

Carrier localizations and transports in nanoscale disordered systems

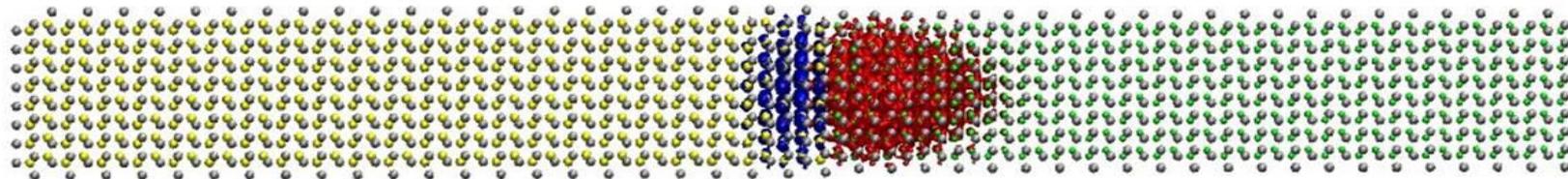
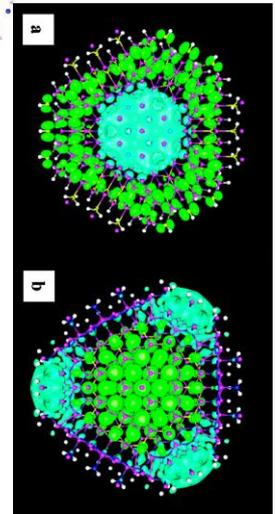
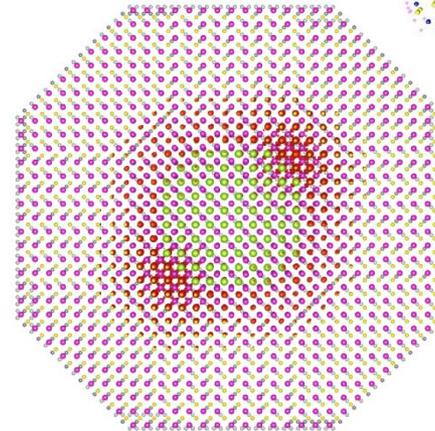
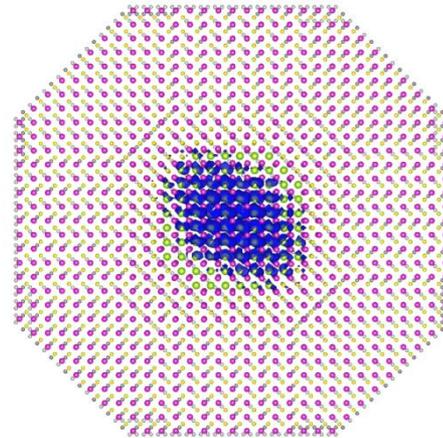
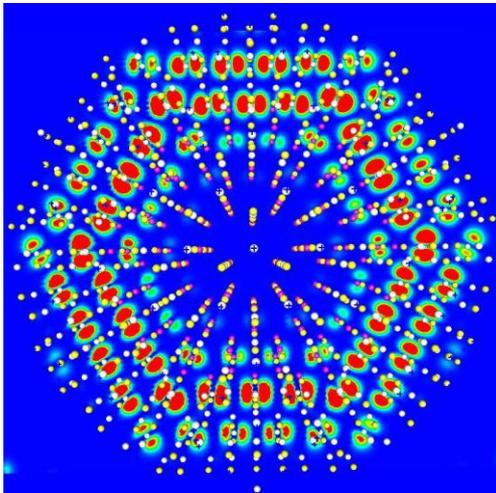
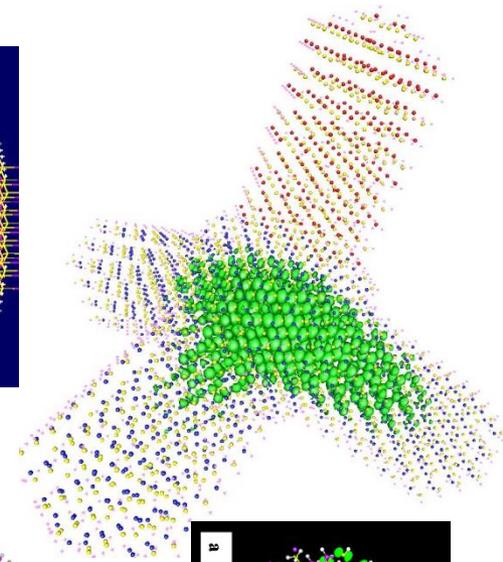
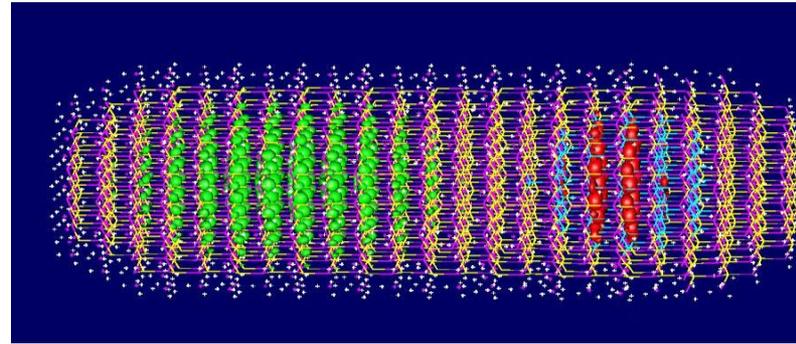
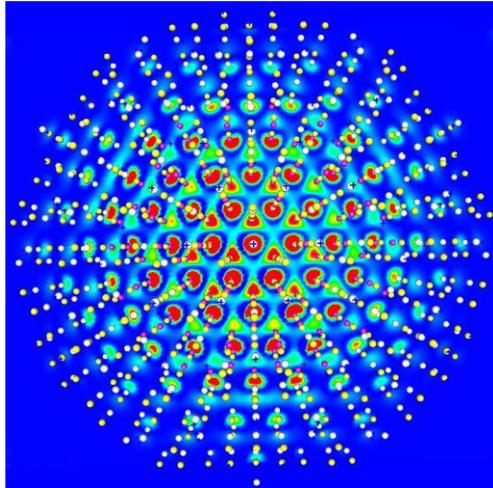
Lin-Wang Wang

Material Science Division
Lawrence Berkeley National Laboratory

US Department of Energy
BES, Office of Science

INCITE Project
NERSC, NCCS, ALCF

Some examples of nanocrystals calculations



- ❖ **Plasmon excitation and decay for a Ag55 nanocluster**
- ❖ **Charge transfer calculation using Marcus theory**
- ❖ **Carrier localization and mobility in hybrid perovskite**

$$i \frac{\partial}{\partial t} \psi(t) = H[R(t)]\psi(t)$$

$$\psi(t) = \sum_i C(i,t)\phi_i(t)$$

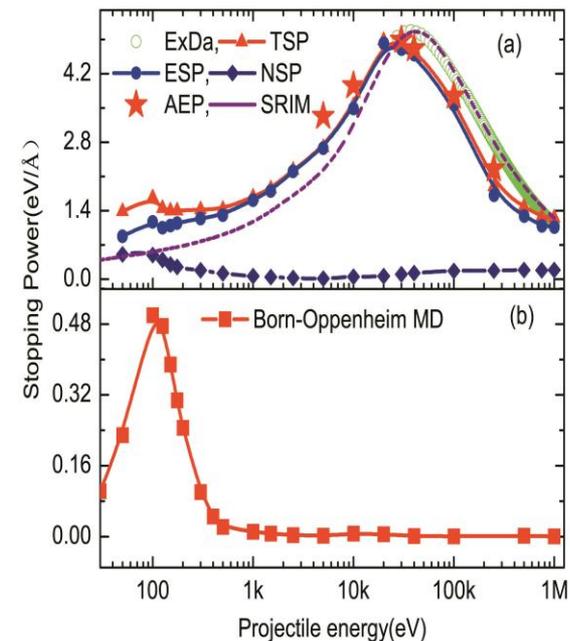
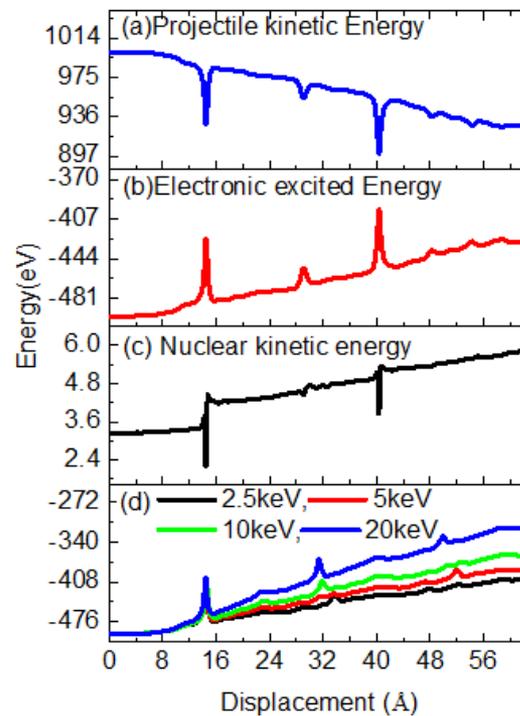
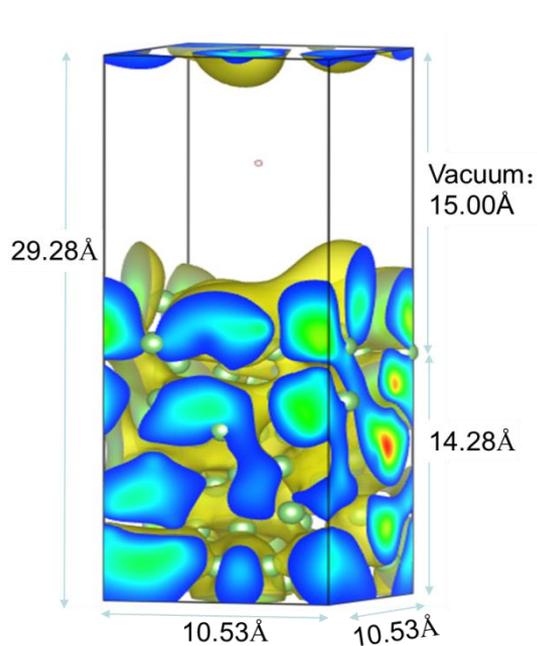
$$H[R(t)]\phi_i(t) = \varepsilon_i(t)\phi_i(t)$$

$$\dot{C}(i,t) = -i\varepsilon_i(t)C(i,t) - \sum_j C(j,t)V_{ij}$$

$$V_{ij} = \left[\langle \phi_i(t) | \phi_j(t + \delta t) \rangle - \delta_{ij} \right] / \delta t$$

This allows us to increase the effective time step to ~0.2fs

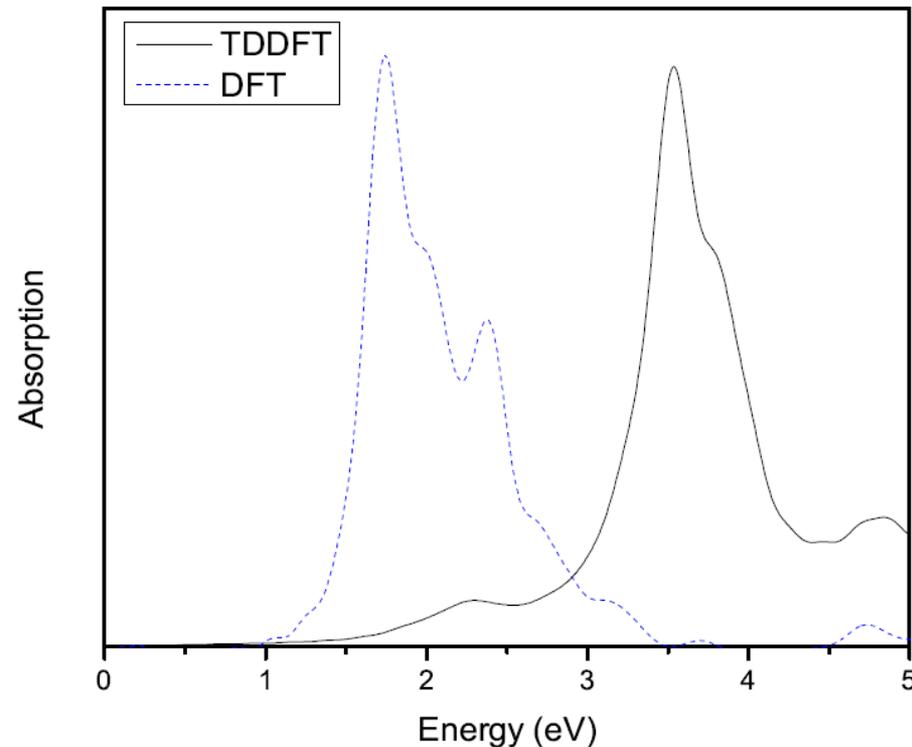
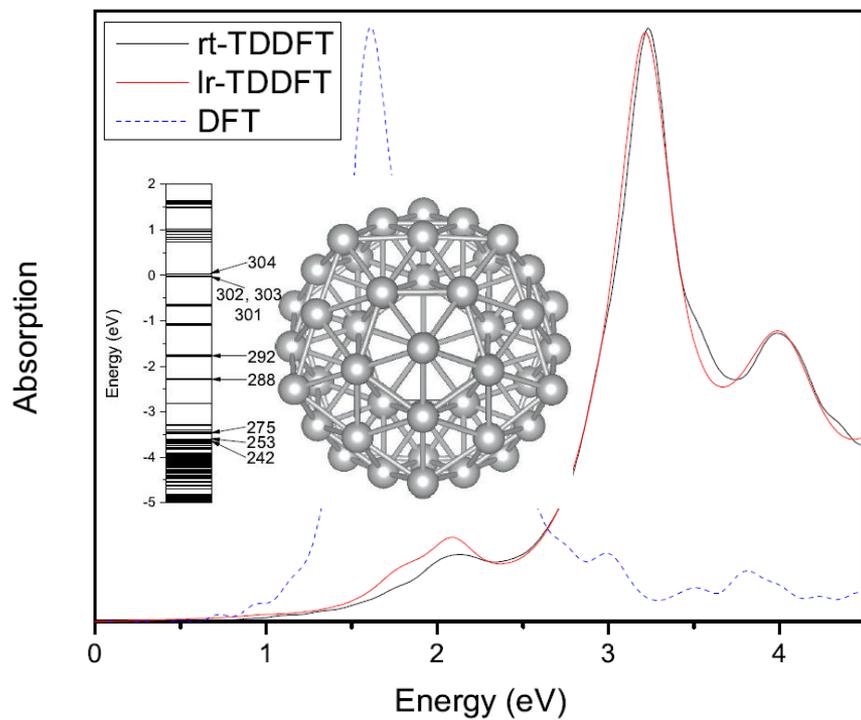
Wang, et.al, P.R.L, 114, 063004 (2015)



