Modeling of transfer rates in hybrid and organic photovoltaic devices

With:

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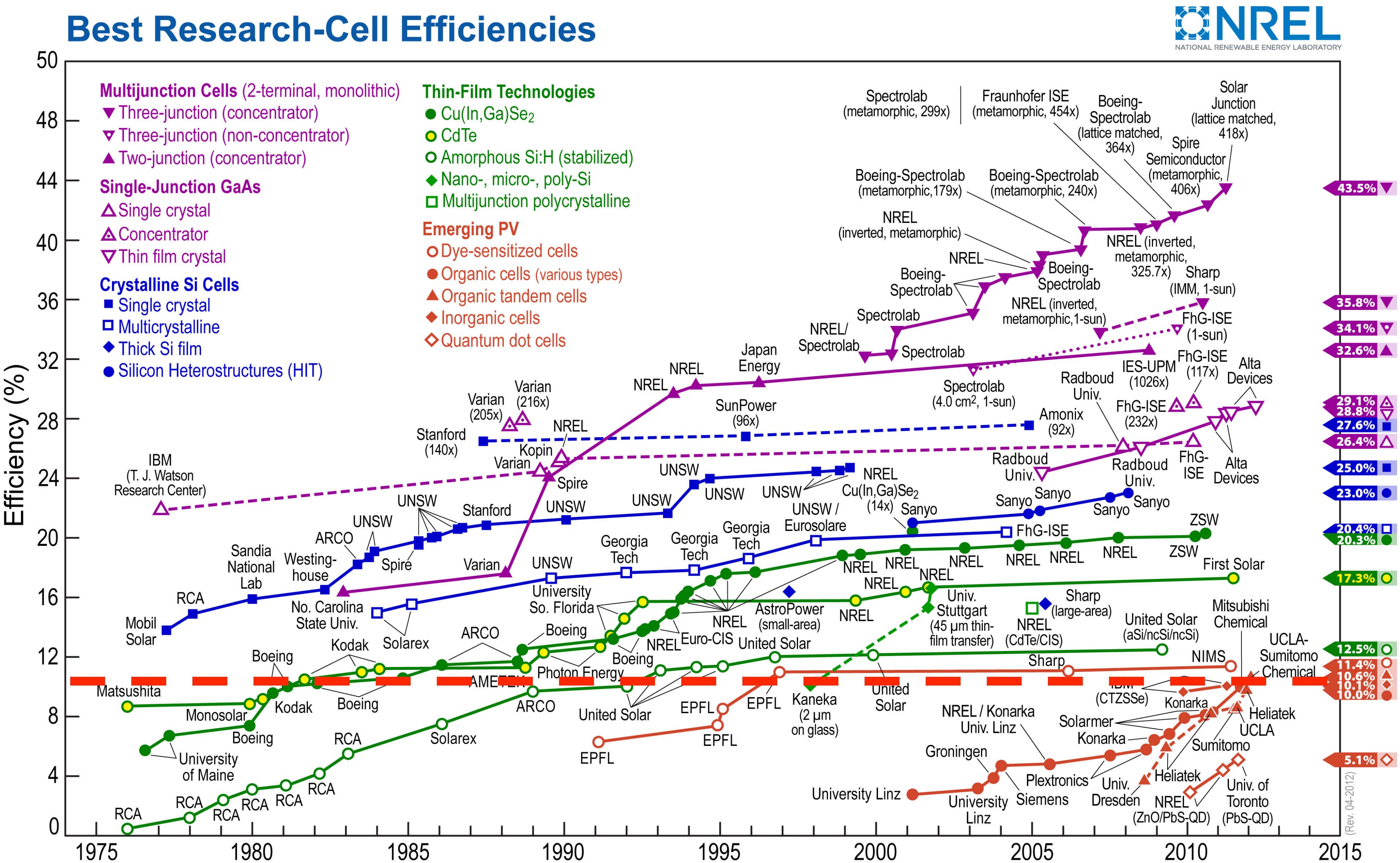
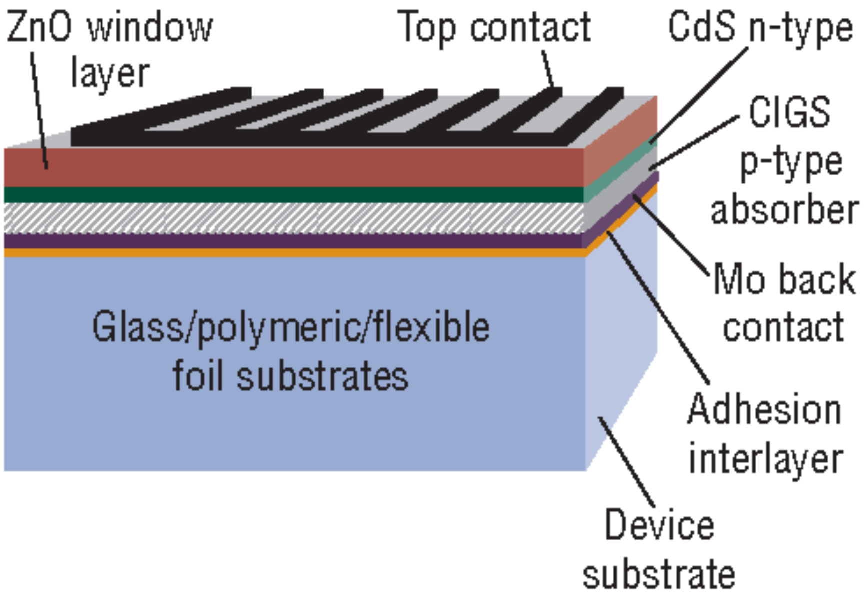
Support: DOE, MGHPCC

IPAM – UCLA, Program on Solar Cells, 23-27 September 2013, Los Angeles, CA



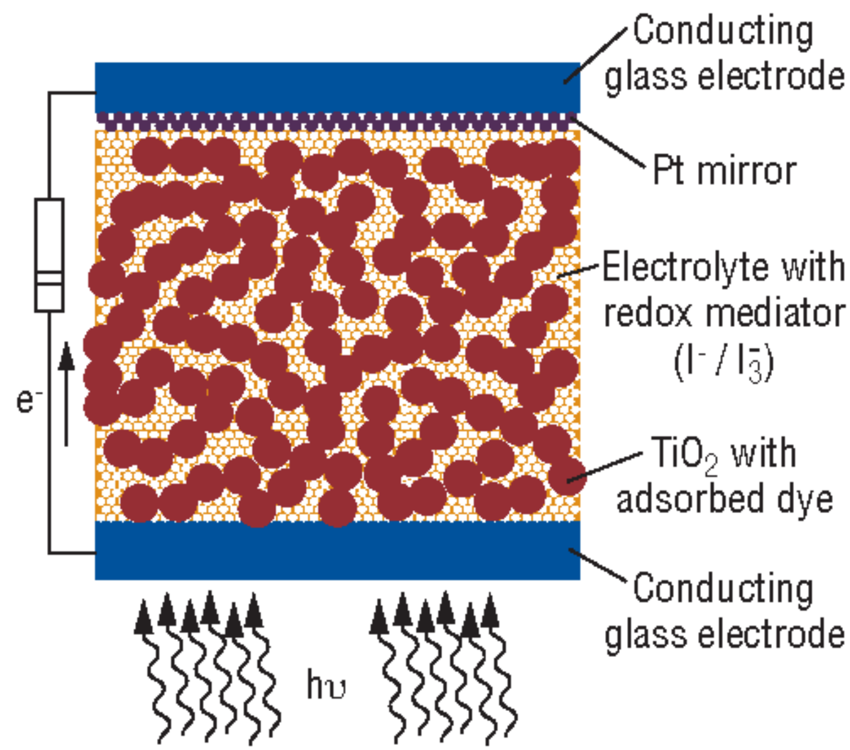
Best Research-Cell Efficiencies
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
Efficiency (%)
Multijunction Cells (2-terminal, monolithic)
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin film crystal
Crystalline Si Cells
Single crystal
Multicrystalline
Thick Si film
Silicon Heterostructures (HIT)
Thin-Film Technologies
Cu(In,Ga)Se2
CdTe
Amorphous Si:H (stabilized)
Nano-, micro-, poly-Si
Multijunction polycrystalline
Emerging PV
Dye-sensitized cells
Organic cells (various types)
Organic tandem cells
Inorganic cells
Quantum dot cells
Spectrolab (metamorphic, 299x)
Fraunhofer ISE (metamorphic, 454x)
Boeing-Spectrolab (lattice matched, 364x)
Solar Junction (lattice matched, 418x)
Spire Semiconductor (metamorphic, 406x)
Boeing-Spectrolab (metamorphic,179x)
Boeing-Spectrolab (metamorphic, 240x)
NREL (inverted, metamorphic)
NREL (inverted, metamorphic, 325.7x)
Sharp (IMM, 1-sun)
NREL (inverted, metamorphic,1-sun)
FhG-ISE (1-sun)
Spectrolab (4.0 cm2, 1-sun)
IES-UPM (1026x)
FhG-ISE (117x)
Alta Devices
FhG-ISE (232x)
Radboud Univ.
Amonix (92x)
SunPower (96x)
Japan Energy
NREL/ Spectrolab
IBM (T. J. Watson Research Center)
Varian (205x)
Varian (216x)
Stanford (140x)
Kopin
Spire
UNSW
Cu(In,Ga)Se2 (14x)
UNSW / Eurosolare
Sanyo
FhG-ISE
ZSW
First Solar
Georgia Tech
University So. Florida
Sandia National Lab
Westing-house
ARCO
No. Carolina State Univ.
Mobil Solar
RCA
Matsushita
Monosolar
Kodak
Boeing
University of Maine
Solarex
AMETEK
Photon Energy
Euro-CIS
United Solar
AstroPower (small-area)
Univ. Stuttgart (45 μm thin-film transfer)
Sharp (large-area)
NREL (CdTe/CIS)
United Solar (aSi/ncSi/ncSi)
Mitsubishi Chemical
UCLA-Sumitomo Chemical
NIMS
IBM (CTZSSe)
Konarka
Heliatek
UCLA
Sumitomo
Kaneka (2 μm on glass)
EPFL
NREL / Konarka Univ. Linz
Solarmer
Groningen
Plextronics
Siemens
University Linz
Univ. Dresden
NREL (ZnO/PbS-QD)
Univ. of Toronto (PbS-QD)
43.5%
35.8%
34.1%
32.6%
29.1%
28.8%
27.6%
26.4%
25.0%
23.0%
20.4%
20.3%
17.3%
12.5%
11.4%
10.6%
10.1%
10.0%
5.1%
(Rev. 04-2012)

