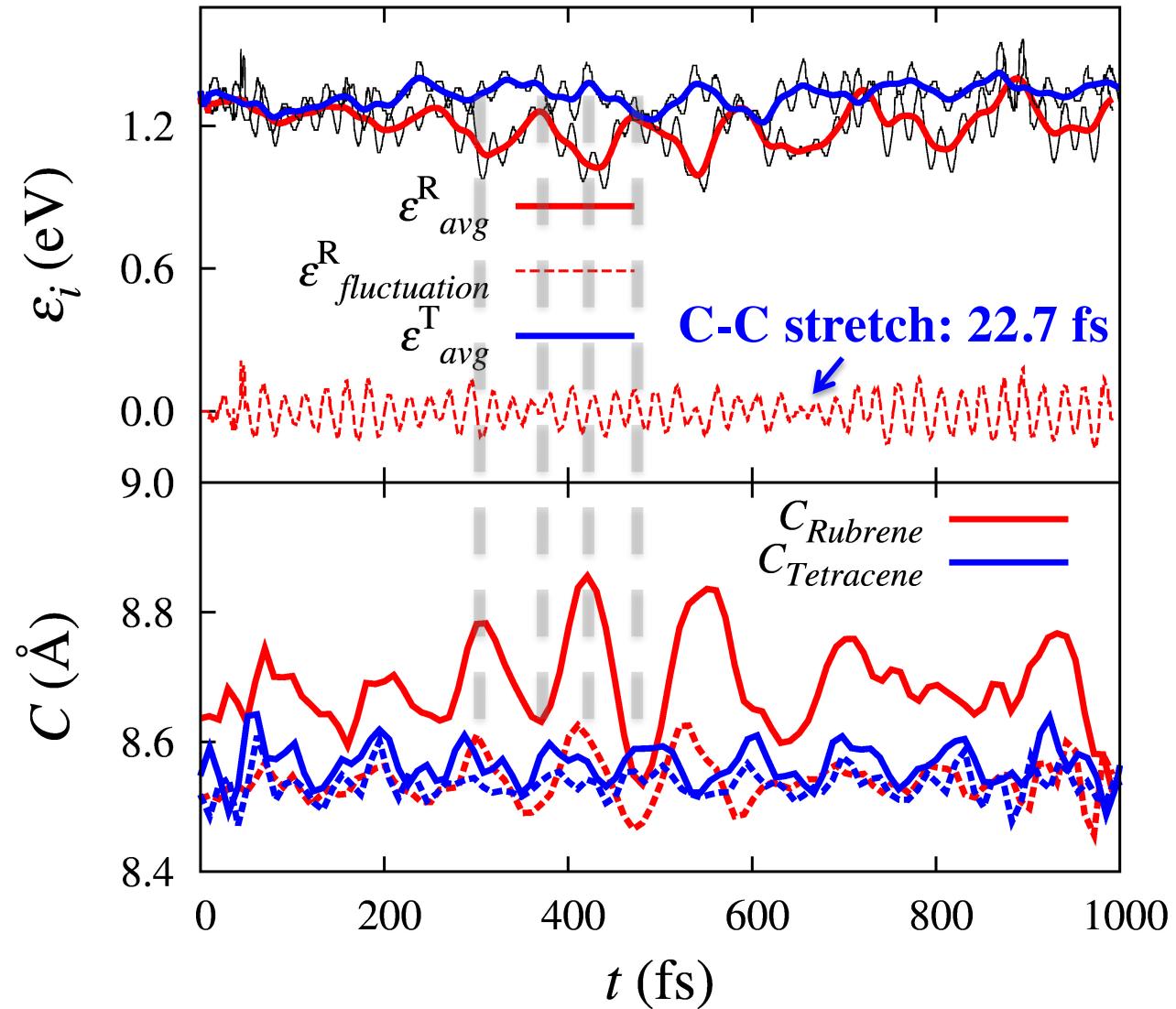
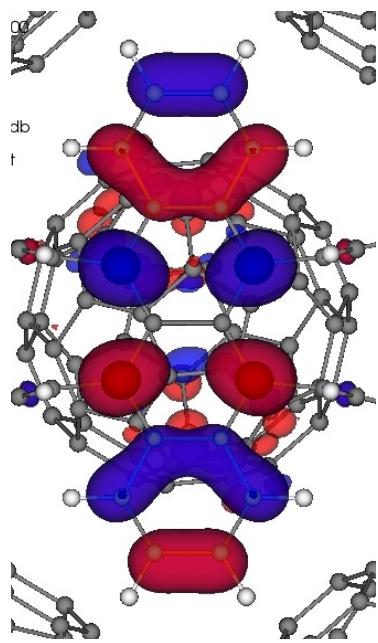
Small level fluctuation → small charge transfer



Large level fluctuation → large charge transfer



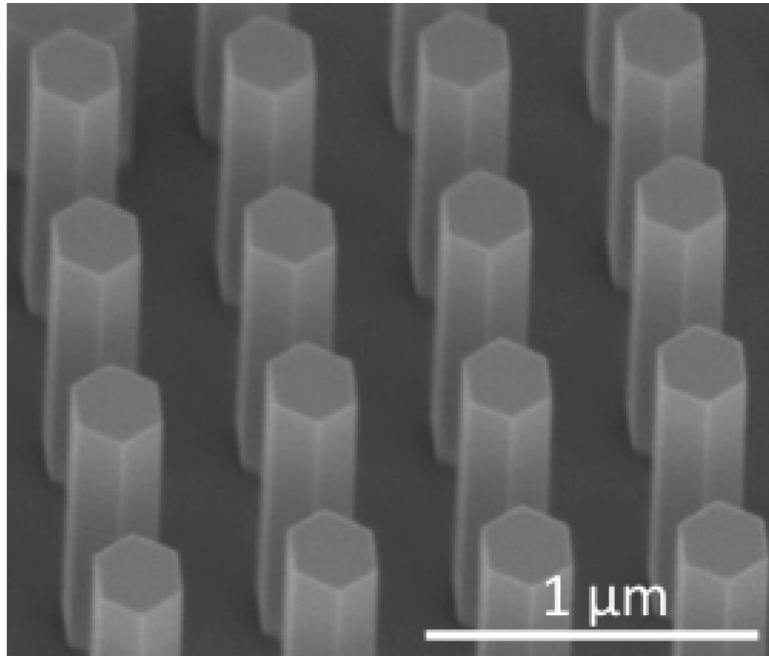
Ring Breathing Modes



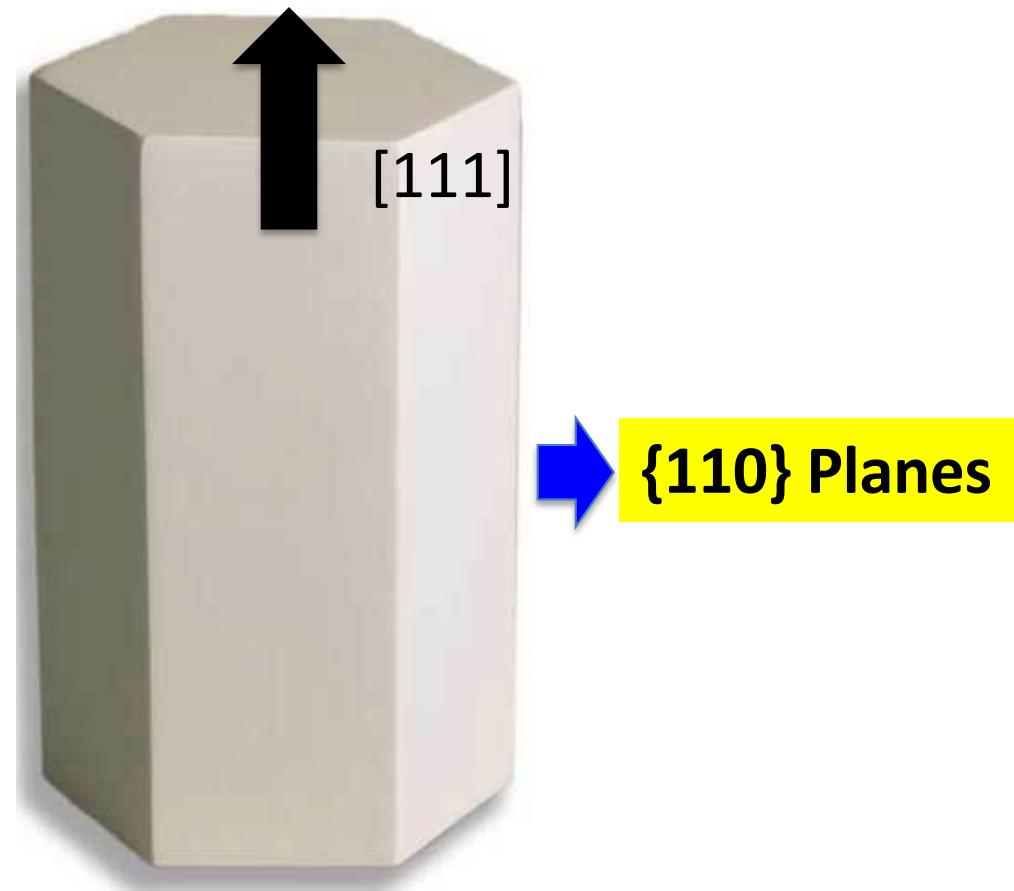
- The phenyl rings expand the inner rings of the backbone & enhances their breathing modes → increased charge transfer

Inorganic Nanowire Photovoltaics (NWPV)

GaAs nanowires under electronic microscopy



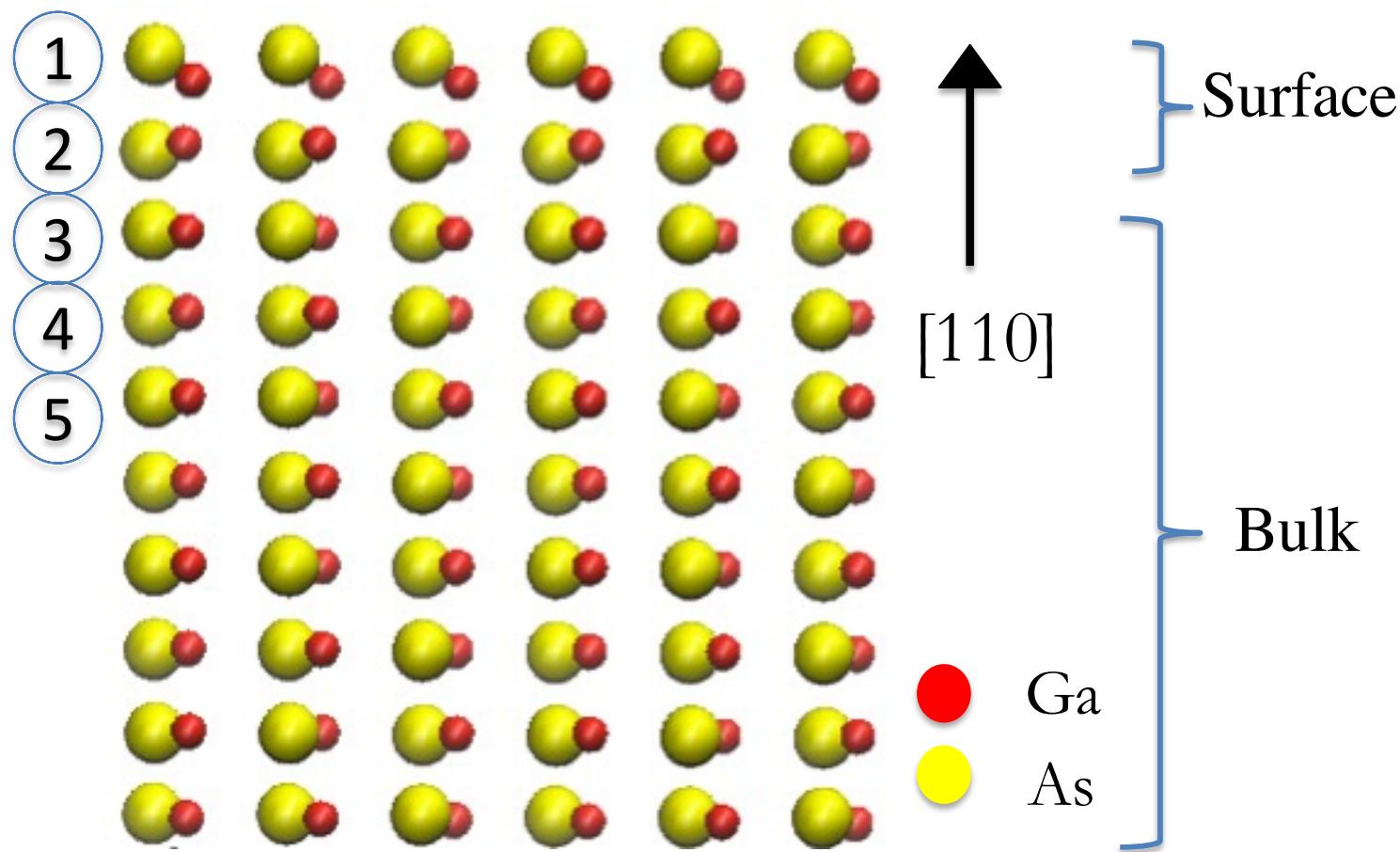
GaAs nanowire with perfect {110} surfaces



Yao et al., ACS Nano 10, 2424 ('16)

NAQMD Simulation of GaAs (110) Surface

Simulation Setup for GaAs (110)

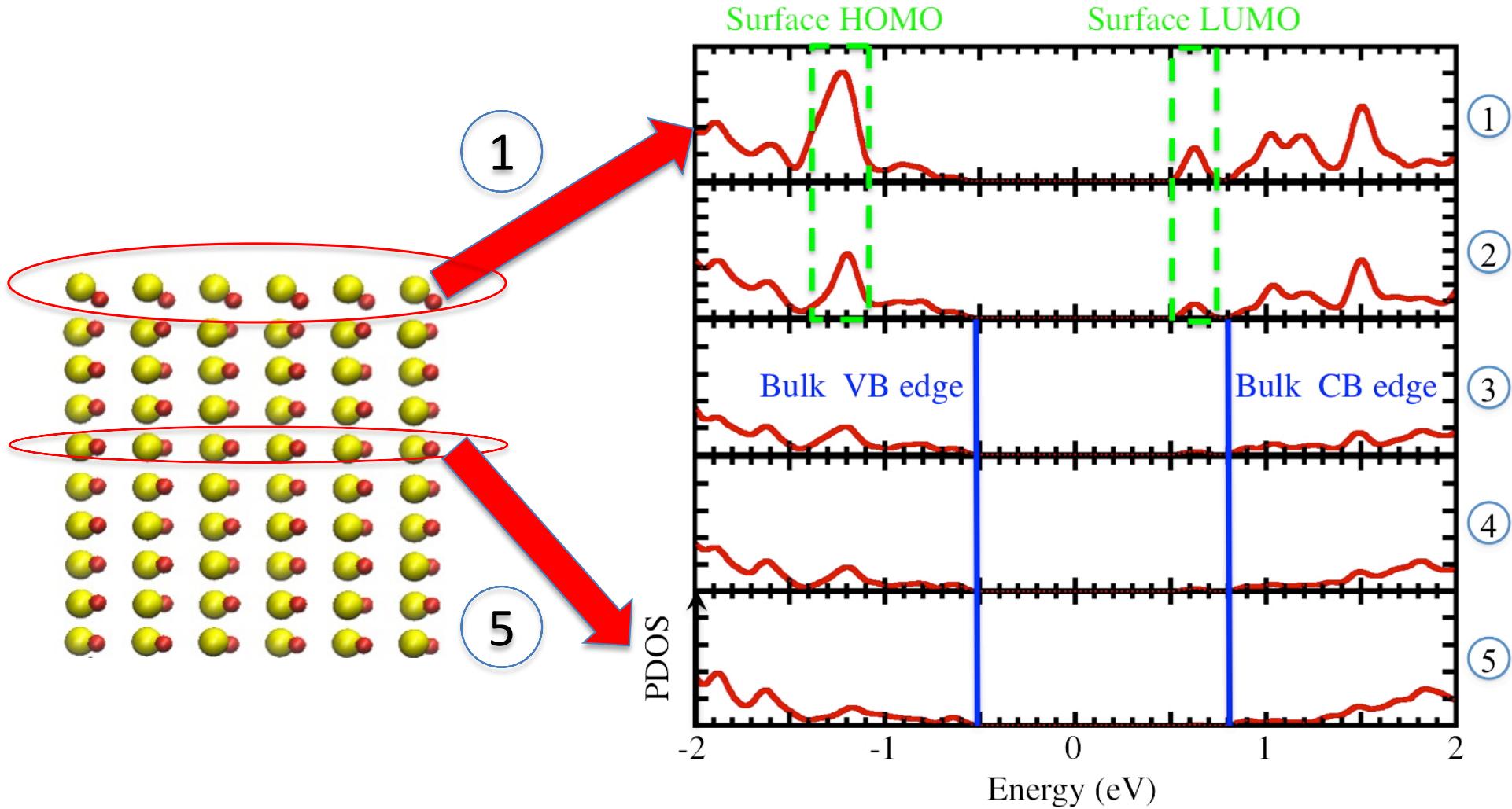


- Definition of surface and bulk
- Atomic bilayers are numbered sequentially

Brown *et al.*, J. Appl. Phys.
117, 054307 ('15)

Electronic Structure at (110) Surface

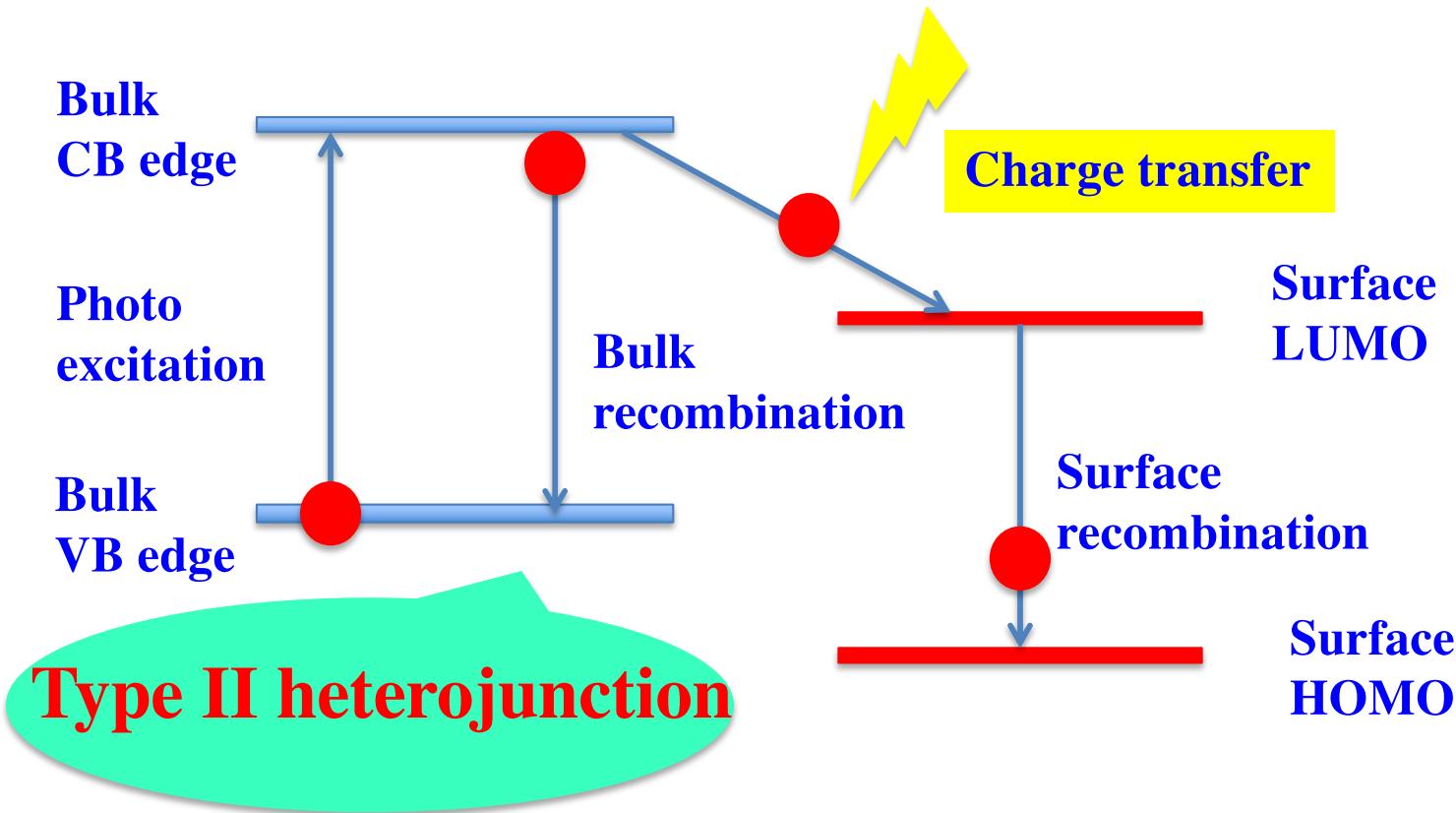
- Electronic partial density of states projected onto the wave functions of atomic bilayers



- Surface relaxation causes spontaneous formation of a type-II (staggered) heterostructure

Staggered Band Alignment Driven Charge Transfer

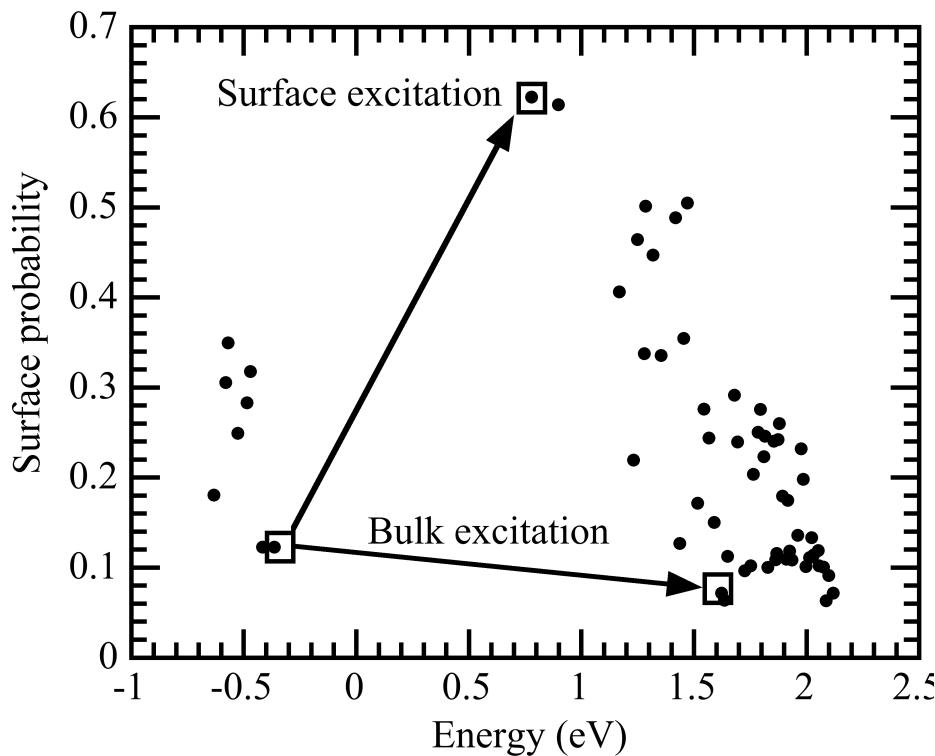
Photo excitation & charge recombination in type II heterojunction



- Staggered band alignment drives a photoexcited electron in the bulk to lower energy surface states, whereas holes remain near the valence-band (VB) edge (which is a bulk state)

Bulk vs. Surface Excitations

- Existence probability of KS wave functions at the surface as a function of the KS energy.
- Two types of excitations by exciting one electron from an occupied orbital to an unoccupied orbital



Existence probability at surface

$$P_i^{\text{surface}} = \int_{\mathbf{r} \in \text{surface}}^{\text{electron}} |\Psi_i(\mathbf{r})|^2 d\mathbf{r}$$

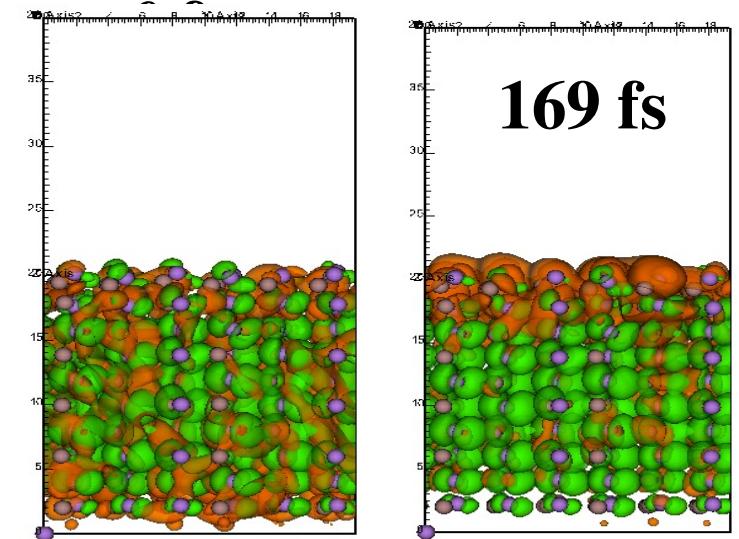
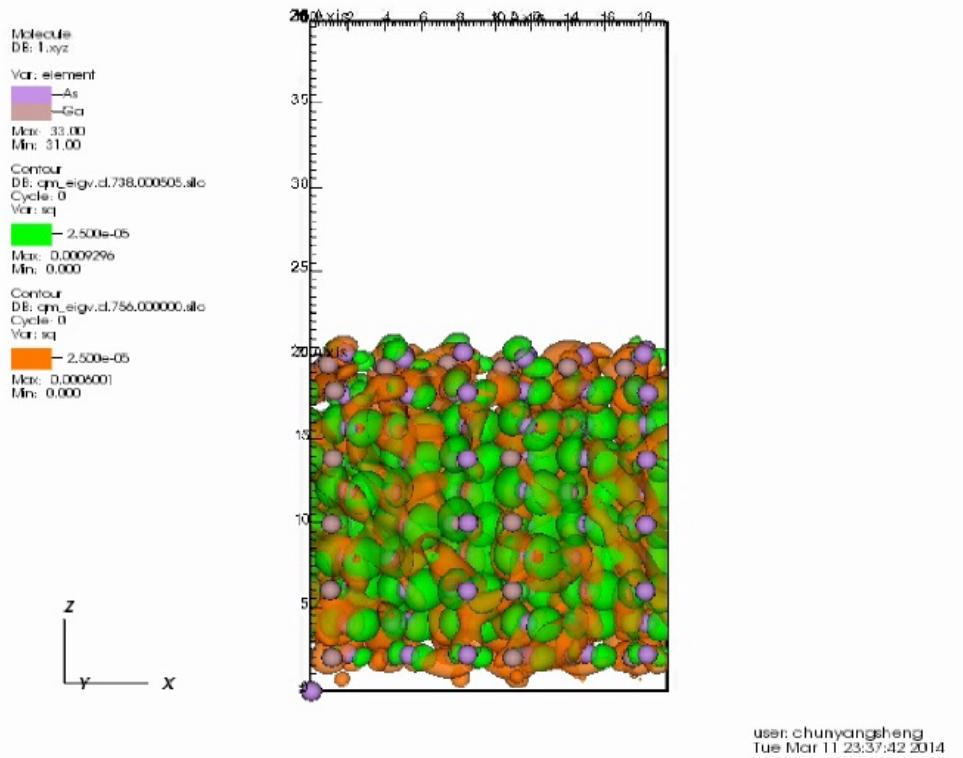
Existence probability at bulk

$$P_i^{\text{bulk}} = \int_{\mathbf{r} \in \text{bulk}}^{\text{electron}} |\Psi_i(\mathbf{r})|^2 d\mathbf{r}$$

Bulk- & surface-excitations are initiated by the transitions denoted by arrows

Carrier Wave Functions & Charge Transfer Rate

Electron (orange) & hole (green) wave functions of the bulk-excitation simulation from time 0 and 169 fs, exhibits homogeneous distribution to surface localization