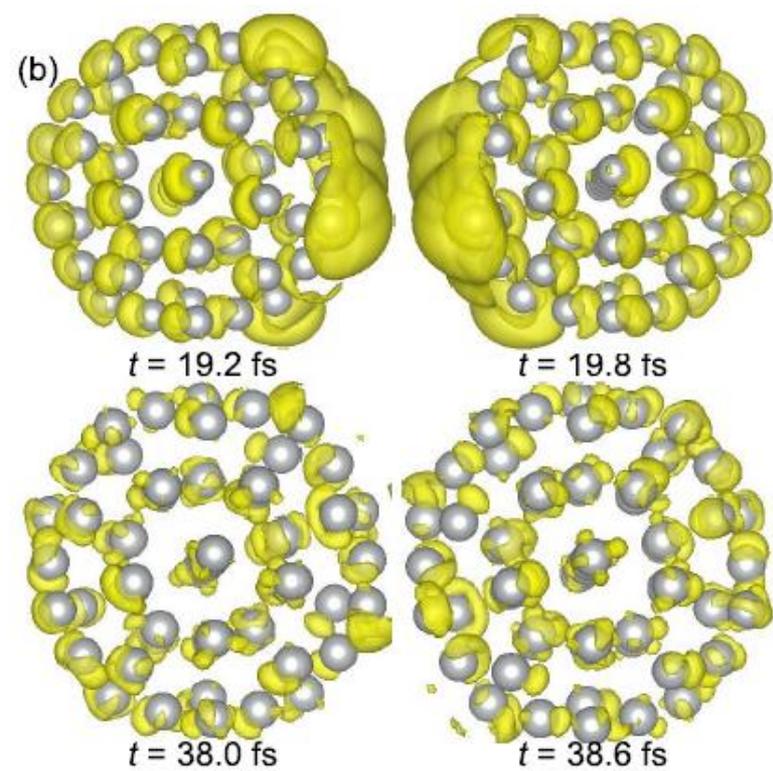
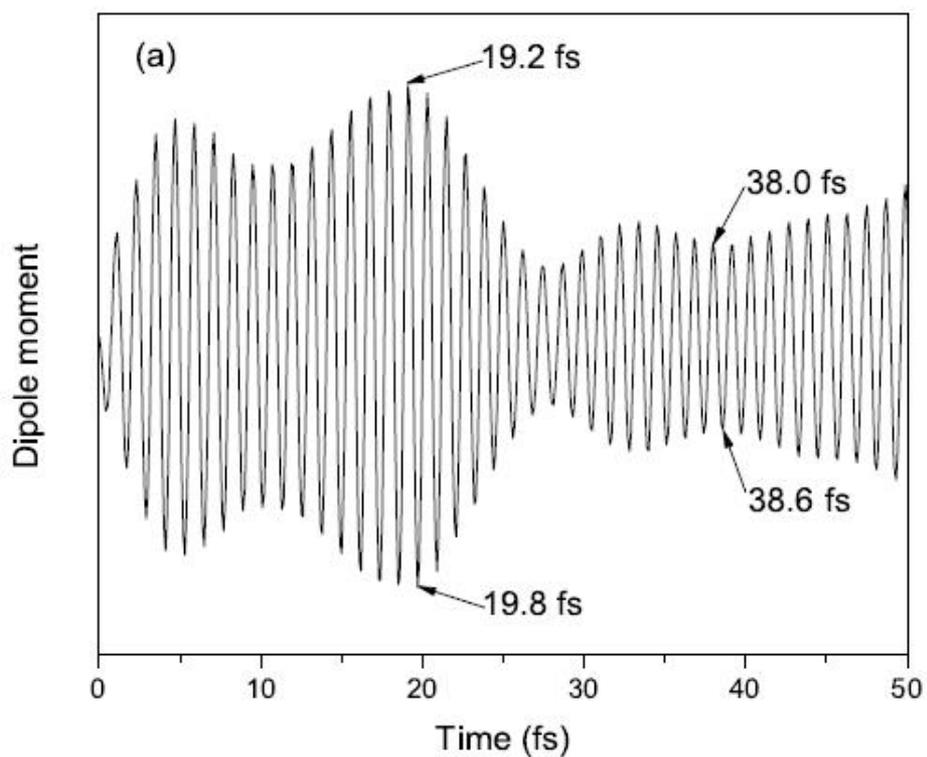
- ◆ Rt-TDDFT agrees with
- ◆ LR-TDDFT

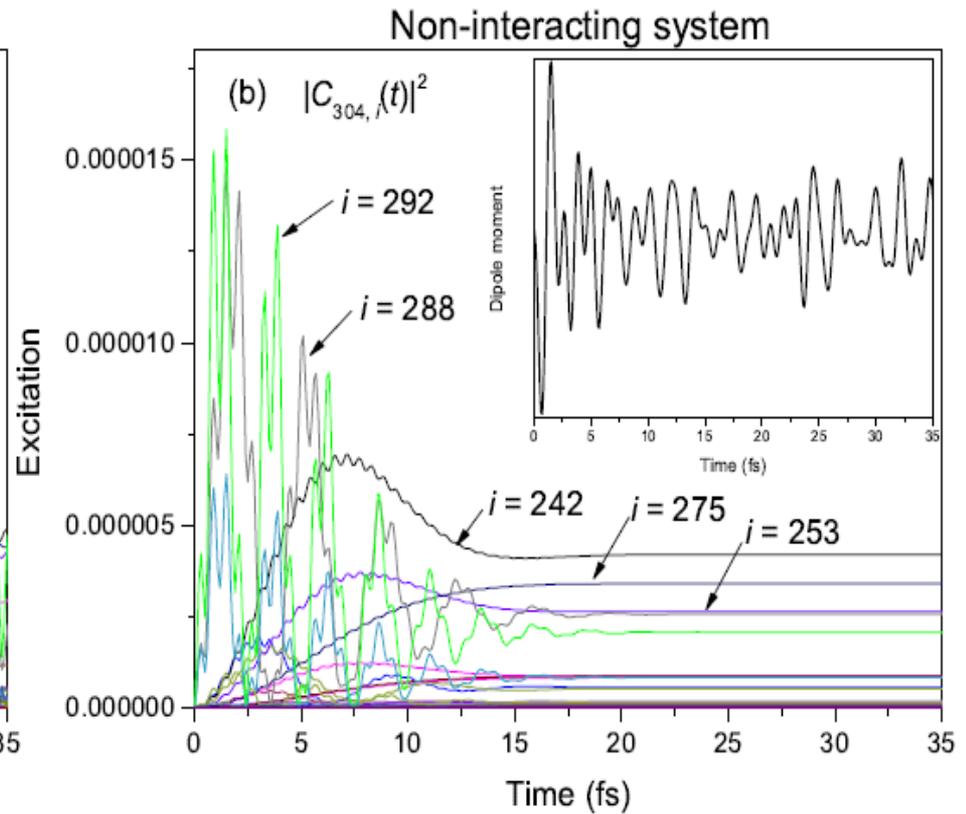
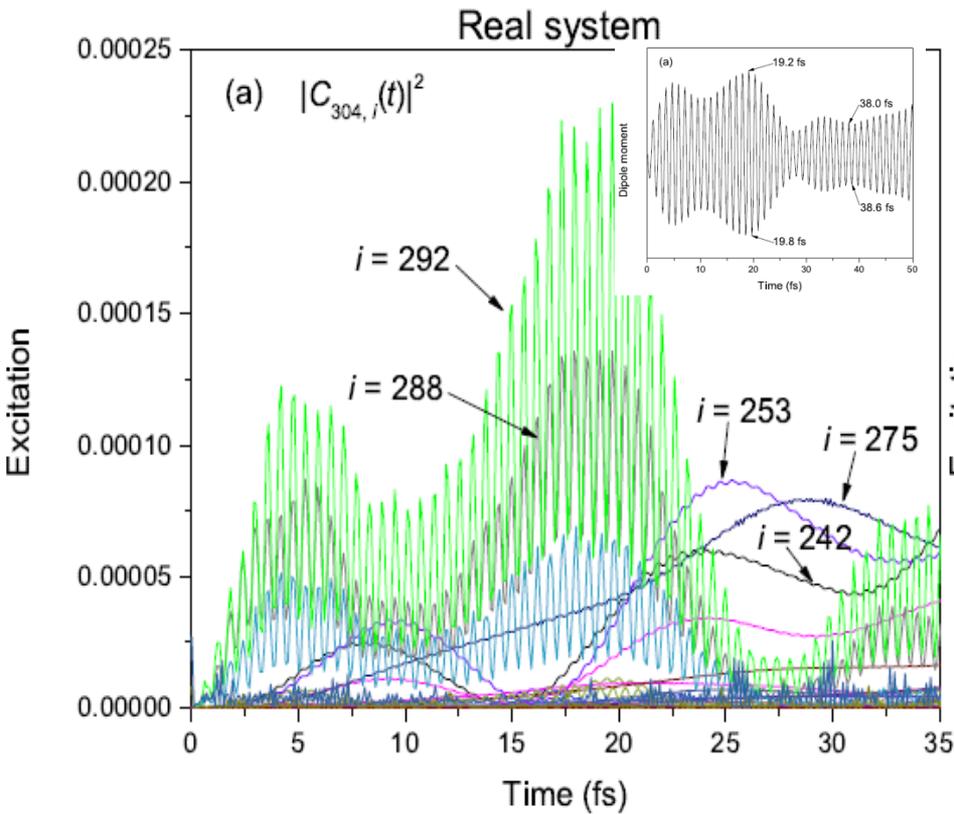
Ag55 cluster

↓ Plasmon peak



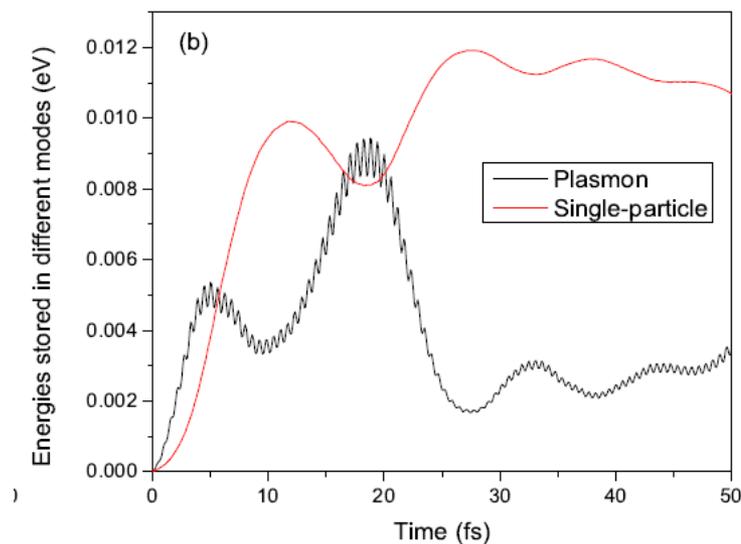
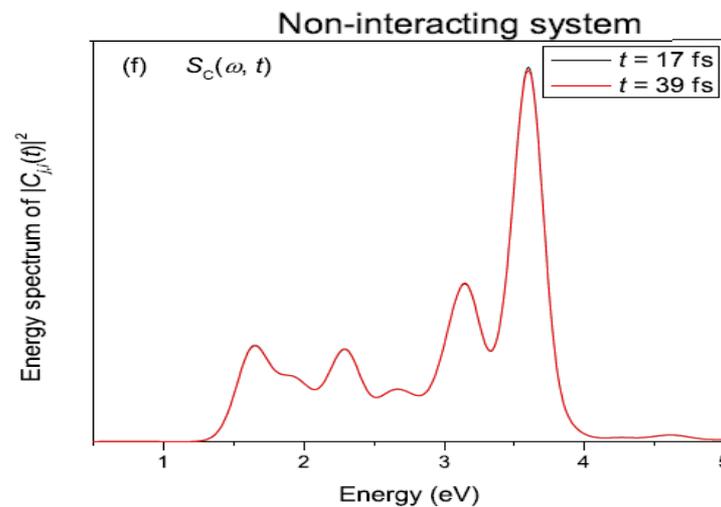
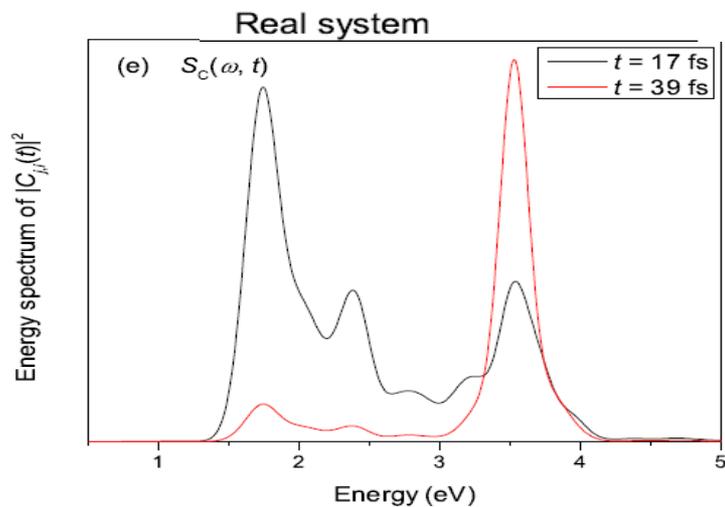
Dipole moment (t)



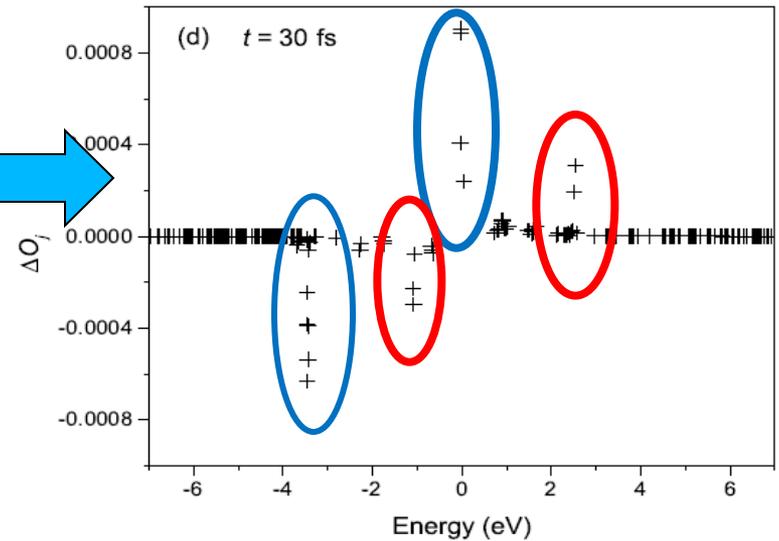
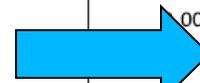
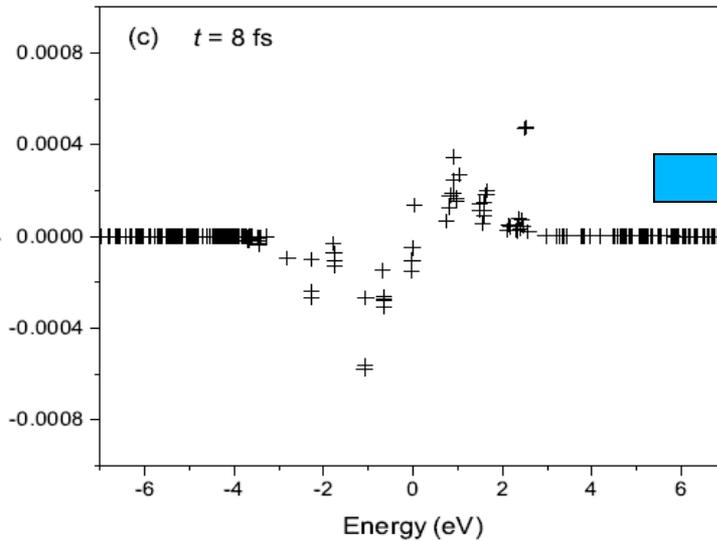