Copper-Indium-Gallium-Selenide cell



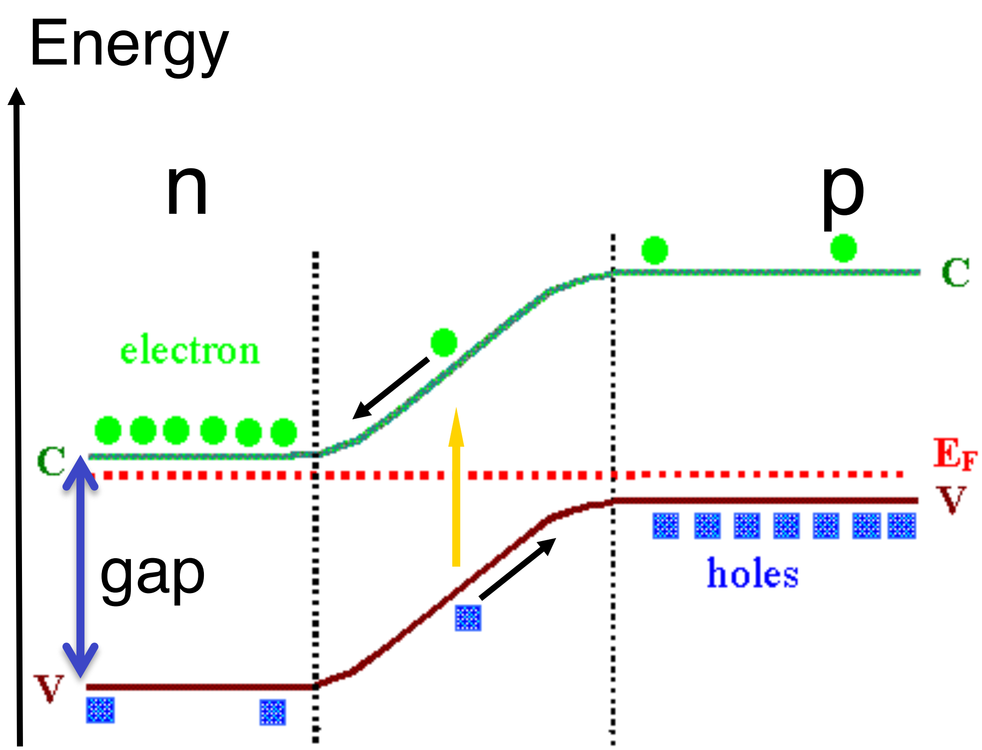
Conventional p-n junction cell
(inorganic)

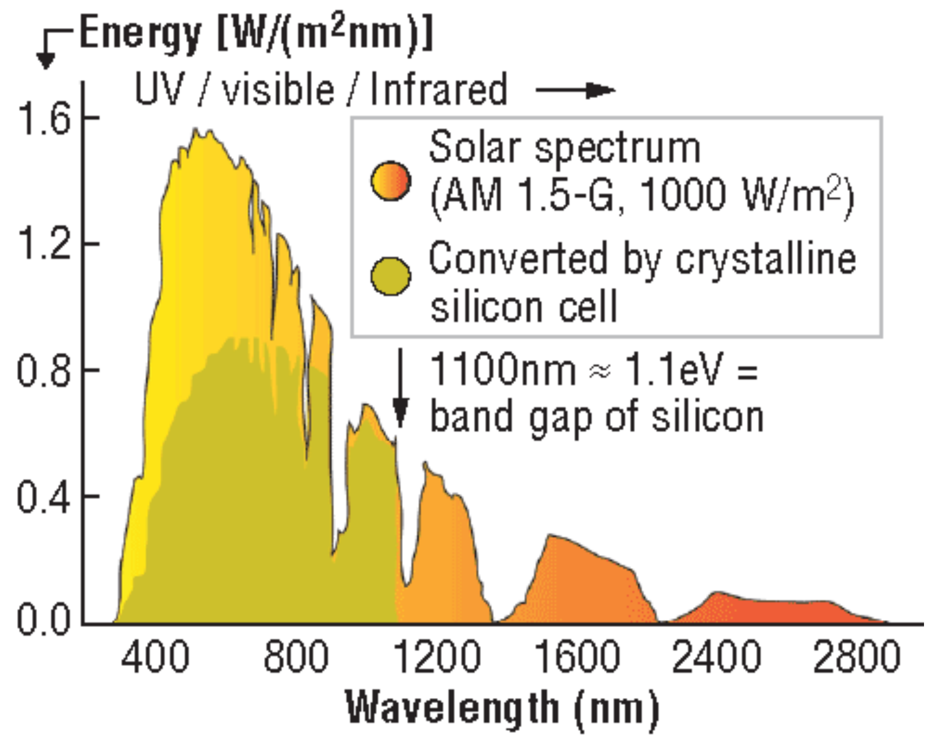
Dye-sensitized cell
(hybrid organic/inorganic)



O'Regan & Graetzel, Nature (1991)

Light absorption by solids: the pn-junction in semiconductors





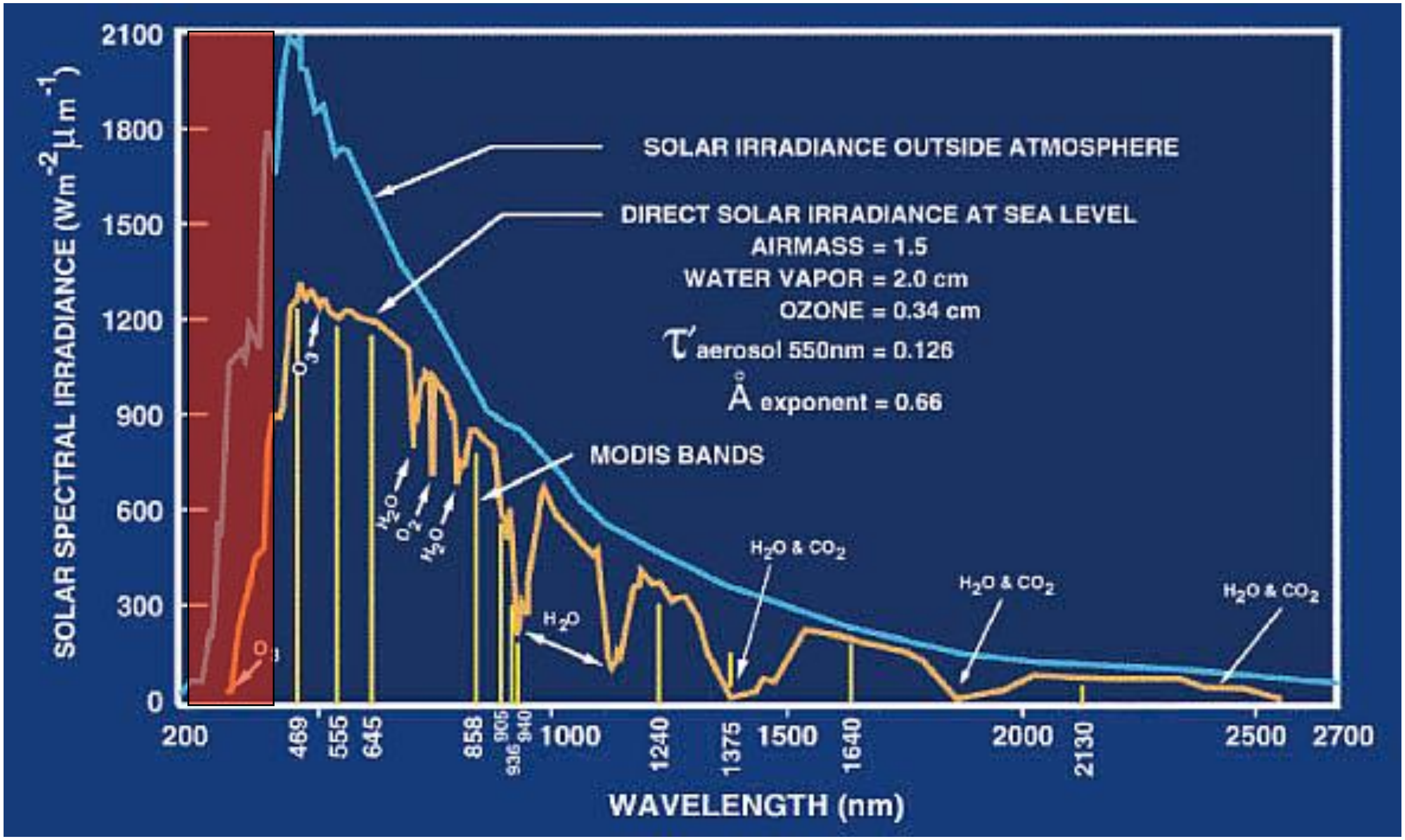
Bulk semiconductor (inorganic)