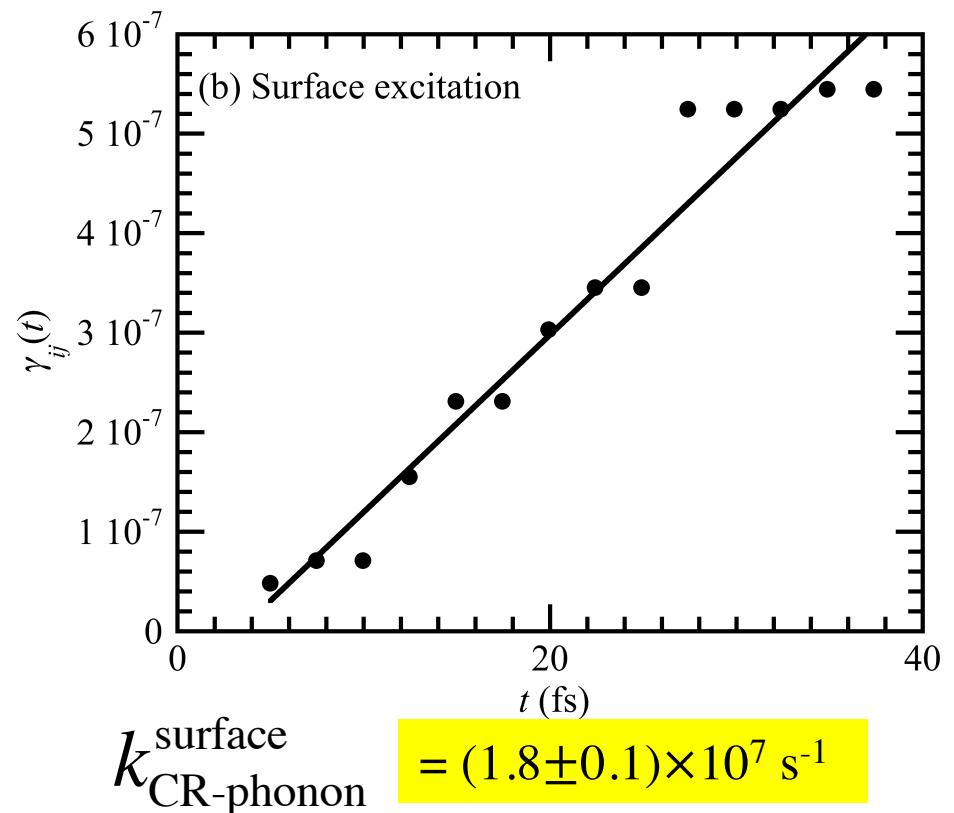
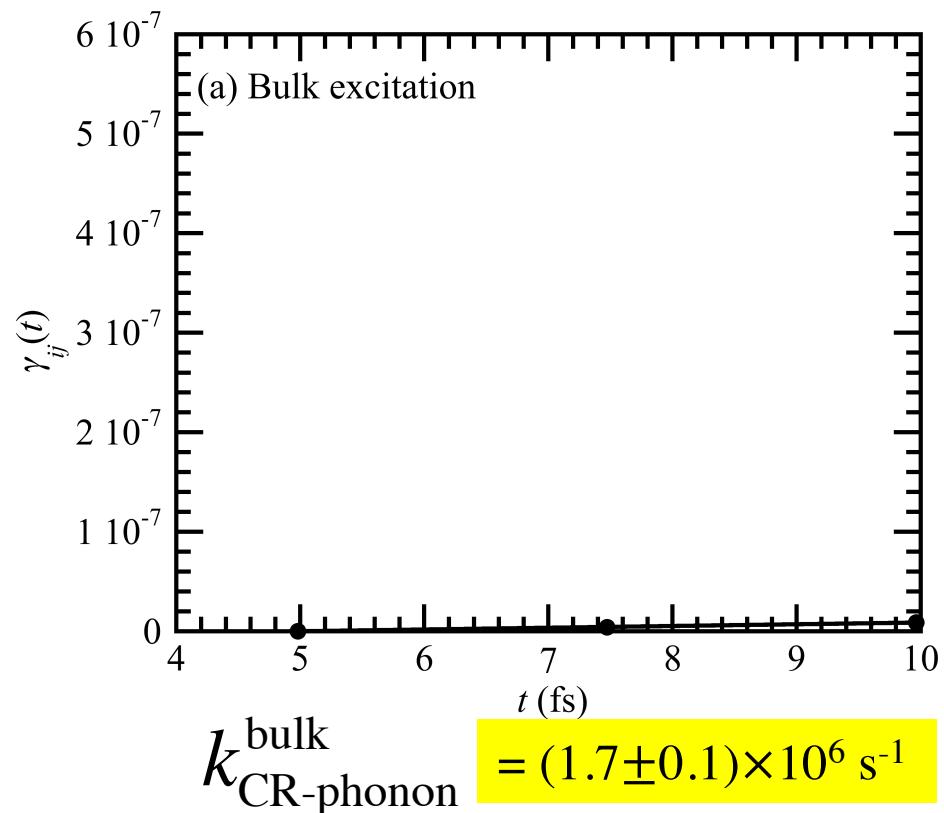


In the NAQMD simulation for bulk excitation, the excited electron quickly transfers to surface

From the time evolution of the surface probability of the excited electron, charge-transfer (CT) rate is estimated to be $k_{CT} = 6.25 \times 10^{12} \text{ s}^{-1}$

Phonon-Assisted Charge Recombination in Bulk

Transition probability $\gamma_{ij}(t)$ from the current excited state i to another state j as a function of time t



Charge-recombination (CR) rate is enhanced by an order-of-magnitude near surface

Spontaneous-Emission CR Rate

$$\gamma_{I,J}^{\text{Dipole}} = \frac{4n(\omega_I - \omega_J)^3 \left| \langle \Phi_I | \hat{\mathbf{r}} | \Phi_J \rangle \right|^2}{3c^3}$$

X. Zhang *et al.*,
PRB **84**, 235208 ('11)

- Bulk

$$R_{\text{CR-SE}} = 2.8 \times 10^2 \text{ (s}^{-1}\text{)}$$

- Surface

$$R_{\text{CR-SE}} = 9.3 \times 10^3 \text{ (s}^{-1}\text{)}$$

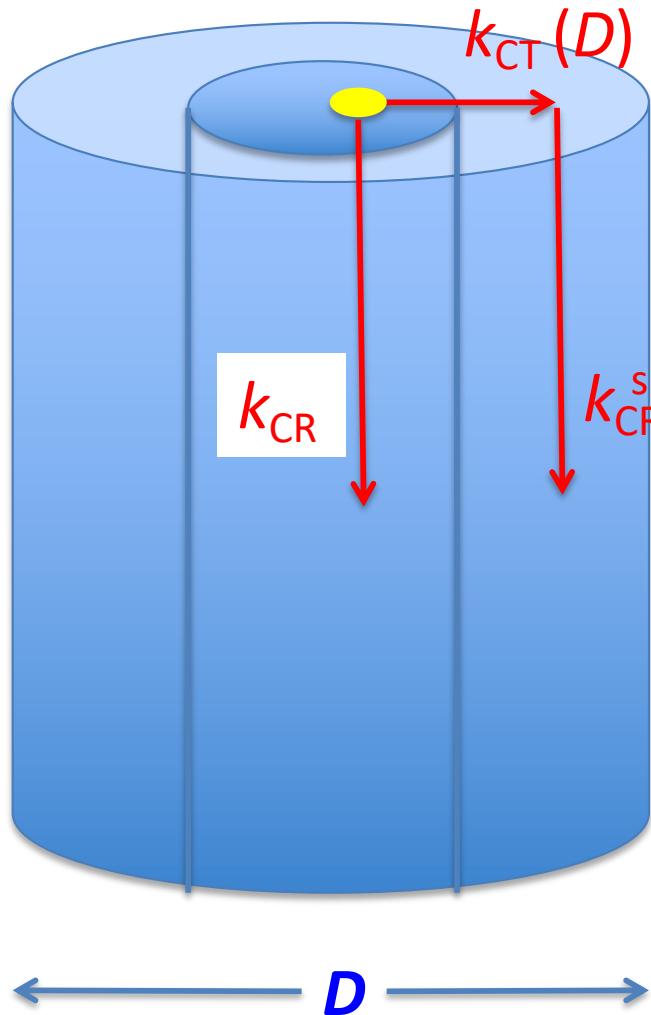
Comparison with phonon assisted CR rates

	Bulk	Surface
Phonon assisted R_{CR}	$1.7 \times 10^6 \text{ (s}^{-1}\text{)}$	$1.8 \times 10^7 \text{ (s}^{-1}\text{)}$
SE R_{CR}	$2.8 \times 10^2 \text{ (s}^{-1}\text{)}$	$9.3 \times 10^3 \text{ (s}^{-1}\text{)}$

Phonon assisted charge recombination is the dominant CR channel

Modelling Carrier-Population Kinetics

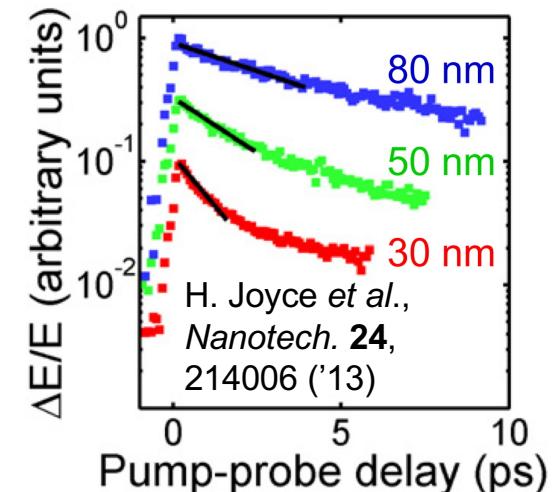
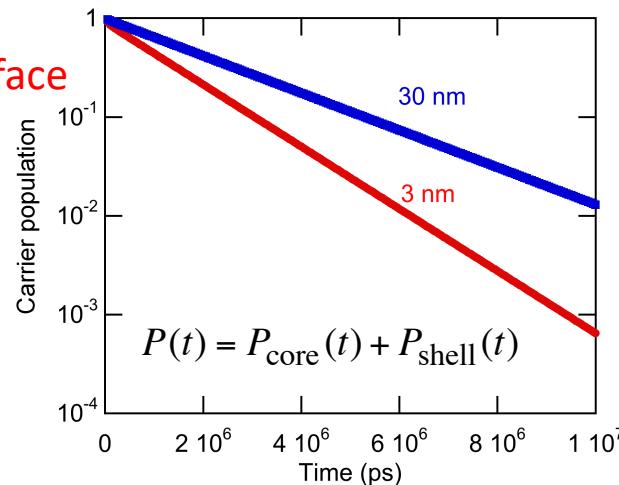
- Core-shell structure GaAs nanowire with diameter D
- Carrier populations at the core & shell
- Electron in the bulk



- CR at surface: 1.8×10^7 (s^{-1})
- CR in bulk : 1.7×10^6 (s^{-1})
- CT rate : 6.25×10^{12} (s^{-1})

kinetic equation for carrier populations:

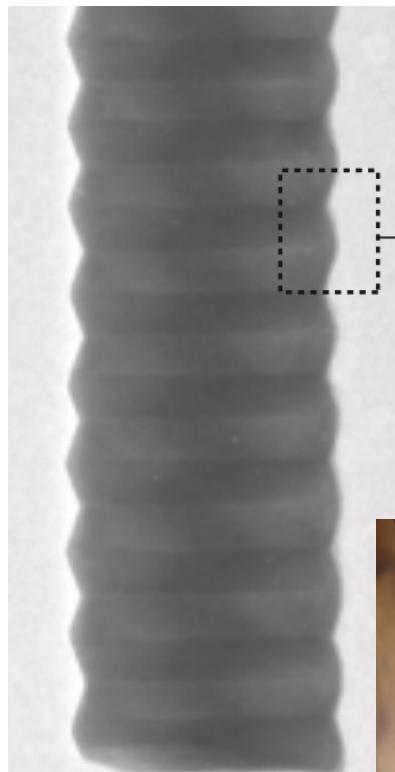
$$\frac{d}{dt} \begin{bmatrix} P_{core} \\ P_{shell} \end{bmatrix} = - \begin{bmatrix} k_{CT}(D) + k_{CR}^{\text{bulk}} & 0 \\ -k_{CT}(D) & k_{CR}^{\text{surface}} \end{bmatrix} \begin{bmatrix} P_{core} \\ P_{shell} \end{bmatrix}$$



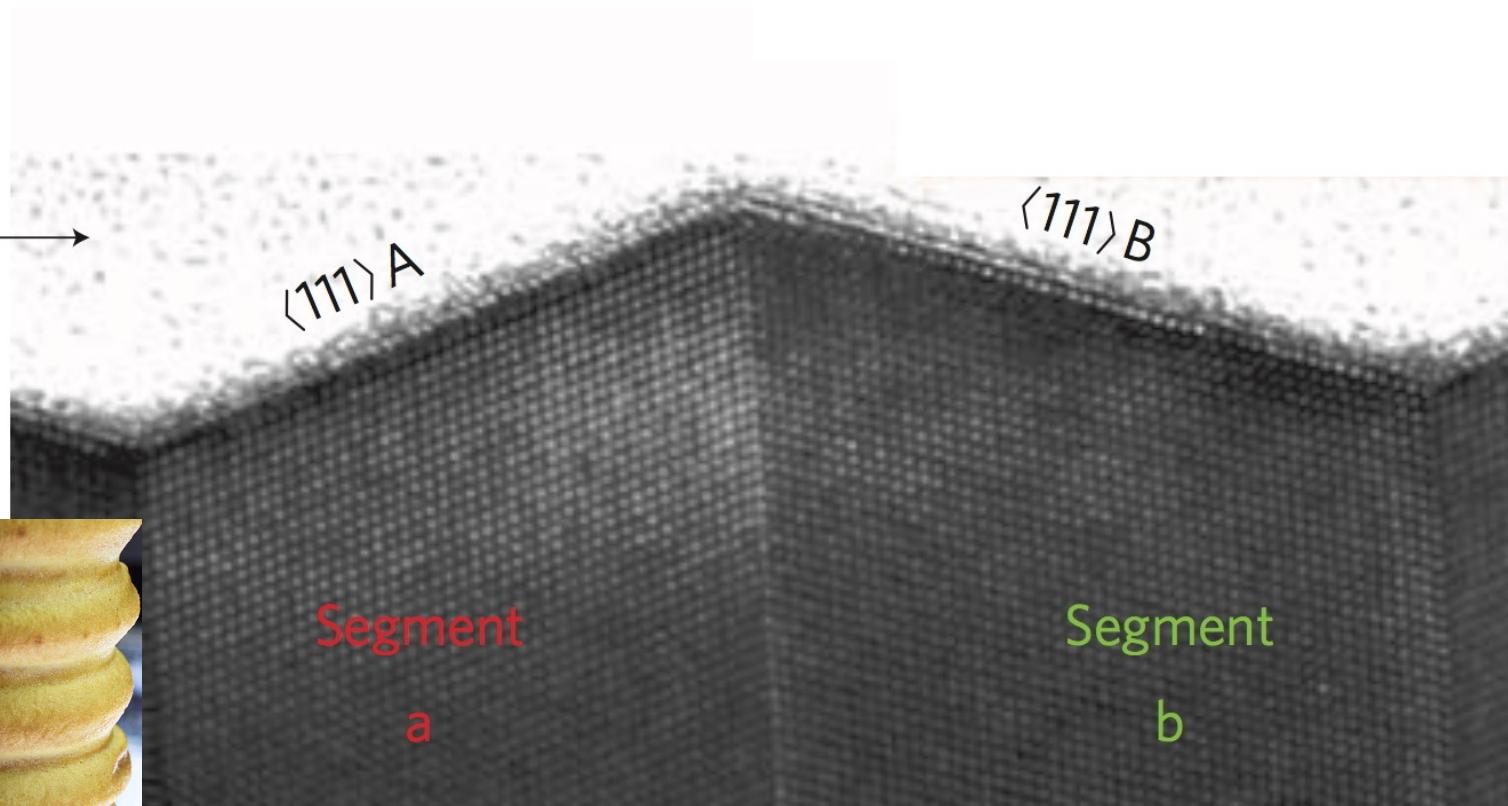
1. Faster decay with decreasing diameter in agreement with experiments
2. Decay time with ideal (110) sidewalls too large → more realistic sidewalls?

Charge Recombination in Twinned NW

SEM image of twinned nanowire



TEM image of twinned nanowire



Real GaAs $\{110\}$ facets contain high density of twin defects

Caroff *et al.*, *Nat. Nanotechnol.* **4**, 50 ('09)

Twin-Twin Attraction

NANO
LETTERS

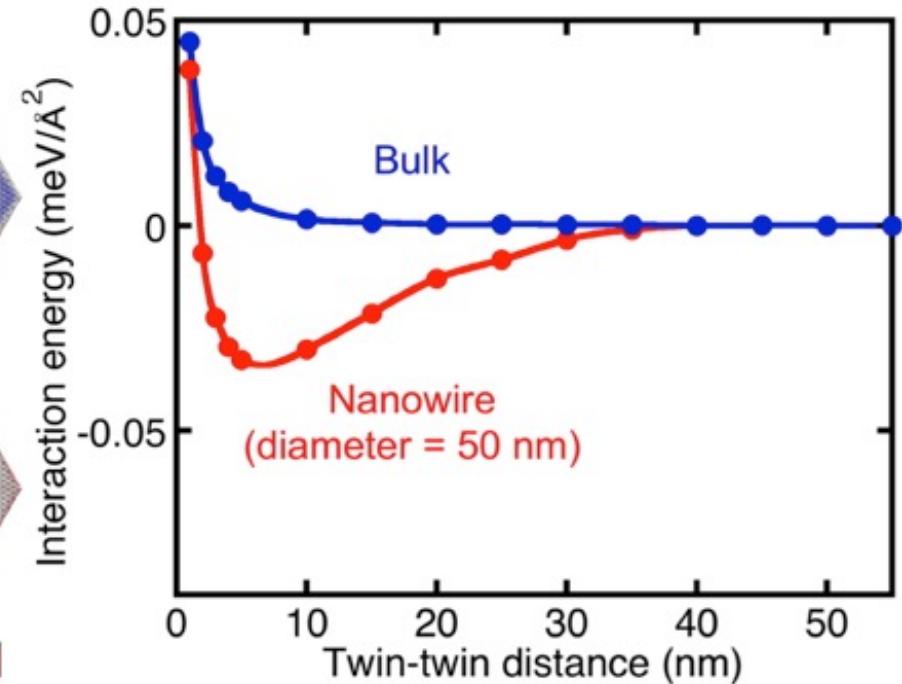
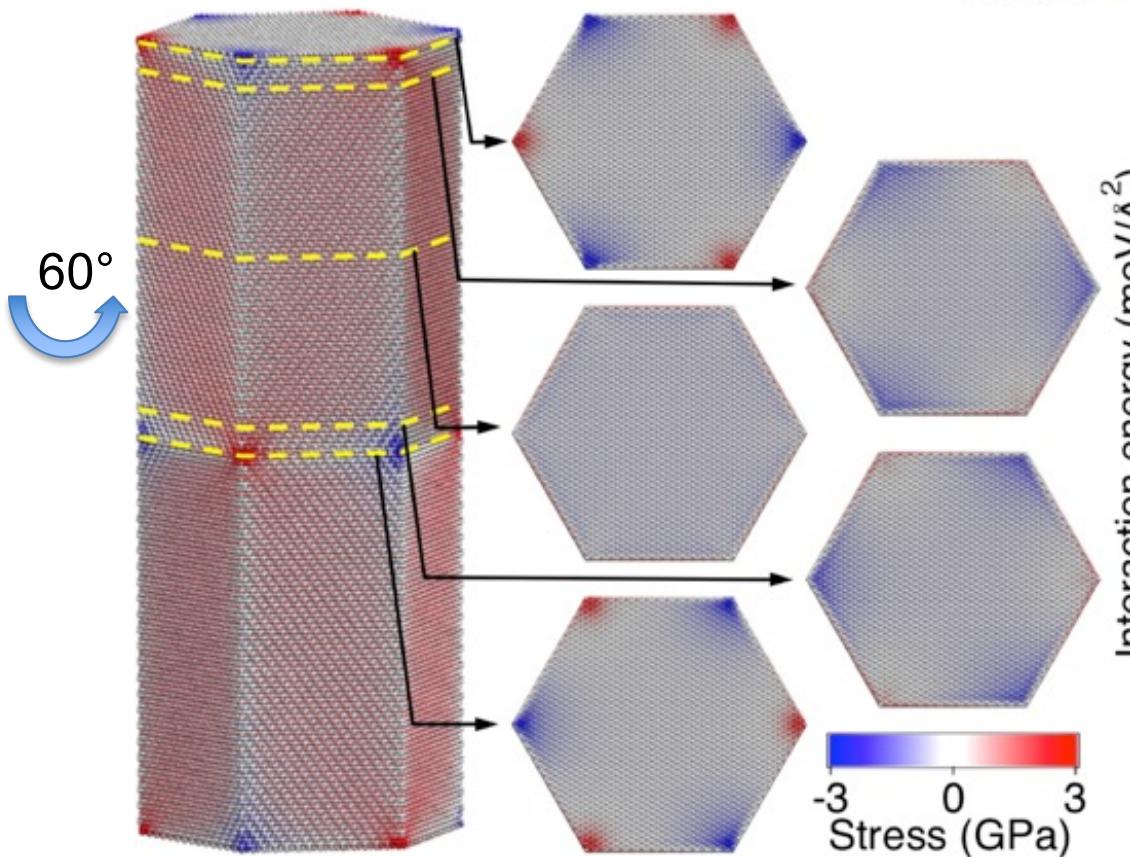
Letter

pubs.acs.org/NanoLett

Self-Replicating Twins in Nanowires

Zaoshi Yuan^{†,‡} and Aiichiro Nakano^{*,†}

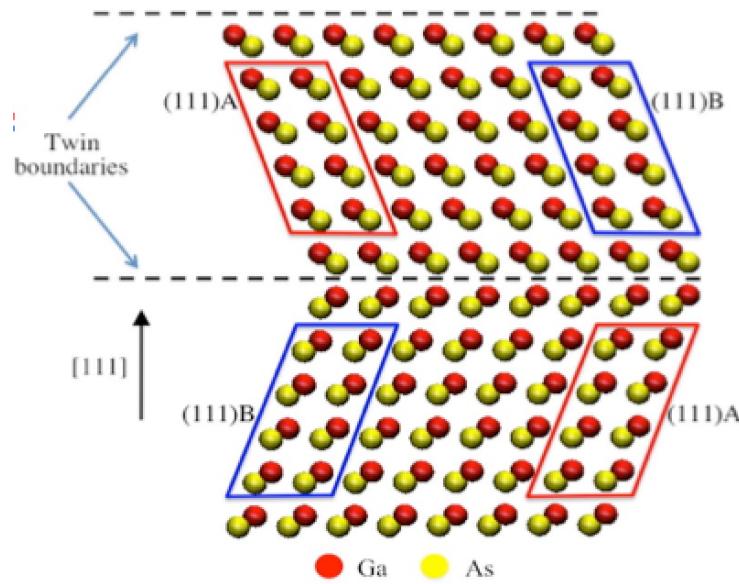
Nano Lett. 2013, 13, 4925–4930



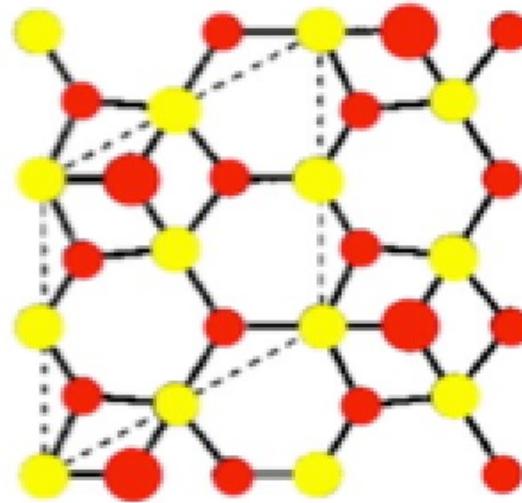
- Twin planes in a [111] GaAs nanowire attain attractive interaction mediated by surface strain → self-replicating generation of a twin superlattice

Twinned GaAs Nanosheet (NS)

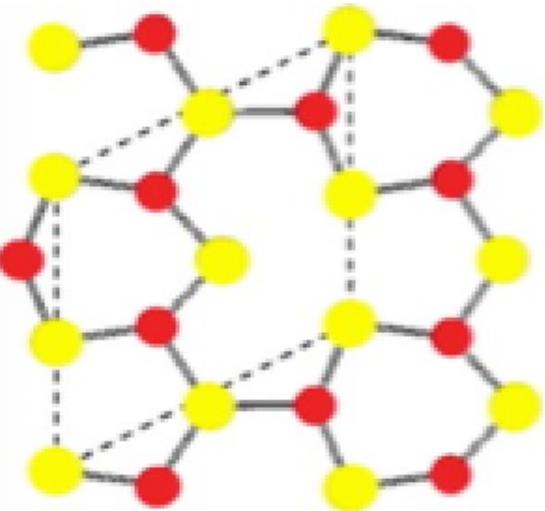
Relaxed GaAs crystal
viewed from the [112]
direction



Top view of the Ga-adatom
reconstruction of GaAs
(111)B surface



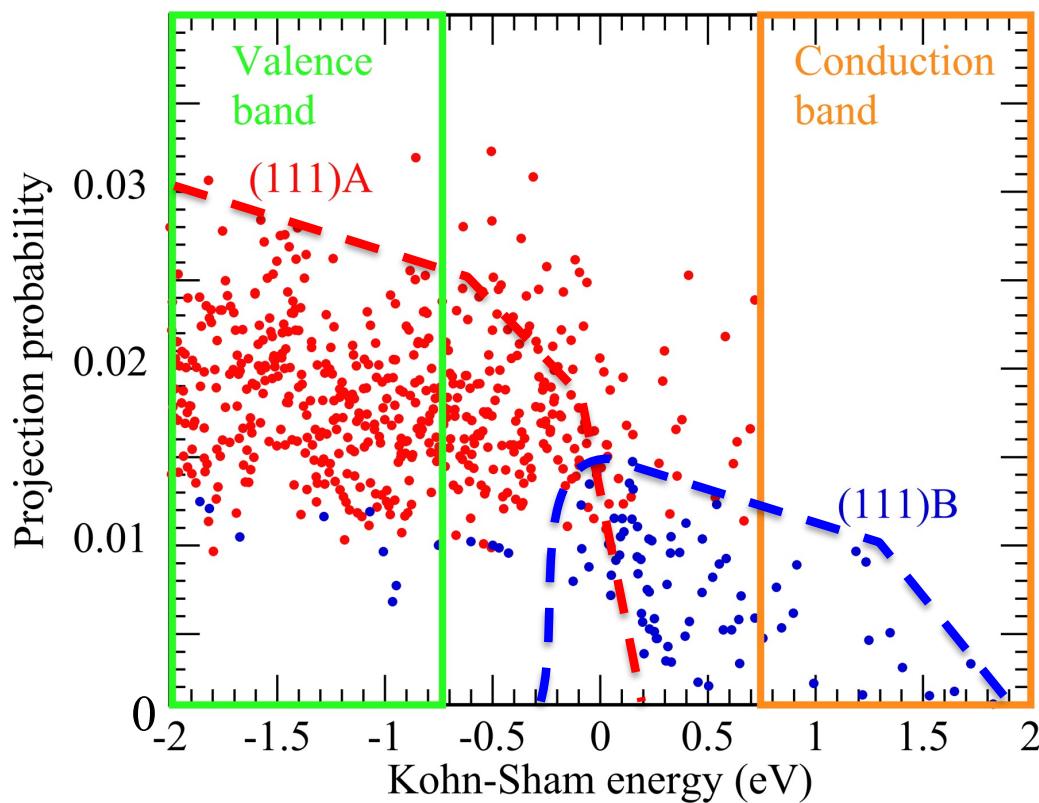
Top view of the Ga-vacancy
reconstruction of (111)A
surface



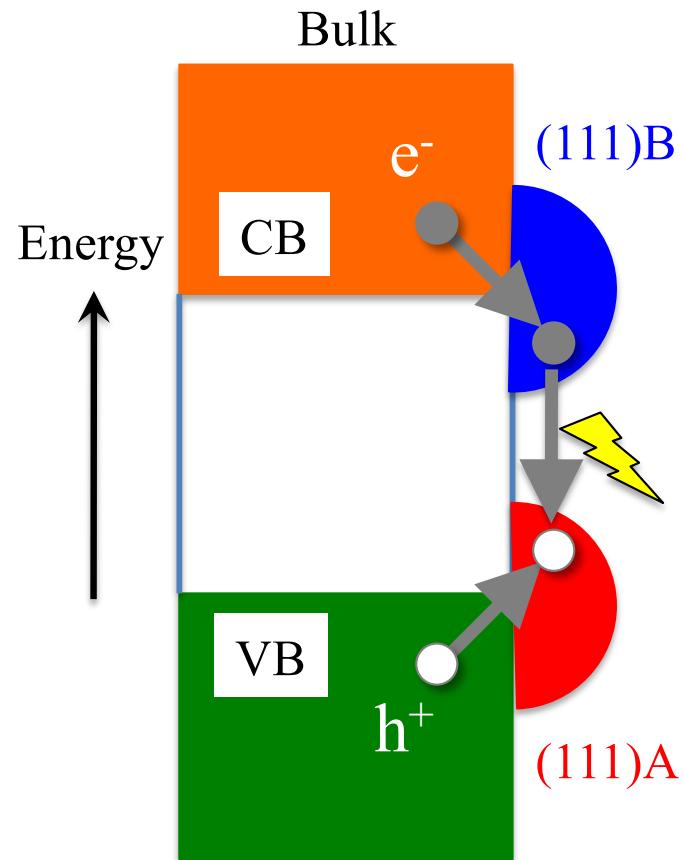
- These energetically lower reconstructed surfaces are charge-neutral
- NS with these reconstructed sidewall surfaces remains stable during quasi-Newton energy minimization