Energy spectrum of $C_{j,i}(t)$

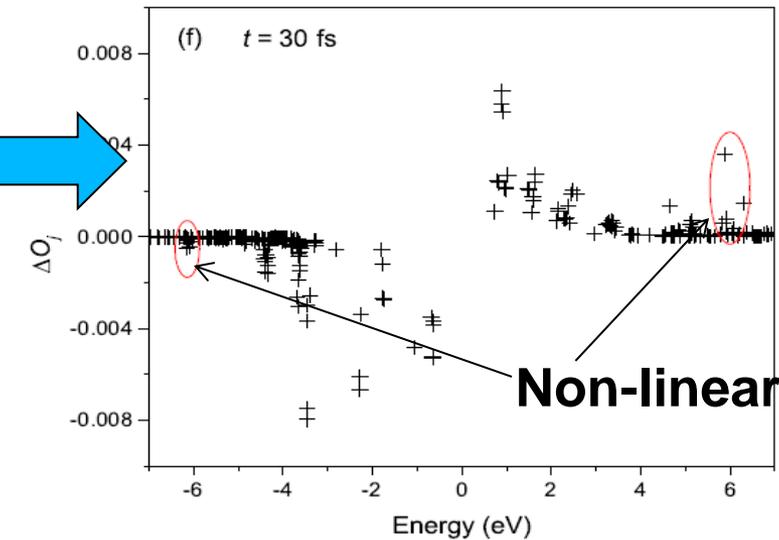
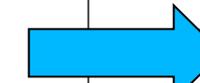
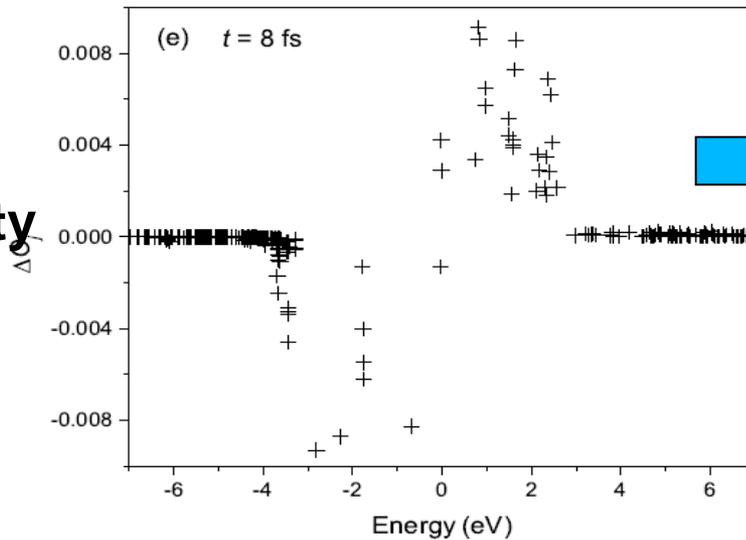
$$S_C(\omega, t) = \sum_{j,i} |C_{j,i}(t)|^2 \delta(\omega - |\omega_j - \omega_i|)$$

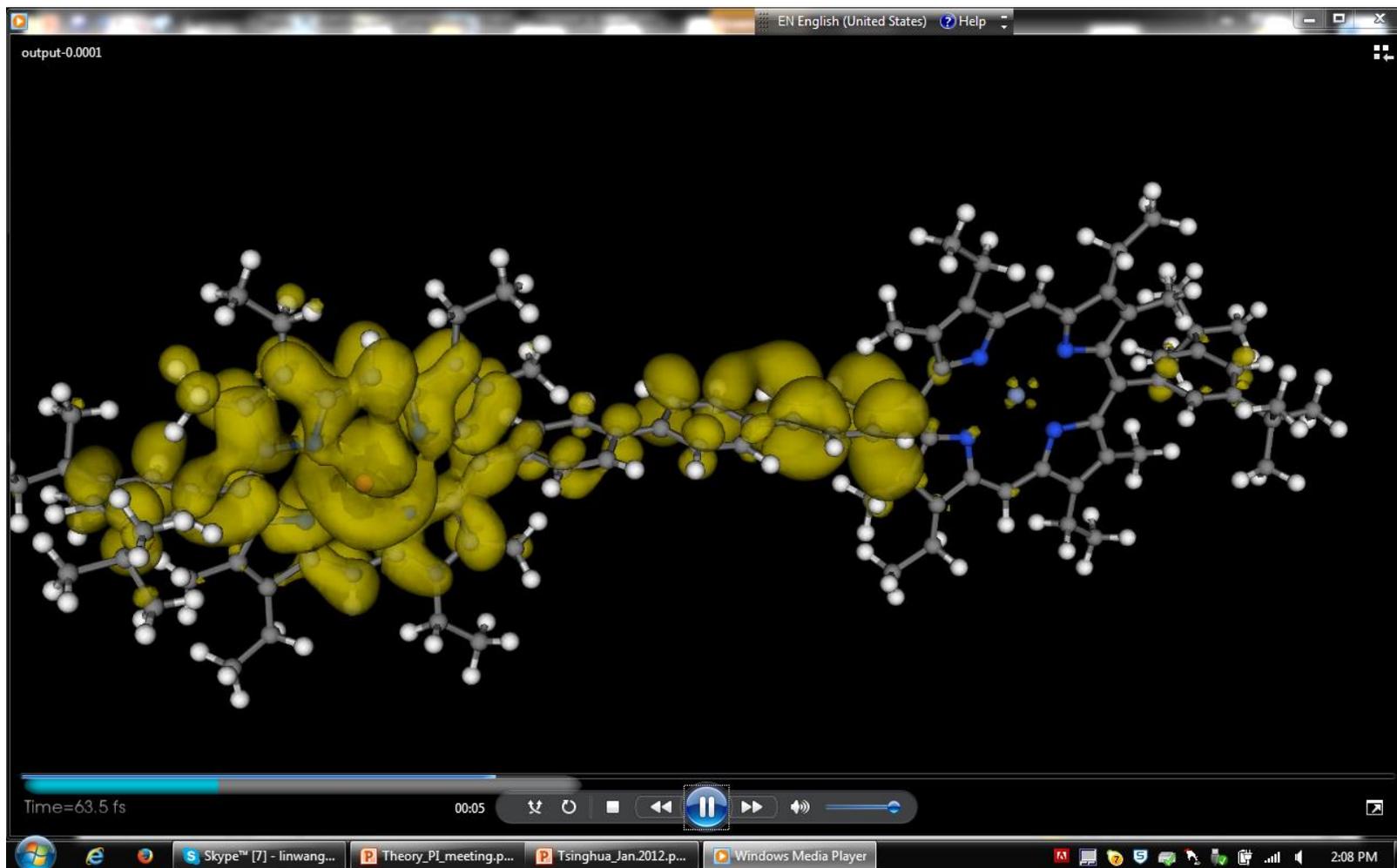


Low-intensity
laser



High-intensity
laser

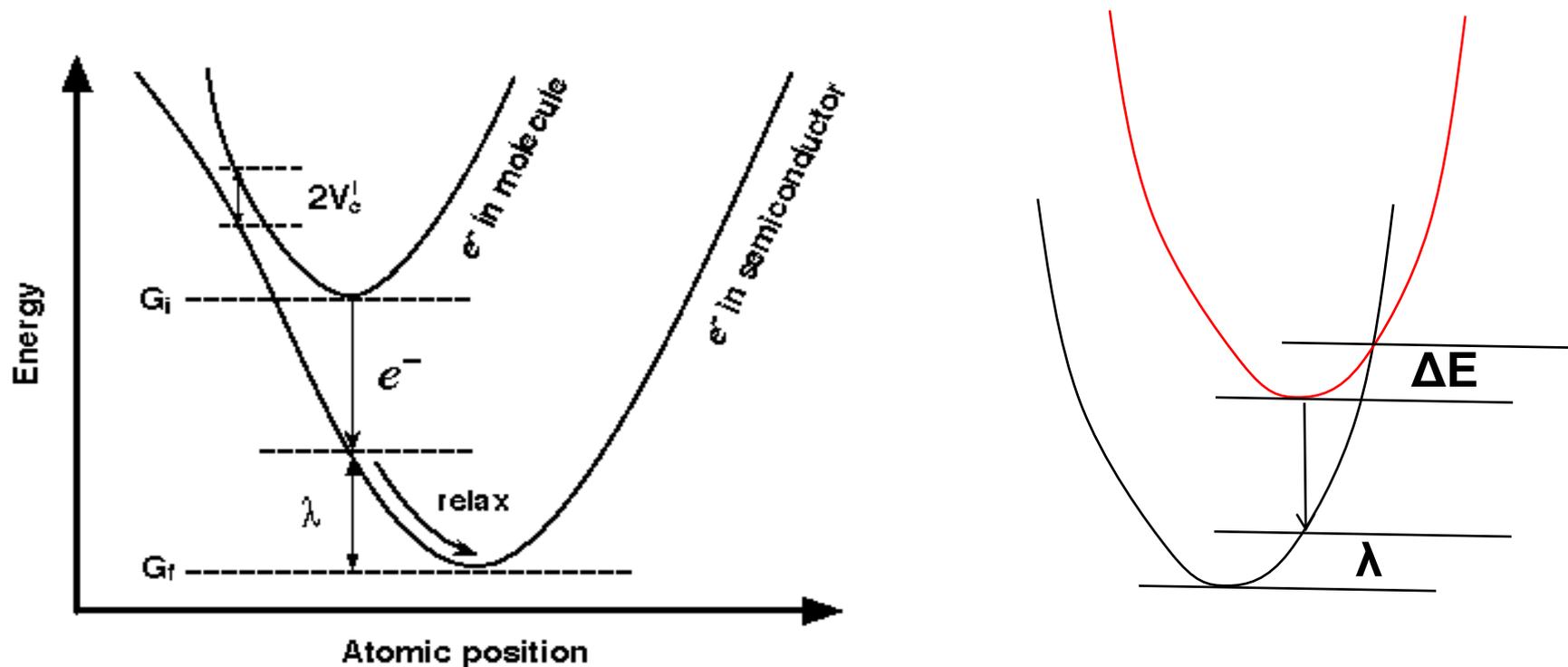




❖ Plasmon excitation and decay for a Ag55 nanocluster

❖ Charge transfer calculation using Marcus theory

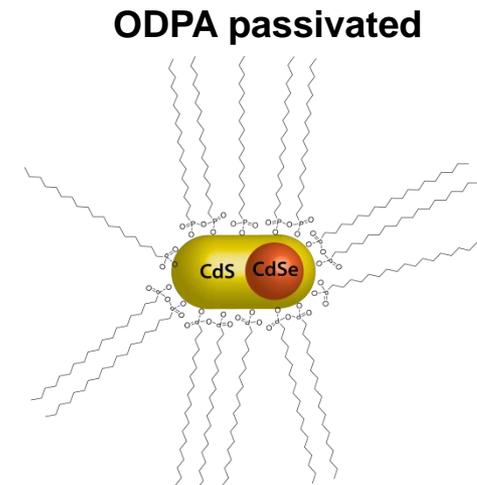
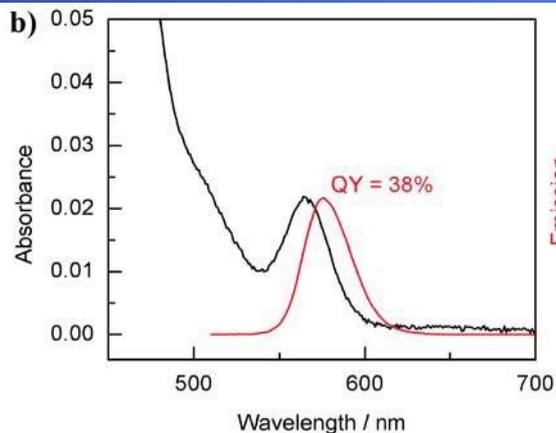
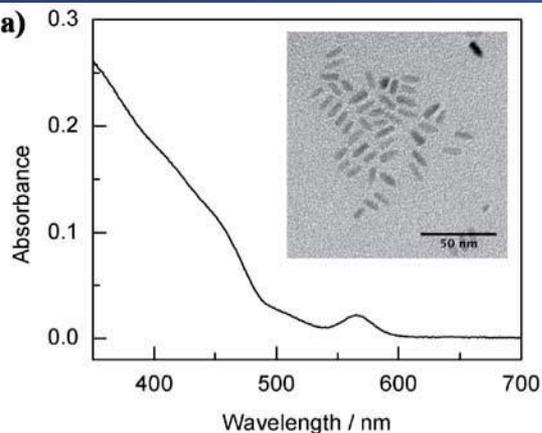
❖ Carrier localization and mobility in hybrid perovskite



$$\text{Rate} = V_{ab}^2 \sqrt{\frac{\pi}{\lambda k T \hbar}} \underbrace{\exp\left[-(\lambda + \varepsilon_a - \varepsilon_b)^2 / 4 \lambda k T\right]}_{\exp(-\Delta E/kT)}$$

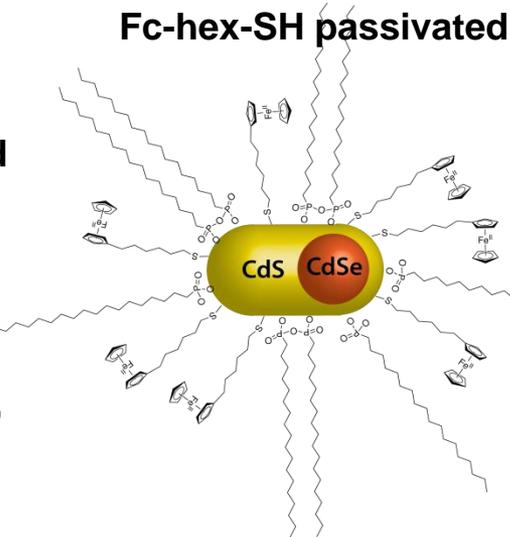
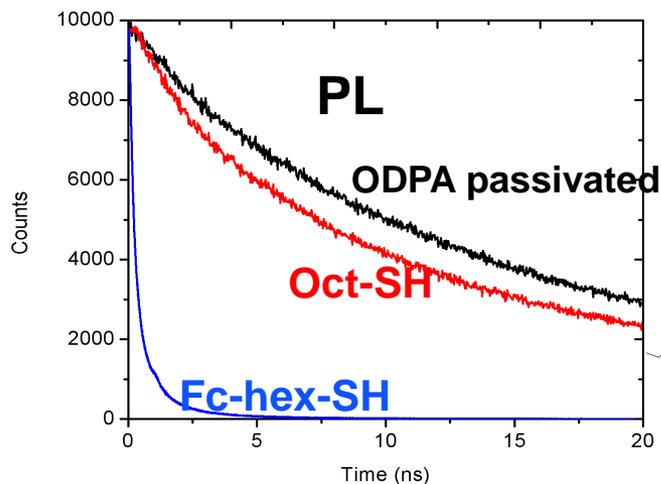
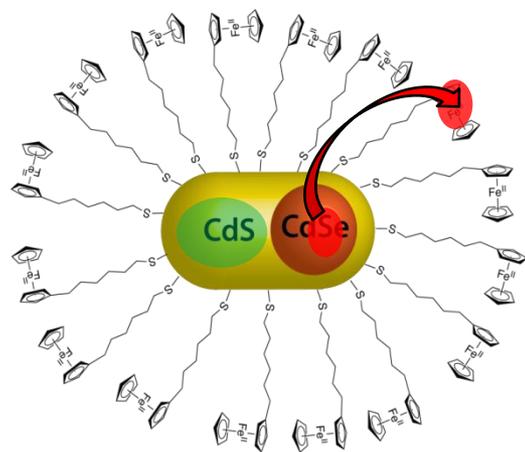
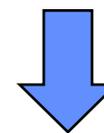
↑
Landau-Zener rate
exp(-ΔE/kT)