- delocalized states (band structure)
- nearly free electrons
- single band-gap

Light absorption by hybrid cells

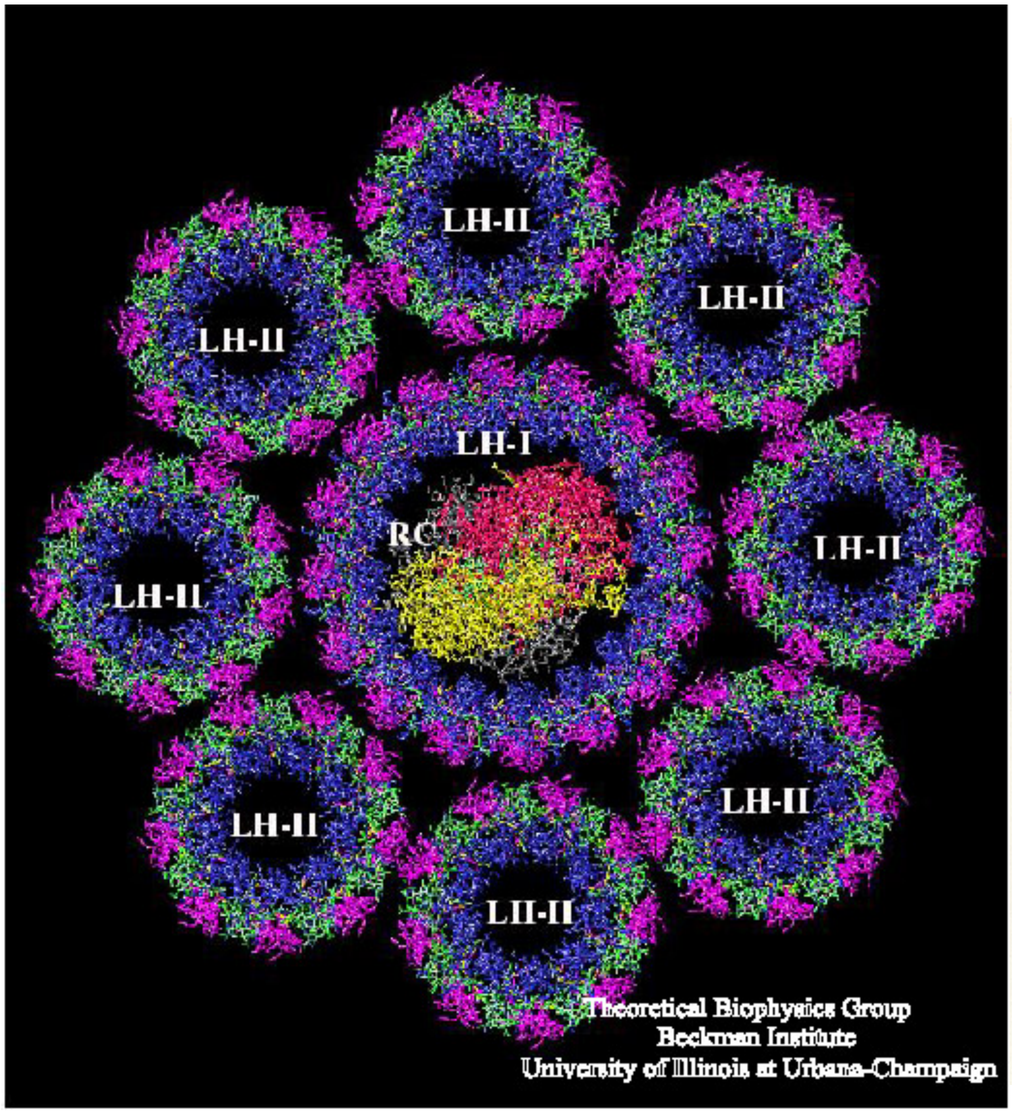
- The Problem: materials for carrier transport with large band gaps

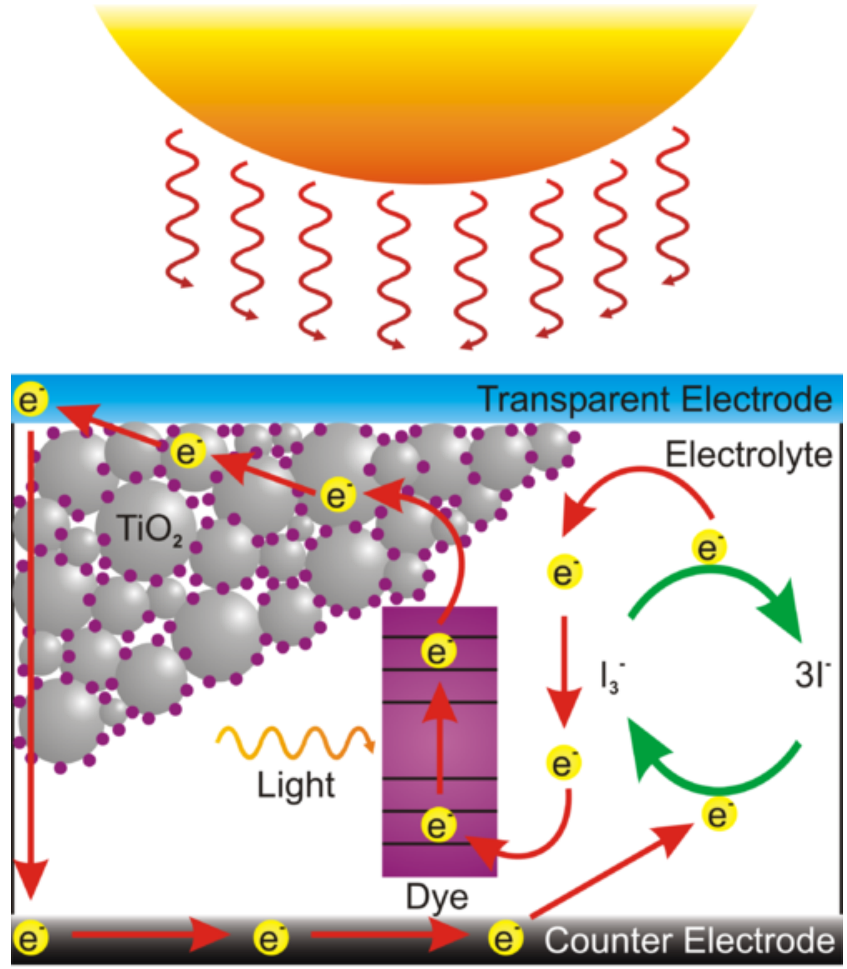
TiO_2 gap = 3.2 eV (200 nm < λ < 400 nm)



solar spectrum

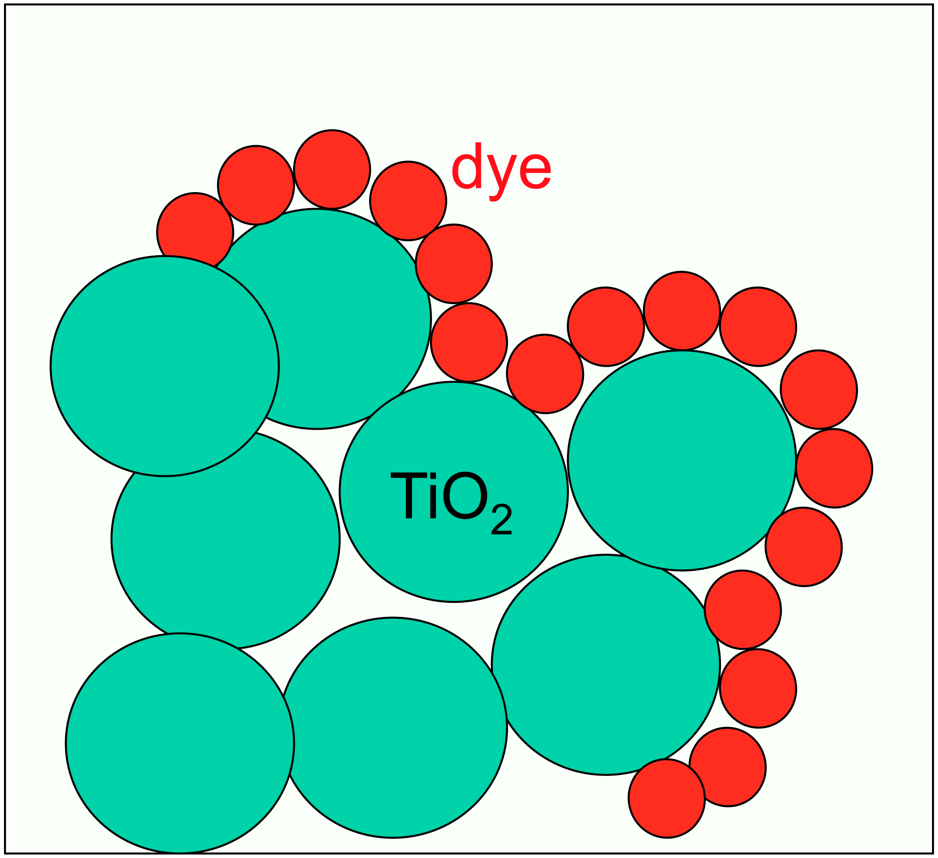
The Principle: separate light-absorption and charge collection processes

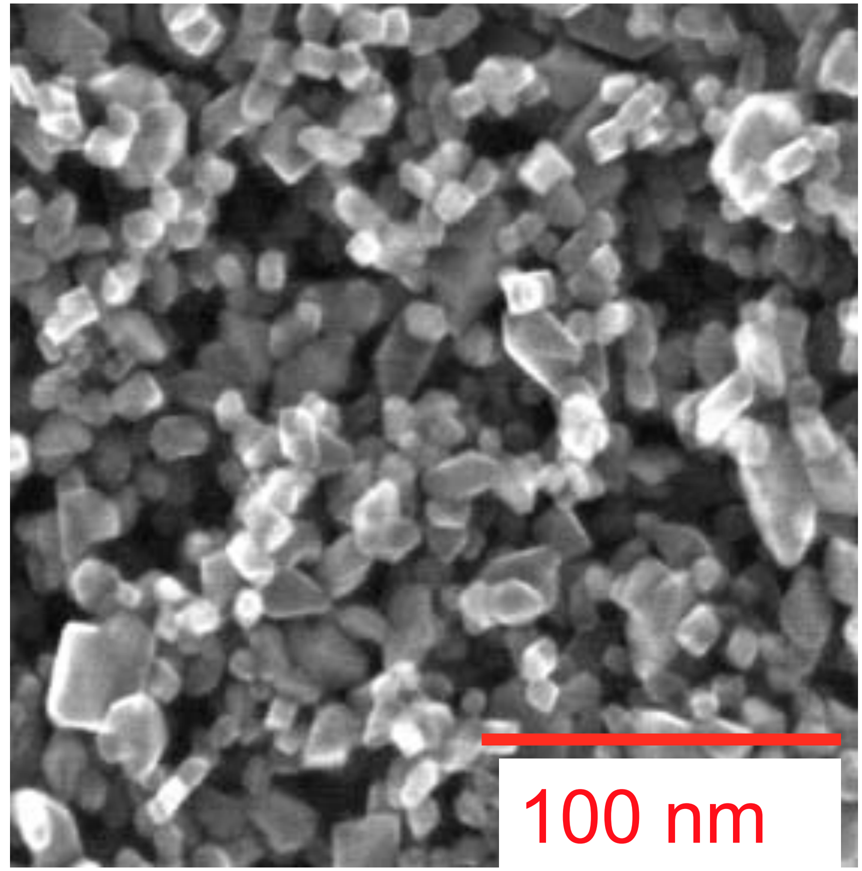




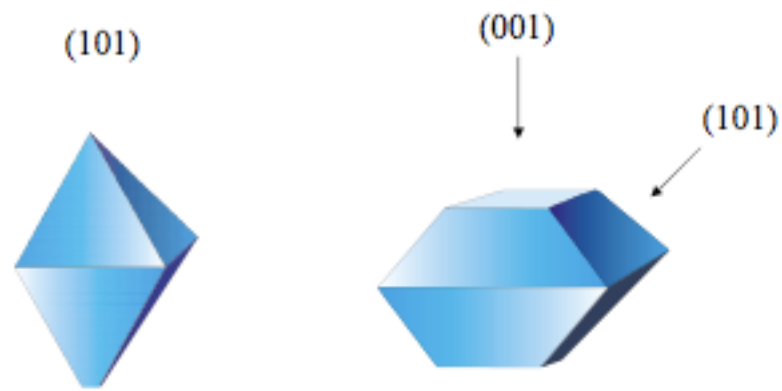
Major issues:
- stability
- efficiency (Inc.Ph.Cur.Eff.)