KS Energy Projection: Band Alignment

Electronic partial densities-of-states (PDOS) projected onto the (111)A and (111)B sidewall



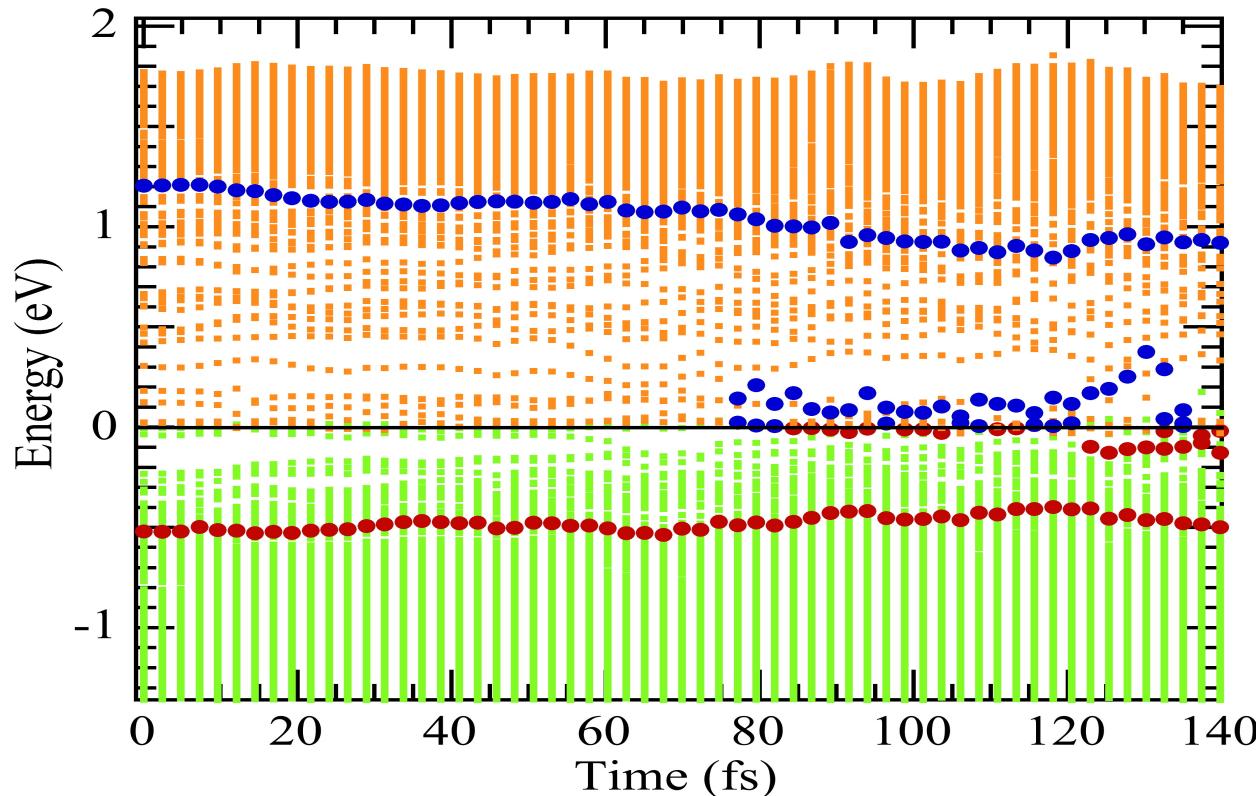
Schematic of the bulk CB (orange) and VB (green) along with (111)A (red) and (111)B (blue) surface-state energies



- Gap states derived from (111)A surfaces are located just above bulk valence band (VB) top
- Gap states derived from (111)B surfaces are located just below bulk conduction band (CB) bottom

Bulk-State Photoexcitation

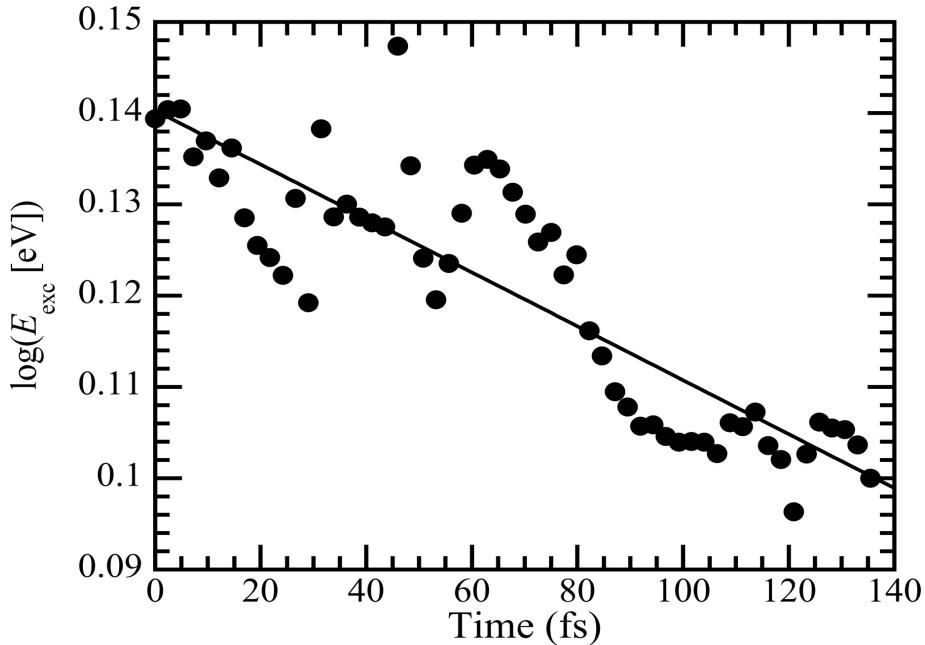
- NAQMD simulation for electron excitation: bulk VB top → bulk CB bottom
- Energy relaxation of photoexcited electron-hole pairs



- Initially, only one electron-hole pair exists
- More electron-hole pairs are created starting at ~80 fs near the Fermi energy

Energy Relaxation on Surface

Logarithm of average excitation energy as a function of time



Average electronic excitation energy as a function of time

$$k_{\text{CR}} = (3.0 \pm 0.2) \times 10^{11} (\text{s}^{-1})$$

Average electronic excitation energy

$$\bar{E}(t) = \frac{\sum_{i=1}^{iF} (2 - n_i(t))(\varepsilon_F(t) - \varepsilon_i(t)) + \sum_{i=iF+1}^{\infty} n_i(t)(\varepsilon_i(t) - \varepsilon_F(t))}{\sum_{i=1}^{iF} (2 - n_i(t)) + \sum_{i=iF+1}^{\infty} n_i(t)}$$

$\varepsilon_i(t)$ is the i th KS energy

Charge recombination rates

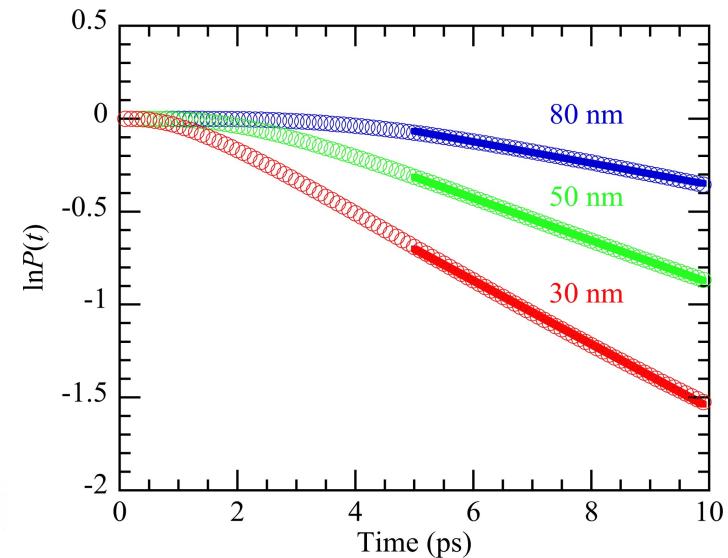
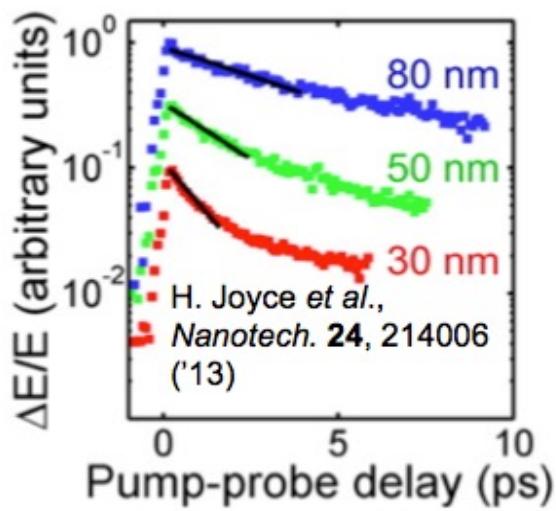
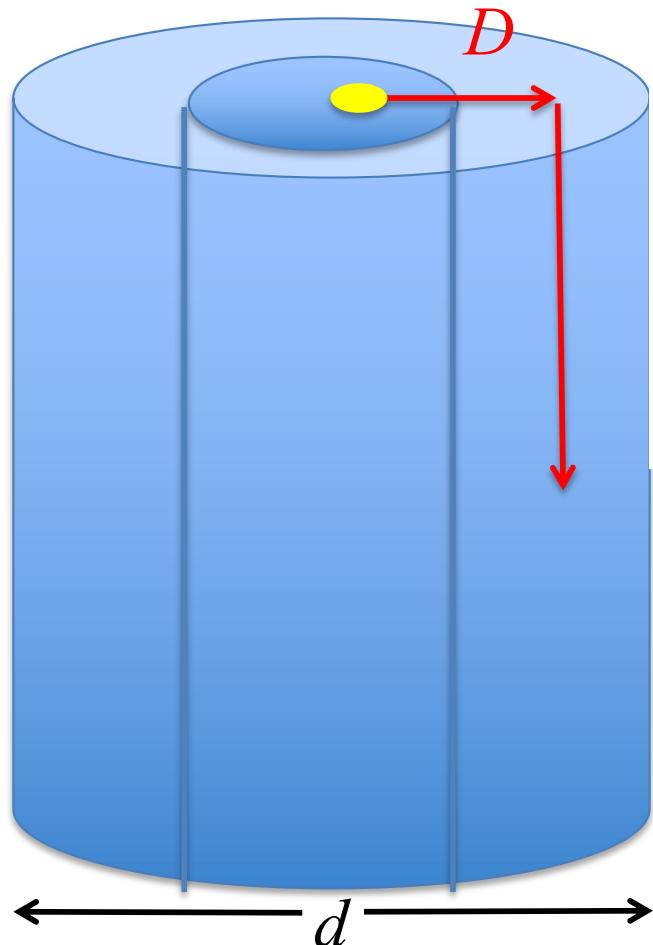
$$k_{\text{CR}} = (3.0 \pm 0.2) \times 10^{11} (\text{s}^{-1}) \quad (111)$$

$$k_{\text{CR}} = (1.8 \pm 0.1) \times 10^7 (\text{s}^{-1}) \quad (110)$$

- Calculated CR rate at (110) surface is orders-of-magnitude smaller
- Much larger CR rate ($\sim 10^{11} \text{ s}^{-1}$) is likely due to the twin superlattice-related surface geometry

Modelling Carrier-Population Kinetics

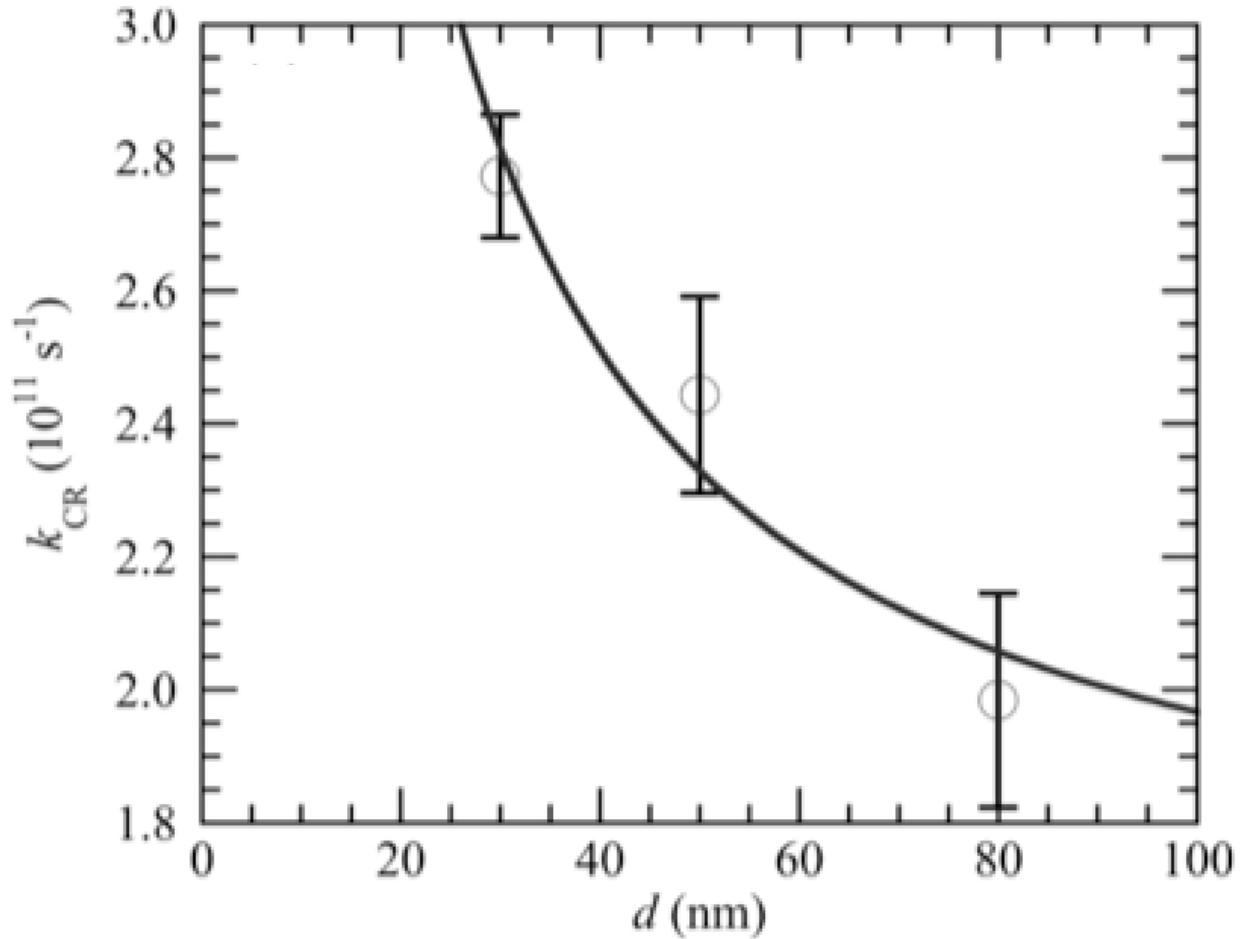
- Core-shell structure GaAs nanowire with diameter D
- Aiming at estimating the surface recombination velocity



1. Faster decay with decreasing diameter in agreement with experiments;
2. Decay time with realistic [111] sidewalls is consistent with experimental data

Surface Recombination Velocity

CR rate as a function of the NW diameter



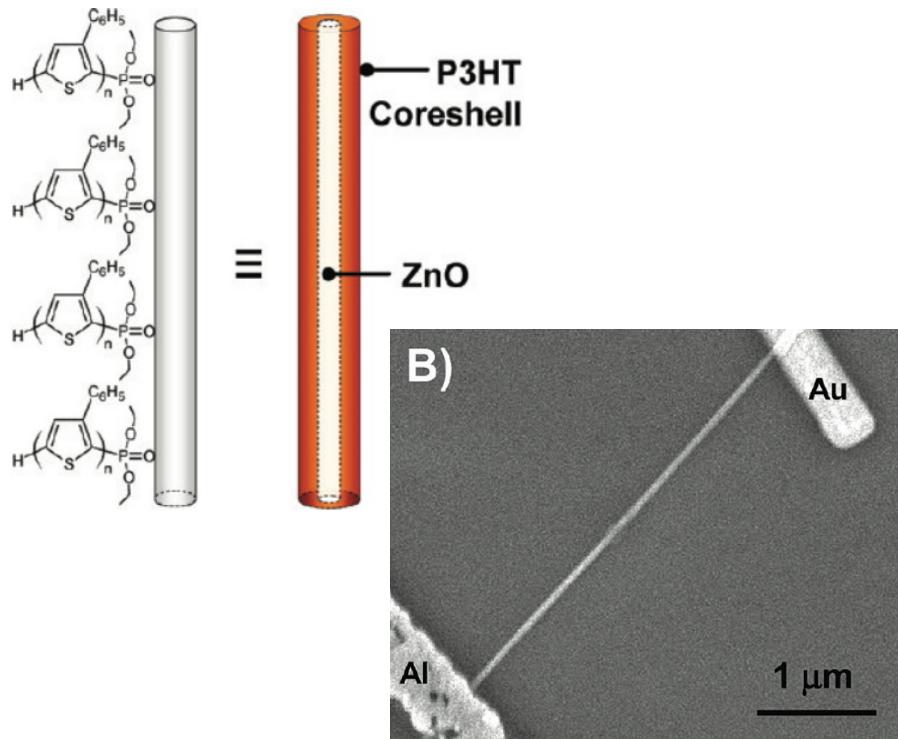
Surface recombination velocity (SRV) in NW

$$k_{CR}(D) = k_{CR}^{\infty} + \frac{4S}{D}$$

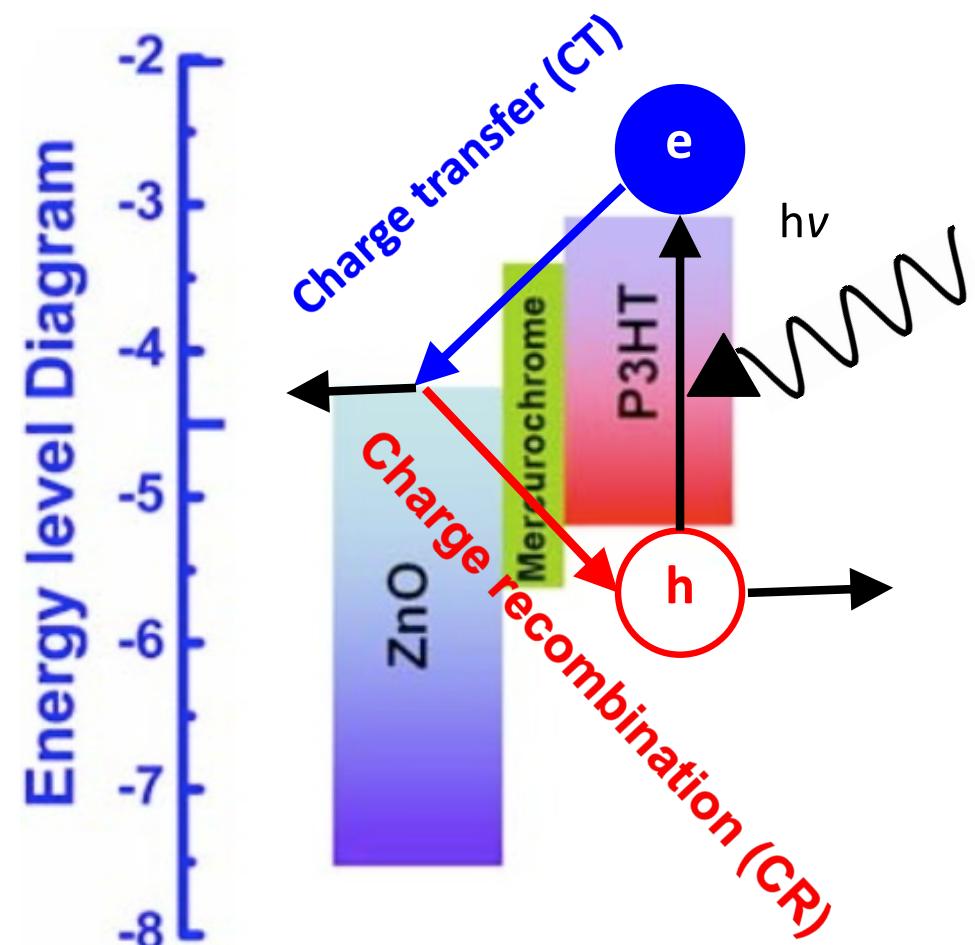
- Calculated SRV = $(3.6 \pm 0.9) \times 10^3 \text{ m/s}$ [Sheng et al., *Appl. Phys. Lett.* **105**, 231602 ('14)]
- Good agreement with the experimental value ($5.4 \times 10^3 \text{ m/s}$) [Joyce et al., *Nanotechnol* **24**, 214006 ('13)]

Hybrid Organic/Inorganic Photovoltaics

- Hybrid P3HT (poly[3-hexylthiophene])/ZnO-nanowire photovoltaics for scalable manufacturing



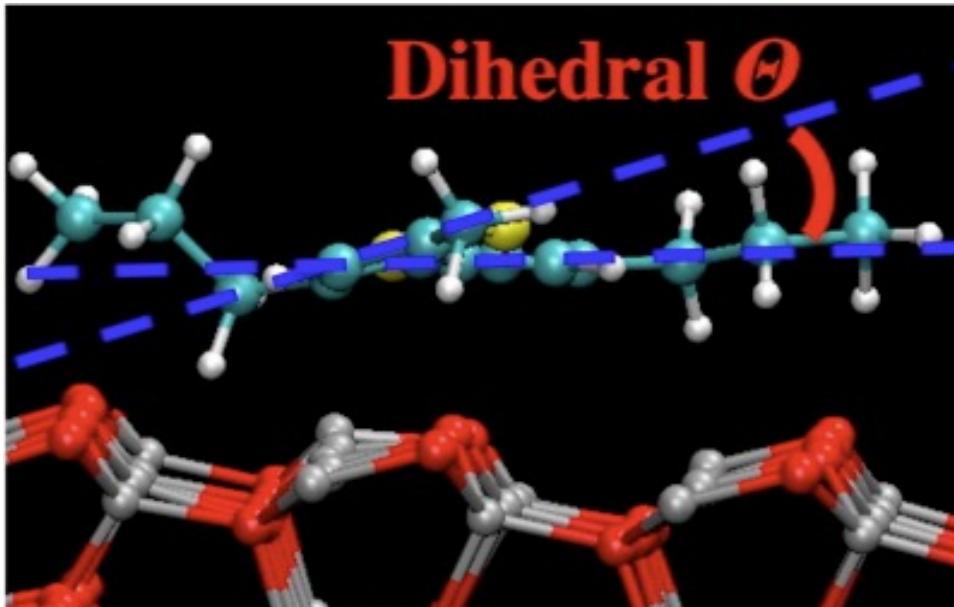
Briseno et al., *Nano Lett.* **10**, 334 ('10)



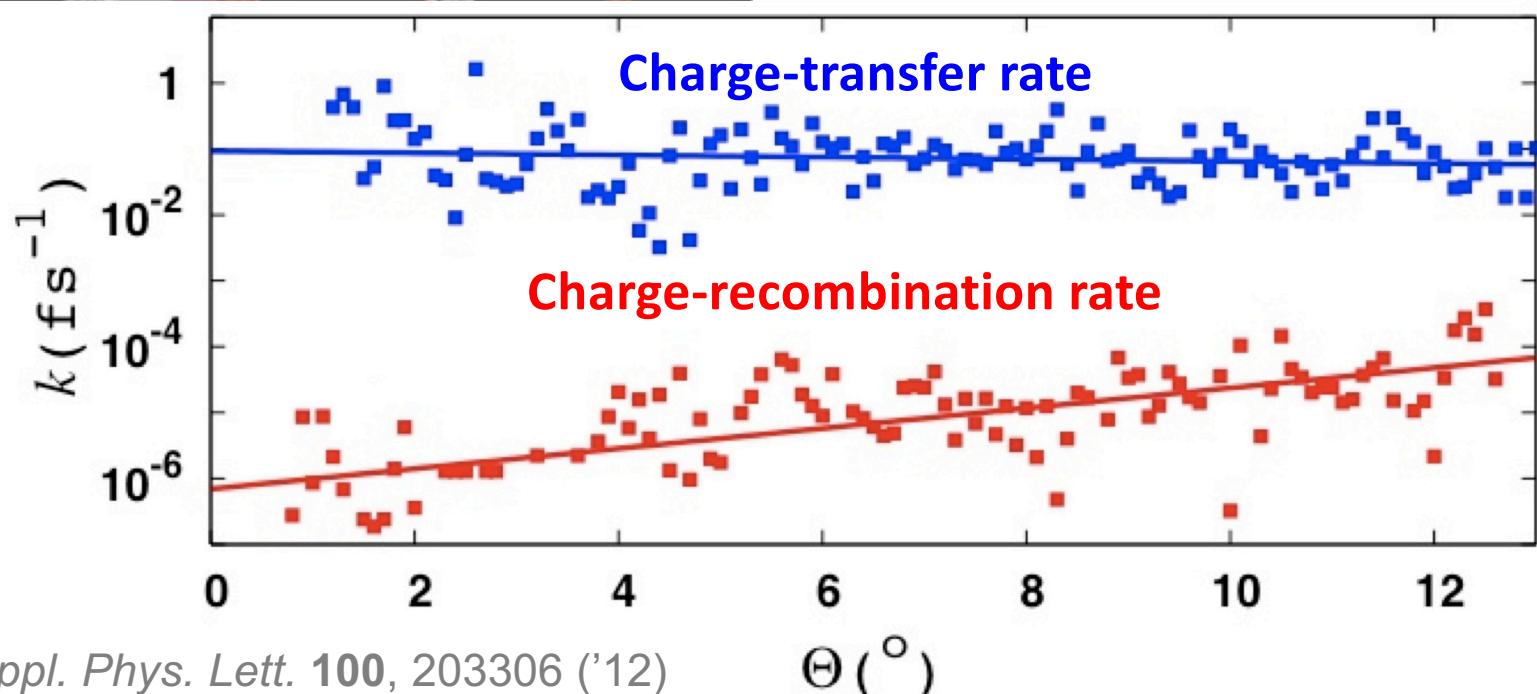
Lin et al., *Appl. Phys. Lett.* **94**, 064308 ('09)

- **Problem:** Interfacial molecular design principles for enhancing charge transfer (CT) & suppressing charge recombination (CR)?