The experiments

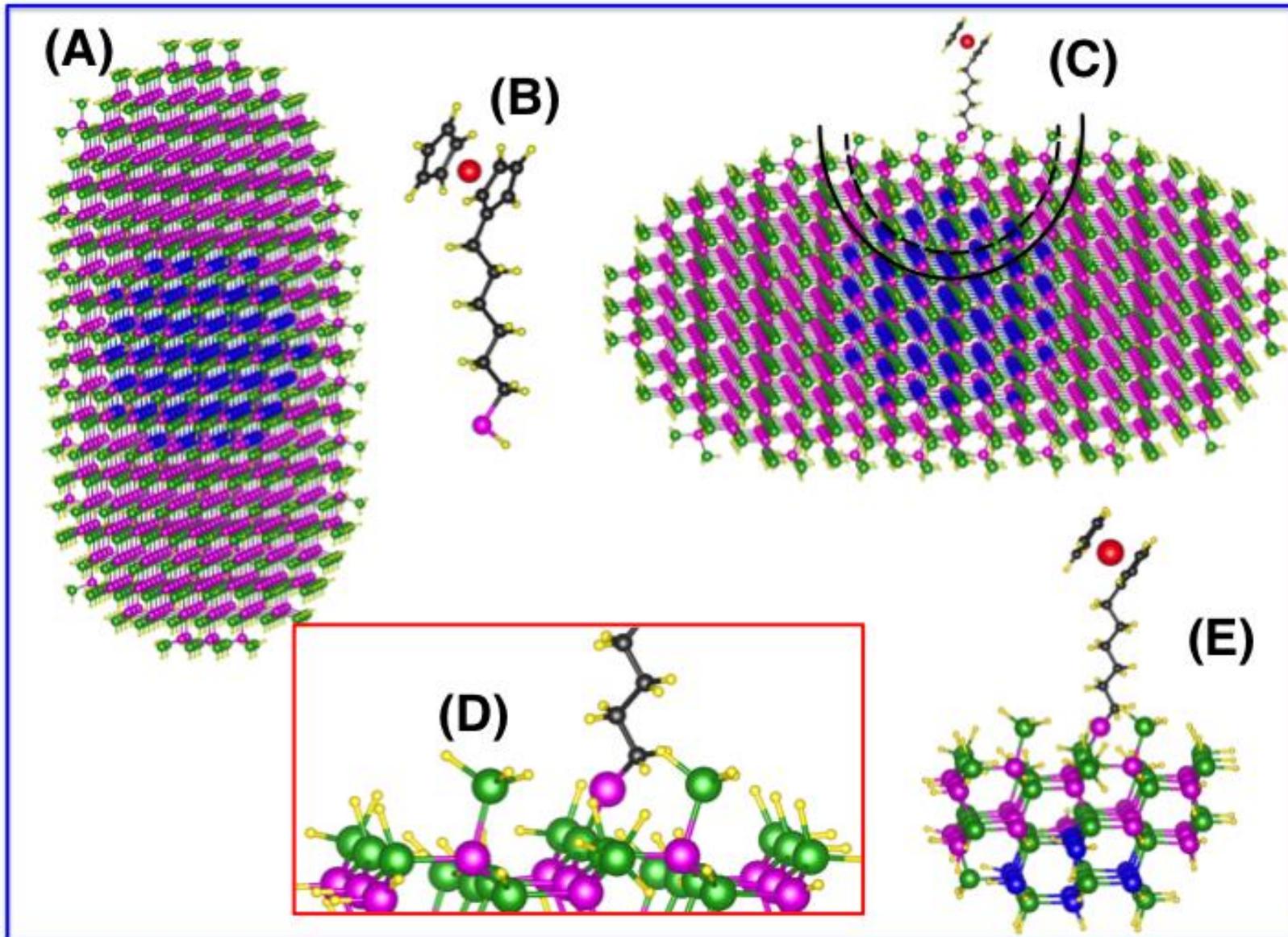


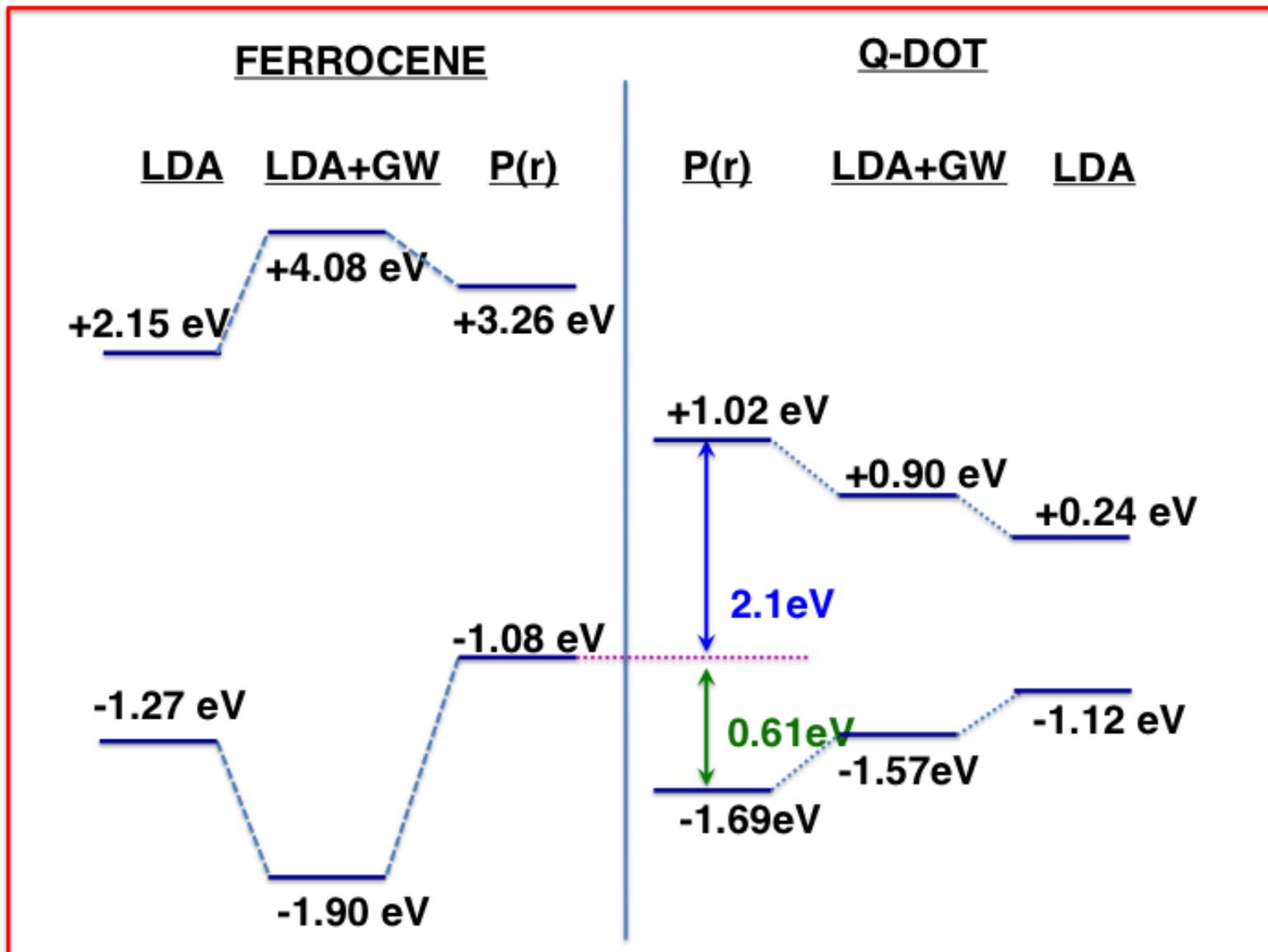
4.4nm wide /11 nm long CdSe/CdS core seeded nanorod

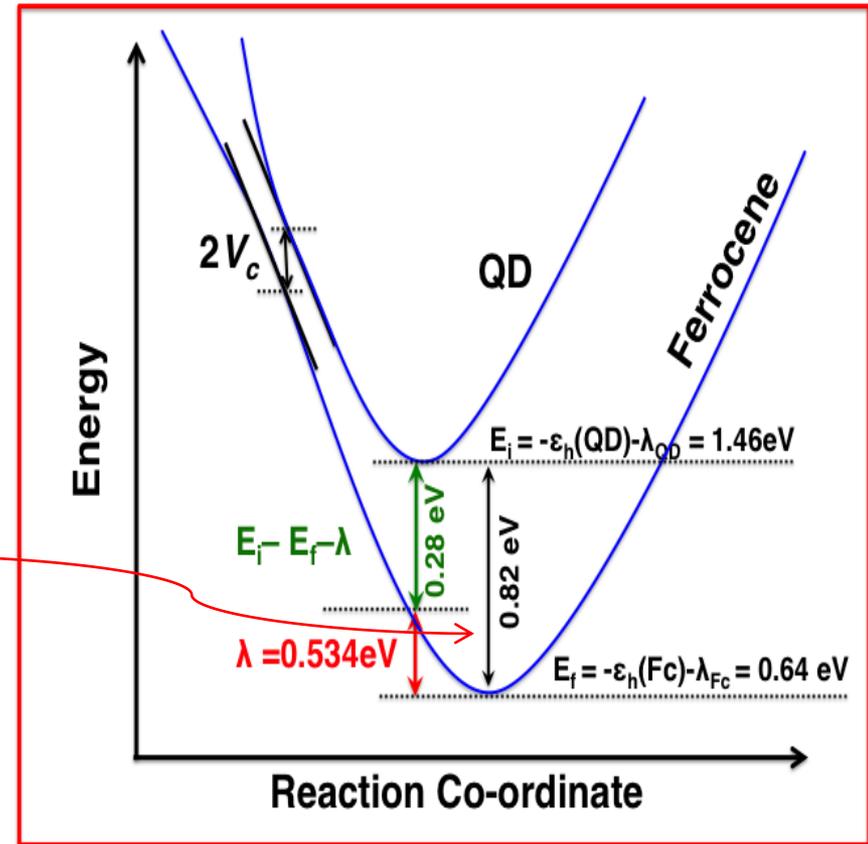
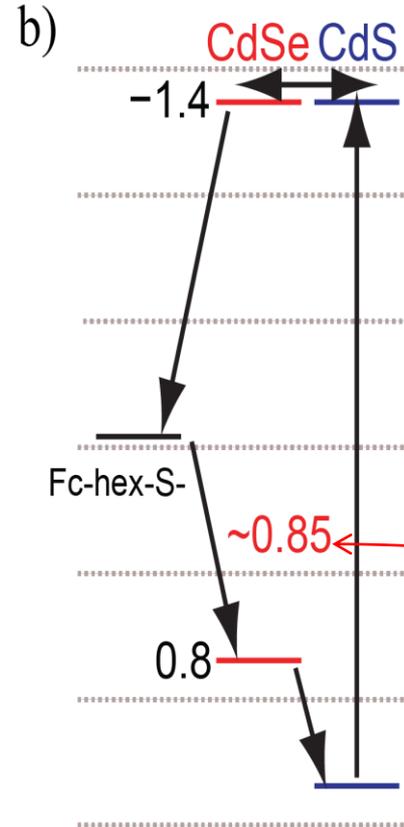
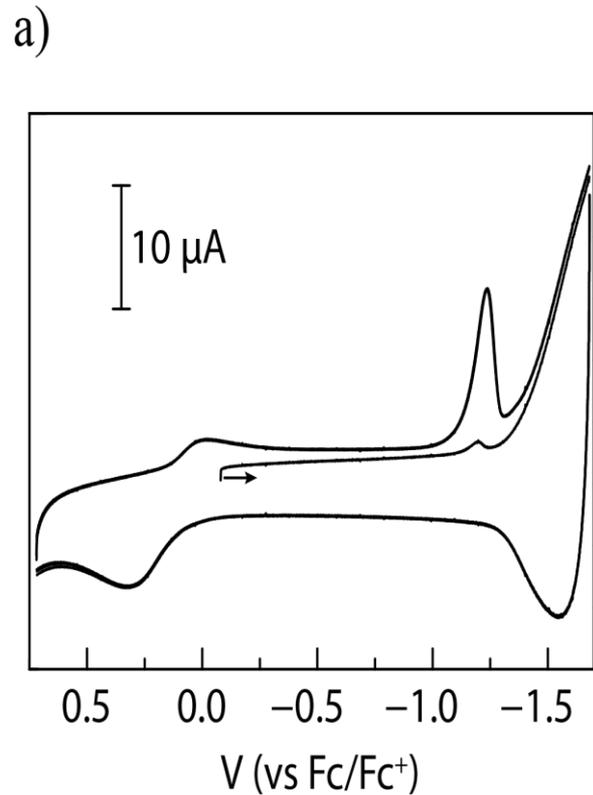
Ligand exchange



CdSe/CdS-Ferrocene system



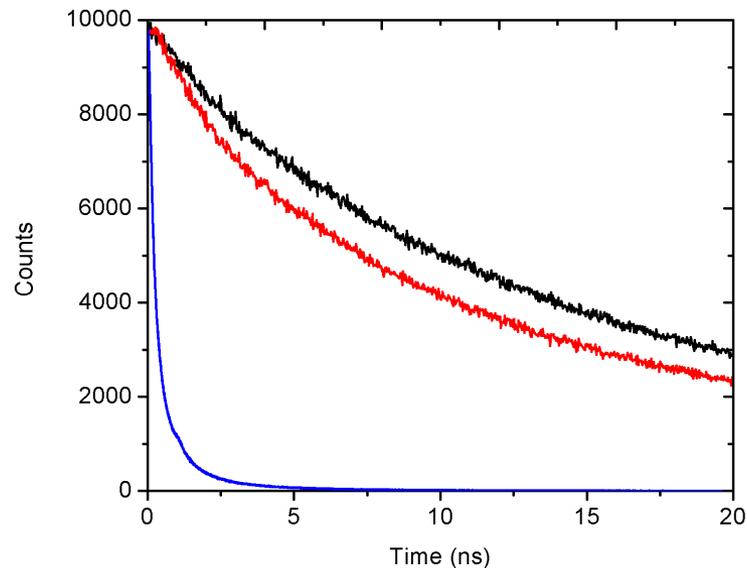
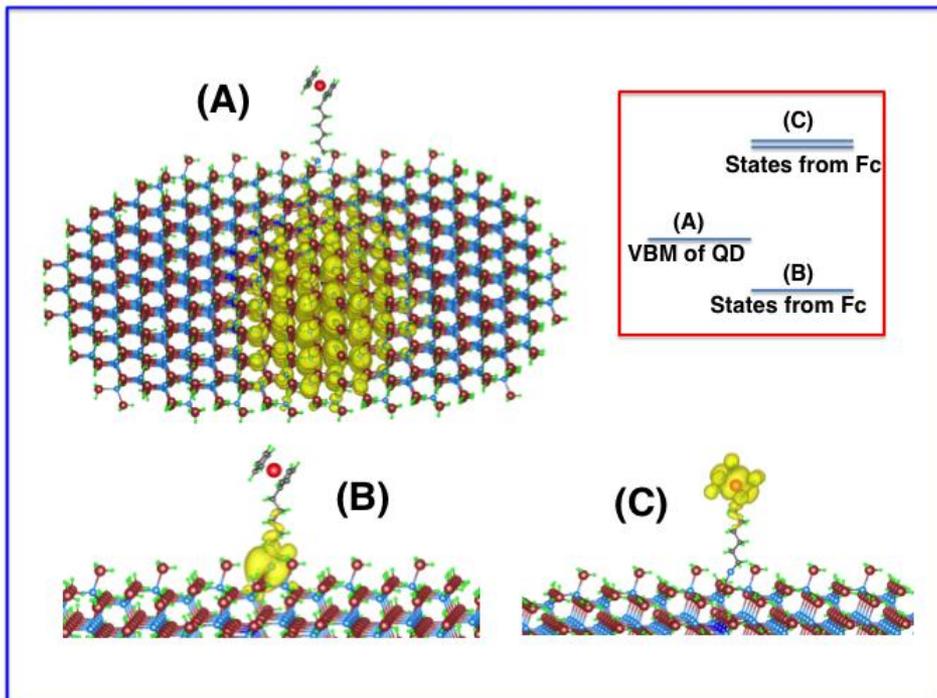