Approximately complete surface coverage (i.e. densest possible packing of dye molecules)





~20 nm sized faccetted anatase nanoparticles



Nano-size: helps in many aspects (e.g. efficiency, transparency, transport, …)

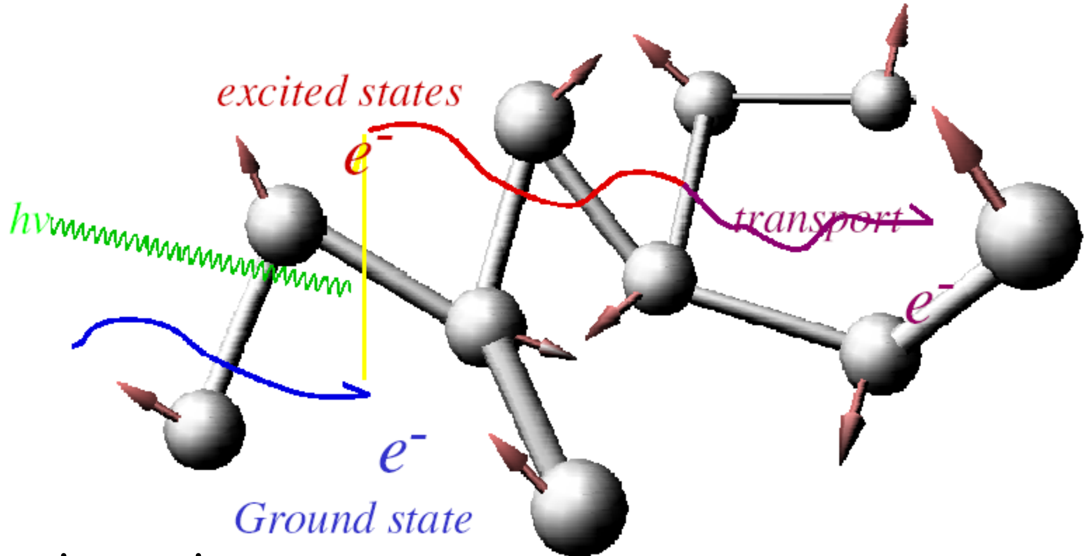
Main issue: coupled electron-ion dynamics

Previous work:

-Schroedinger eq. with model Hamiltonian
Thoss, Miller, Stock, JCP (2000);
Rego& Batista, JACS (2003);…

-semiempirical Hamiltonian (tight-binding)
Allen et al., JMO (2003);…

-ground state DFT + TDDFT
Prezhdo et al., PRL (2005); JACS (2007)…



Ours: self-consistent TDDFT with atomic motion

Meng & Kaxiras, J. Chem. Phys. (2008).

Coupled electron-ion dynamics

Similar to: Miyamoto *et al.*; Rubio *et al.*; Tavernelli *et al.*.

$$\begin{cases} i\hbar\dfrac{\partial\phi_j(\mathbf{r},t)}{\partial t} = \left[-\dfrac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} + v_{ext}(\mathbf{r},t) + \displaystyle\int\dfrac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \sum_I \dfrac{Z_I}{|\mathbf{r}-\mathbf{R}^{cl}_I|} + v_{xc}[\rho](\mathbf{r},t)\right]\phi_j(\mathbf{r},t) \\ M_J\dfrac{d^2\mathbf{R}^{cl}_J(t)}{dt^2} = -\nabla_{\mathbf{R}^{cl}_J}\left[V^J_{ext}(\mathbf{R}^{cl}_J,t) - \displaystyle\int\dfrac{Z_J\rho(\mathbf{r},t)}{|\mathbf{R}^{cl}_J-\mathbf{r}|}d\mathbf{r} + \sum_{I\neq J}\dfrac{Z_JZ_I}{|\mathbf{R}^{cl}_J-\mathbf{R}^{cl}_I|}\right] \end{cases}$$

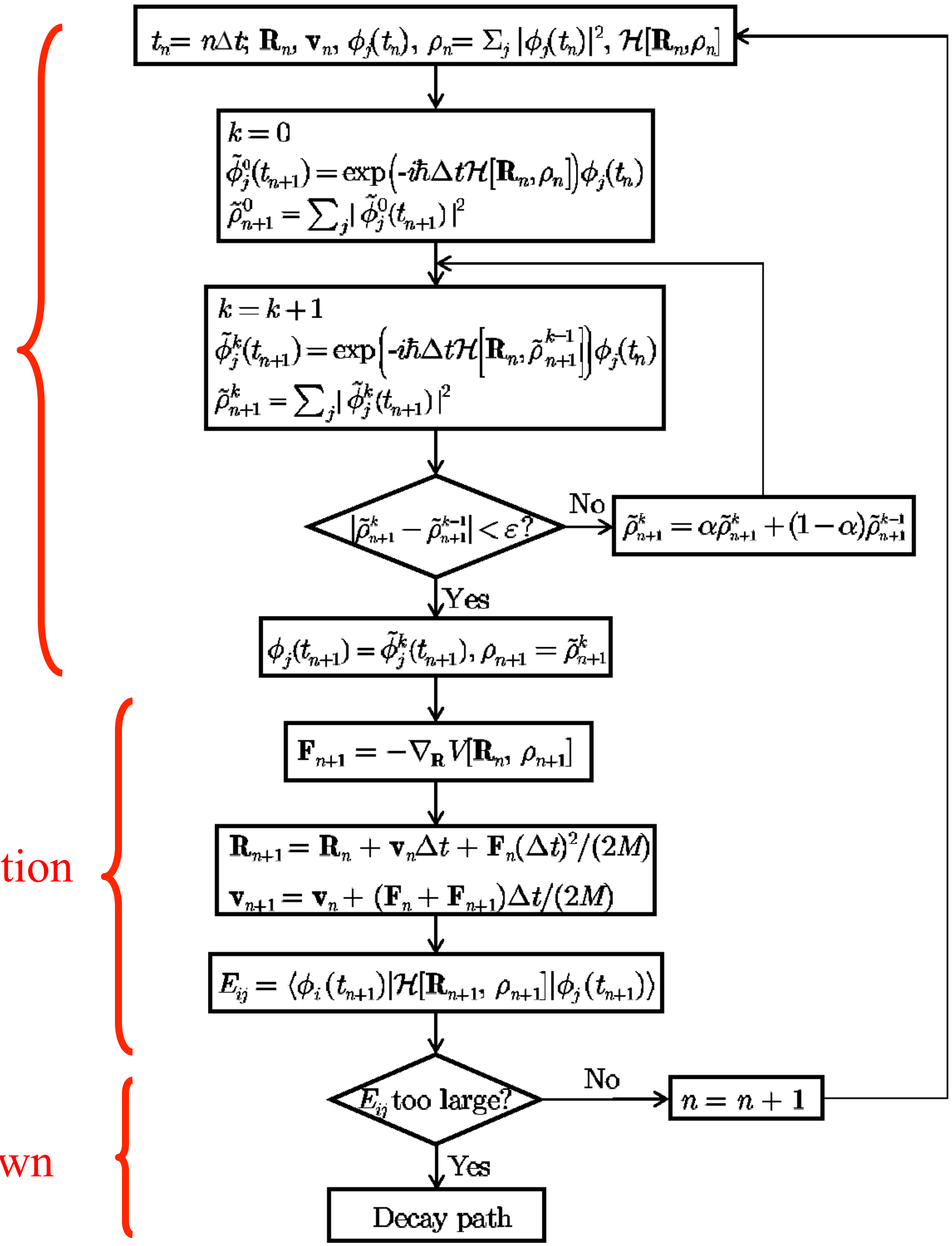
Propagation of electrons in time (TDSE) + Ehrenfest dynamics for ions