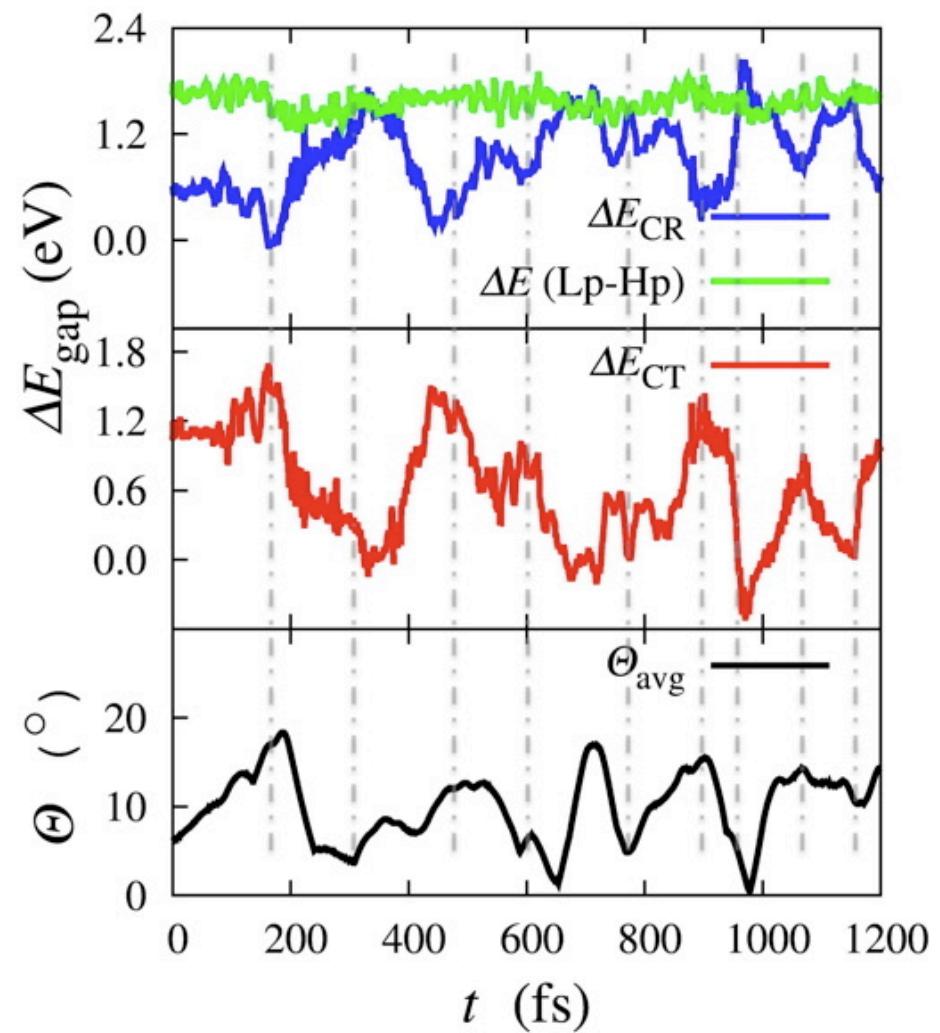
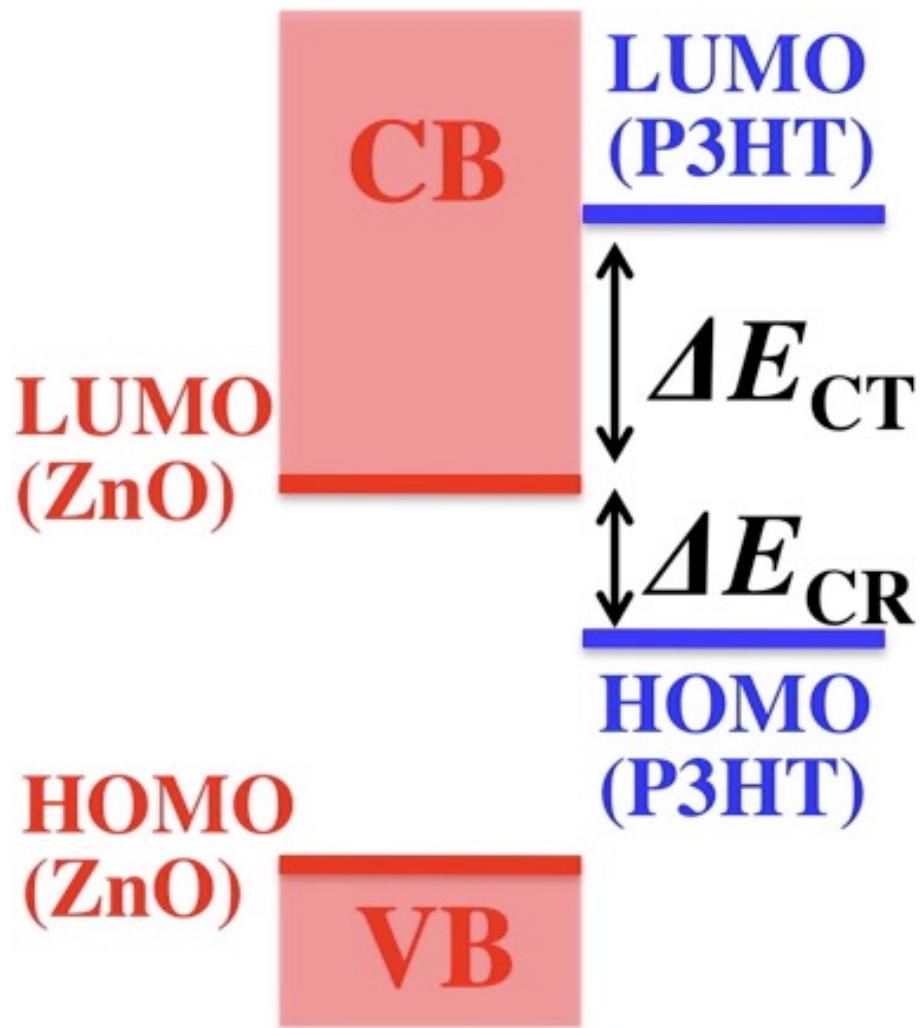
Effects of Molecular Disorder on CT/CR



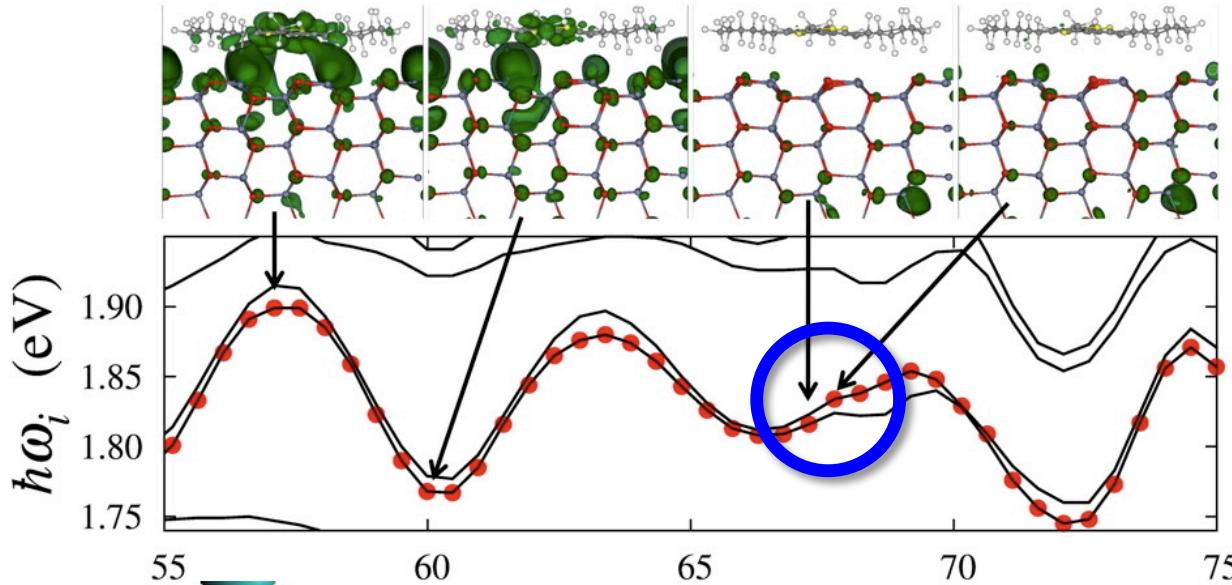
- 552-atom nonadiabatic quantum molecular dynamics simulation of P3HT on ZnO (10̄10)
- Twisting of P3HT (static disorder) increases charge-recombination (CR) rate, but not affects charge-transfer (CT) rate



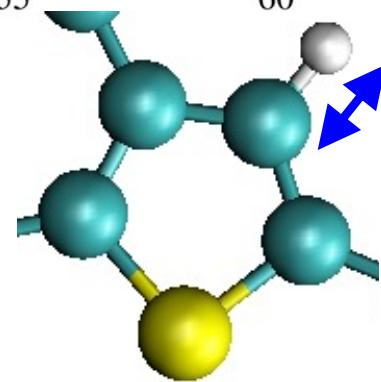
Molecular Mechanism



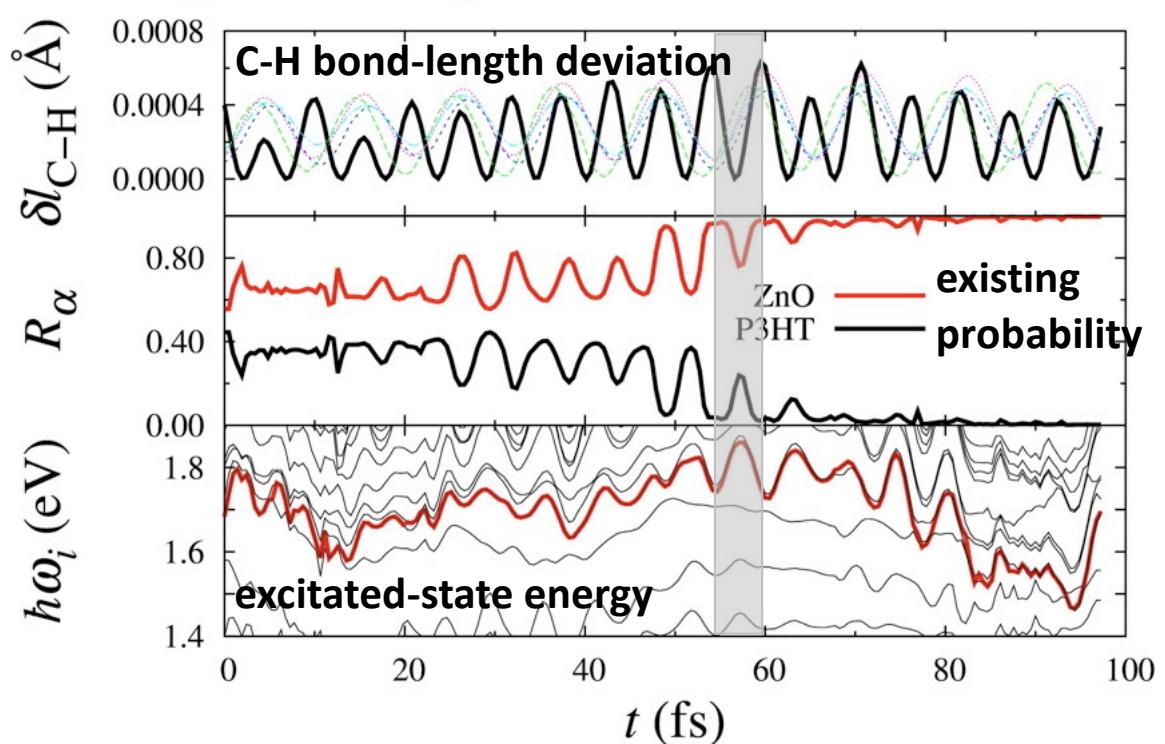
Effect of Dynamic Disorder



- Energy-level fluctuation of period ~ 6 fs assists electronic transition



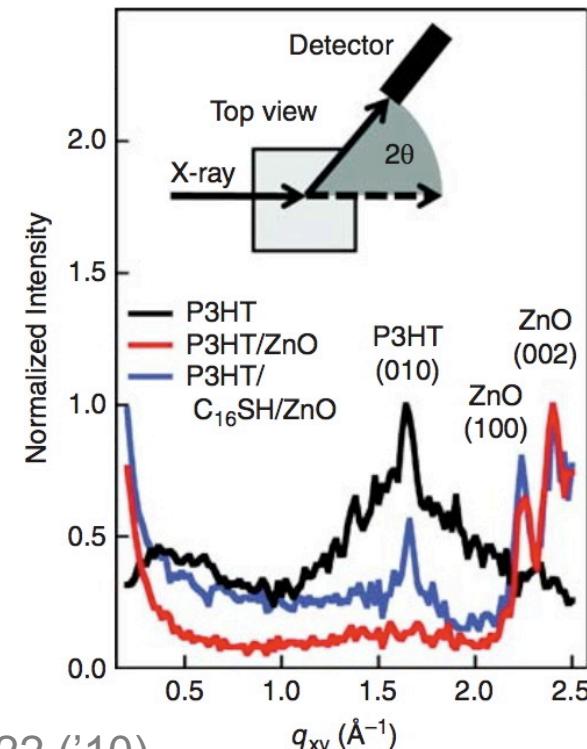
- Thermal vibration of C-H bonds on the backbone chain around their equilibrium length assists charge transfer



Interfacial Molecular-Design Principle

- *Static disorder* of P3HT conformation is *detrimental* to the efficiency of hybrid P3HT/ZnO photovoltaics by increasing the charge-recombination rate
- *Dynamic disorder* (i.e., thermal fluctuation of C-H bonds in P3HT) is *essential* for high efficiency by assisting charge transfer
- A design principle for efficient photovoltaics—weak interfacial bonding: (1) avoid *static disorder*; (2) promote *dynamic disorder*
- Example: Grazing incidence x-ray diffraction & photocurrent measurements show increase of photocurrent with improved P3HT crystallinity near P3HT/ZnO interfaces due to the insertion of an alkane-thiol self-assembled monolayer

Sample	J_{sc} (mA/cm ²)
Unmodified	0.28 ± 0.011
C ₁₈ SH	0.42 ± 0.020

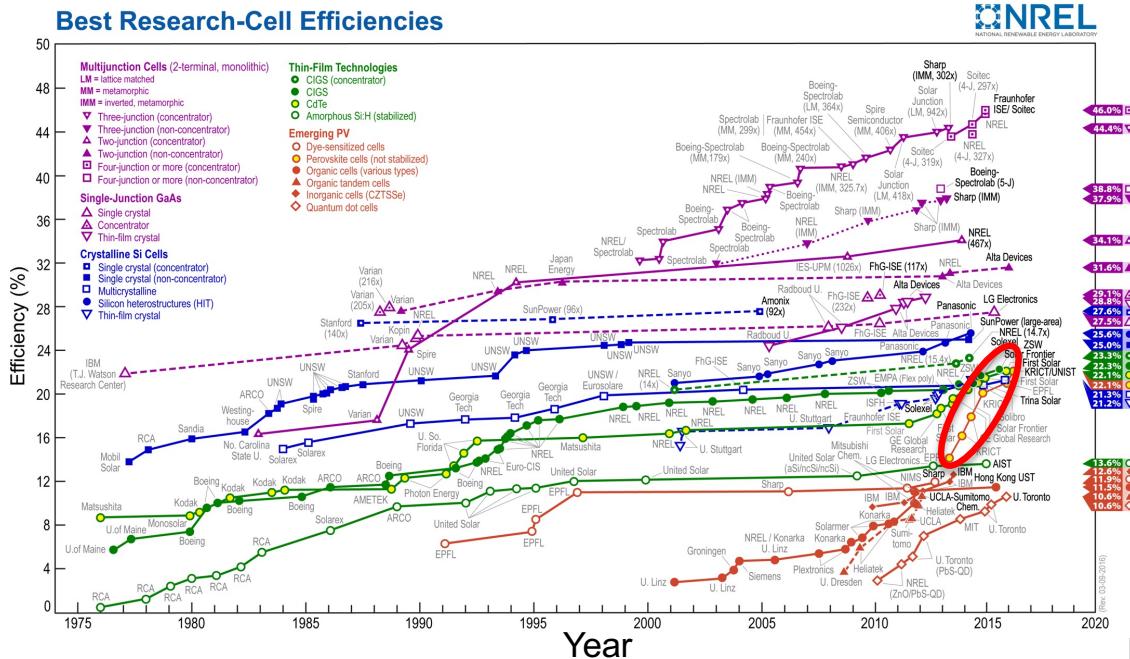


Hsu & Lloyd, MRS Bulletin 35, 422 ('10)

Photoexcited Carriers in MAPbI_3

- Organometal halide perovskites (*e.g.* methylammonium lead iodide, $\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3) for solar cells with high power conversion efficiency > 20%

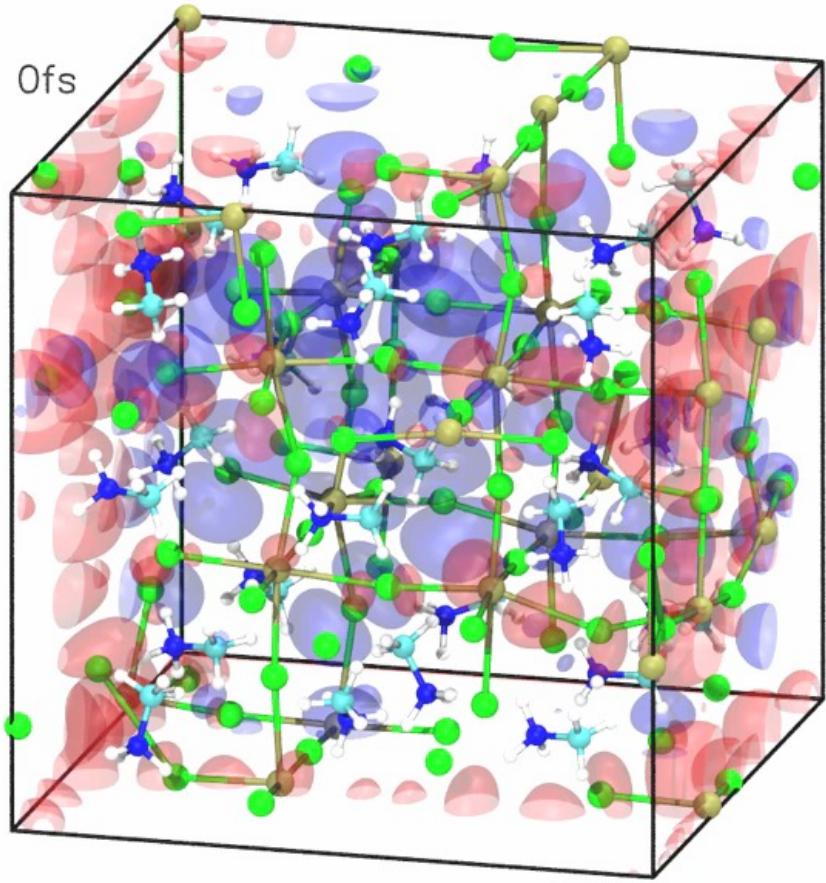
Stranks & Snaith, *Nat. Nanotechnol.* **10**, 391 ('15)



- Nonadiabatic QMD simulation

Pb & I sublattices act as disjunct pathways for rapid & balanced transport of free electrons & holes—electron (63% Pb-6p) & hole (90% I-5p); diffusion coefficients $D_e = (1.16 \pm 0.31) \times 10^{-2} \text{ cm}^2/\text{s}$ & $D_h = (1.01 \pm 0.42) \times 10^{-2} \text{ cm}^2/\text{s}$

Expt: $D_e = (1.7 \pm 1.1) \times 10^{-2} \text{ cm}^2/\text{s}$ & $D_h = (1.1 \pm 0.7) \times 10^{-2} \text{ cm}^2/\text{s}$ [Stranks *et al.*, *Science* **342**, 341 ('13)]

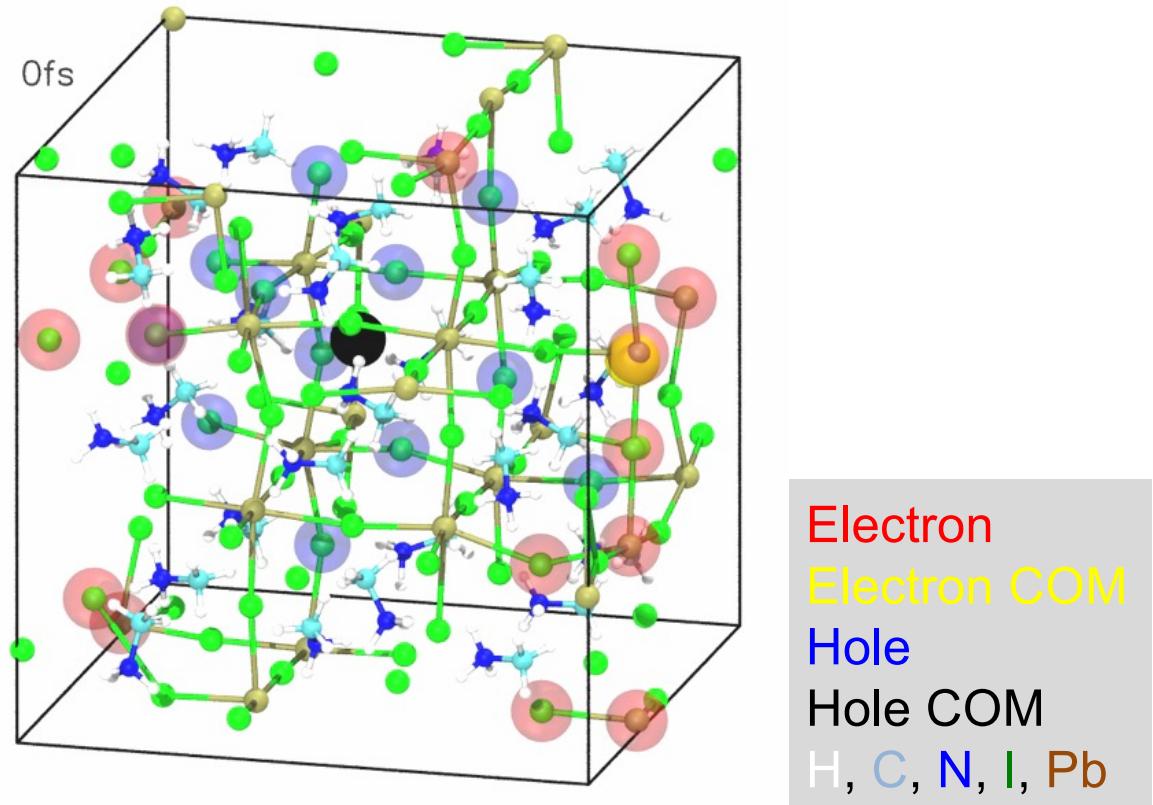
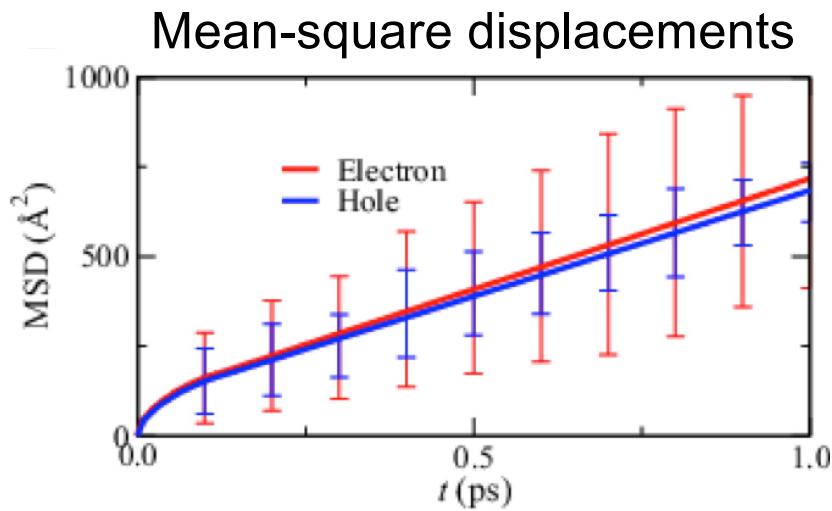


Quasi-electron Quasi-hole H, C, N, I, Pb

Rapid & Balanced Carrier Transport

- Separate electron & hole express lanes are the key nanostructural feature for rapid & balanced carrier transport: $D_e = (1.16 \pm 0.31) \times 10^{-2} \text{ cm}^2/\text{s}$ & $D_h = (1.01 \pm 0.42) \times 10^{-2} \text{ cm}^2/\text{s}$

Expt: $D_e = (1.7 \pm 1.1) \times 10^{-2} \text{ cm}^2/\text{s}$ & $D_h = (1.1 \pm 0.7) \times 10^{-2} \text{ cm}^2/\text{s}$ [Stranks et al., *Science* '13]

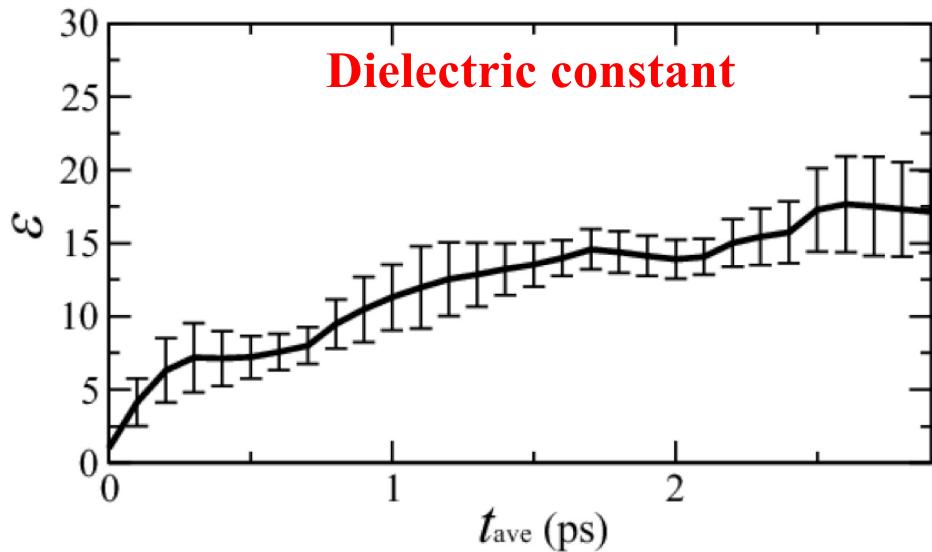


$$x_{\text{COM-PBC}} = \frac{L}{2\pi} \text{Im} \ln \int d\mathbf{r} |\psi(\mathbf{r})|^2 \exp(i \frac{2\pi}{L} x)$$

- Small radiative recombination rate: $\tau^{-1}/\rho = (1.99 \pm 0.43) \times 10^{-12} \text{ cm}^3/\text{s}$

Hakamata et al., *Sci. Rep.* 5, 19599 ('16)

Screening Role of Methylammonium Sublattice

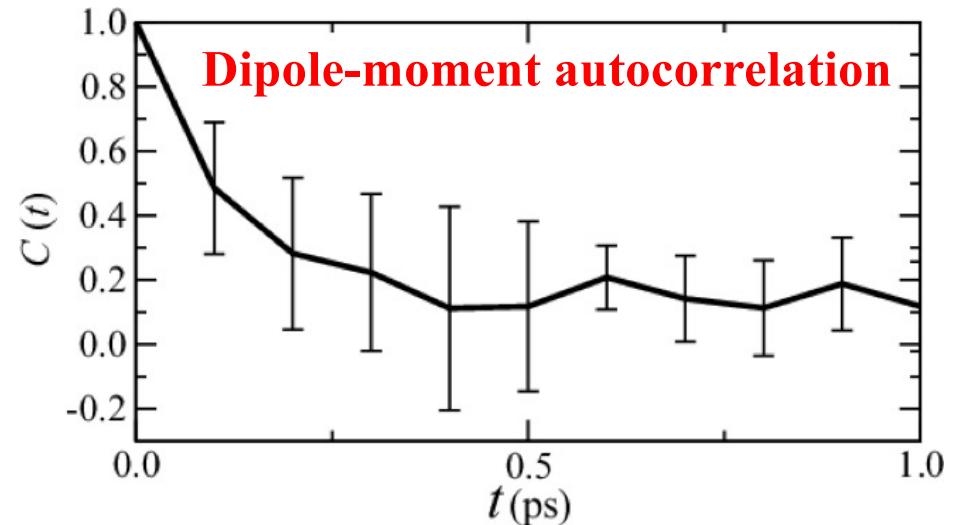


$$\epsilon = 1 + \frac{4\pi}{3k_B TV} (\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2)$$

time average
dipole moment

cf. $\epsilon_{\text{expt}}(10^{12} \text{ Hz}) = 7\text{-}10$

Lin *et al.*, *Nat. Photonics* **9**, 106 ('15)



$$C(t) = \frac{\langle \mathbf{M}(t + t_0) \cdot \mathbf{M}(t_0) \rangle}{\langle \mathbf{M}(t_0) \cdot \mathbf{M}(t_0) \rangle}$$