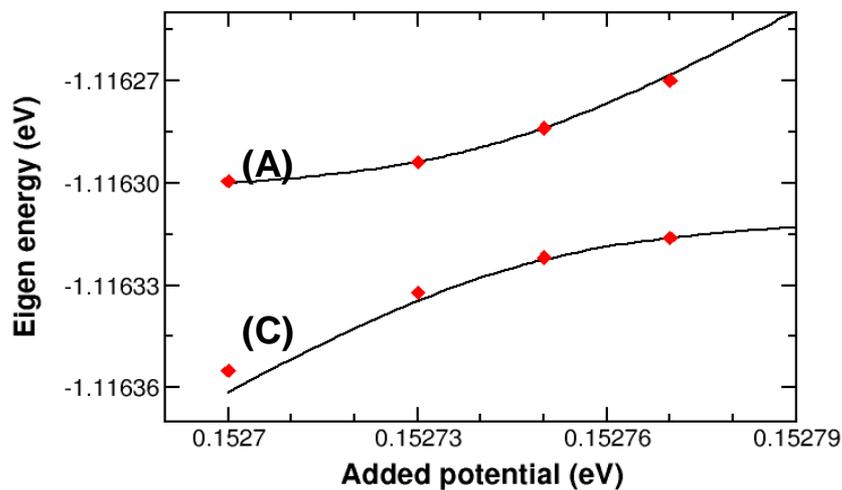
system	λ_{cc}^{at}	λ_{cc}^{sol}	λ_{CT}^{sol}
Ferrocene	48	390	348
QD	138	93	(meV)

$$E_i = E(N) - [\epsilon_h(QD) + \lambda_{QD}]$$

$$E_f = E(N) - [\epsilon_h(Fc) + \lambda_{Fc}]$$



Experimental rate: **1/141 ps – 1/610 ps**

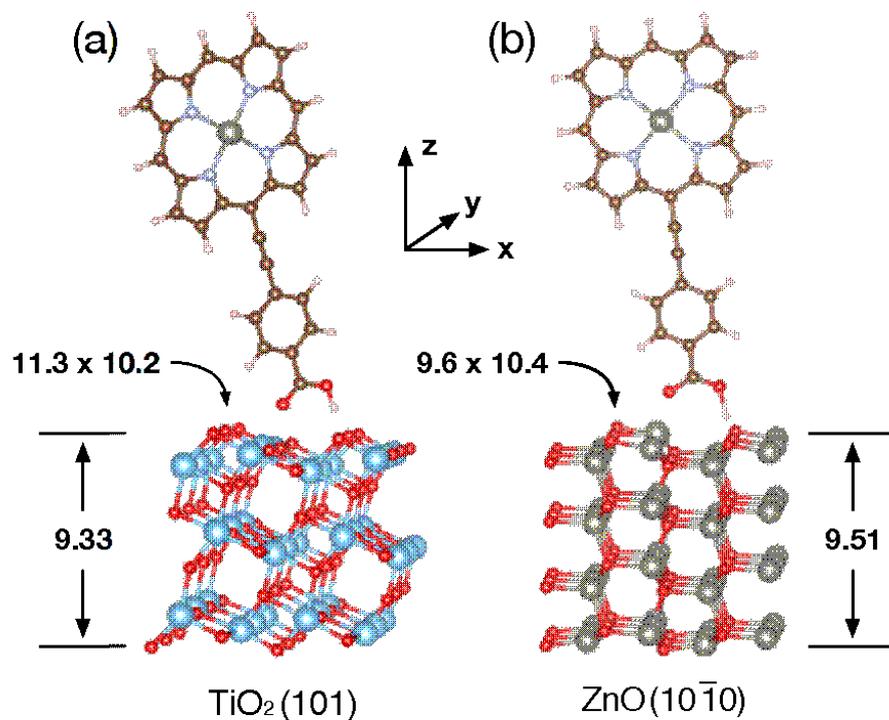


$$Rate = V_{ab}^2 \sqrt{\frac{\pi}{\lambda k T \hbar}} \exp[-(\lambda + \varepsilon_a - \varepsilon_b)^2 / 4 \lambda k T]$$

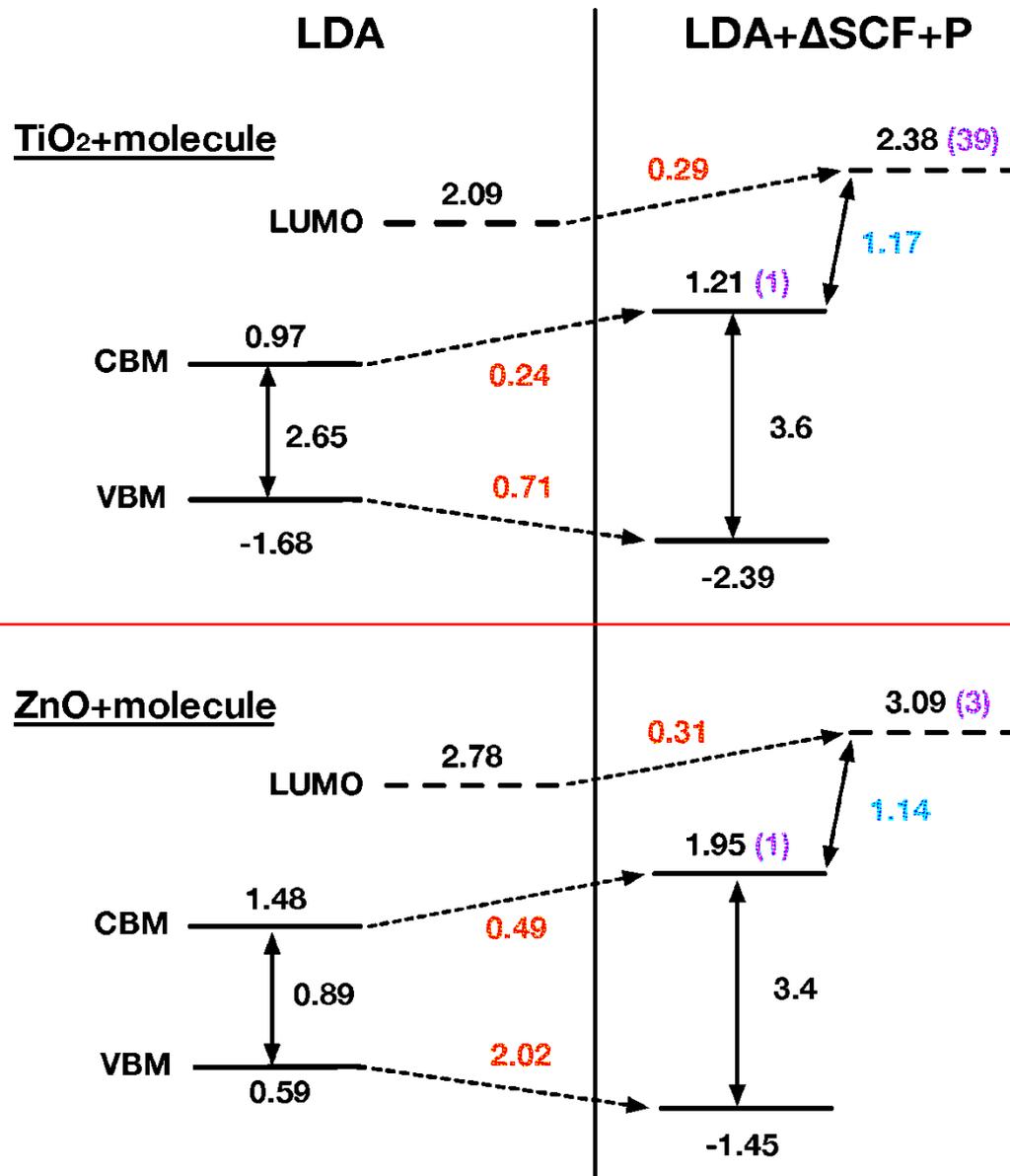
Calculated rate = **1/388 ps**

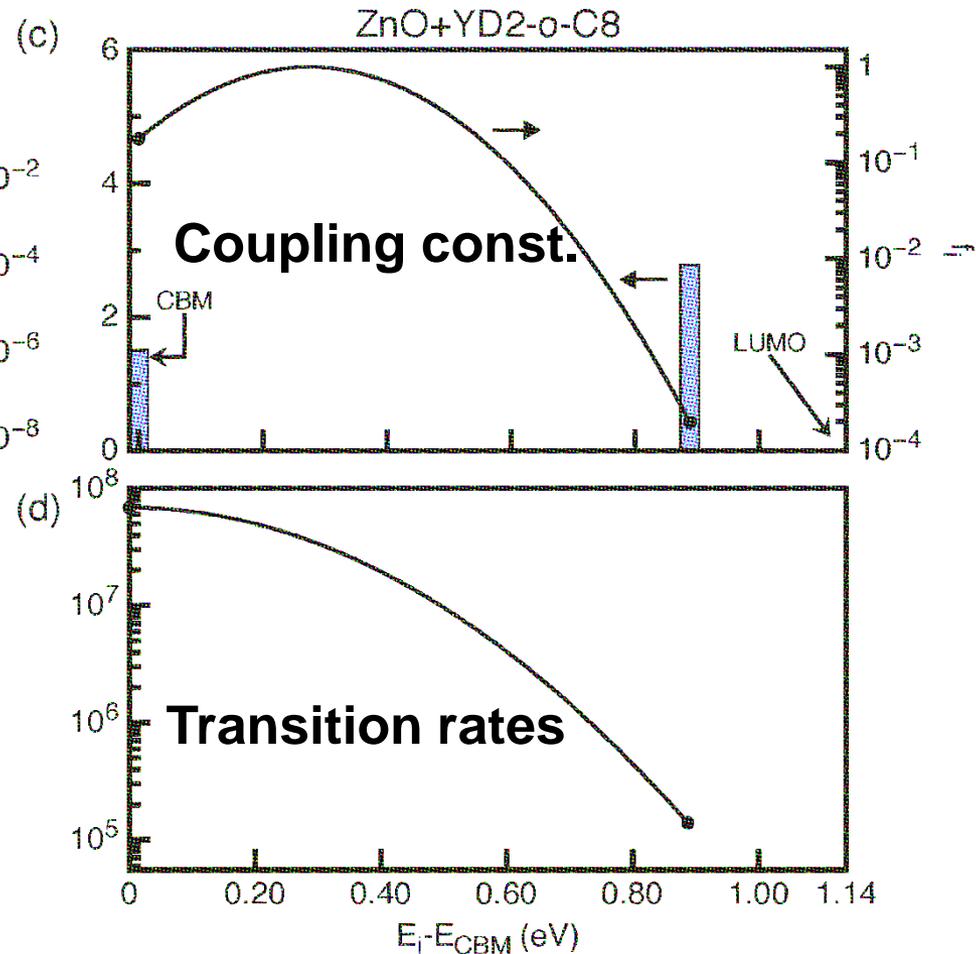
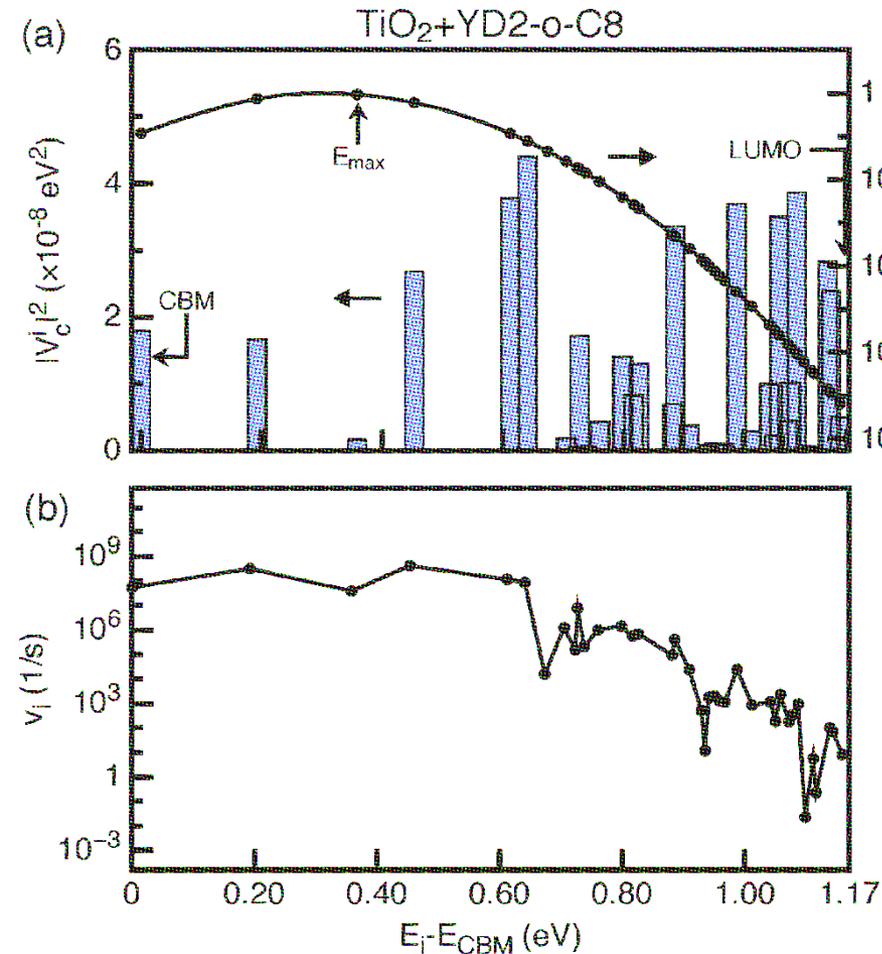
Dye sensitized solar cell: Why TiO₂ is better

- ❖ ZnO has much higher electron mobility
- ❖ The band gap and alignments for ZnO, TiO₂ are similar
- ❖ Like to replace TiO₂ with ZnO
- ❖ But experimentally, they found TiO₂ is much better