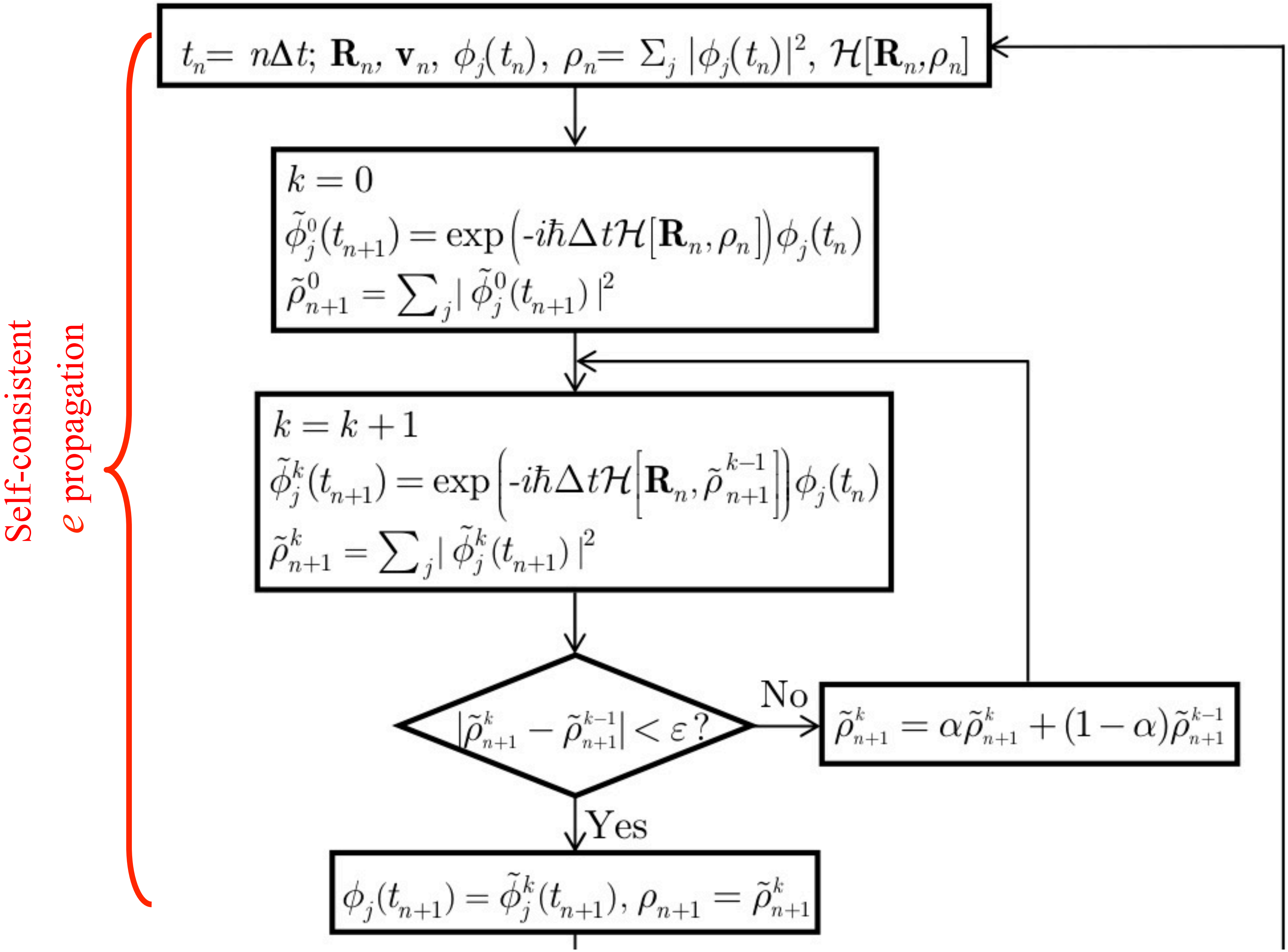
Computational flowchart

Self-consistent
e propagation

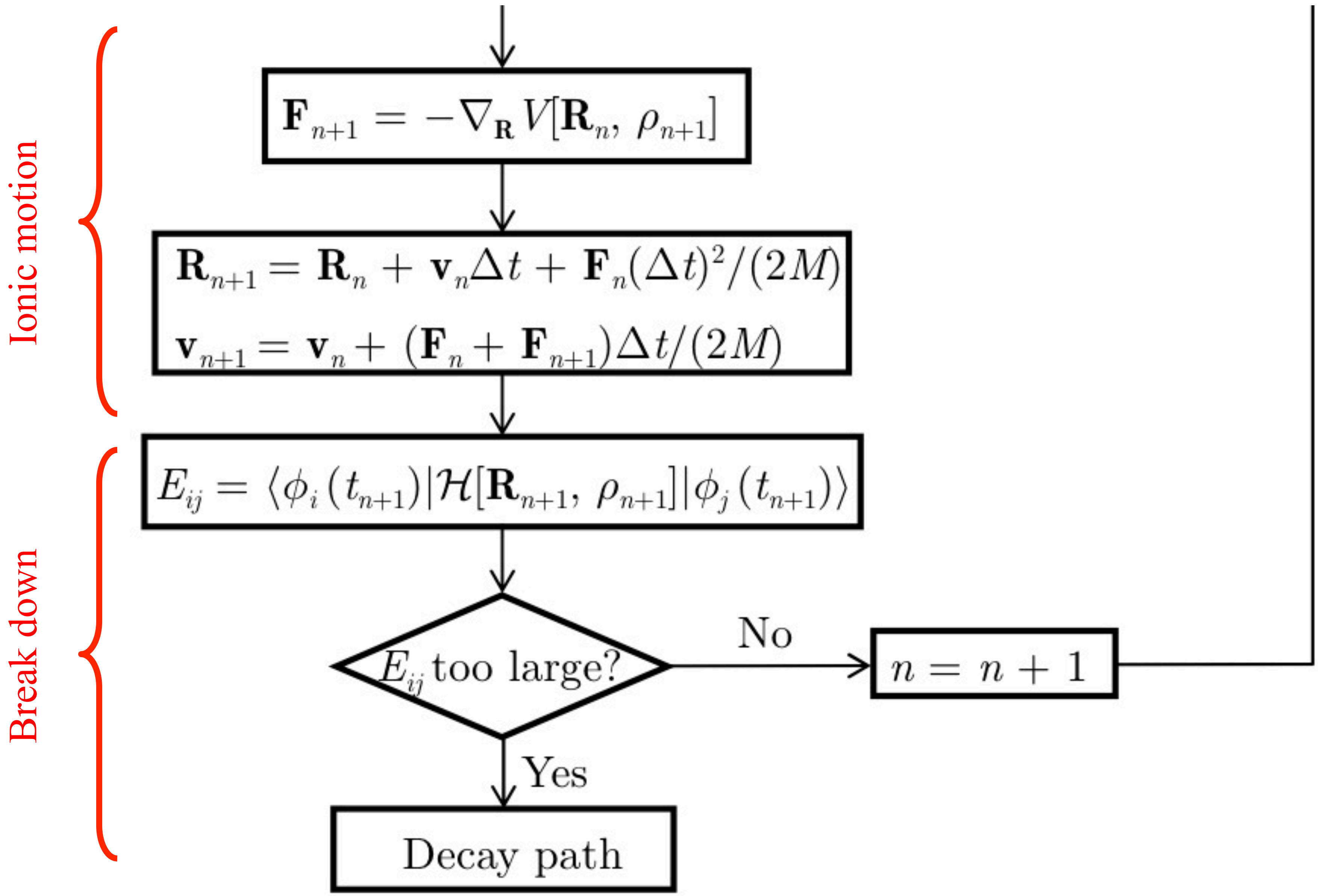
Ionic motion

Break down

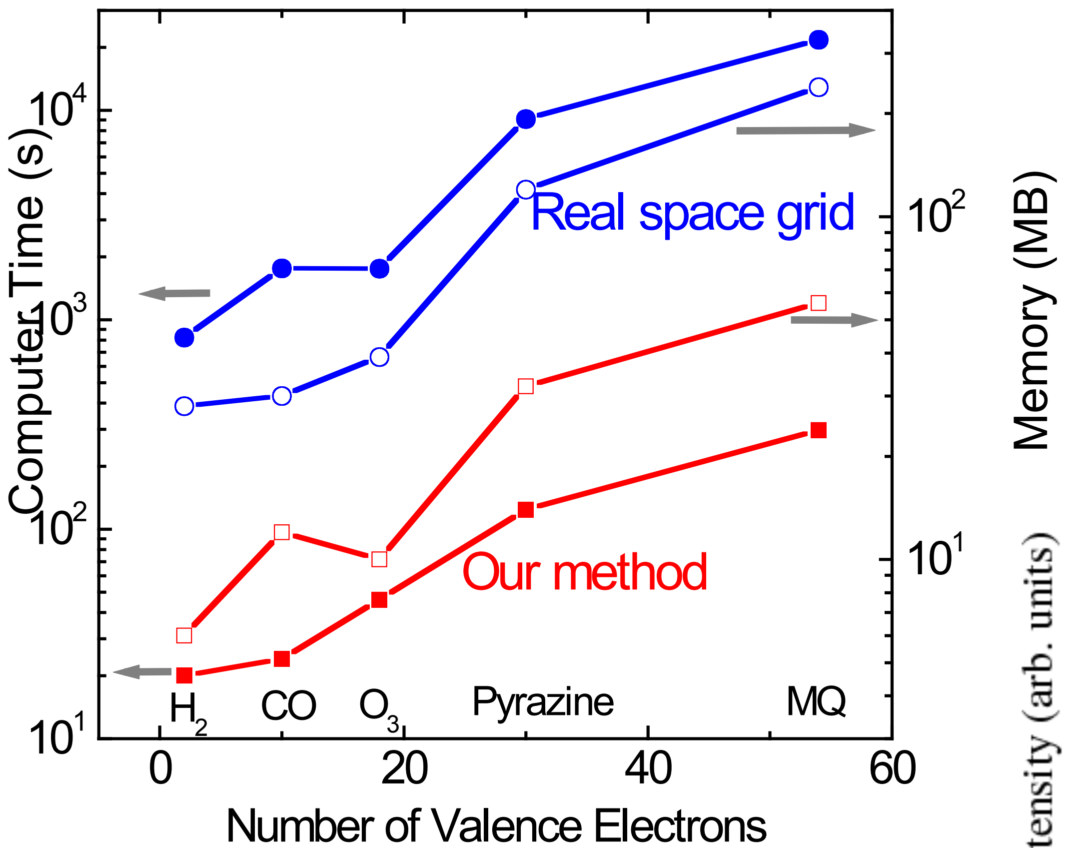


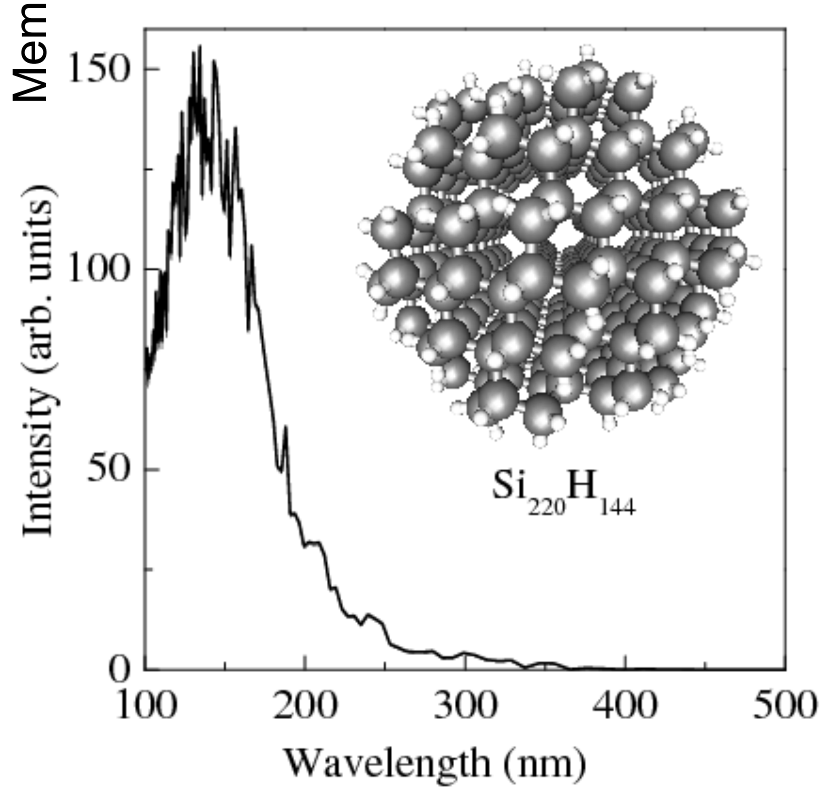


$t_n = n\Delta t$; $\mathbf{R}_n$, $\mathbf{v}_n$, $\phi_j(t_n)$, $\rho_n = \Sigma_j |\phi_j(t_n)|^2$, $\mathcal{H}[\mathbf{R}_n, \rho_n]$
$k = 0$
$\tilde{\phi}_j^0(t_{n+1}) = \exp\left(-i\hbar\Delta t\mathcal{H}[\mathbf{R}_n, \rho_n]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^0 = \sum_j |\tilde{\phi}_j^0(t_{n+1})|^2$
$k = k+1$
$\tilde{\phi}_j^k(t_{n+1}) = \exp\left(-i\hbar\Delta t\mathcal{H}\left[\mathbf{R}_n, \tilde{\rho}_{n+1}^{k-1}\right]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^k = \sum_j |\tilde{\phi}_j^k(t_{n+1})|^2$
$|\tilde{\rho}_{n+1}^k - \tilde{\rho}_{n+1}^{k-1}| < \varepsilon$?
No
$\tilde{\rho}_{n+1}^k = \alpha\tilde{\rho}_{n+1}^k + (1-\alpha)\tilde{\rho}_{n+1}^{k-1}$
Yes
$\phi_j(t_{n+1}) = \tilde{\phi}_j^k(t_{n+1})$, $\rho_{n+1} = \tilde{\rho}_{n+1}^k$
Self-consistent
e propagation