Rapid response time ~ 1 ps

cf. $\tau_{\text{expt}} = 2$ ps

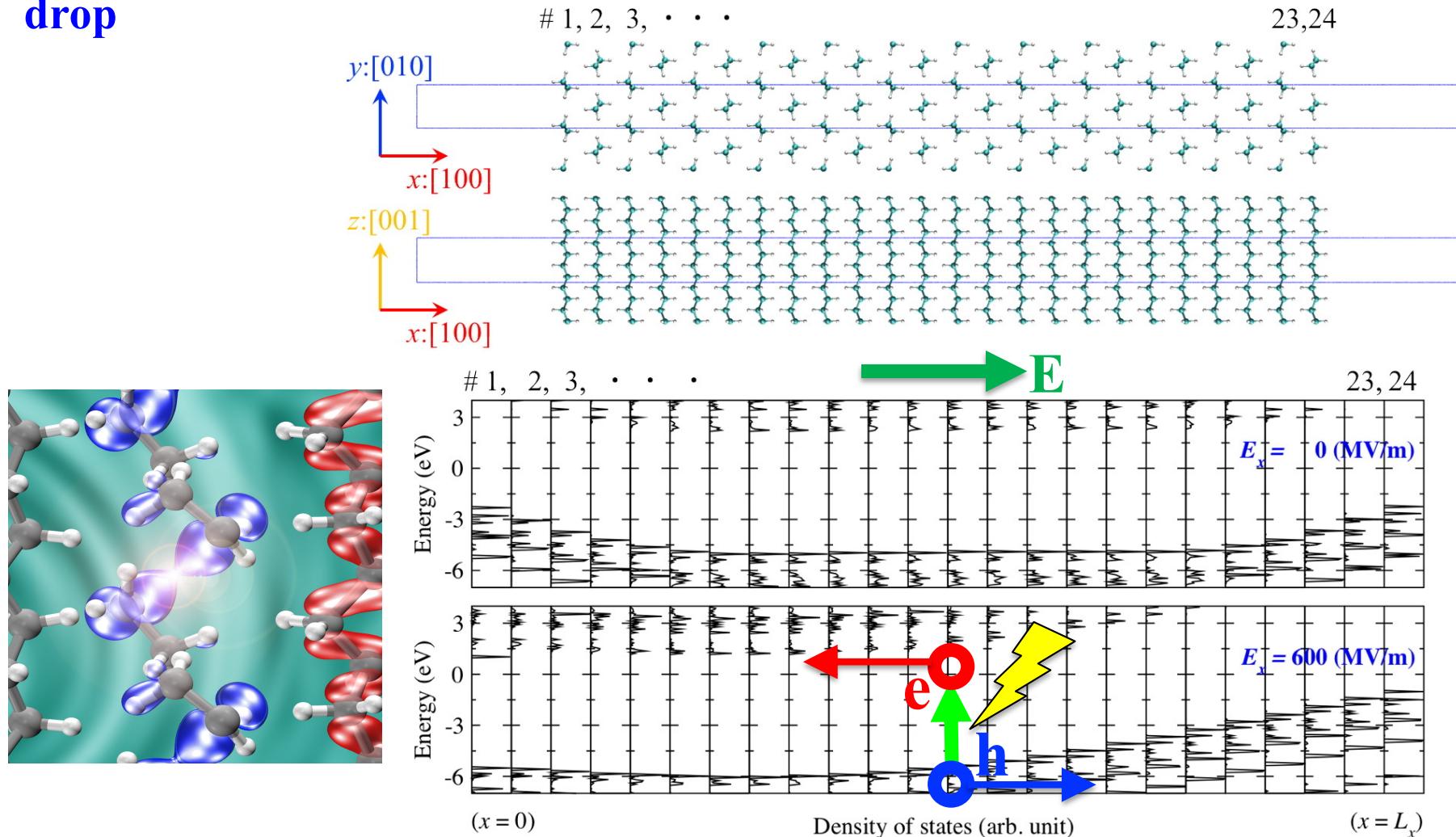
Deschler *et al.*, *JPCL* **5**, 1421 ('15)

- Large dielectric constant of MA sublattice causes small exciton binding energy, **0.012 ± 0.009 eV** (experimental upper bound = **0.05 eV** [D'Innocenzo *et al.*, *Nat. Commun.* **5**, 3586 ('14)])
- MA sublattice quickly screens out electrostatic electron-hole attraction to unbind an exciton & generate free carriers within **1 ps** [*cf.* Zhu *et al.*, *Science* **353**, 1409 ('16)]

Hakamata *et al.*, *Sci. Rep.* **5**, 19599 ('16)

Dielectric Breakdown of Polyethylene

- NAQMD simulation of hot electrons & holes in polyethylene (PE) slab under electric field (600 MV/m)
- Projected electronic density-of-states (DOE) shows band bending & voltage drop

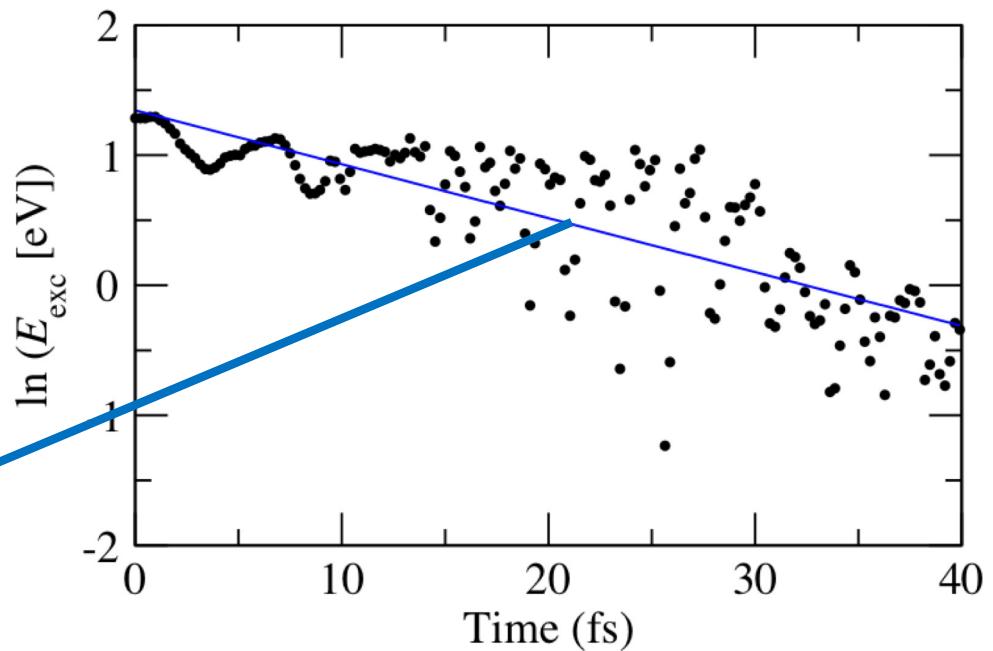
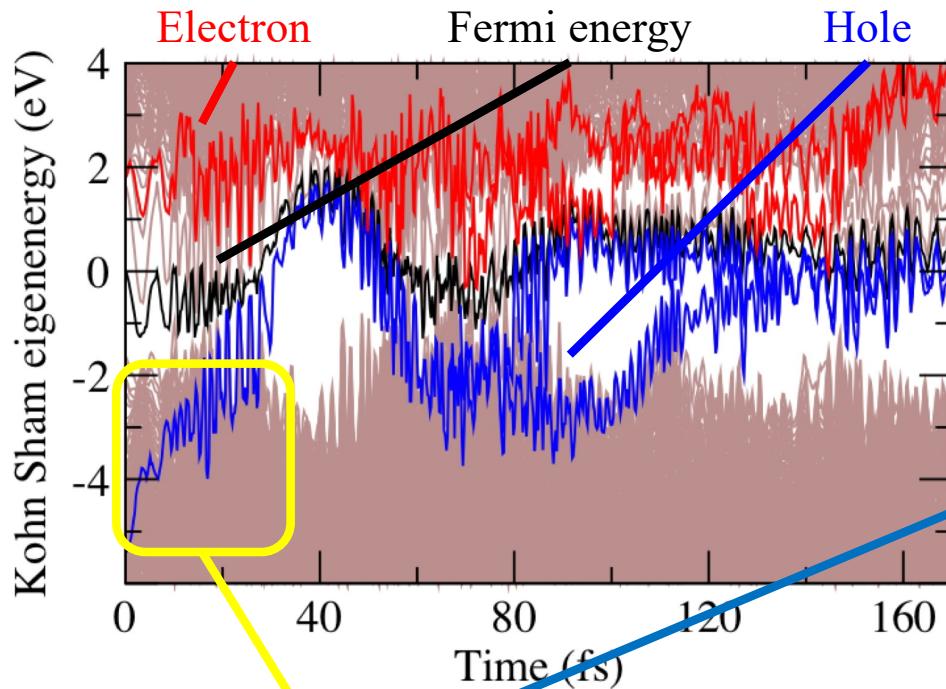


Kumazoe et al., J. Phys. Chem. Lett. **10**, 3937 ('19); ibid. **11**, 352 ('20)

Rapid Energy Dissipation of Hot Carriers

- Time evolution of Kohn-Sham energies & average excitation energy

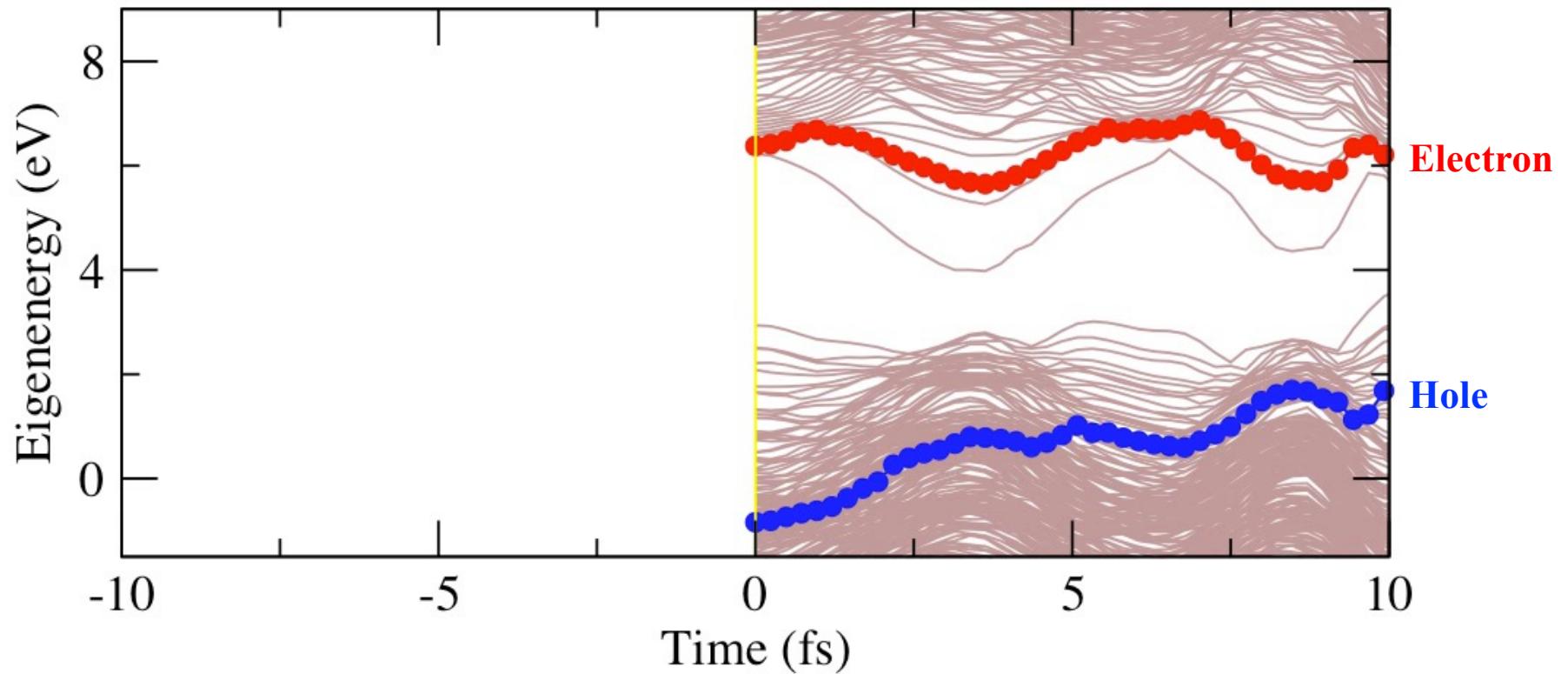
$$E_{\text{exc}}(t) = \frac{\sum_i f_i(t) \varepsilon_i(t) \Theta(\varepsilon_i(t)) - \sum_i (1 - f_i(t)) \varepsilon_i(t) \Theta(-\varepsilon_i(t))}{\sum_i f_i(t) \Theta(\varepsilon_i(t)) + \sum_i (1 - f_i(t)) \Theta(-\varepsilon_i(t))}$$



- Hot carrier relaxes to the band edge within 20 fs at a rate of $k = 4.1 \times 10^{13} \text{ s}^{-1}$ due to strong electron-phonon scattering

Field-Induced Electron & Hole Dynamics

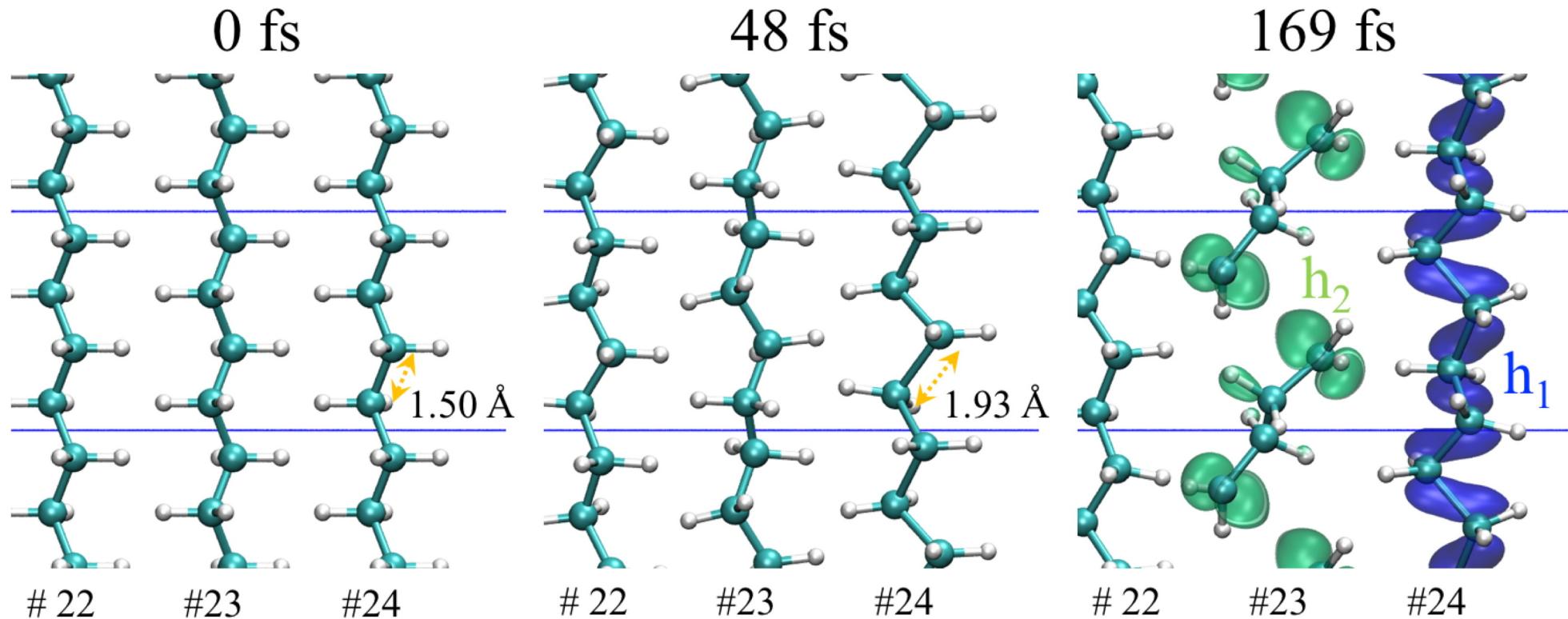
- Time evolution of Kohn-Sham energies shows carrier multiplication



- Electron (red) & hole (blue) wave functions; holes travel to a slab surface & localize on C-H bonds

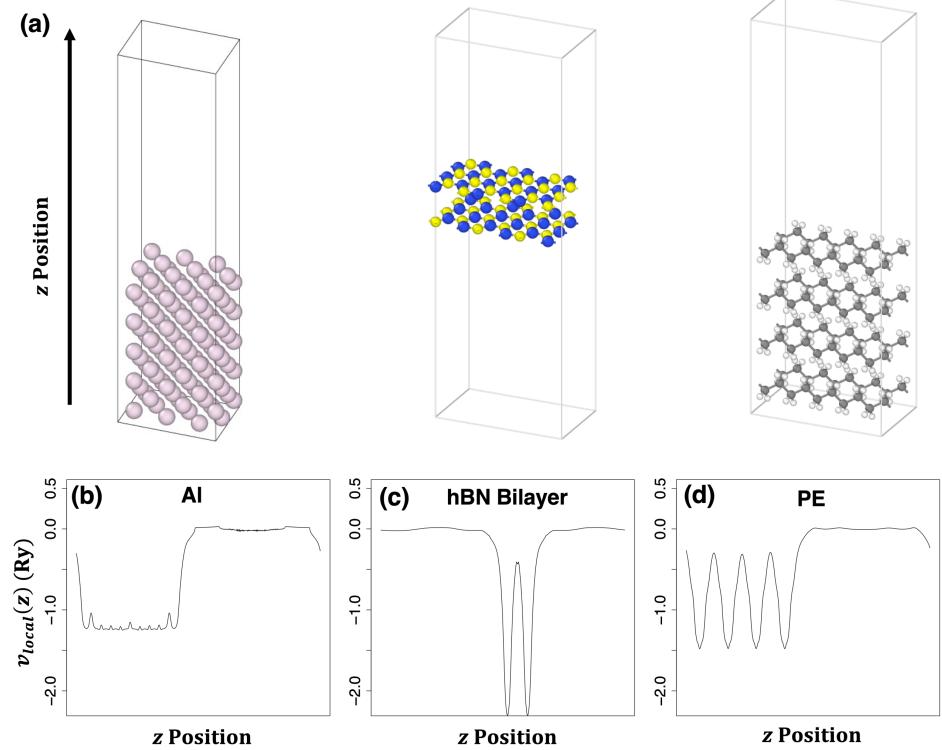
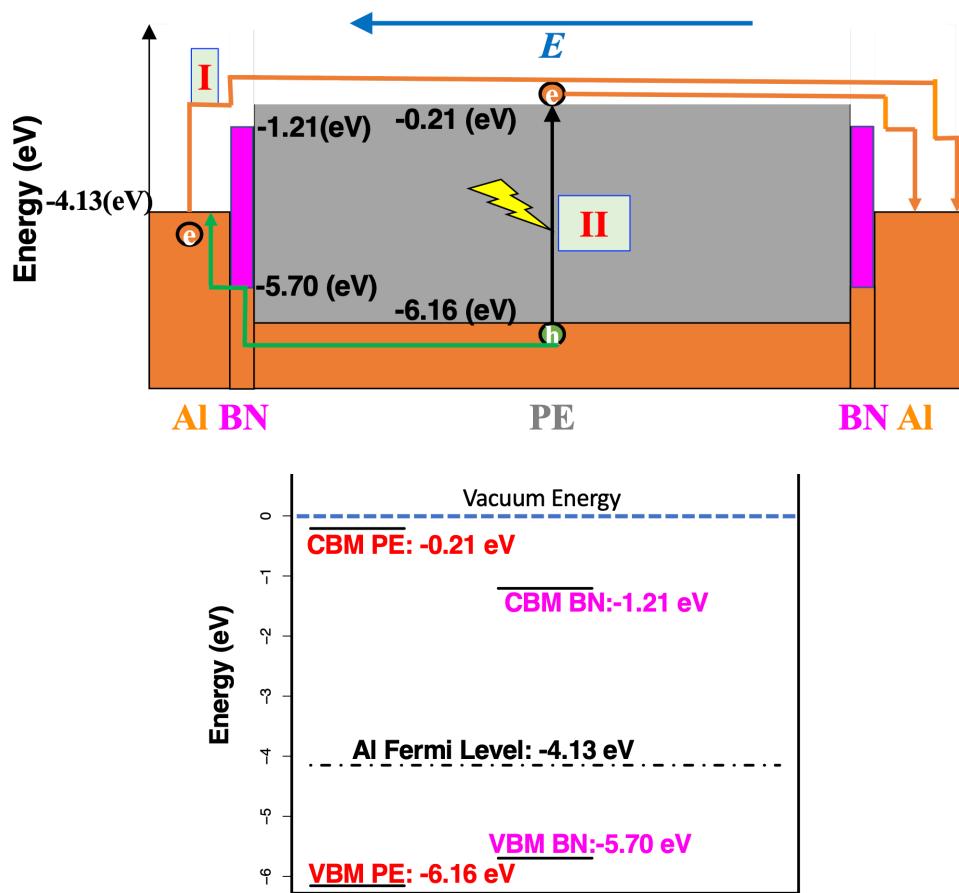
Hot-Carrier Chemistry

- Highly-localized holes are driven to the low-voltage surface by electric field, causing the elongation & cleavage of C-C bonds



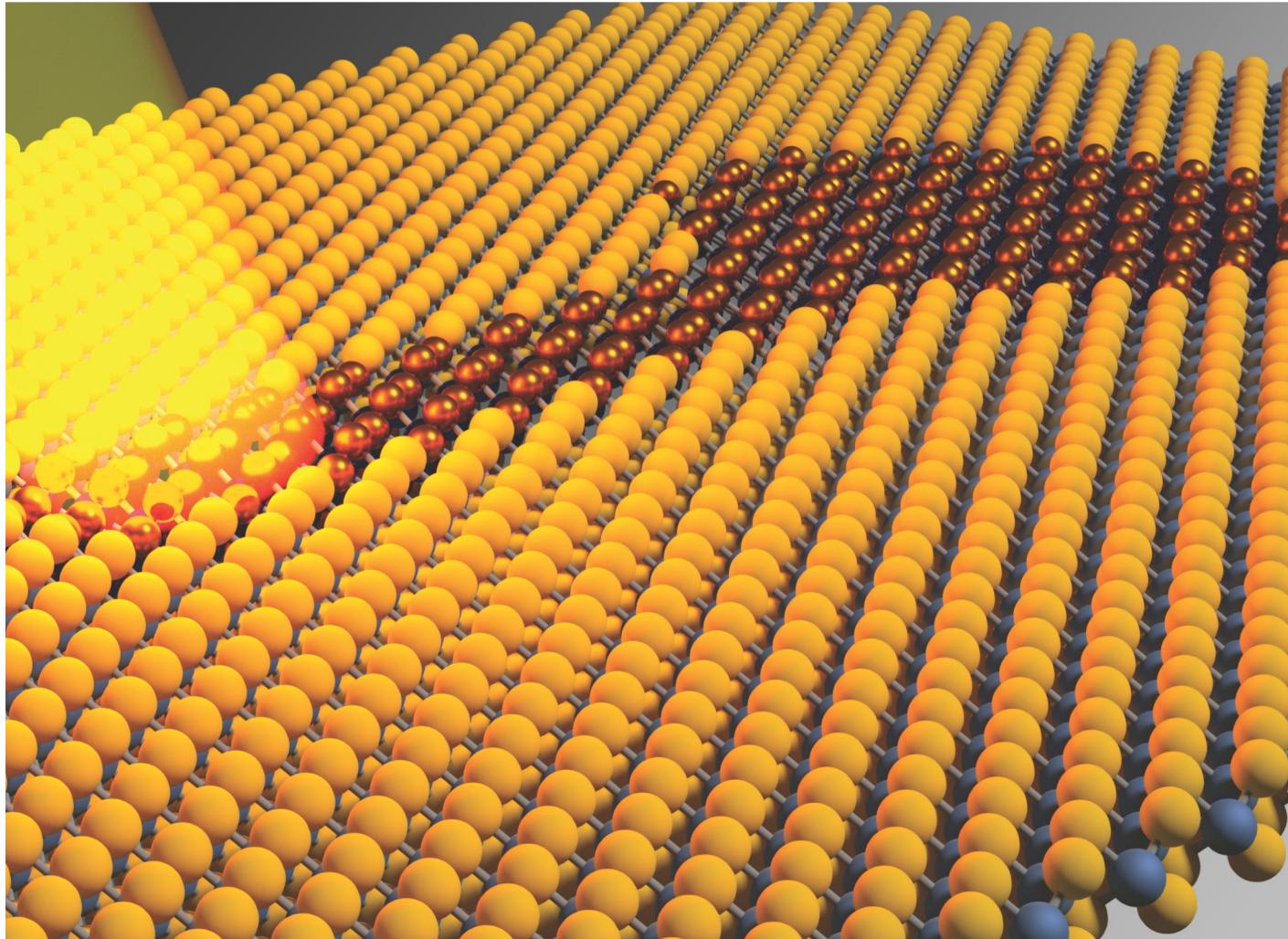
Breakdown-Resistant Coating

- NAQMD shows that coating polyethene (PE) with hexagonal boron nitride (hBN) traps hot carriers injected from metal electrode, thereby mitigating detrimental dielectric breakdown



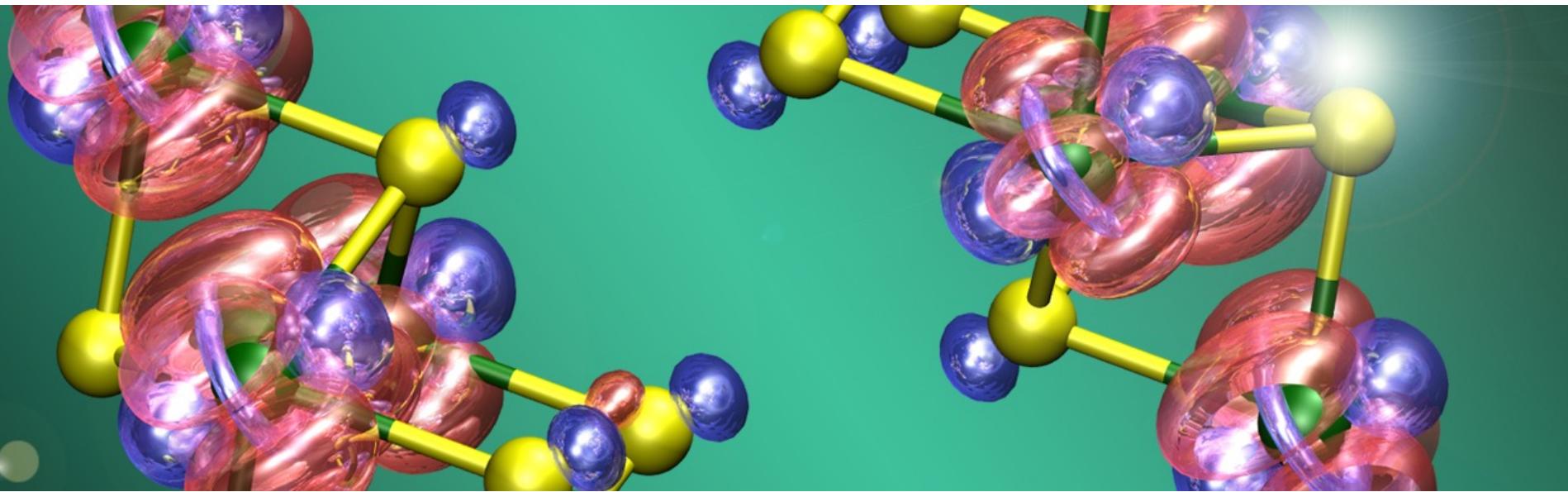
Ultrafast Control of Quantum Materials

Goal: Use ultrafast laser pulses to transform material structures & properties
(e.g., semiconductor-to-metal) on demand