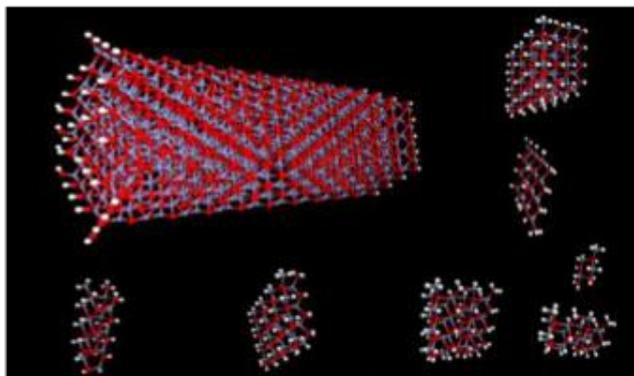
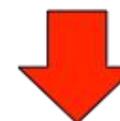
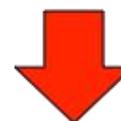
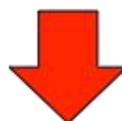
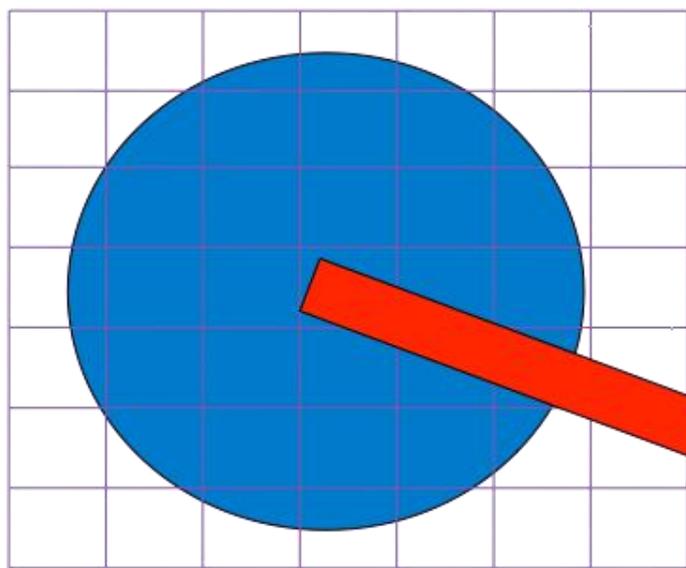
Eigen energy correction from LDA results

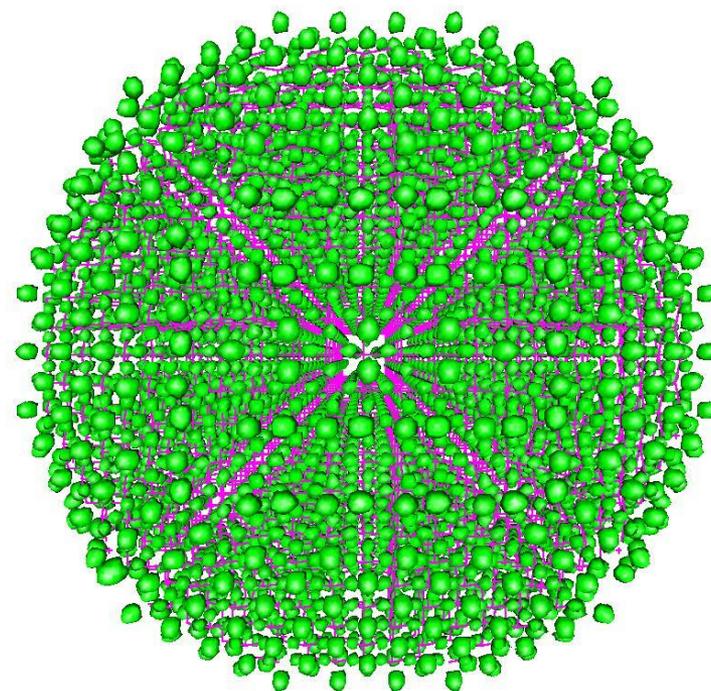
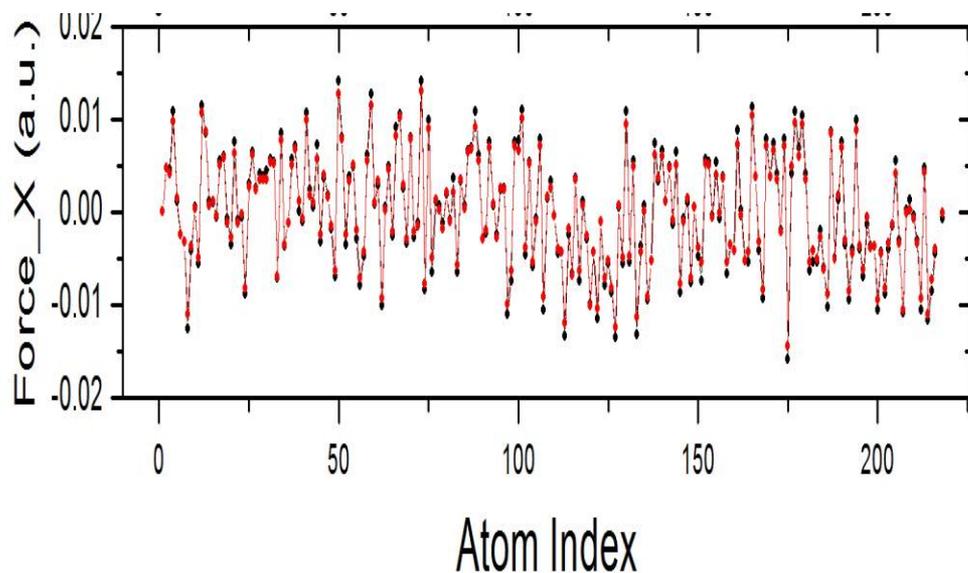




- ❖ Plasmon excitation and decay for a Ag55 nanocluster
- ❖ Charge transfer calculation using Marcus theory
- ❖ Carrier localization and mobility in hybrid perovskite

The parallelization of LS3DF

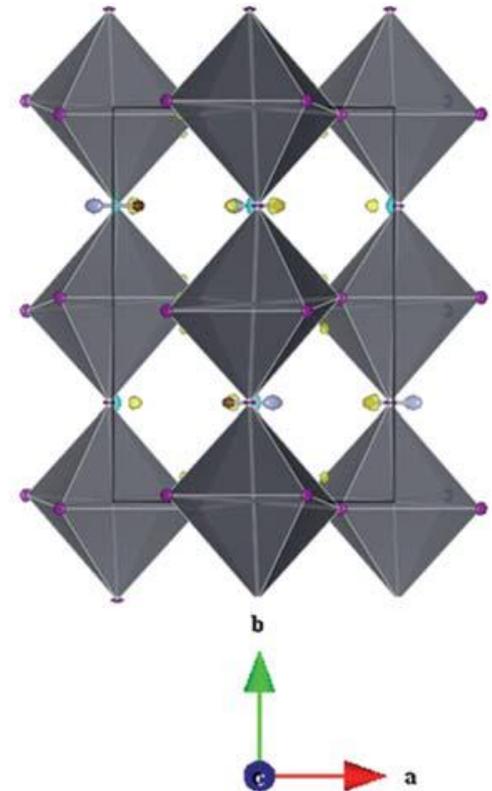
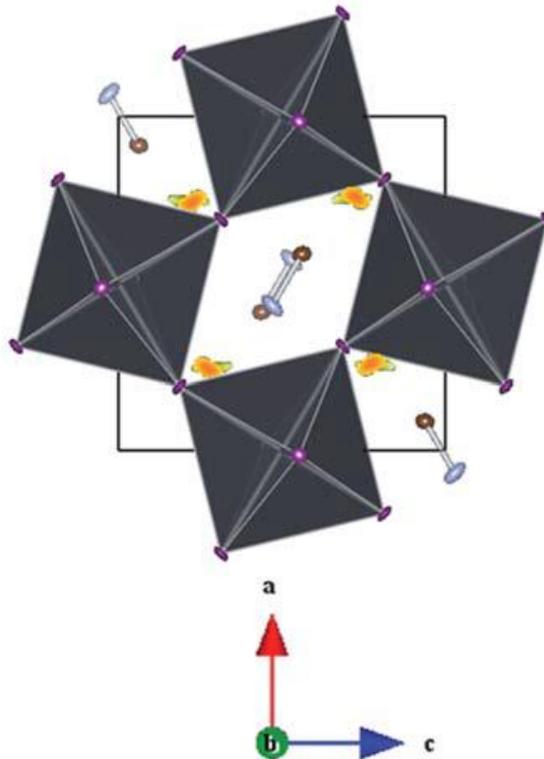
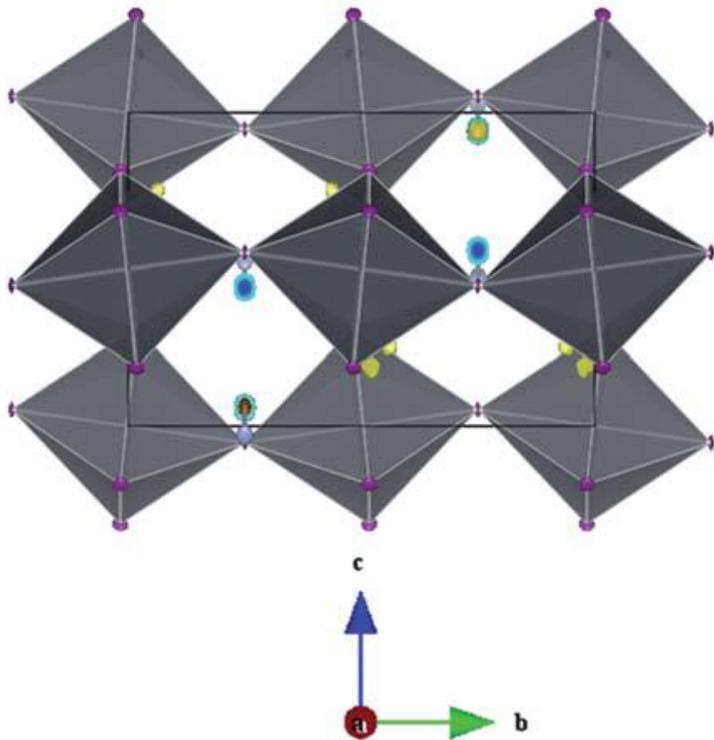




**For a 5000 atom system,
It takes about ~10 minutes
per atomic relaxation step
using 50,000 processors**

Plane-Wave nonlocal Pseudopotential calculations ($E_{\text{cut}}=30\text{Ryd}$)

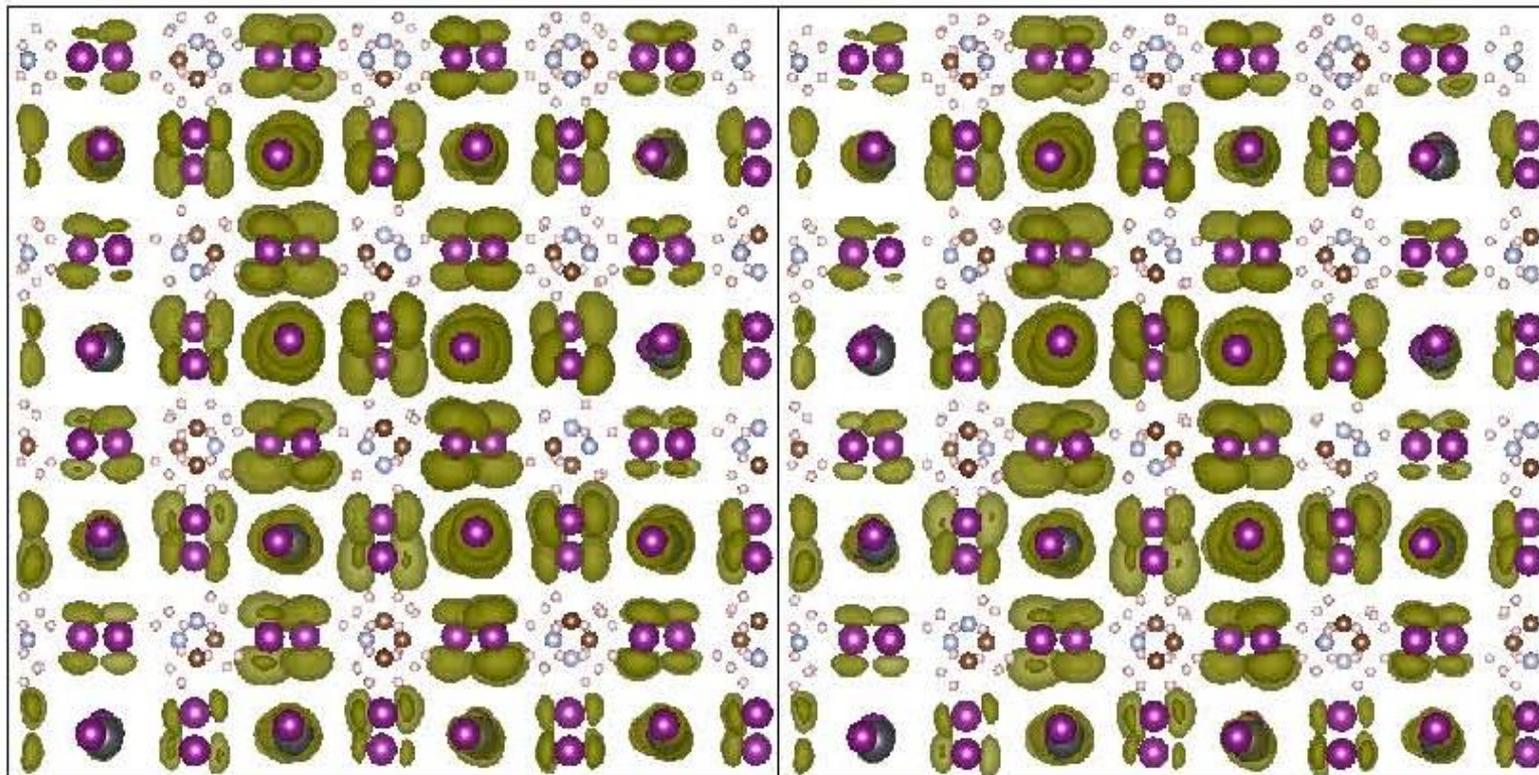
- ❖ There is no experimental evidence for the ferroelectricity
- ❖ The CH_3NH_3 has random orientation (8 possible directions)
- ❖ What is the electronic effects of this random orientation?