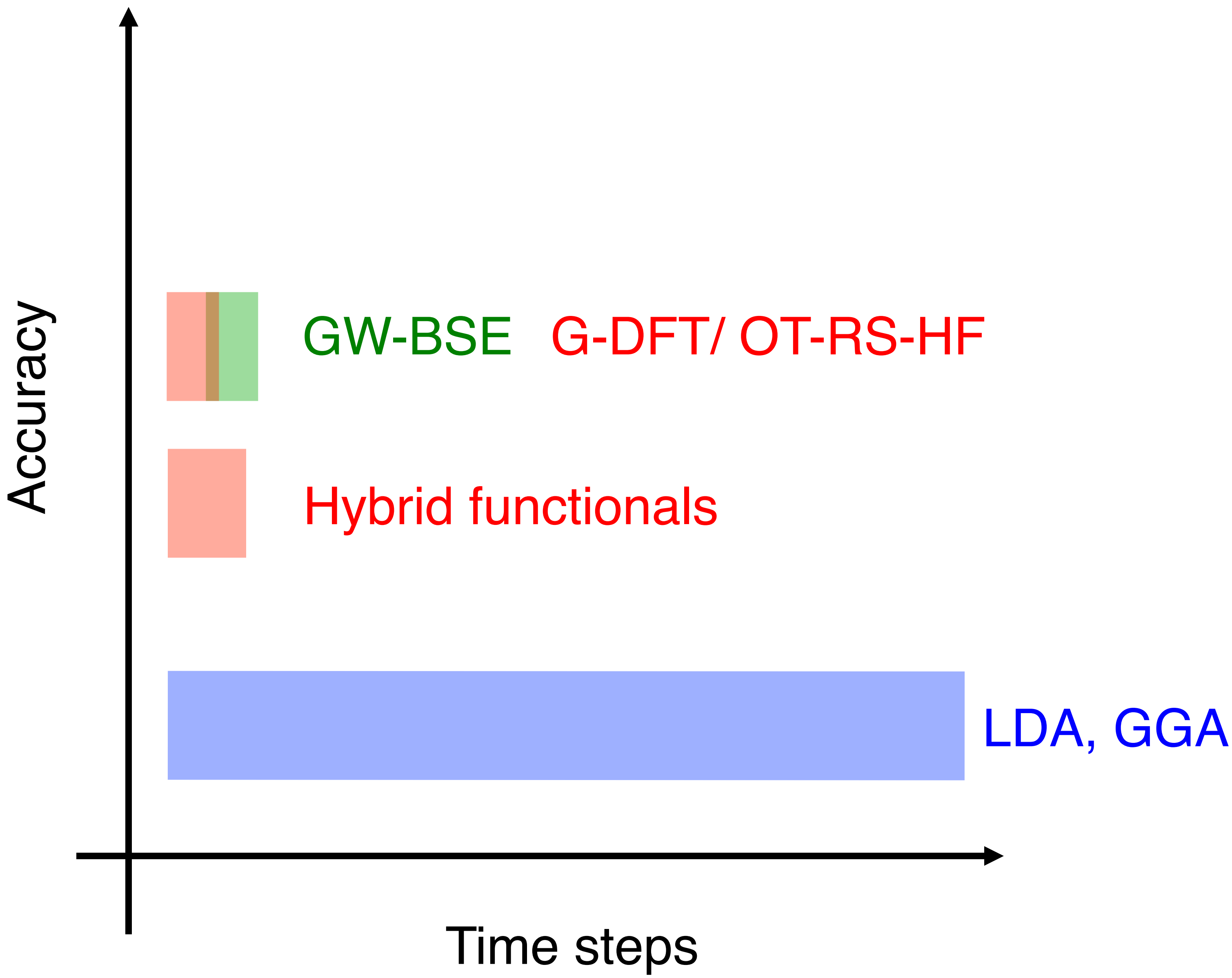

Ionic motion
$\mathbf{F}_{n+1} = -\nabla_{\mathbf{R}} V[\mathbf{R}_n, \rho_{n+1}]$
$\mathbf{R}_{n+1} = \mathbf{R}_n + \mathbf{v}_n \Delta t + \mathbf{F}_n (\Delta t)^2/(2M)$
$\mathbf{v}_{n+1} = \mathbf{v}_n + (\mathbf{F}_n + \mathbf{F}_{n+1}) \Delta t/(2M)$
Break down
$E_{ij} = \langle \phi_i(t_{n+1}) | \mathcal{H}[\mathbf{R}_{n+1}, \rho_{n+1}] | \phi_j(t_{n+1}) \rangle$
E_{ij} too large?
No
$n = n + 1$
Yes
Decay path

Code performance (compared to standard code - "octopus")