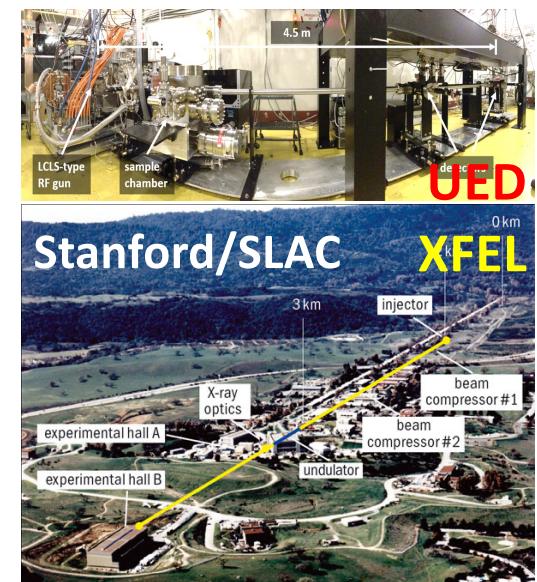


A. Krishnamoorthy *et al.*, *Nanoscale* **10**, 2742 ('18); journal cover

Simulation-Experiment Synergy



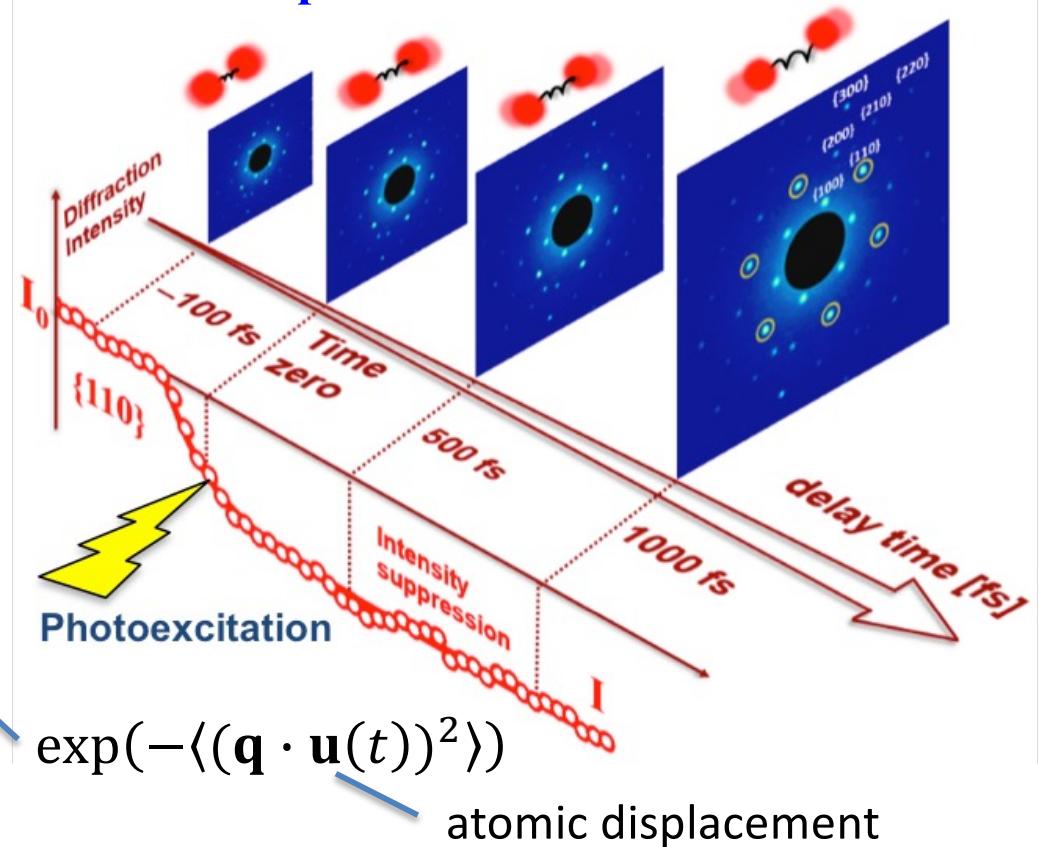
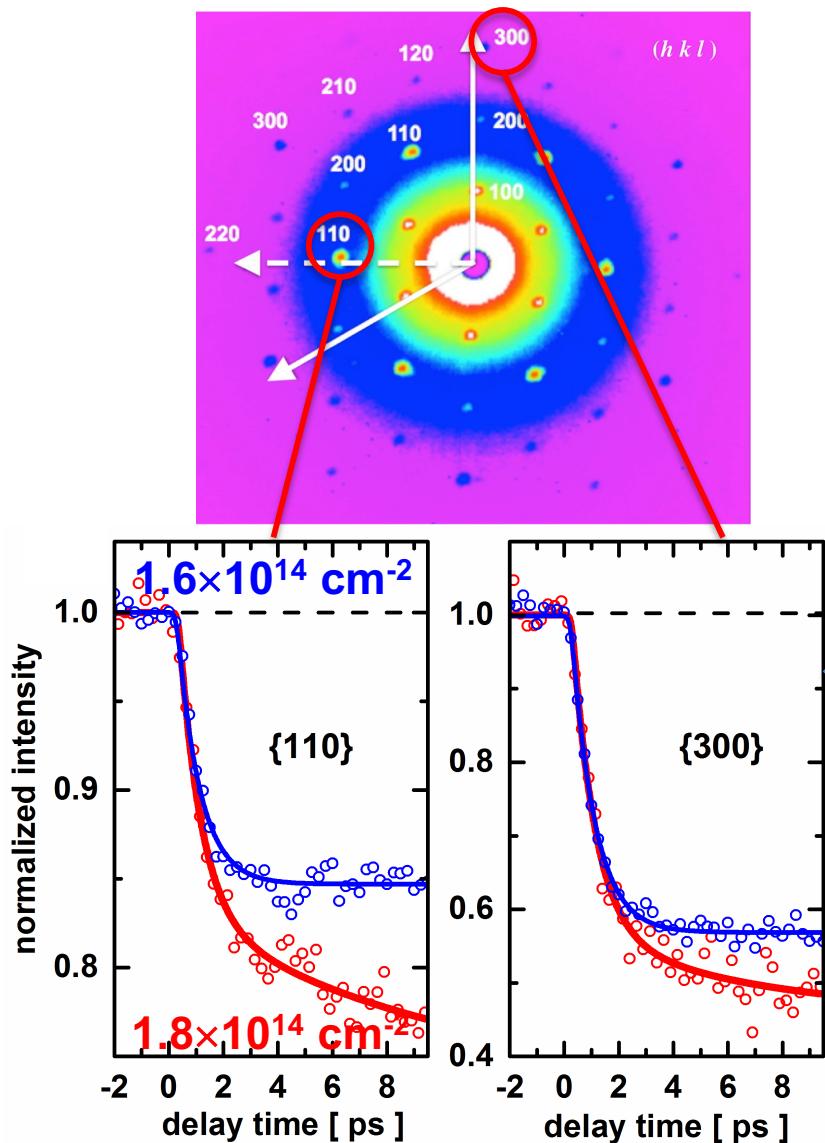
- In ultrafast ‘electron & X-ray cameras,’ laser light hitting a material is almost completely converted into nuclear motions — key to switching material properties on & off at will for future electronics applications.
- High-end nonadiabatic quantum molecular dynamics simulations reproduce the ultrafast energy conversion at exactly the same space & time scales, and explain it as a consequence of photo-induced phonon softening.



Ultrafast electron diffraction: M. F. Lin *et al.*, *Nature Commun.* **8**, 1745 ('17)
X-ray free-electron laser: I. Tung *et al.*, *Nature Photon.* **13**, 425 ('19)

Ultrafast Coupled Electron-Lattice Dynamics

- Ultrafast electron diffraction experiment shows nearly perfect energy conversion from electronic excitation to lattice motions within ps

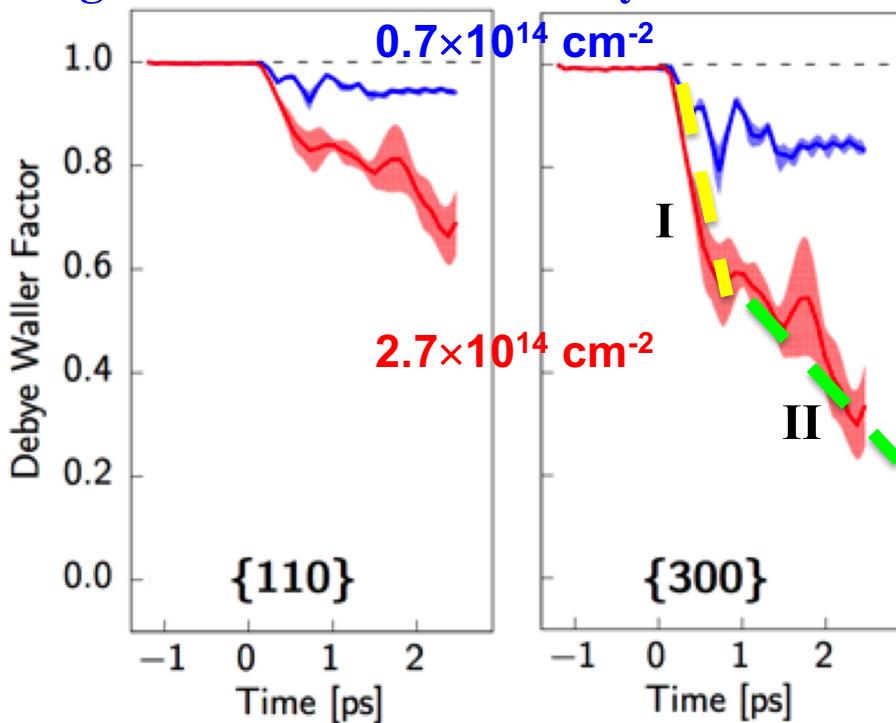


- Dynamics of Debye-Waller factor reveals rapid disordering for both {300} & {110} peaks
- Transition from mono- to bi-exponential decay at higher electron-hole density

M.F. Lin *et al.*, *Nature Commun.* 8, 1745 ('17)

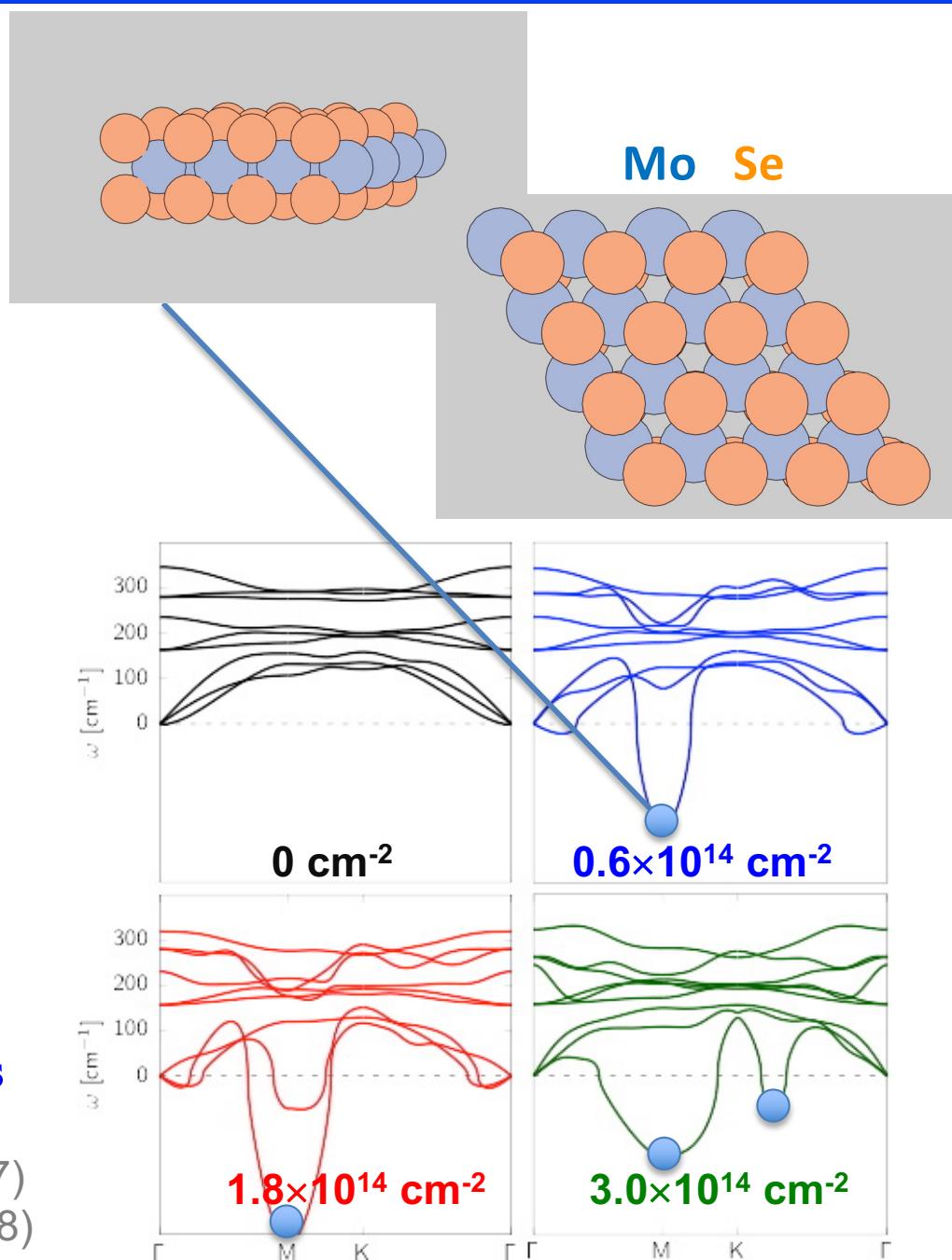
Strong Electron-Lattice Coupling in MoSe₂

- NAQMD simulations reproduce (1) rapid photo-induced lattice dynamics & (2) mono- to bi-exponential transition at higher electron-hole density



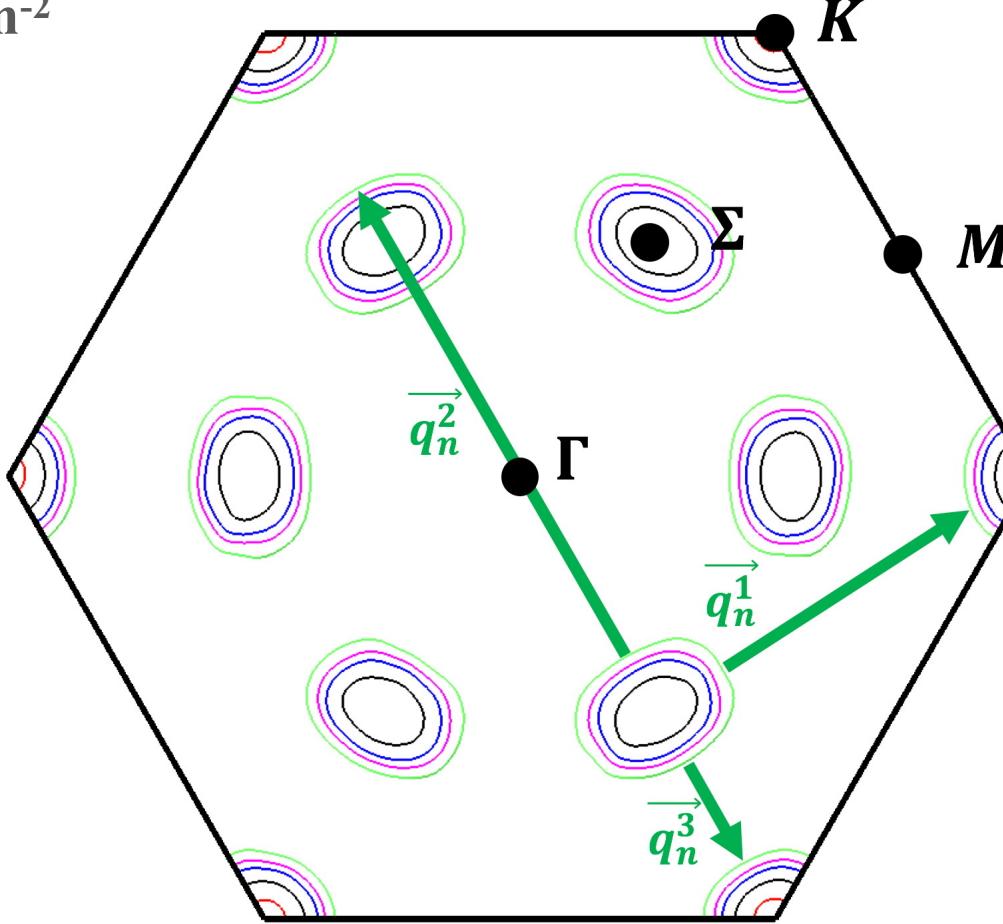
- Rapid lattice dynamics is explained by the softening of M-point (1/2 0 0) phonon
- Bi-exponential transition is explained by the softening of additional phonon modes at higher electron-hole densities

Lin et al., *Nature Commun.* **8**, 1745 ('17)
Bassman et al., *Nano Lett.* **18**, 4653 ('18)



Electronic Origin of Phonon Softening

- Electronic Fermi surface for the electron-hole density $n(\text{e-h})$ ranging from 0.2 to $2 \times 10^{14} \text{ cm}^{-2}$

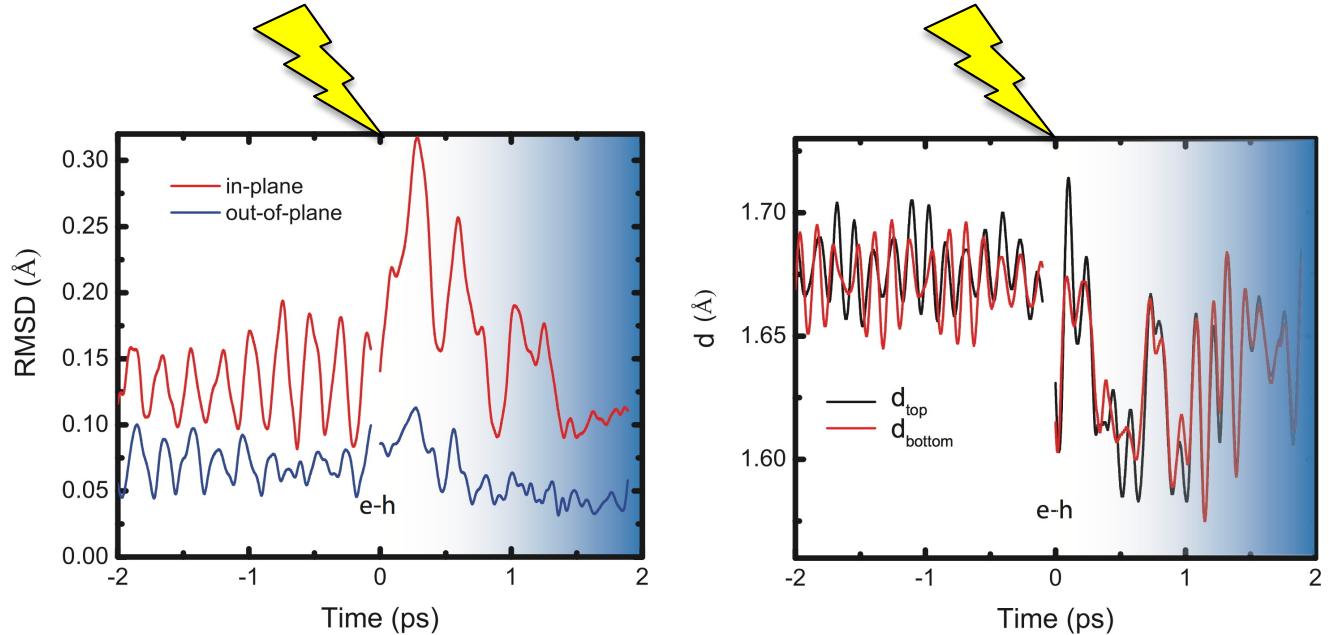
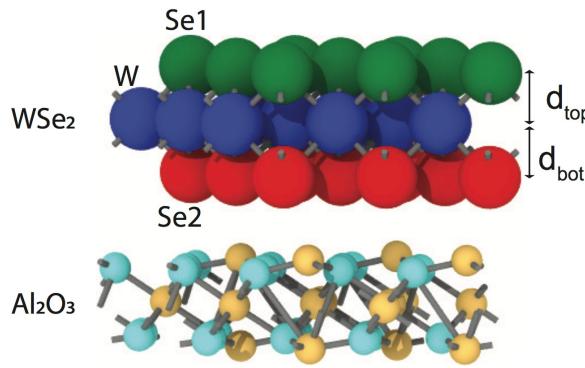


$$n(\text{e-h}) = 0.22, 1, 2, 3, 4 \times 10^{14} \text{ cm}^{-2}$$

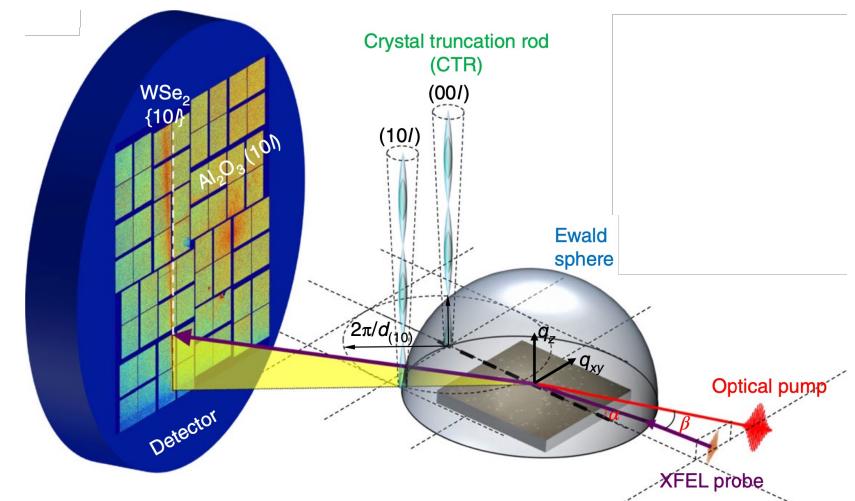
- While the Fermi surface is localized at K-points at minimal excitation (red), it occupies Σ -pockets at larger $n(\text{e-h})$ (black & blue), enabling electron scattering by emitting \vec{q}_n^1 (M), \vec{q}_n^2 (Σ) and \vec{q}_n^3 (K) phonons

WSe₂ Monolayer on Al₂O₃ Substrate

- NAQMD simulation to study photoexcitation dynamics of WSe₂ monolayer on Al₂O₃ substrate



- Enhanced in-plane atomic displacements upon photoexcitation
- Photo-induced intralayer contraction of W-Se distances
- Good agreement with femtosecond surface X-ray scattering experiments at Stanford SLAC/LCLS

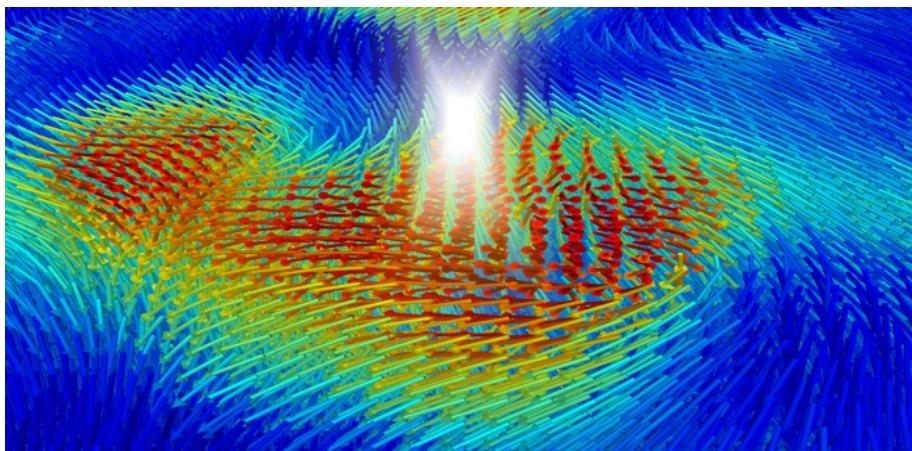
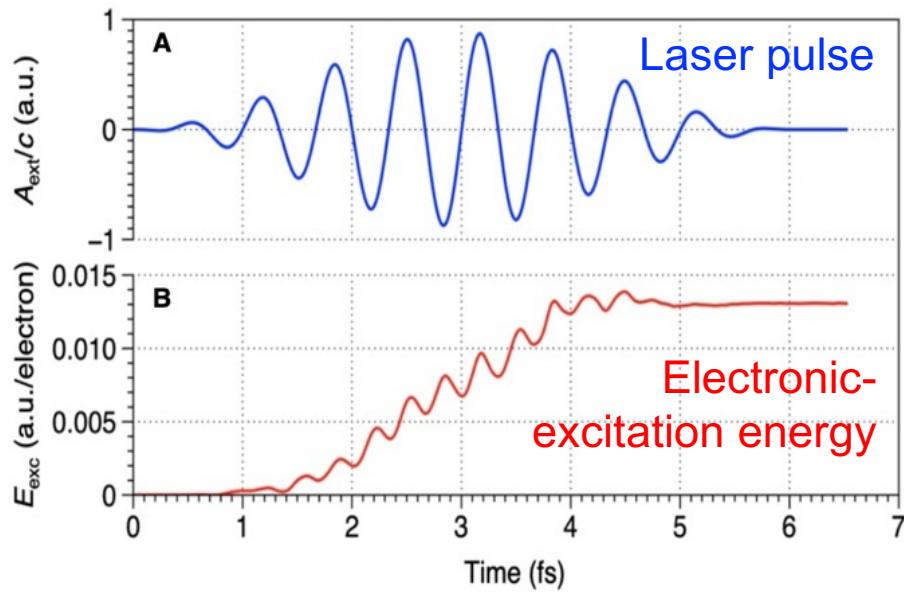


Tung et al., *Nature Photonics* **13**, 425 ('19);

Kumazoe et al., *J. Phys.: Condens. Matter* **30**, 32LT02 ('18)

Ferroelectric Opto-Toptronics

- Quantized ferroelectric topology is protected against thermal noise → ultralow-power opto-electronics



- Ehrenfest NAQMD simulation of photoexcited PbTiO_3 shows rapid thermalization of electron excitation energy into Fermi distribution within a few femtoseconds