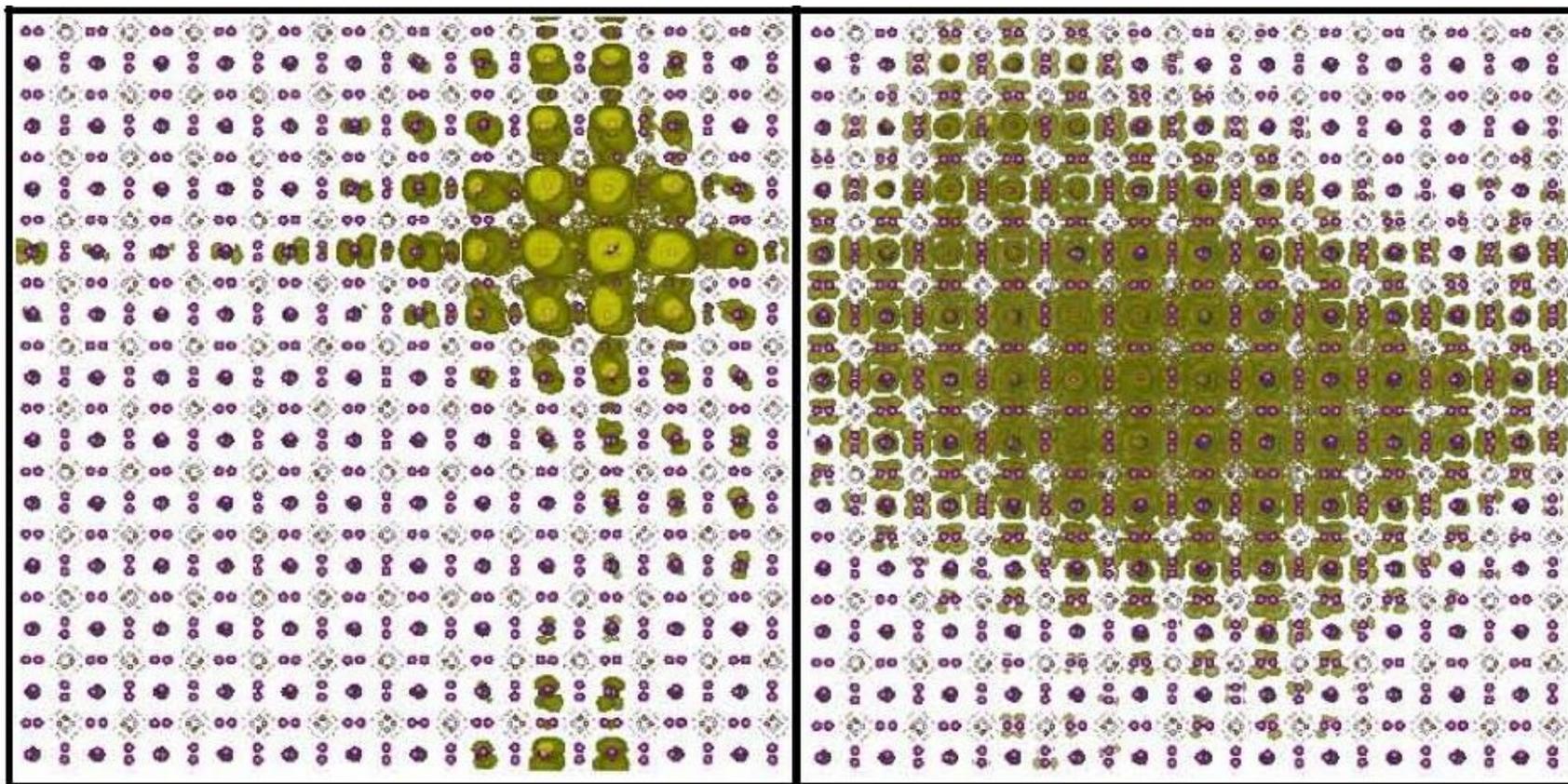
Comparison between LS3DF and direct DFT

LS3DF

PEtot



Hybrid (CH₃NH₃)PbI₃ perovskite: electron localization



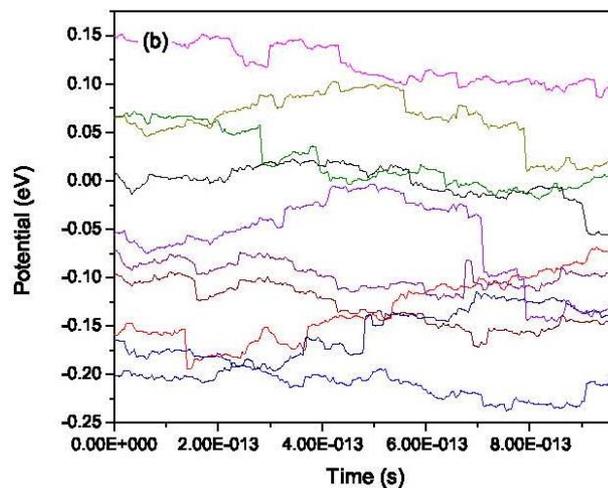
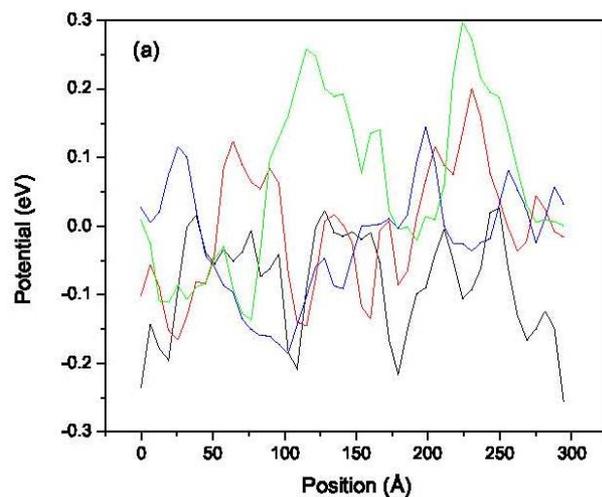
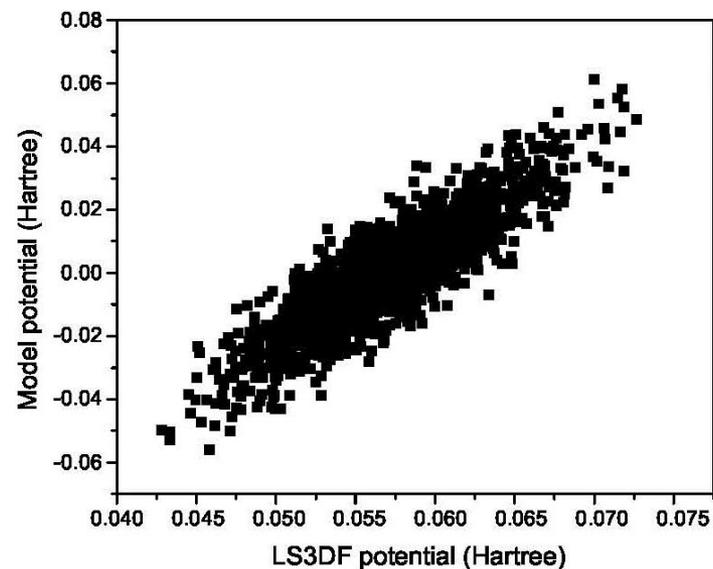
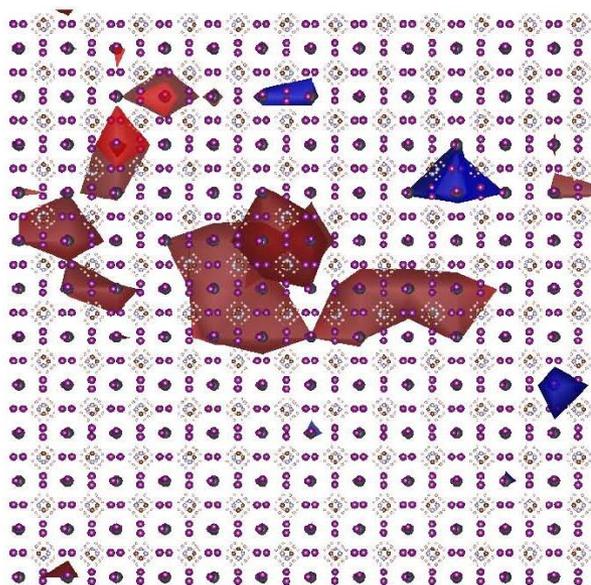
CBM

VBM

~20,000 atoms

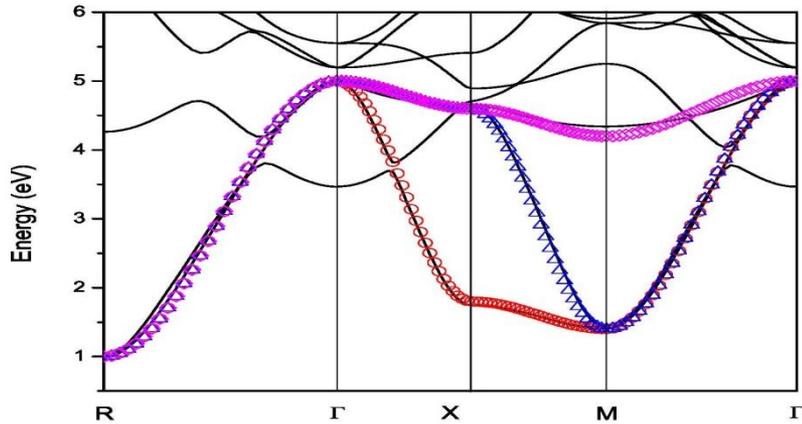
Using 60,000 processors, takes < 1 hour

Molecule orientation fluctuation cause electrostatic potential fluctuation

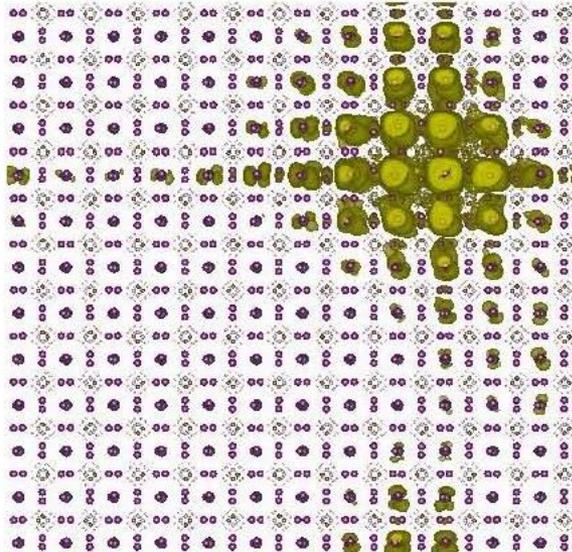


**Comparison between the DFT
calculated potential and model
dipole moment potential**

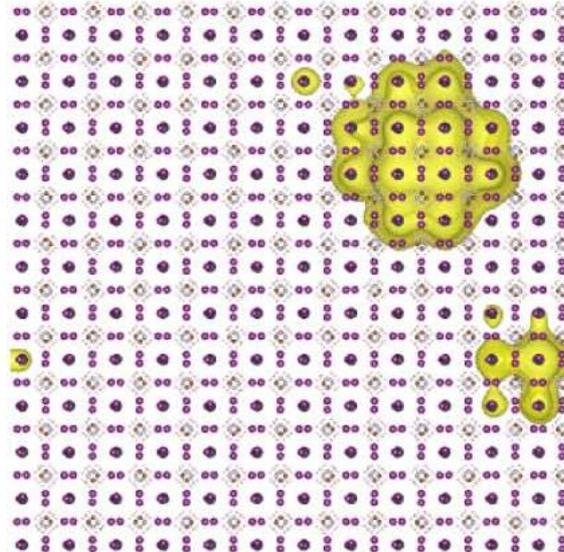
Tight-binding fitting of the MAPbI₃ Hamiltonian



ab initio



tight binding

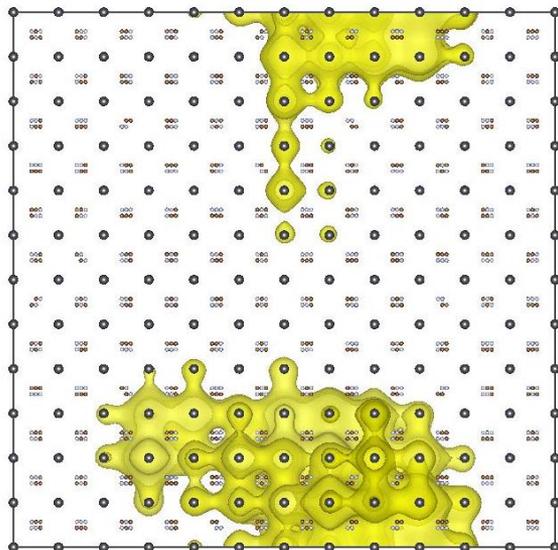


$$i \frac{\partial \varphi}{\partial t} = H(t) \varphi$$

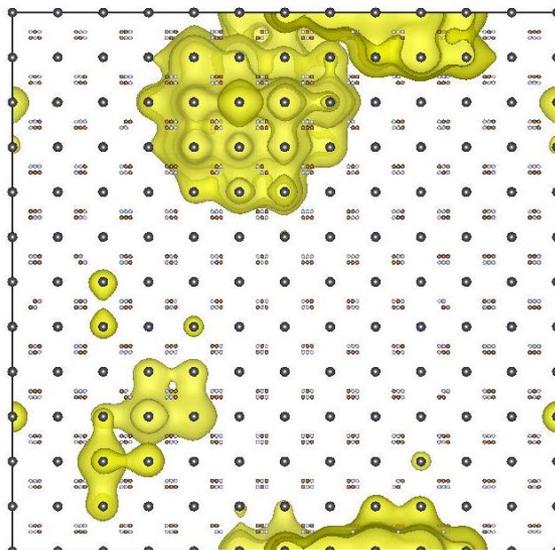
$$\psi(t + \Delta t) = \exp[-iH(t)\Delta t] \psi(t)$$

$$R^2(t) = \langle \psi(t) | (r - r_0)^2 | \psi(t) \rangle$$

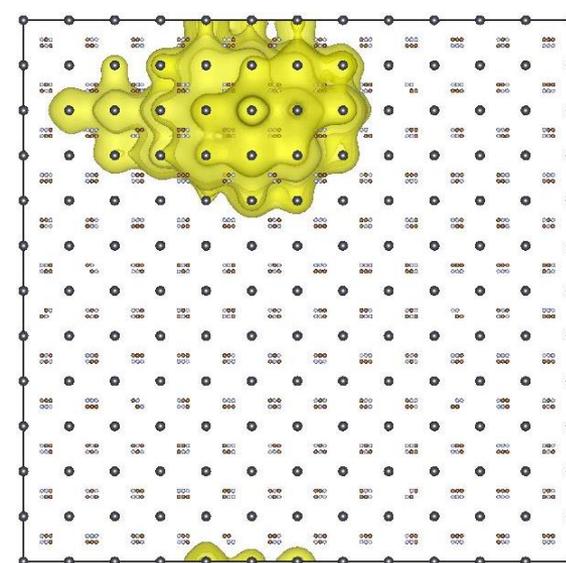
H(t) is determined by CH₃NH₃ random flopping



$t = 0$



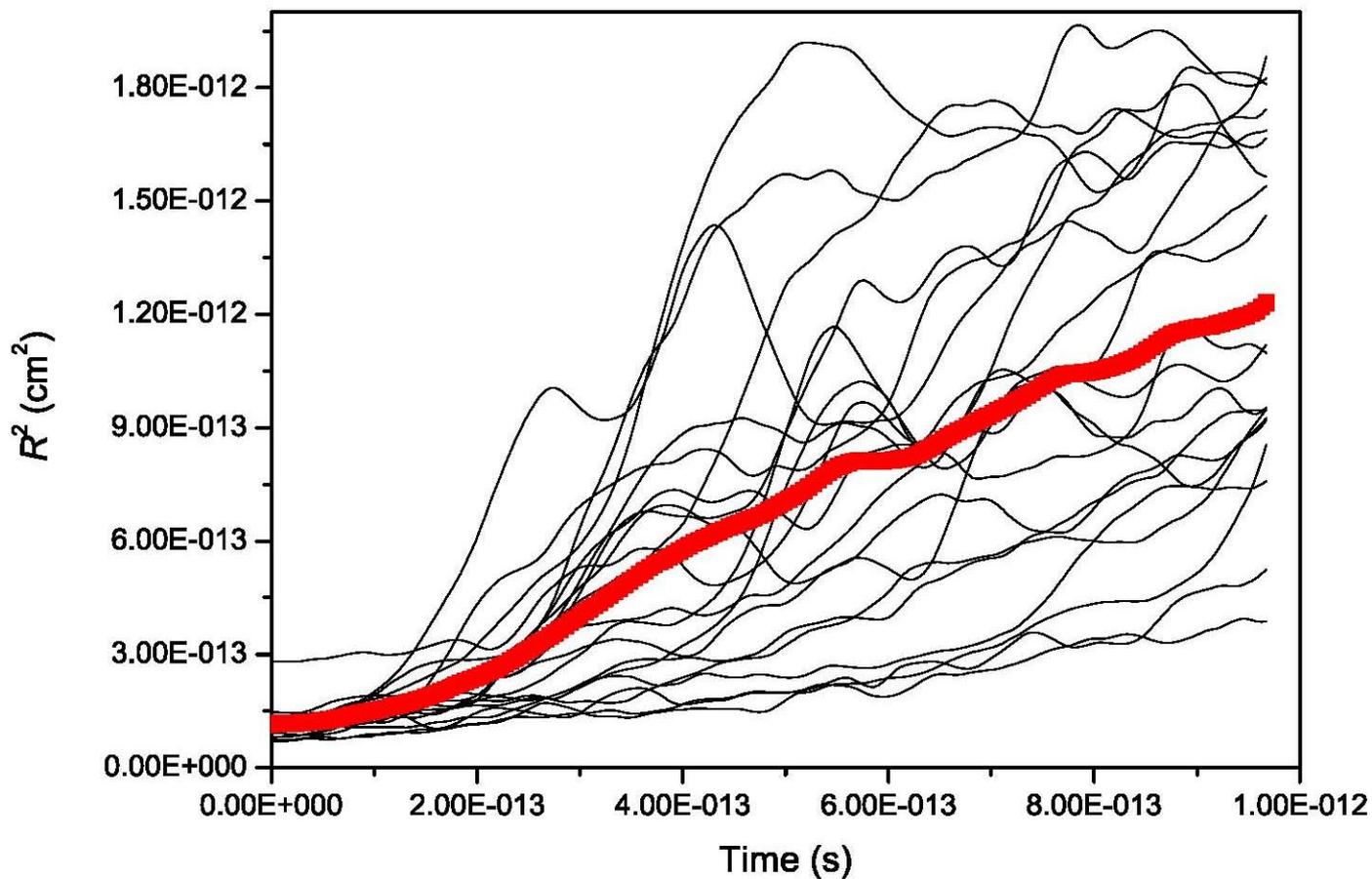
$t = 50000$ a.u.