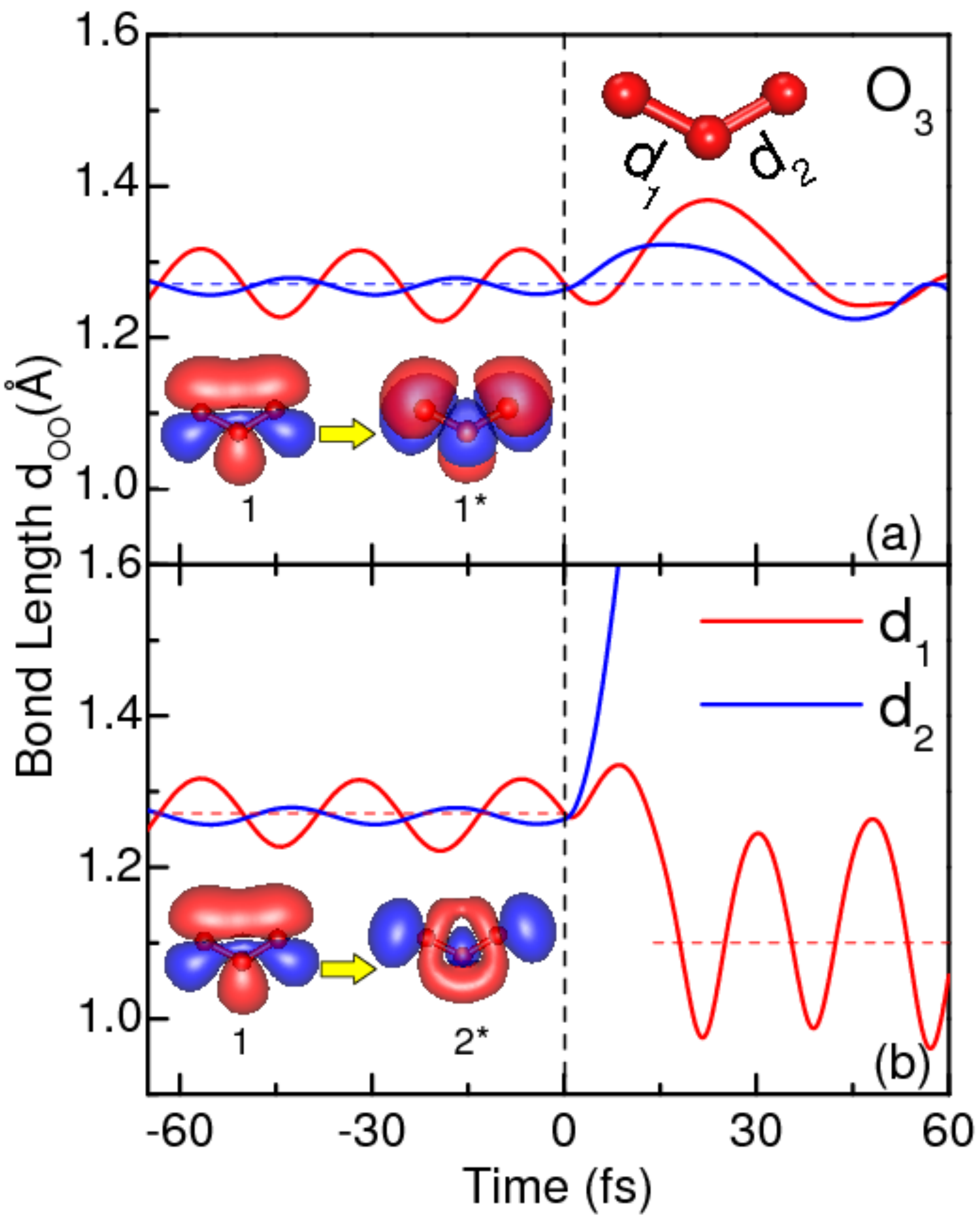


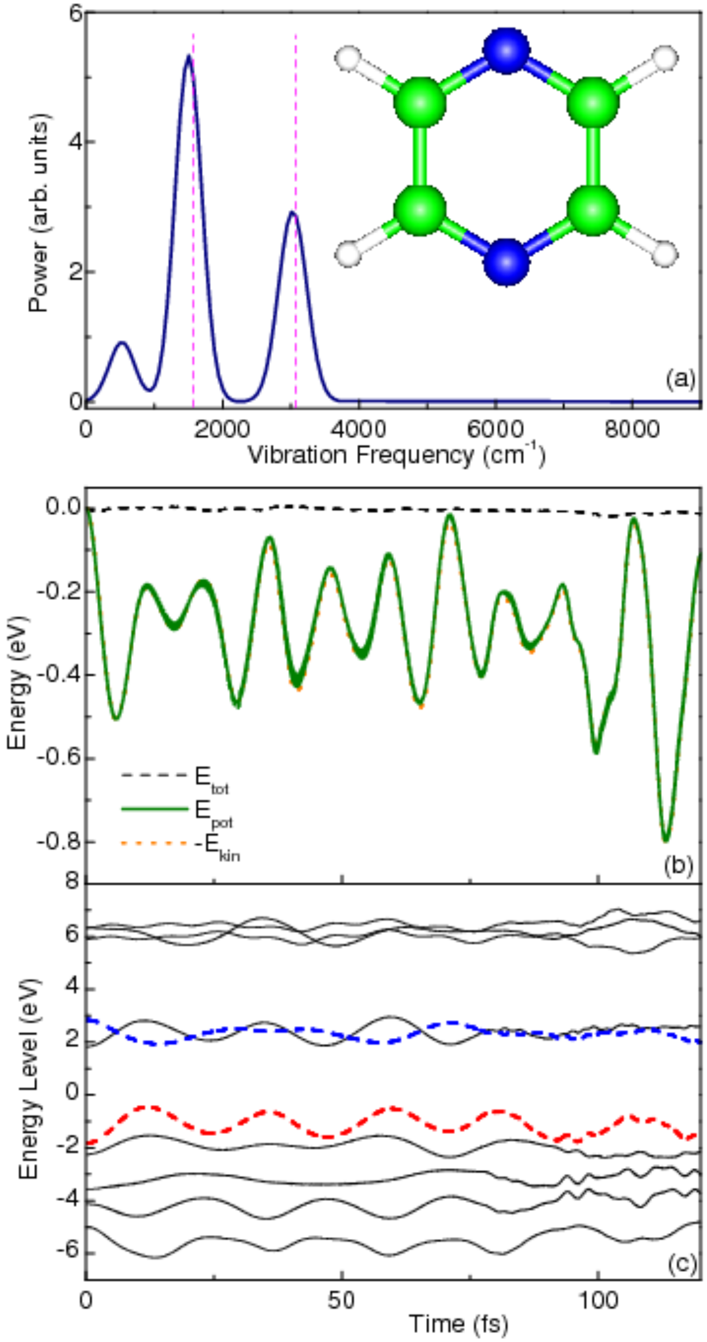


~ 500 atoms

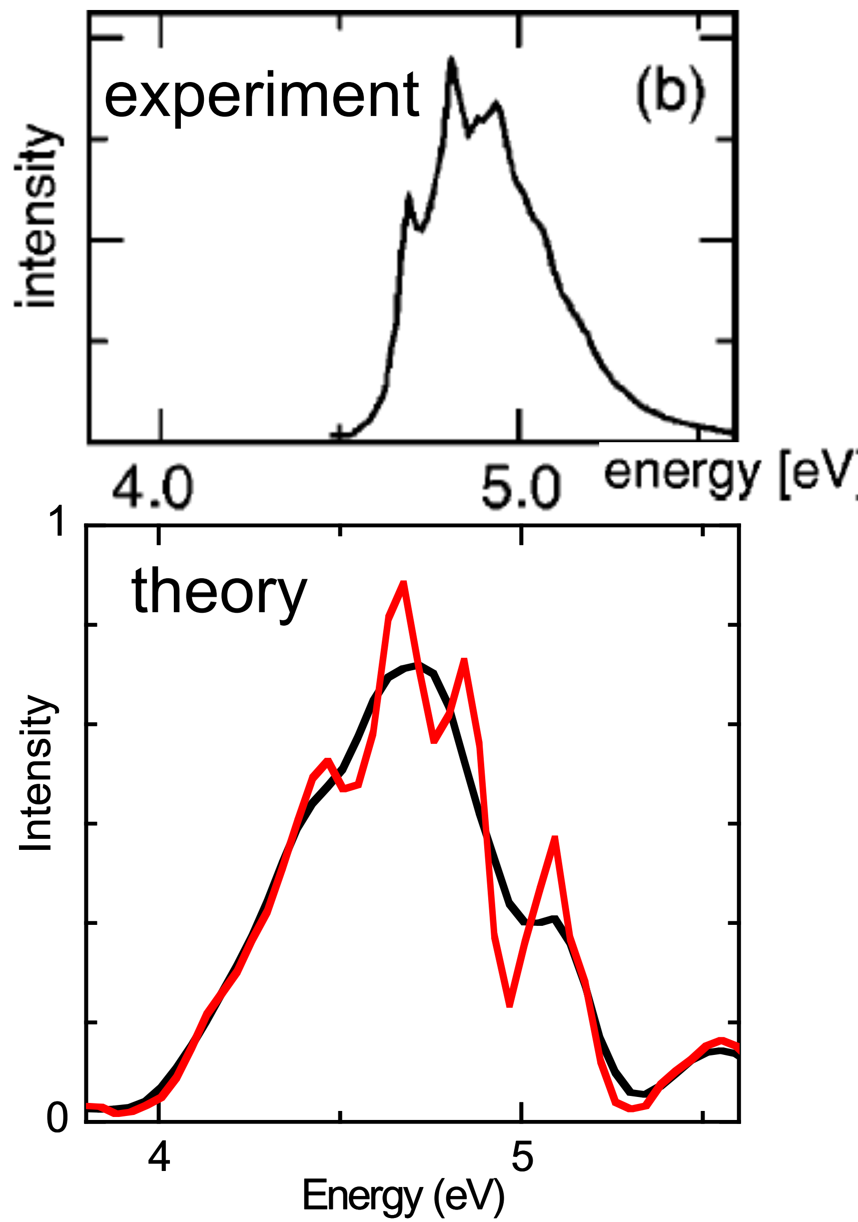

Accuracy
GW-BSE
G-DFT/ OT-RS-HF
Hybrid functionals
LDA, GGA
Time steps

Tests: ozone molecule - photo-dissociation

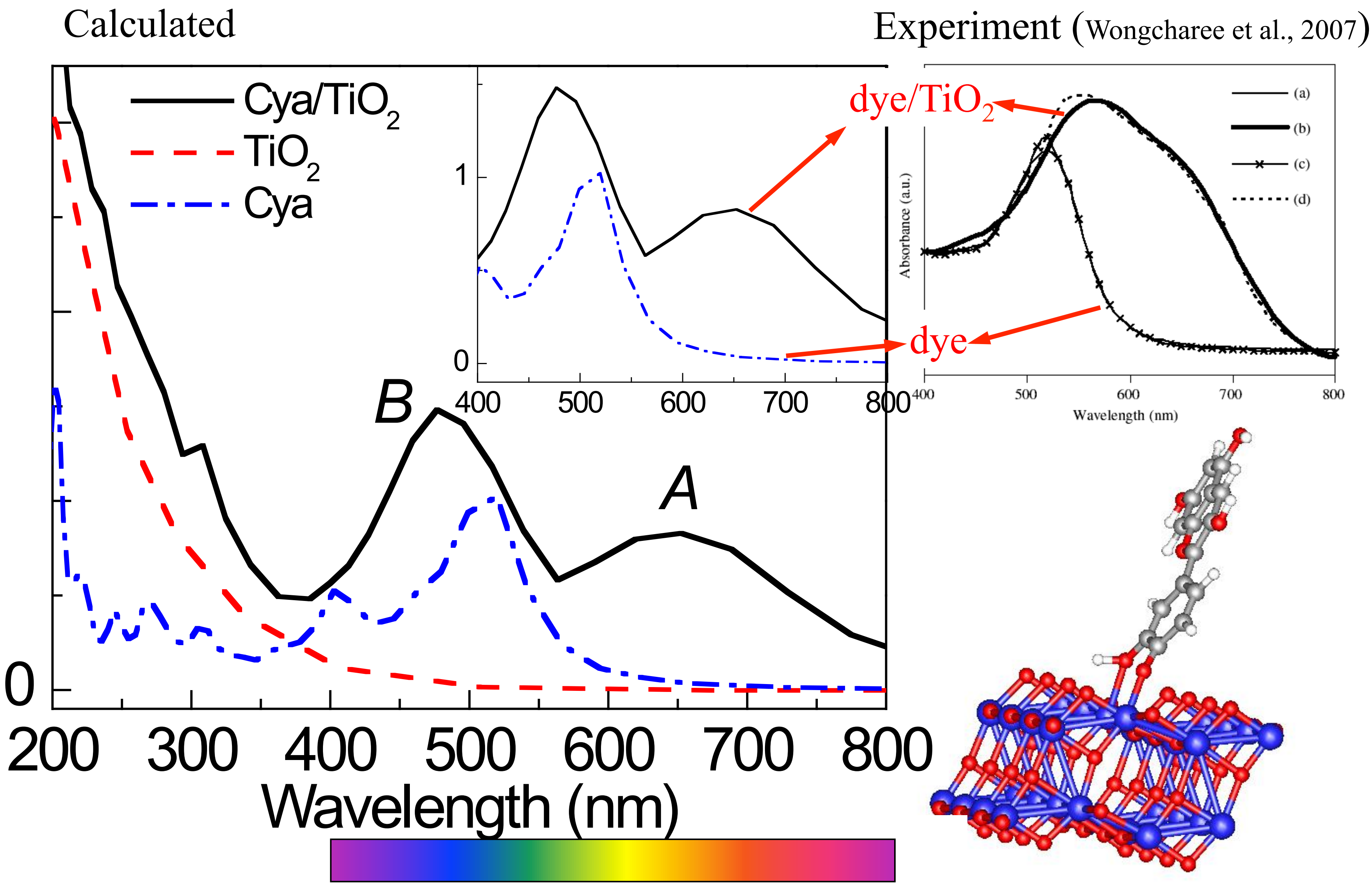




Test: spectrum of pyrazine

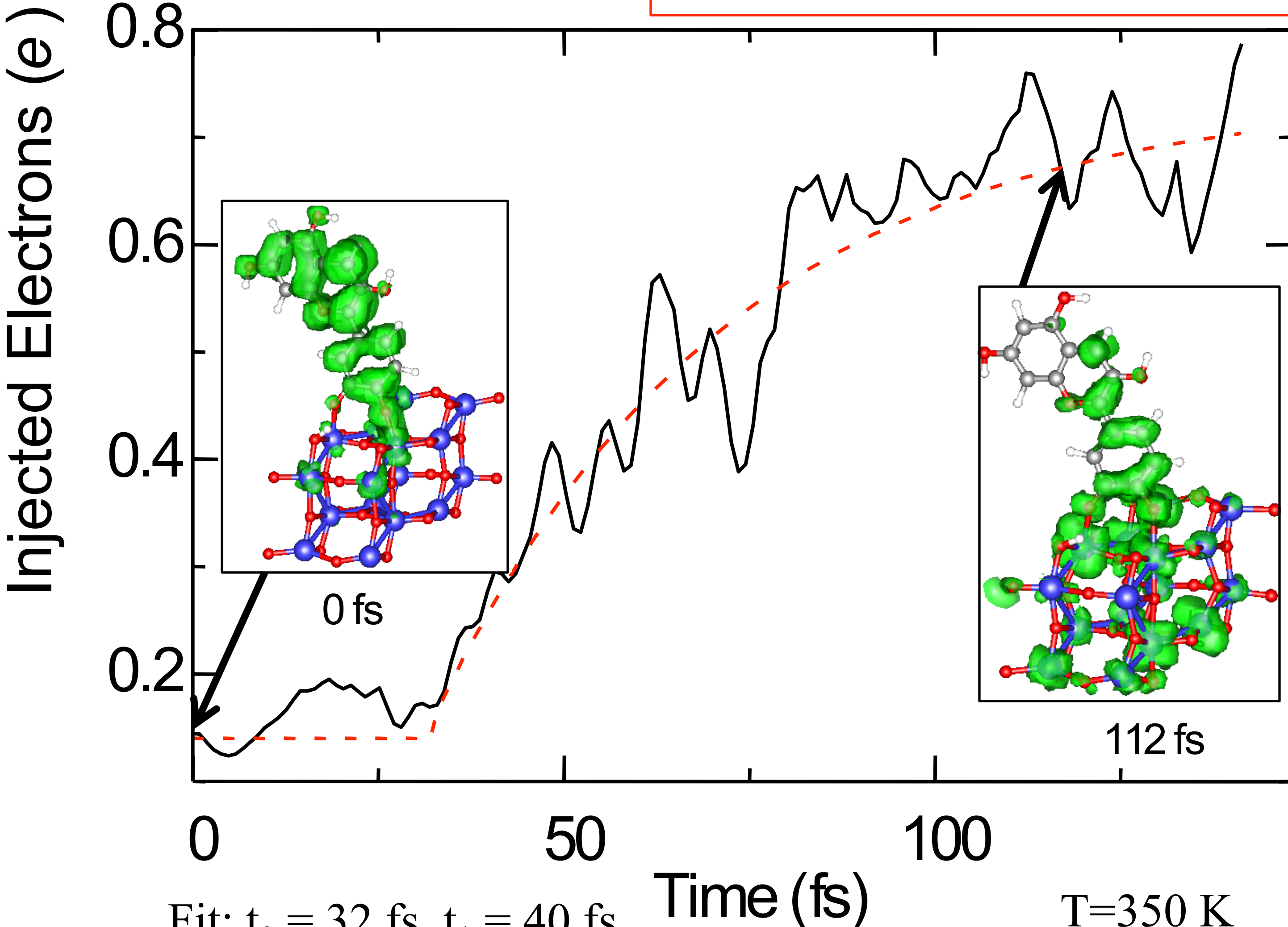