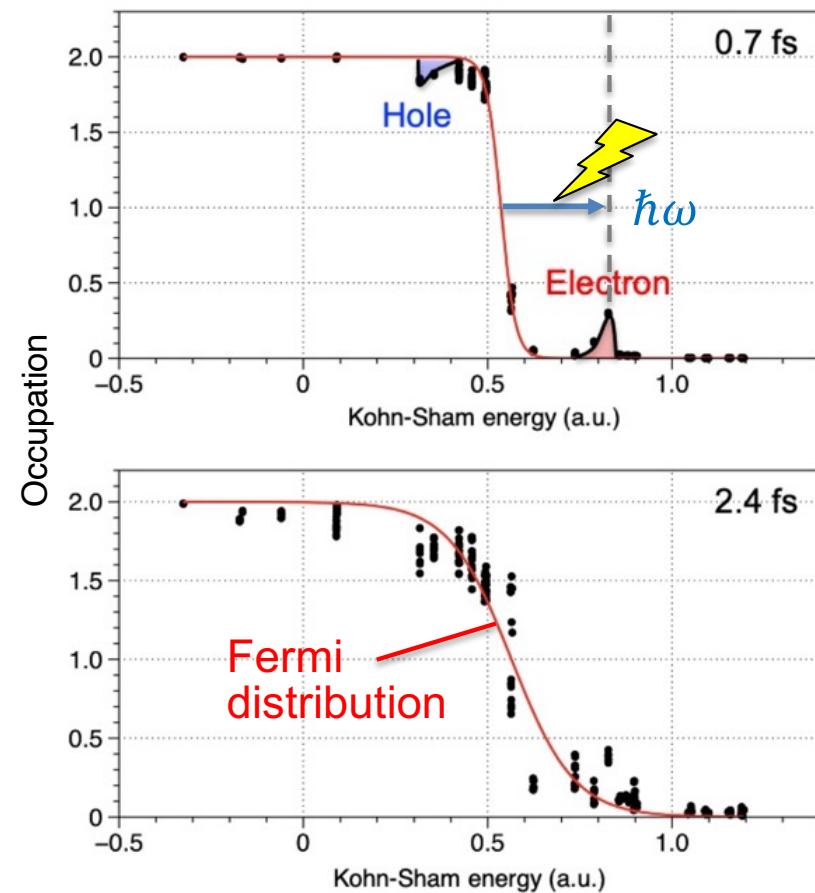
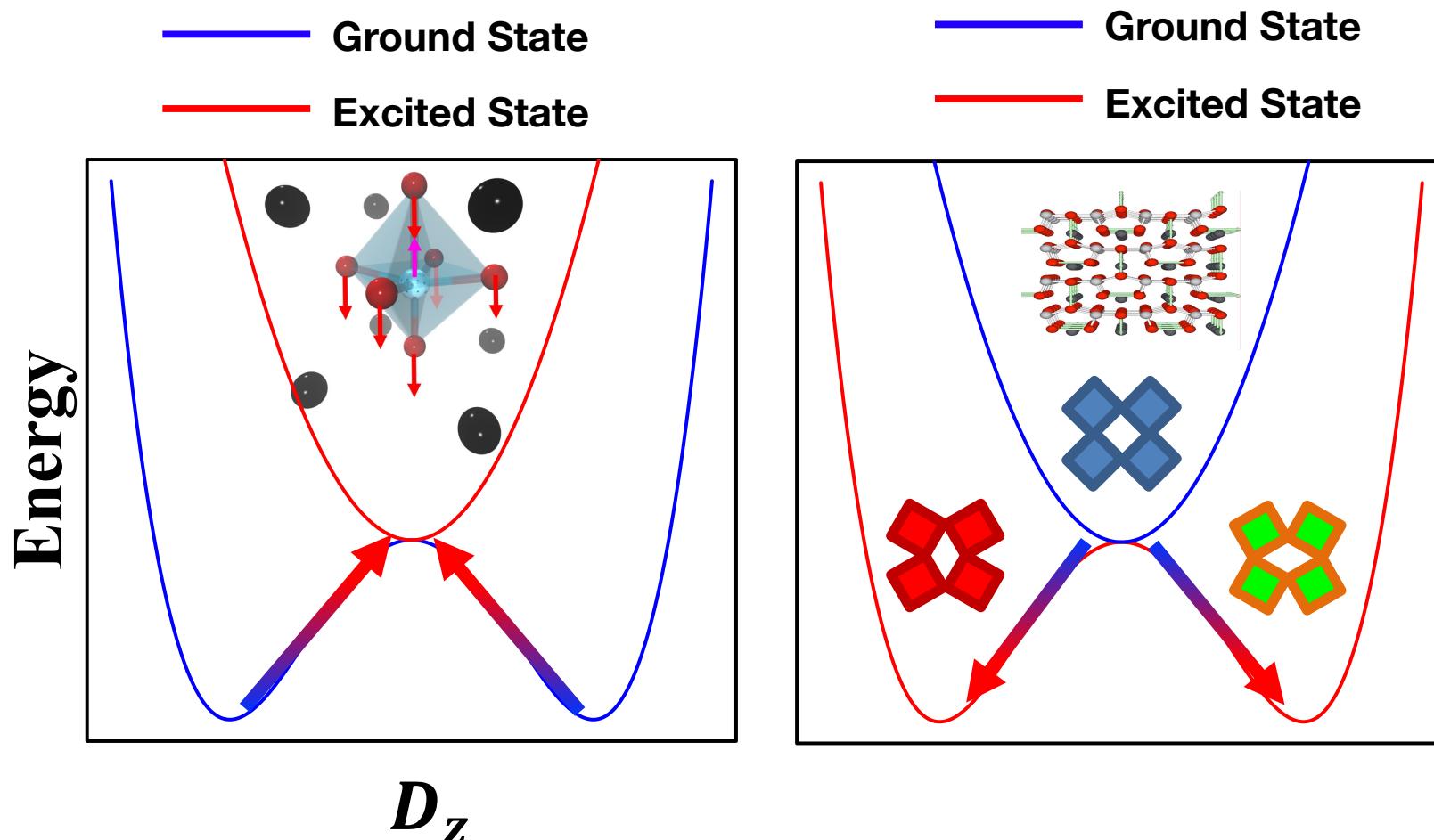
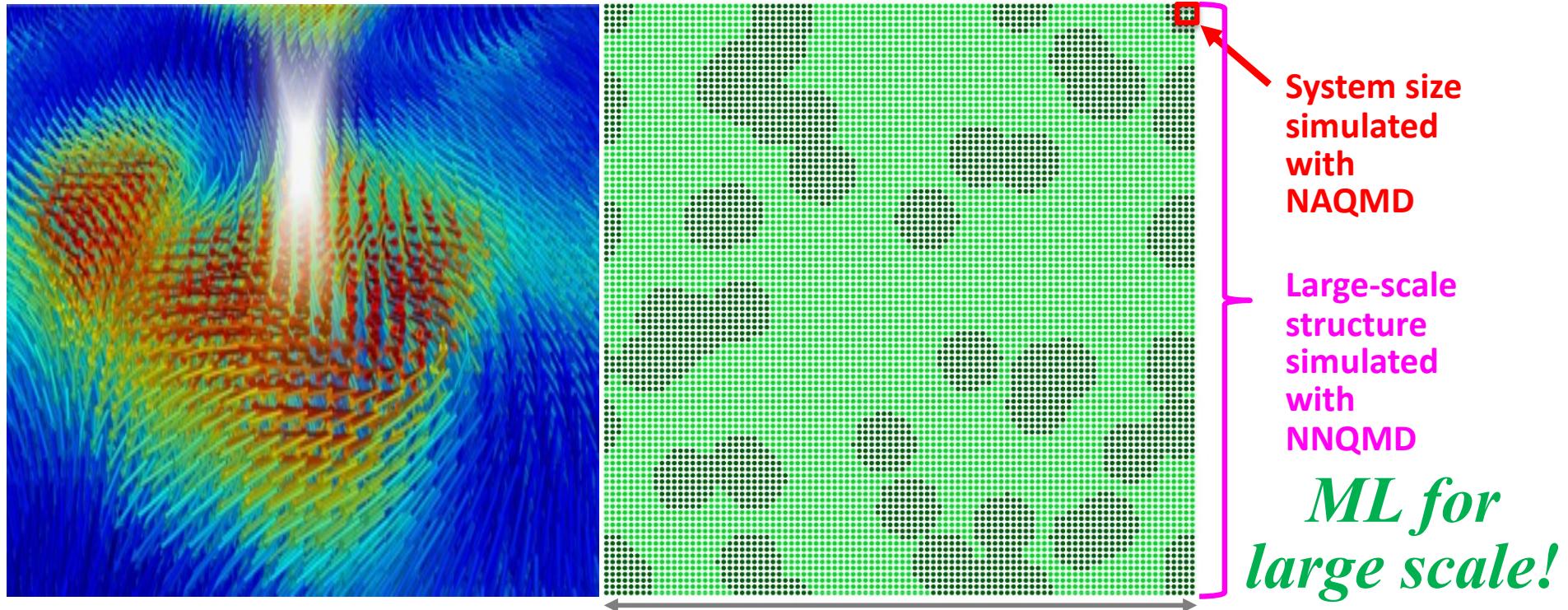


Photo-induced Matter

- Surface-hopping & Fermi-temperature NAQMD simulations show the disappearance of a ferroelectric order parameter & emergence of a new rotational order parameter due to the excited-state energy landscape



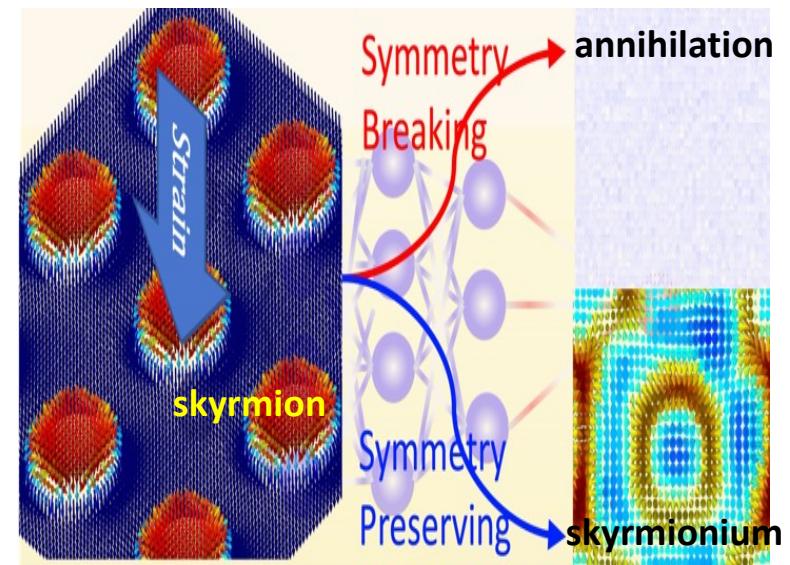
Multiscale Ferroelectric Opto-Toptronics



- Billion-atom neural-network quantum molecular dynamics (NNQMD) trained by NAQMD revealed photo-induced topological phase-transition dynamics (*cf.* Kibble-Zurek mechanism in cosmology)
- Symmetry-controlled skyrmion-to-skyrmionium* switching

*Composite of skyrmions with opposite topological charges

Linker *et al.*, *Science Adv.* **8**, eabk2625 ('22);
JPCL **13**, 11335 ('22); *Nano Lett.* **23**, 7456 ('23)



Optical Retinal Neuron

- Interplay between electronic band alignment & charge transfer rates of photoexcited carriers gives rise to intrinsic negative differential resistance (NDR) at a graphene/silicon interface under illumination, thus enabling oscillatory retinal neurons (ORN) to perform in-sensor image computing without external power in the era of ubiquitous AI in sustainable society

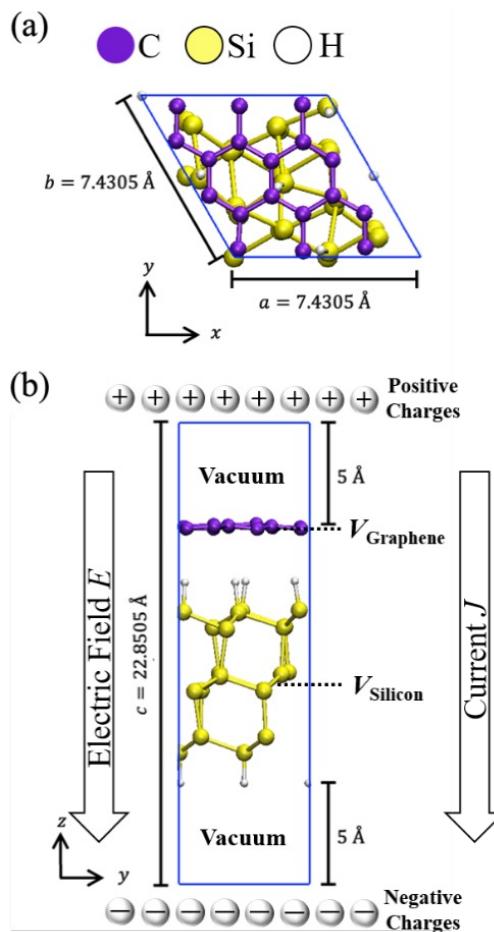
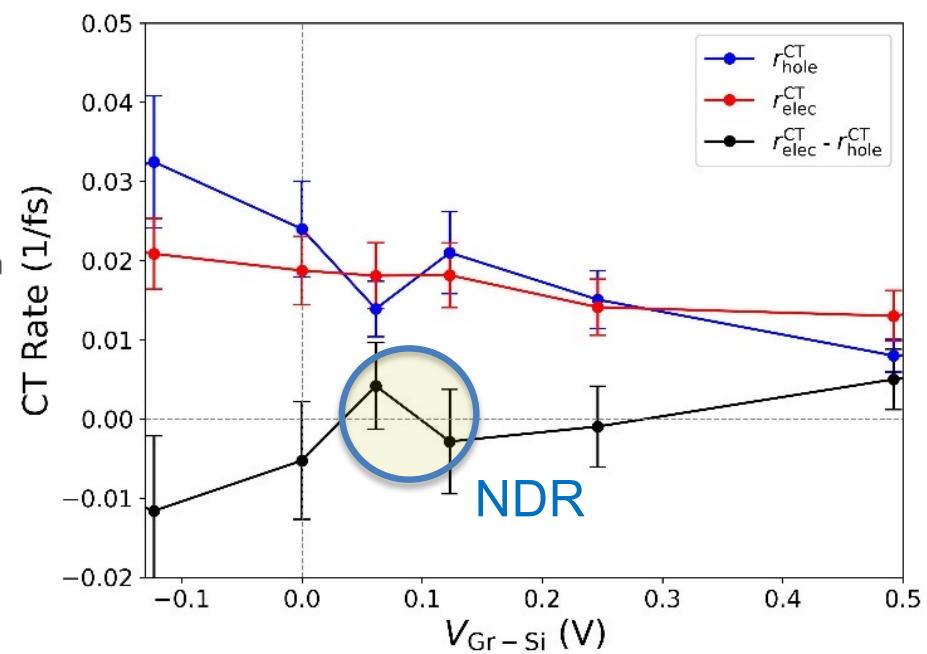
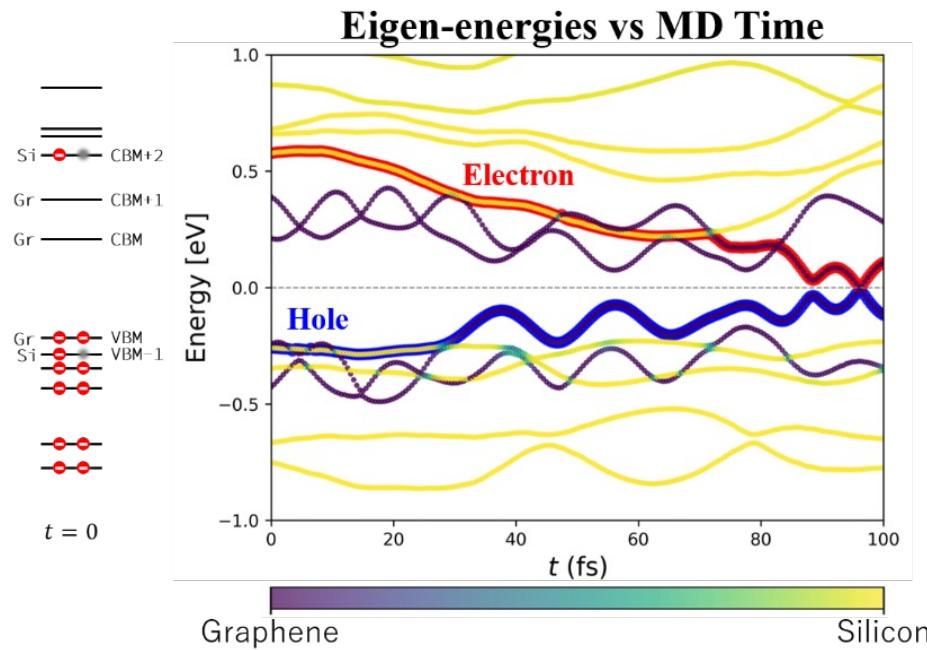


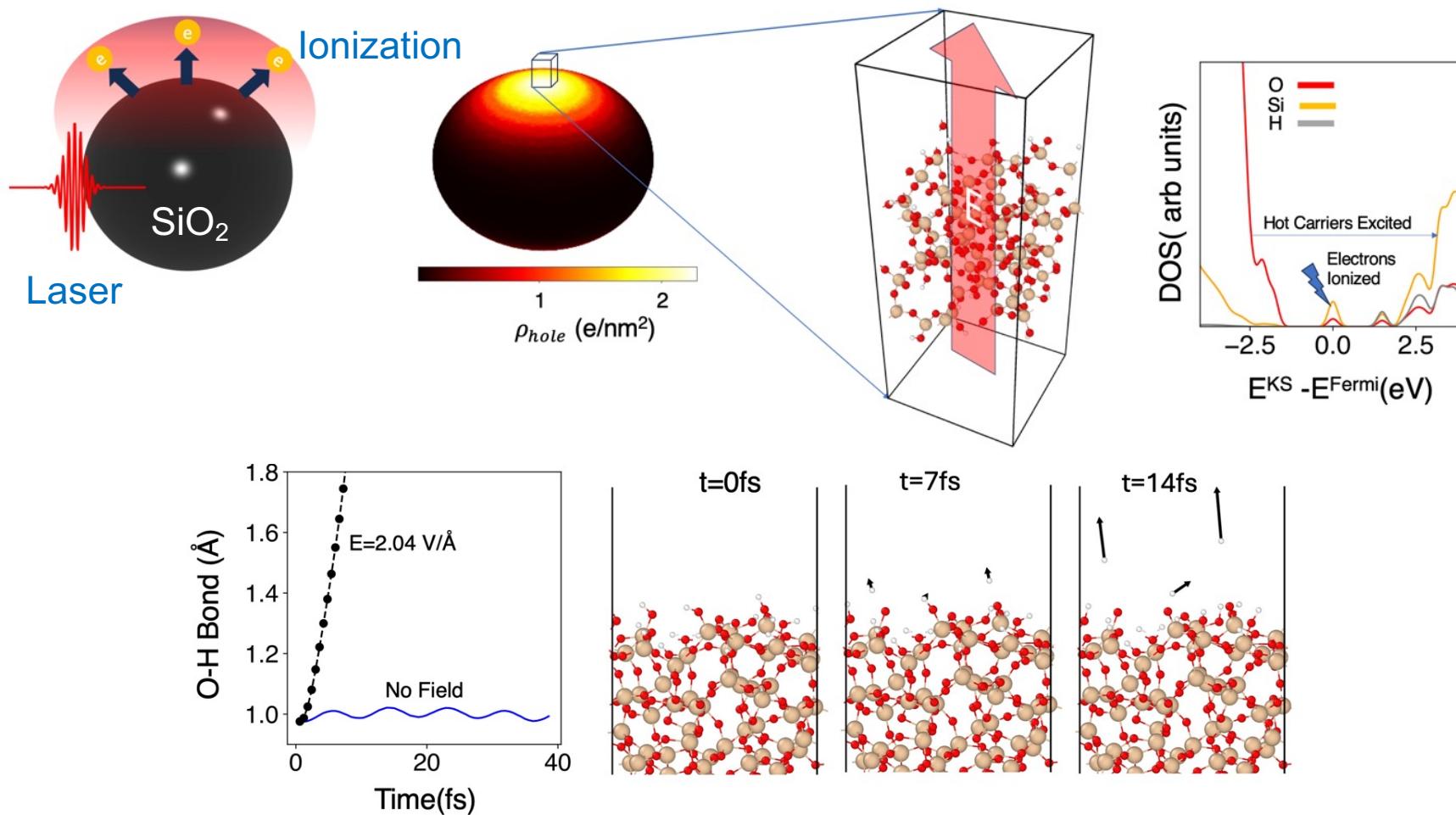
Photo-Induced NDR

- NAQMD simulation of an electron-hole pair photoexcited in Si substrate exhibits nonlinear voltage dependence of electron & hole charge-transfer (CT) rates to graphene, which explains photoinduced NDR in experiments



Laser-Driven Surface Chemistry

- NAQMD simulation shows enhanced O-H breakage on a hydrogenated surface of a laser-ionized SiO_2 nanoparticle



II. Advanced NAQMD

Many-Body Excited States

- Surface-hopping NAQMD with adiabatic Kohn-Sham basis does not represent many-body excited states such as an exciton (*i.e.*, electron-hole pair bound by electrostatic attraction)
- Linear-response time-dependent density-functional theory (LR-TDDFT) obtains many-body electronic excitation energies as poles of the frequency-dependent electron-hole-pair response function [Casida, '95]

Excitonic Effects: LR-TDDFT

- Excited electron-hole pairs within the linear-response time-dependent density functional theory (LR-TDDFT)

$$\delta V(t) = \delta v_{kl\tau}(t) \hat{a}_{k\tau}^+ \hat{a}_{l\tau} \xrightarrow{\hspace{10em}} \delta P_{ij\sigma}(t) = \delta \langle \Phi(t) | \hat{a}_{i\sigma}^+ \hat{a}_{j\sigma} | \Phi(t) \rangle$$

$$\chi_{ij\sigma,kl\tau}(t-t') = \delta P_{ij\sigma}(t)/\delta v_{kl\tau}(t')$$

electron hole

- Excitation energies from the poles of the response function $\chi_{ij\tau,kl\sigma}(\omega)$

$2N_{\text{unoccupied}} N_{\text{occupied}} \times 2N_{\text{unoccupied}} N_{\text{occupied}}$ matrix eigenequation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B}^* \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix} = \hbar\omega_I \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix}$$

***I*-th excitation energy**

Kohn-Sham energy

$$A_{ia\sigma,jb\tau} = \delta_{\sigma,\tau} \delta_{i,j} \delta_{a,b} (\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) + K_{ia\sigma,jb\tau} \quad B_{ia\sigma,jb\tau} = K_{ia\sigma,bj\tau}$$

$$K_{ia\sigma,i'a'\sigma'} = \iint \psi_{i\sigma}^*(\mathbf{r}) \psi_{a\sigma}(\mathbf{r}) \left(\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{\text{xc}}}{\delta \rho_\sigma(\mathbf{r}) \delta \rho_{\sigma'}(\mathbf{r}')} \right) \psi_{i'\sigma'}(\mathbf{r}') \psi_{a'\sigma'}^*(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

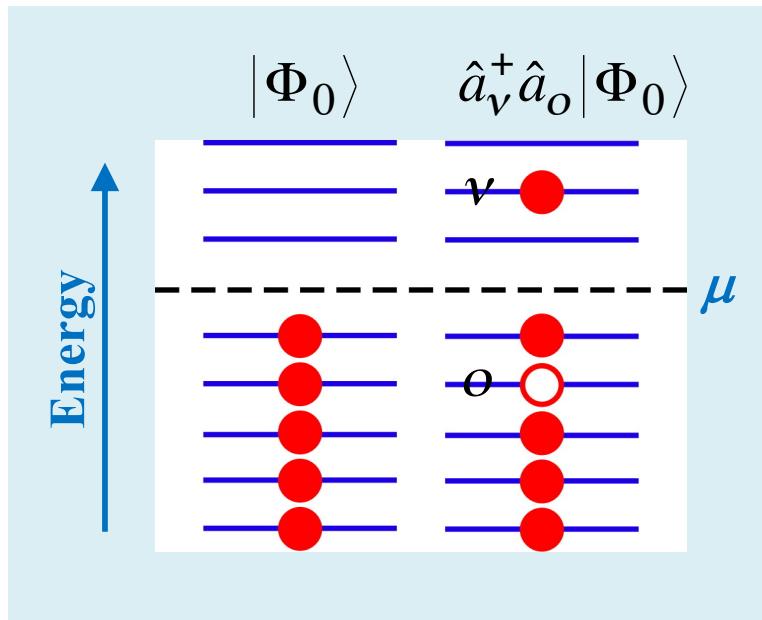
Coulomb & exchange-correlation interaction matrix elements

Electronic Excited States

- I -th excited state

$$|\Phi_I(\mathbf{r}; \mathbf{R})\rangle = \sum_{i \in \{\text{occupied}\}} \sum_{a \in \{\text{unoccupied}\}} \sum_{\sigma} \sqrt{\frac{\varepsilon_{a\sigma} - \varepsilon_{i\sigma}}{\hbar\omega_I}} (X_{I,ia\sigma} + Y_{I,ia\sigma}) \hat{a}_{a\sigma}^+ \hat{a}_{i\sigma} |\Phi_0(\mathbf{r}; \mathbf{R})\rangle$$

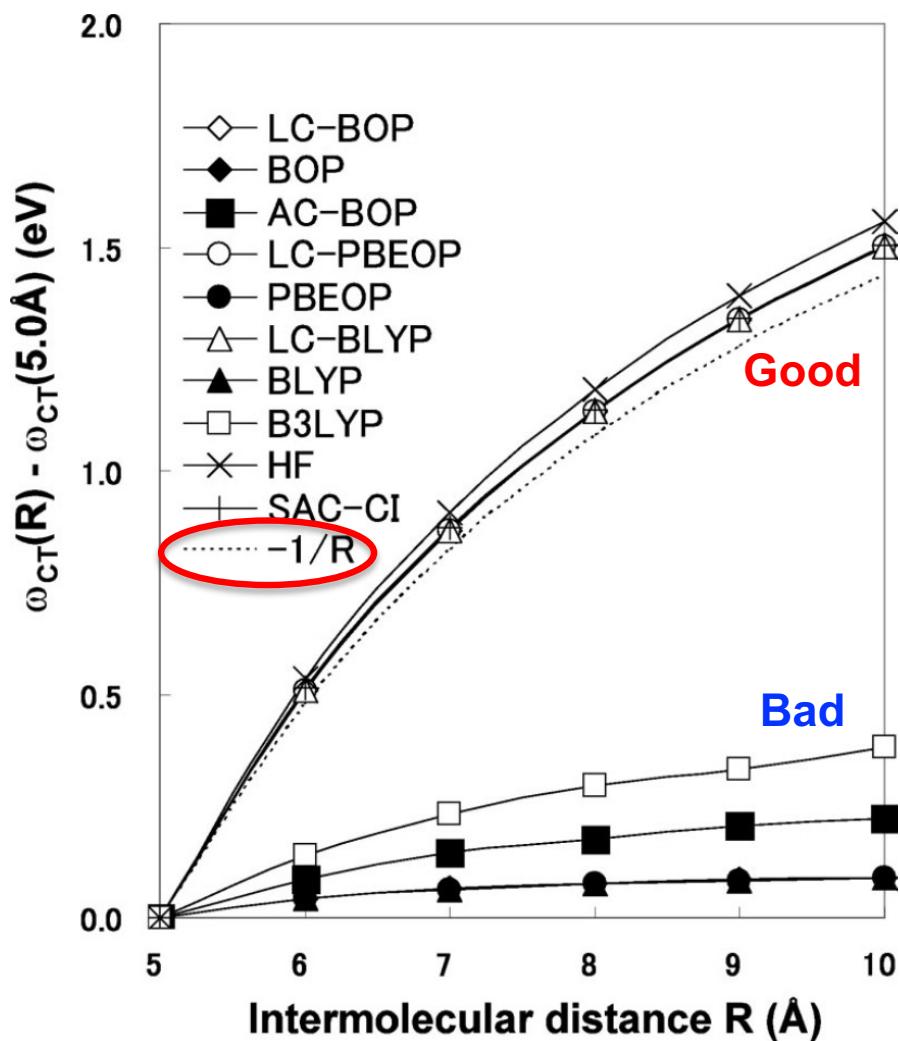
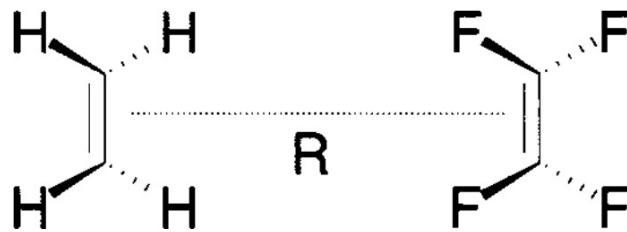
electron-hole pair ground state



See notes on (1) general time-dependent perturbation, (2) density response with time-dependent Kohn-Sham basis, (3) Fourier transform of step function, (4) excitation energies by LR-TDDFT, (5) many-body wave function

Many-Body Effects: Excitons

- Incorporating exact-exchange is indispensable for LR-TDDFT to describe $1/R$ binding energy of charge-transfer excitation (where electron moves from a donor to a spatially separated acceptor)
- Exchange integral is responsible for the $1/R$ attraction



Drew et al., J. Chem. Phys. 119, 2943 ('03); Tawada et al., J. Chem. Phys. 120, 8425 ('04)

See notes on (1) range-separated exact-exchange functional,
(2) excited-state forces, (3) excitation-energy balance sheet

Accelerating Exact-Exchange Computation

- Exact-exchange computation is highly compute-intensive: $O(N^5)$

$$(si|it) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_s^*(\mathbf{r}_1) \phi_i(\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \phi_i^*(\mathbf{r}_2) \phi_t(\mathbf{r}_2)$$

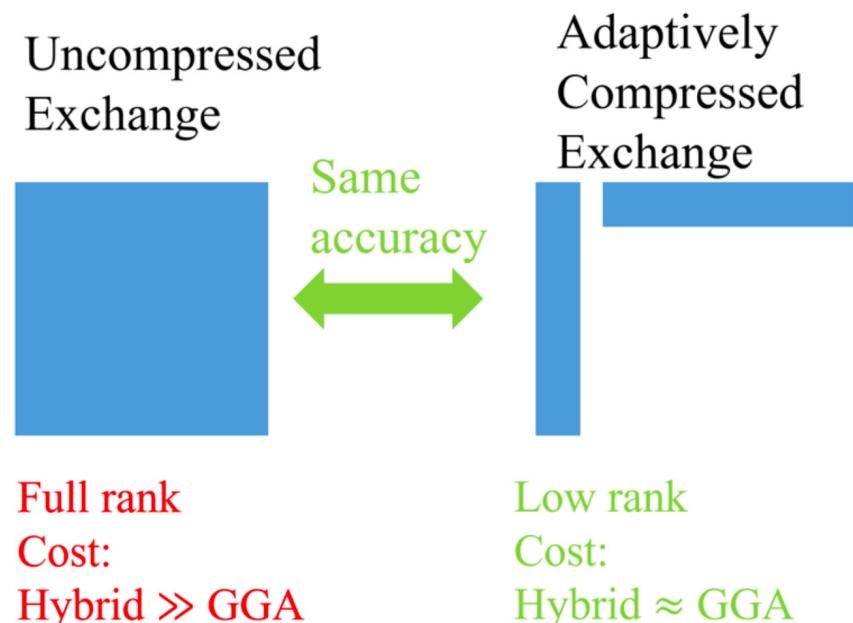
- Resolution-of-identity (ROI, closure by projection to a small augmenting basis set) or density-fitting approach reduces its computation to $O(N^4)$

Weigend, *Phys. Chem. Chem. Phys.* **4**, 4285 ('02)

$$(si|it) \cong \sum_{P,Q} (si|P)(P|Q)^{-1}(Q|it)$$

- Adaptive compression (or low-rank tensor product) to reduce the complexity to near GGA-type computation?