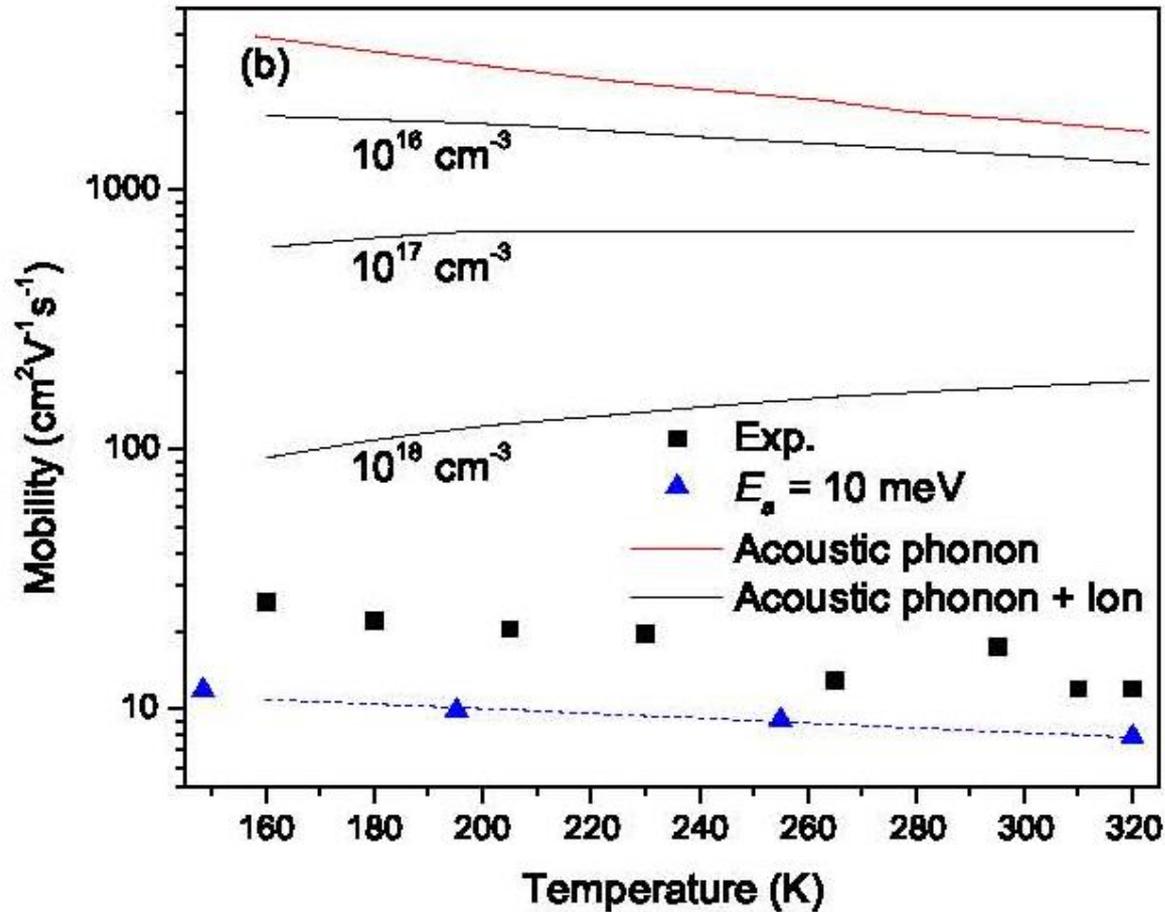
$t = 50000$ a.u.
Adiabatic state

1 flip per molecule per ps

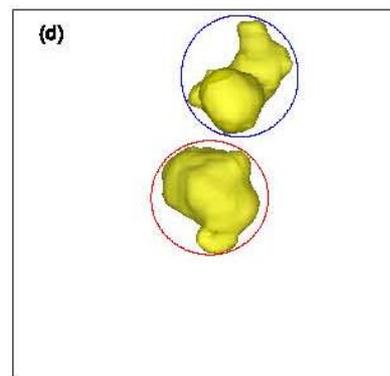
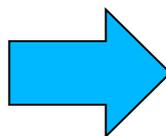
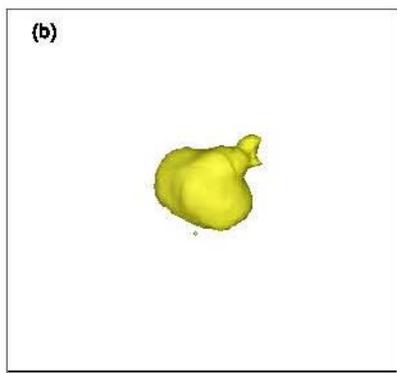
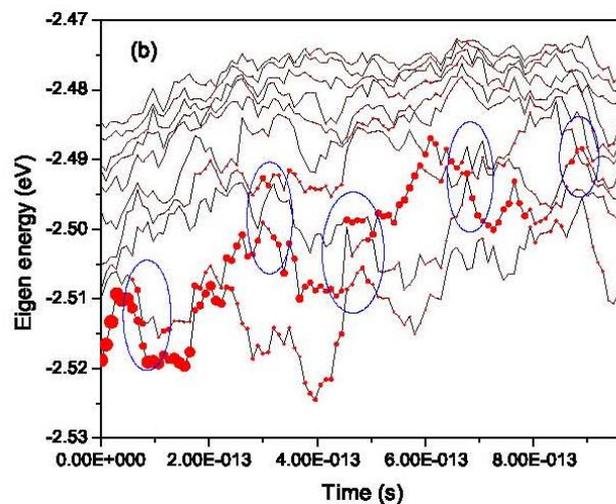
The calculation of diffusion constant from: $R^2(t)$



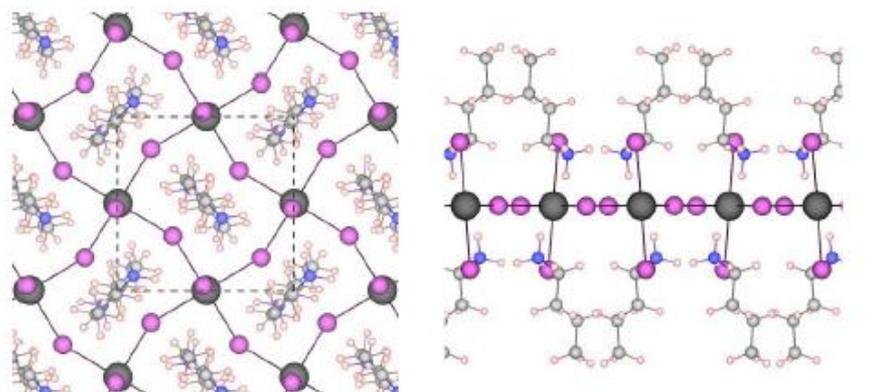
Comparison with experiments



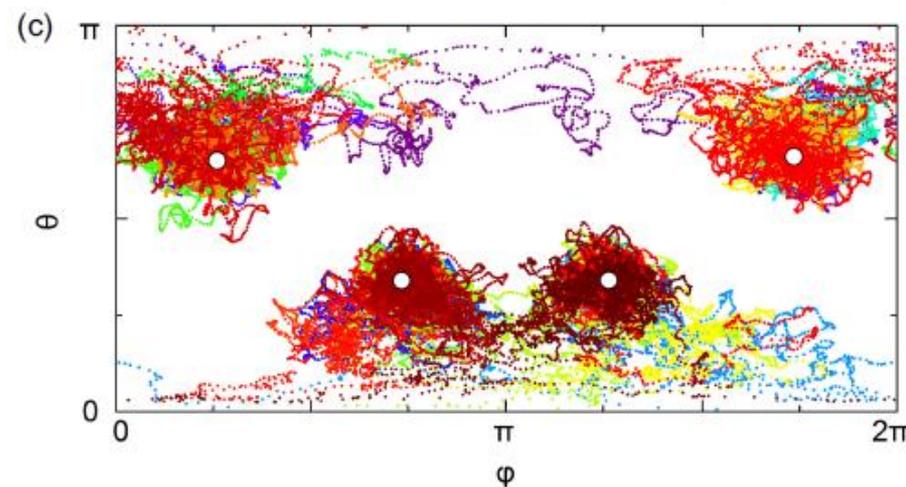
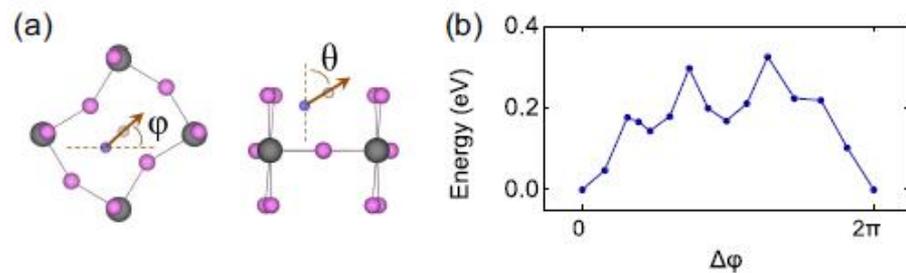
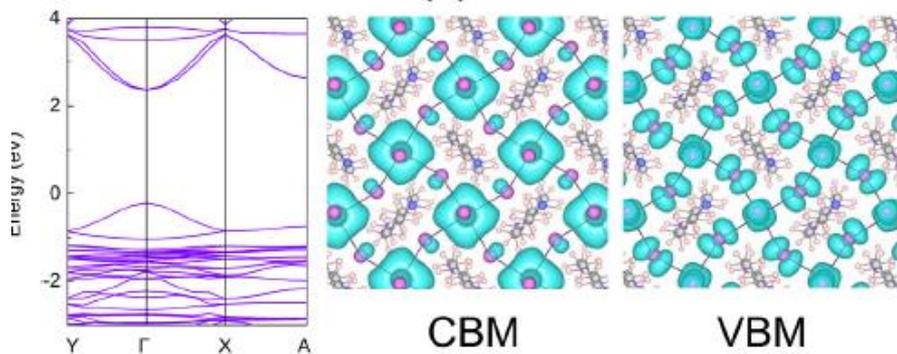
What causes the electron diffusion?

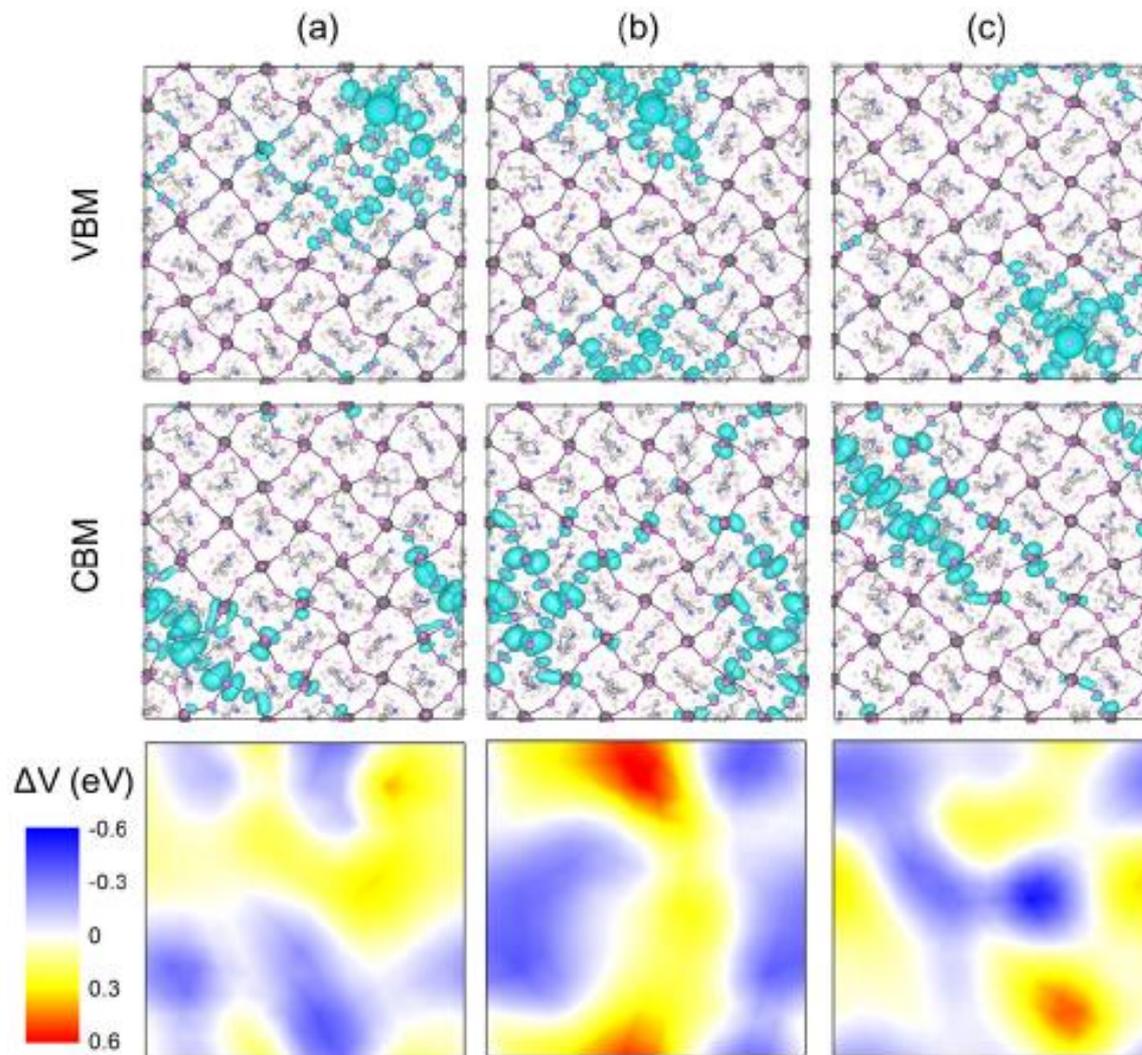


- ❖ Each adiabatic state does not drift quickly, but their energy fluctuates
- ❖ When the energies of two nearby states crossing each other, the electron makes a hop.



(a)





Thanks!