Lin, *J. Chem. Theory Comput.* **12**, 2242 ('16)



Application: Optical Absorption Spectrum

- Oscillator strength calculated by the linear-response TDDFT

I-th excitation energy

Polarizability:

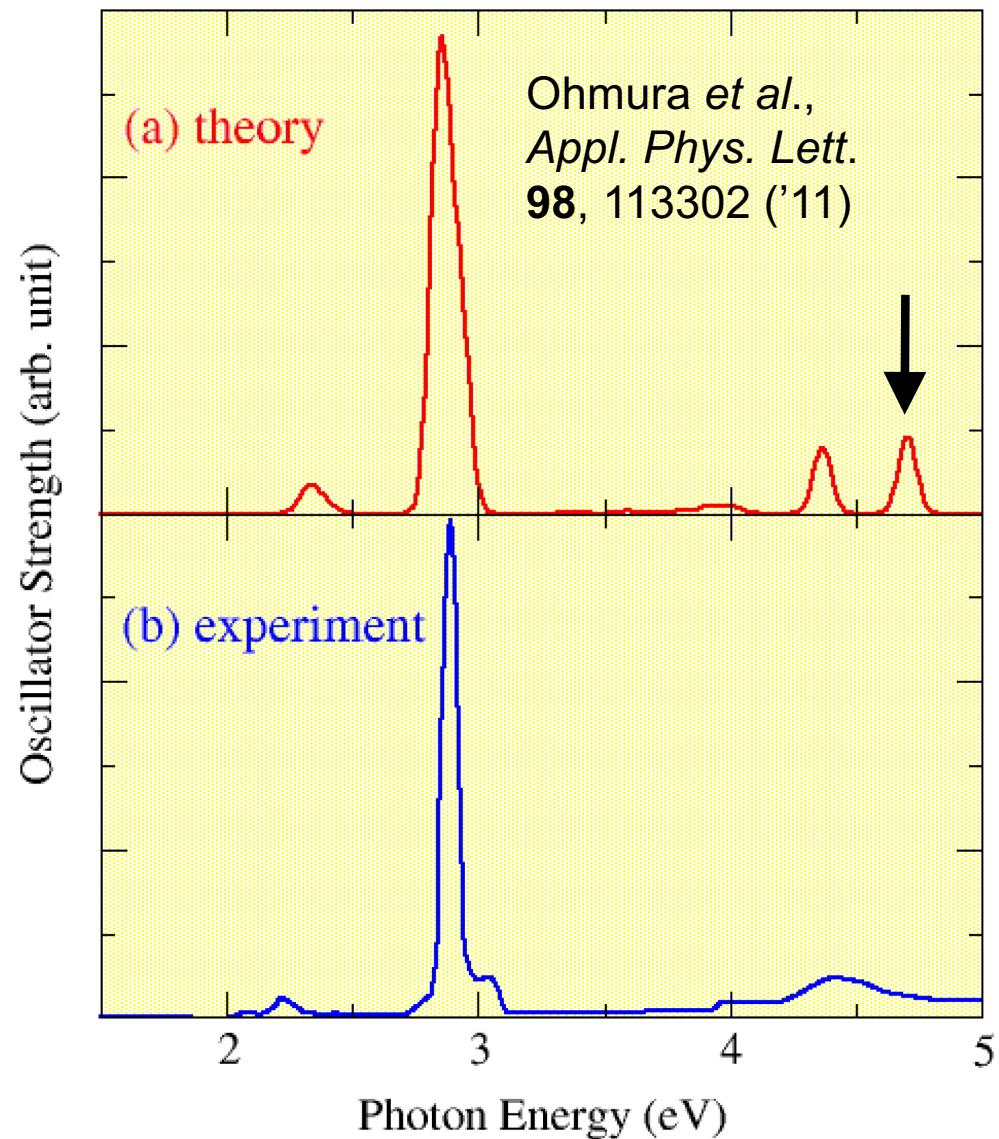
$$\alpha(\omega) = \sum_I \frac{f_I}{\omega - \omega_I}$$

Oscillator strength:

$$f_I = \frac{2\omega_I}{3} \sum_{\alpha=x,y,z} |\langle 0 | \hat{\alpha} | I \rangle|^2$$

I-th excited state

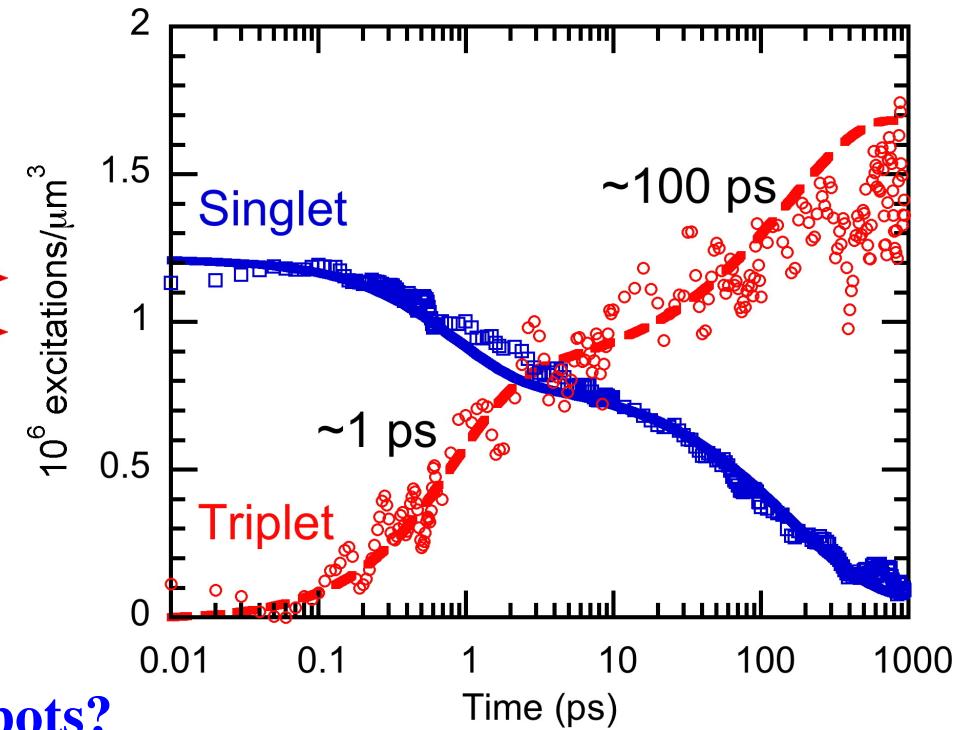
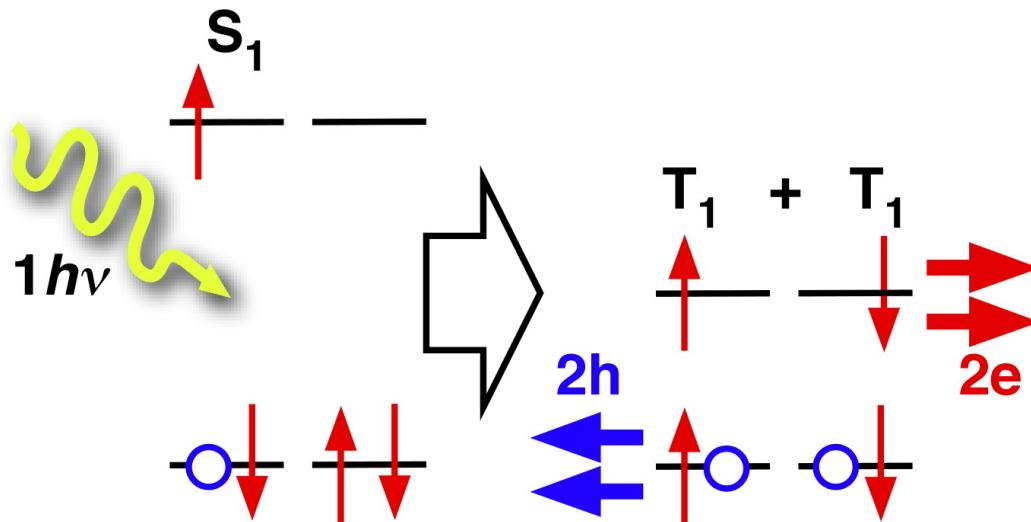
See [08Casida-TDDF-LR.pdf](#)



- Excellent agreement with experimental data [Akai et al., '06]

Singlet Fission in Amorphous DPT

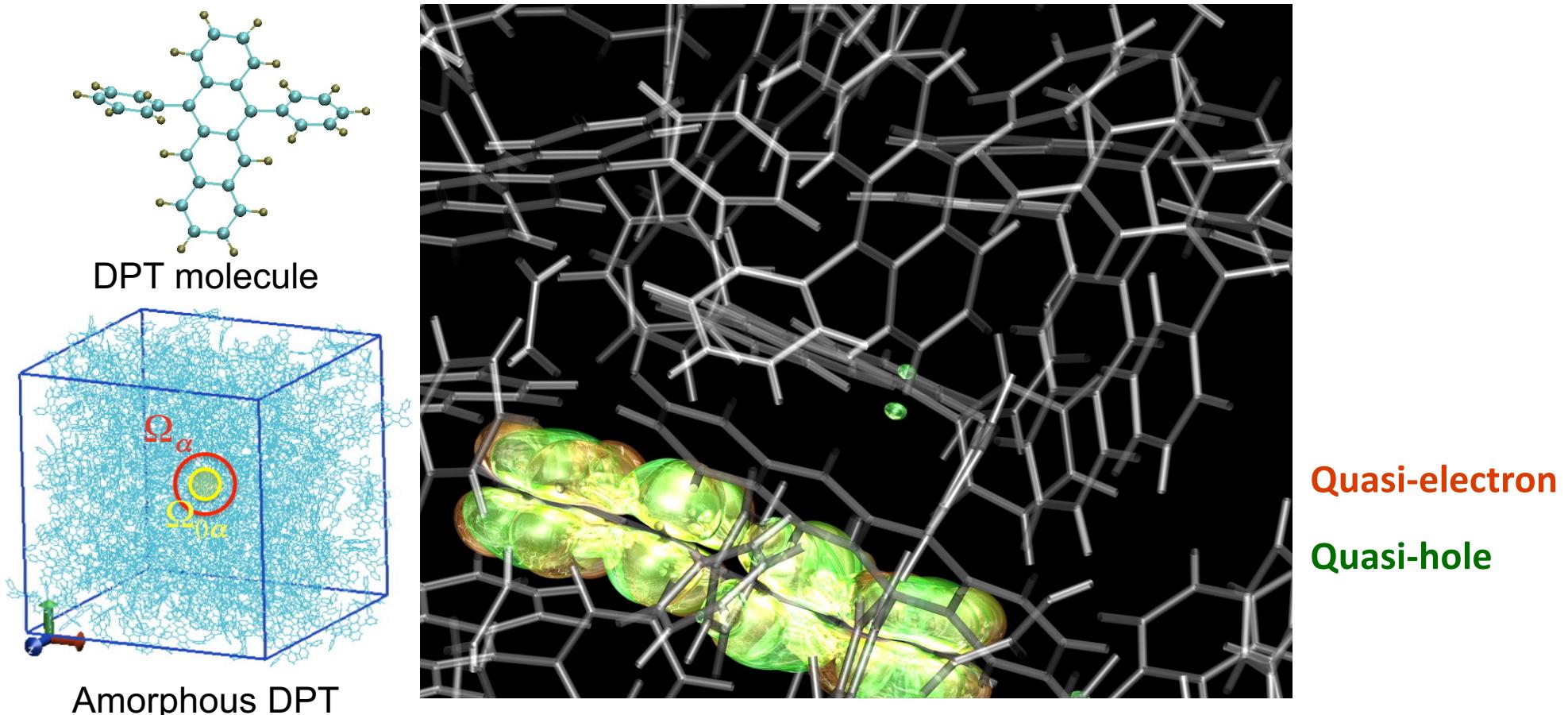
- Photo-current doubling by splitting a singlet exciton into 2 triplet excitons
- Singlet fission (SF) in mass-produced disordered organic solid
→ efficient low-cost solar cells
- Exp'l breakthrough: SF found in amorphous diphenyl tetracene (DPT)
- Ultrafast transient absorption measurements identified *two time-scales* (1 & 100 ps) for exciton population dynamics
- Hypothesis: Existence of *SF hot spots* [S. T. Roberts *et al.*, JACS 134, 6388 ('12)]



- Problem: *Molecular origin of SF hot spots?*

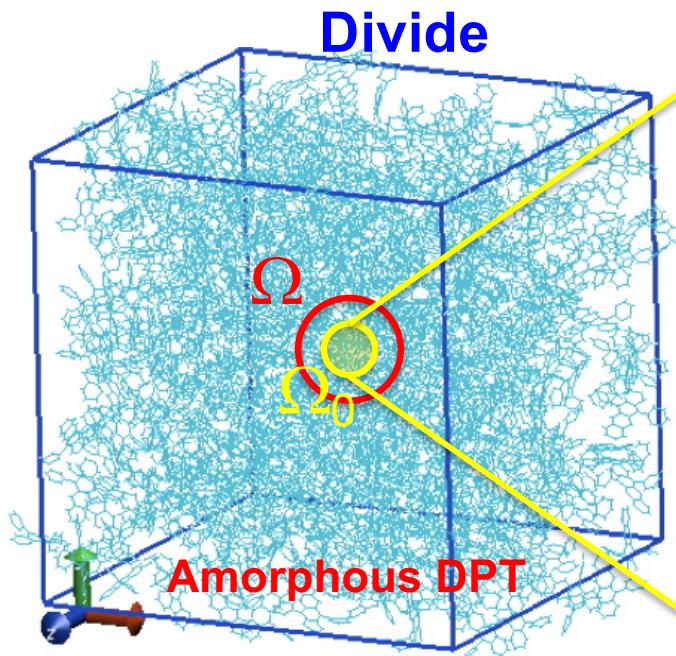
Singlet Fission in Amorphous DPT

- Photo-current doubling by splitting a singlet exciton into 2 triplet excitons
- Singlet fission in mass-produced disordered organic solid → efficient low-cost solar cells
- Experimental breakthrough: SF found in amorphous diphenyl tetracene (DPT)

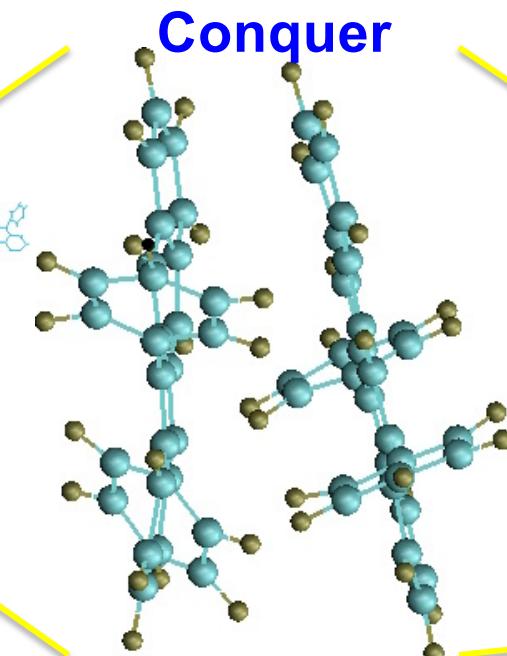


- Divide-conquer-recombine nonadiabatic QMD (phonon-assisted exciton dynamics) + time-dependent perturbation theory (singlet-fission rate) + kinetic Monte Carlo calculations of exciton population dynamics in 6,400-atom amorphous DPT

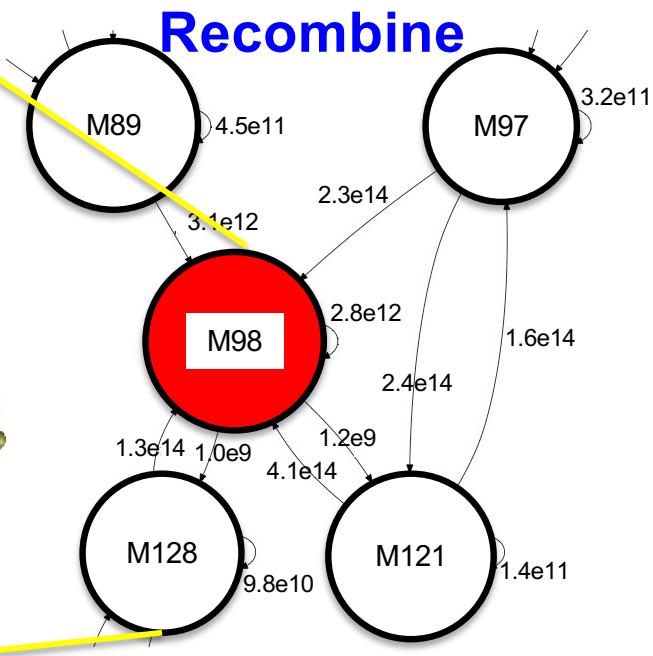
Divide-Conquer-Recombine Electronic Excitation



Molecular Dynamics

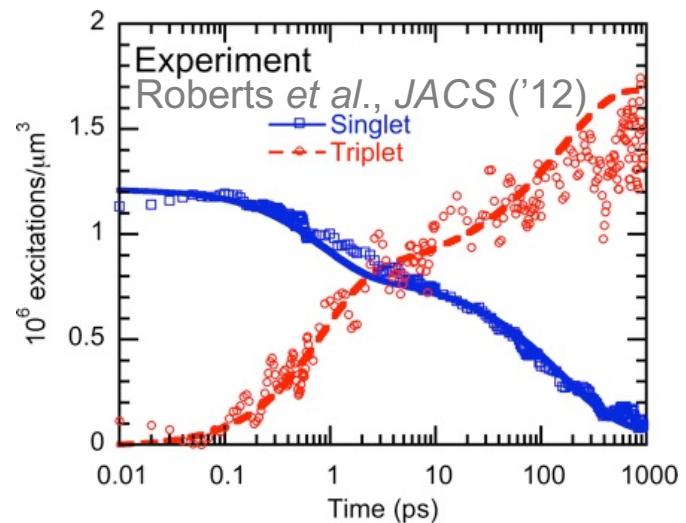
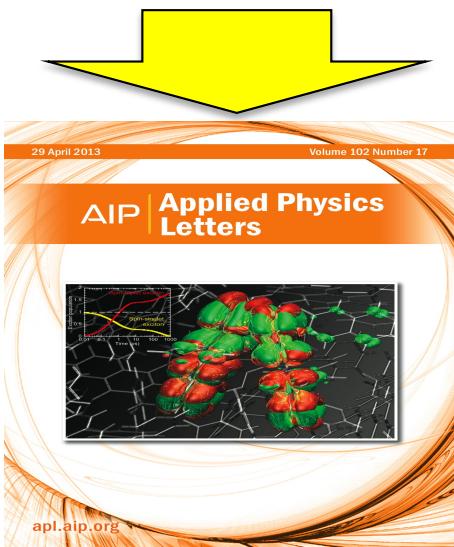
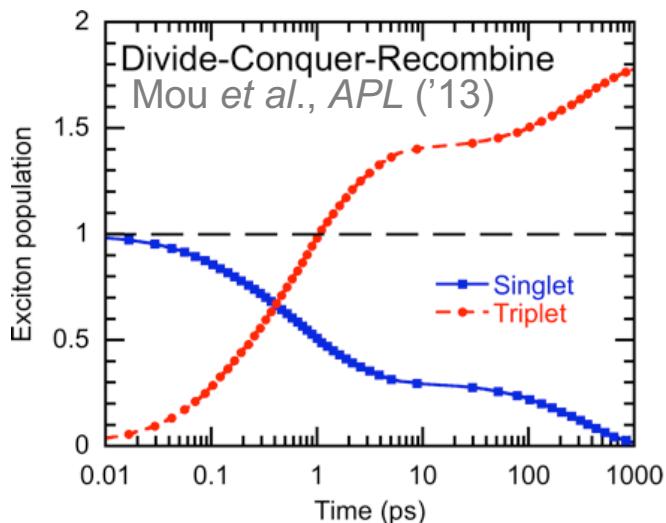


Quantum Molecular Dynamics



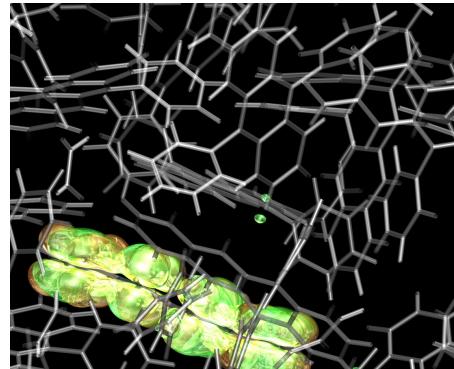
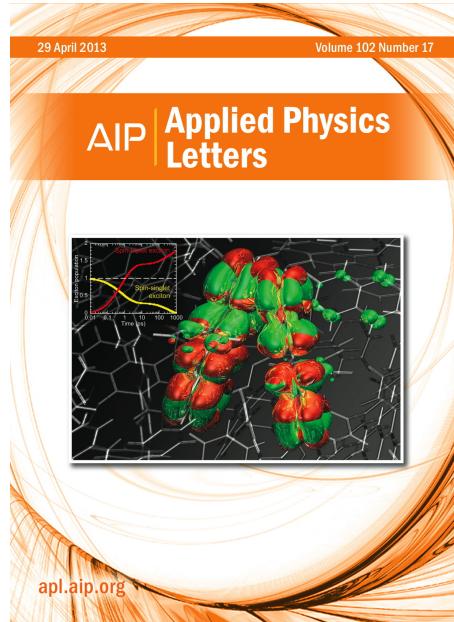
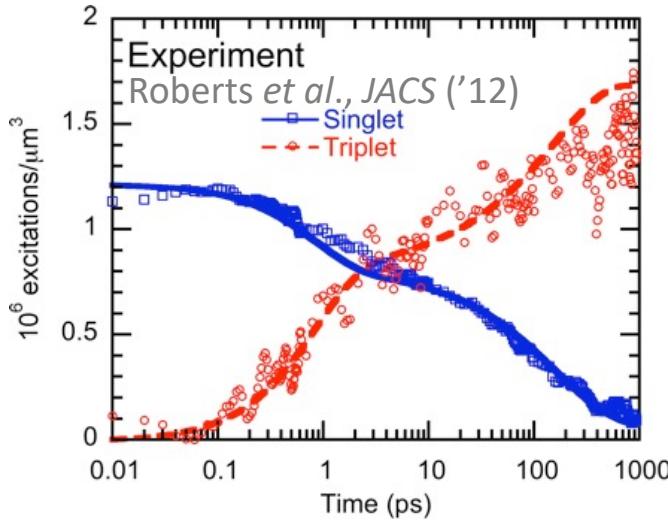
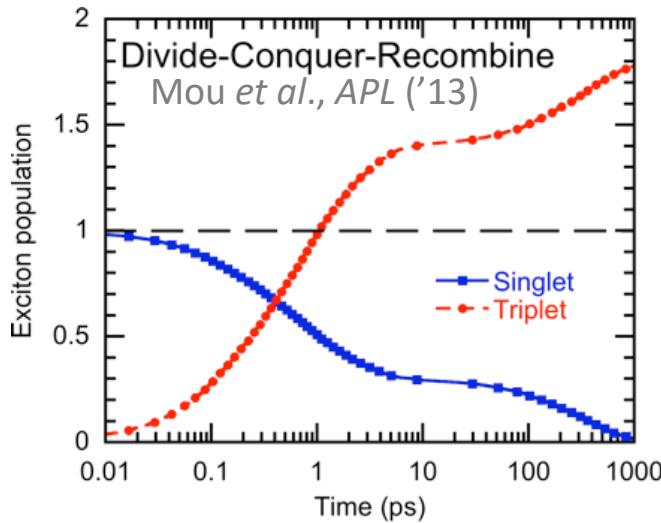
Kinetic Monte Carlo

Experimental Length & Time Scales

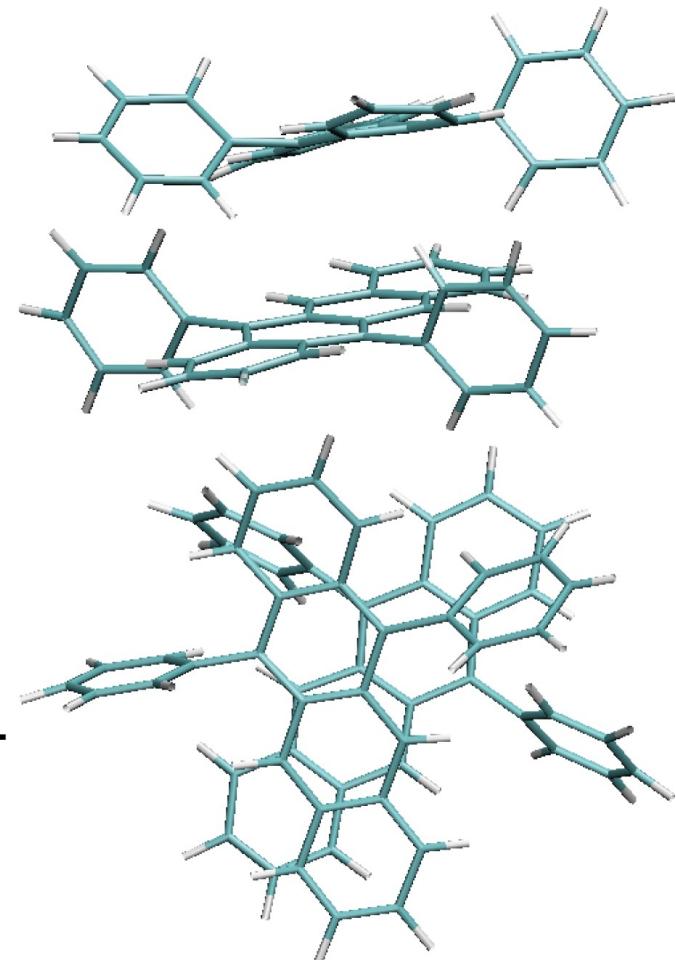


Singlet-Fission Hot Spot

- Nonadiabatic quantum molecular dynamics simulations not only reproduced experimentally measured exciton population dynamics but also revealed unknown molecular geometry of singlet fission hot spots



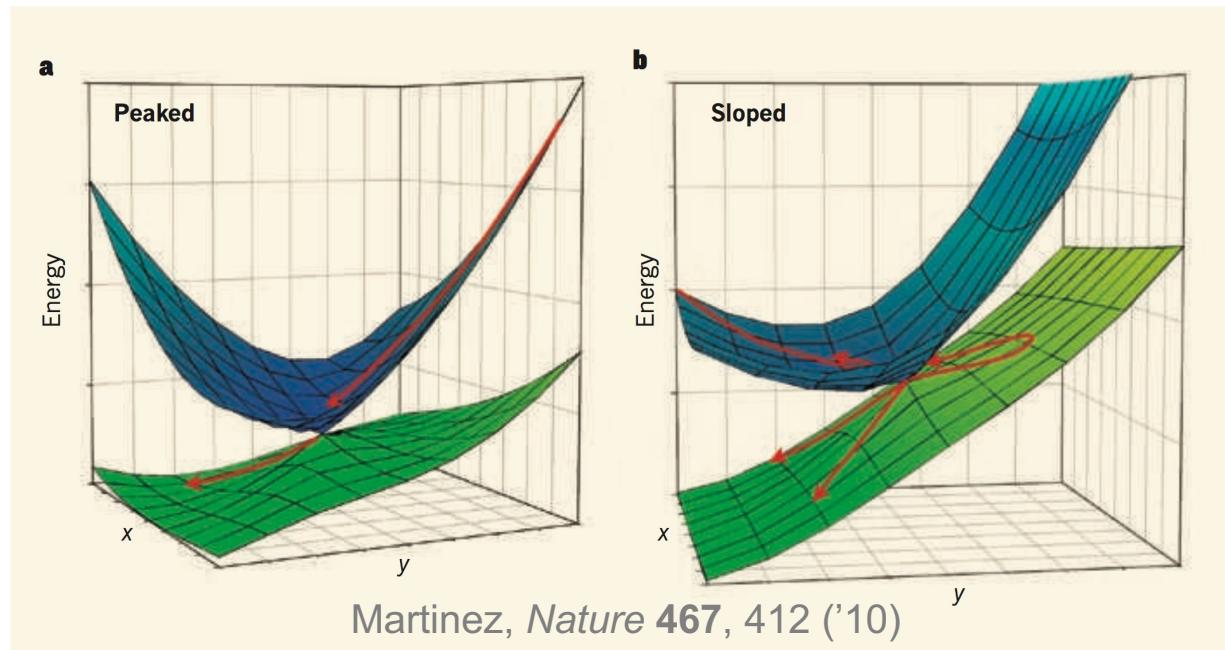
Side view
Top view



Caveats

- While the current QXMD code can excite many independent electron-hole pairs, the many-body treatment within LR-TDDFT is restricted to one electron-hole pair (divide-conquer-recombine approach to simulate many interaction electron-hole pairs is under construction)
- The current TDDFT xc functionals cannot adequately describe certain phenomena like conical intersection

Levine *et al.*, *Mol. Phys.* **104**, 1039 ('06); Yang *et al.*, *J. Phys. Chem. Lett.* **7**, 2407 ('16)



Beyond Adiabatic XC Kernel

- Time-dependence of the exchange-correlation (xc) functional in time-dependent density functional theory (TDDFT) is commonly ignored (adiabatic xc kernel)
- Time-dependence like memory effects has been modeled by parametrizing higher-order dynamic correlations in dynamic mean-field theory (DMFT), also incorporating spin-flipping processes

Acharya *et al.*, Phys. Rev. Lett. 125, 017202 ('20)