Optical absorption (TDDFT)



Charge injection dynamics:

$$\chi = \int d\mathbf{r} |\tilde{\psi}(\mathbf{r})|^2, \qquad \tilde{\psi}(\mathbf{r}) = \sum_{j \in \mathrm{TiO_2}} c_j \phi_j(\mathbf{r}),$$



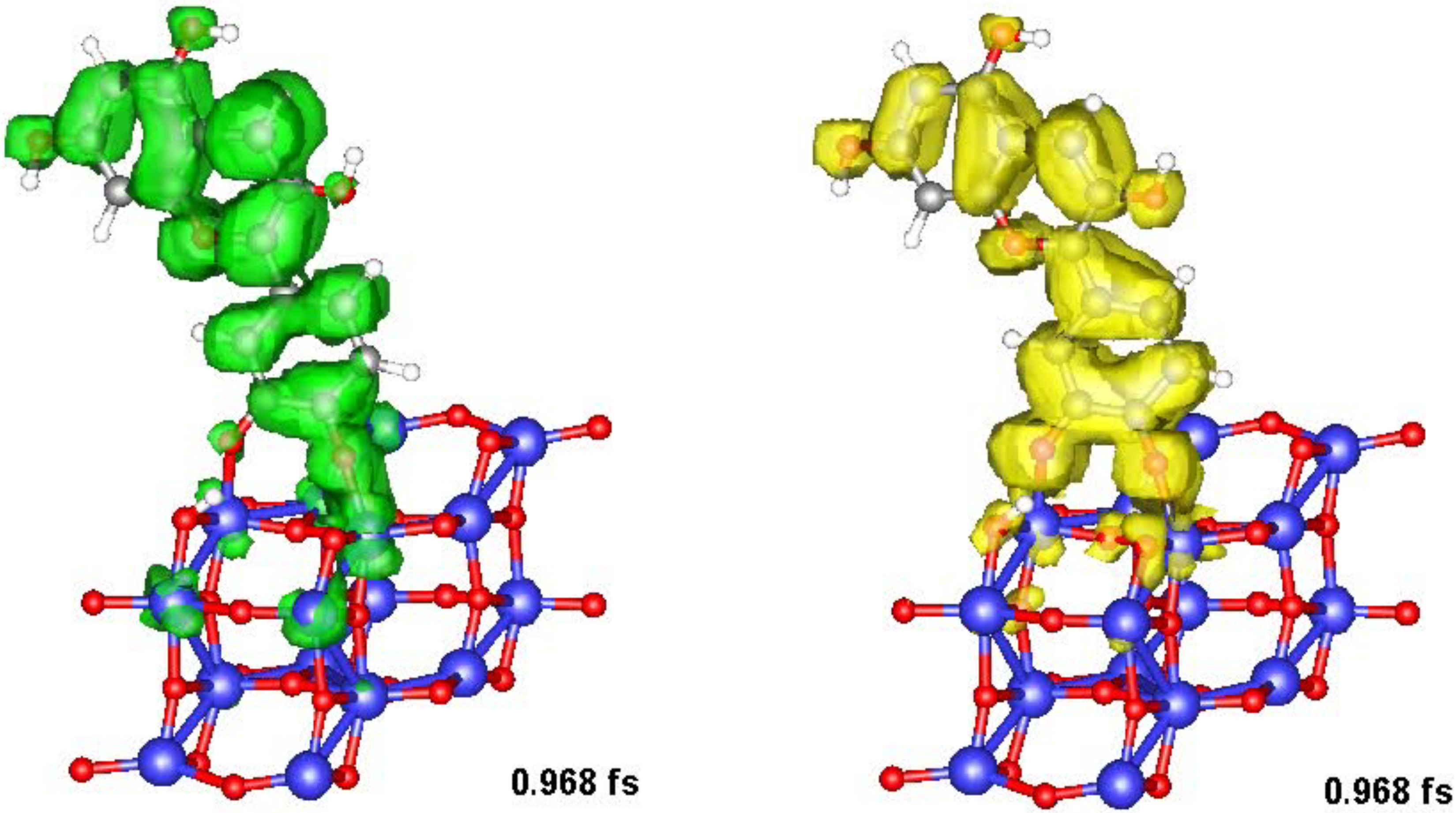
Fit: t_0 = 32 fs, t_1 = 40 fs

Expt.[a] : <100 fs

[a] Cherepy et al., JPCB (1997).

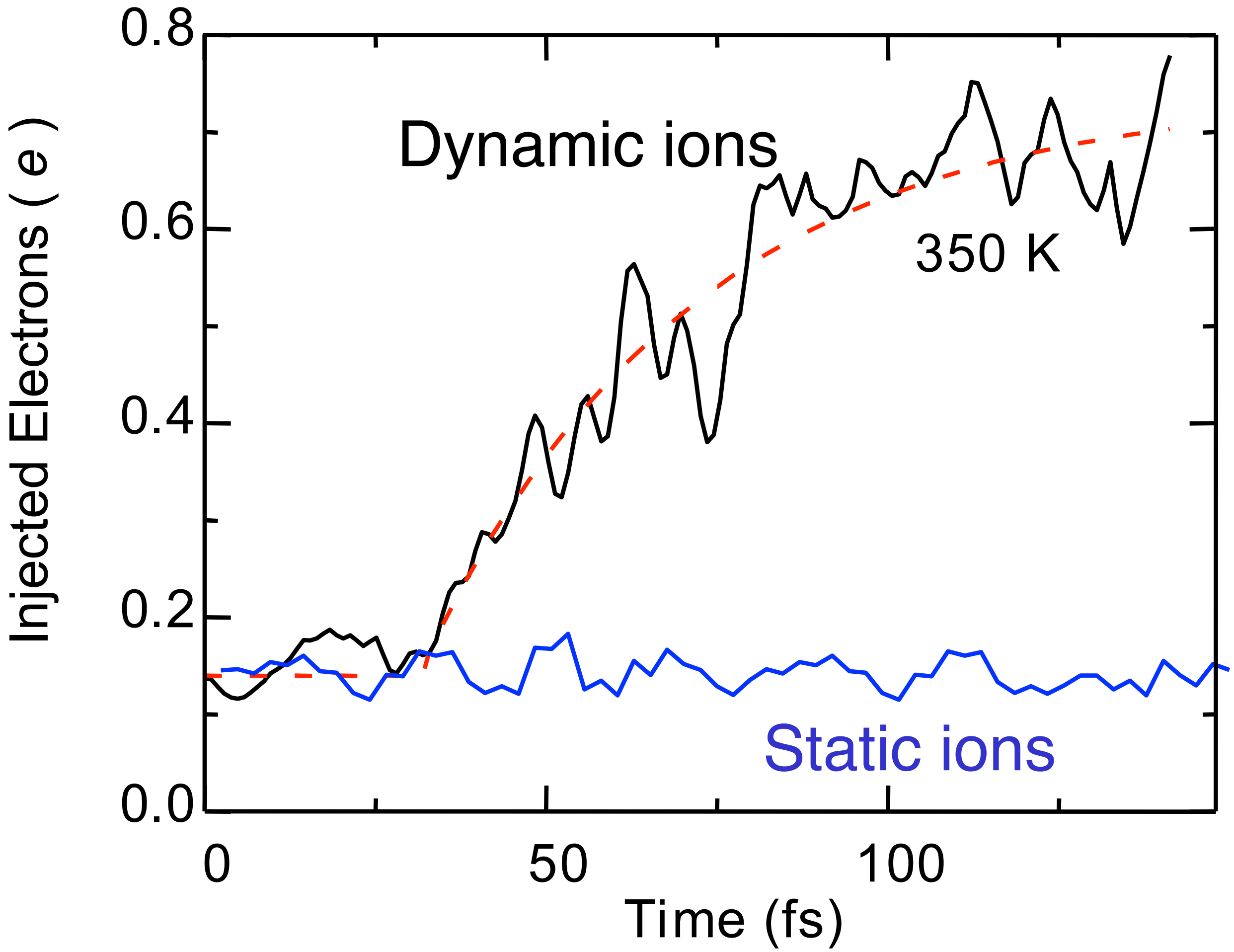
T=350 K

δt=0.02419 fs

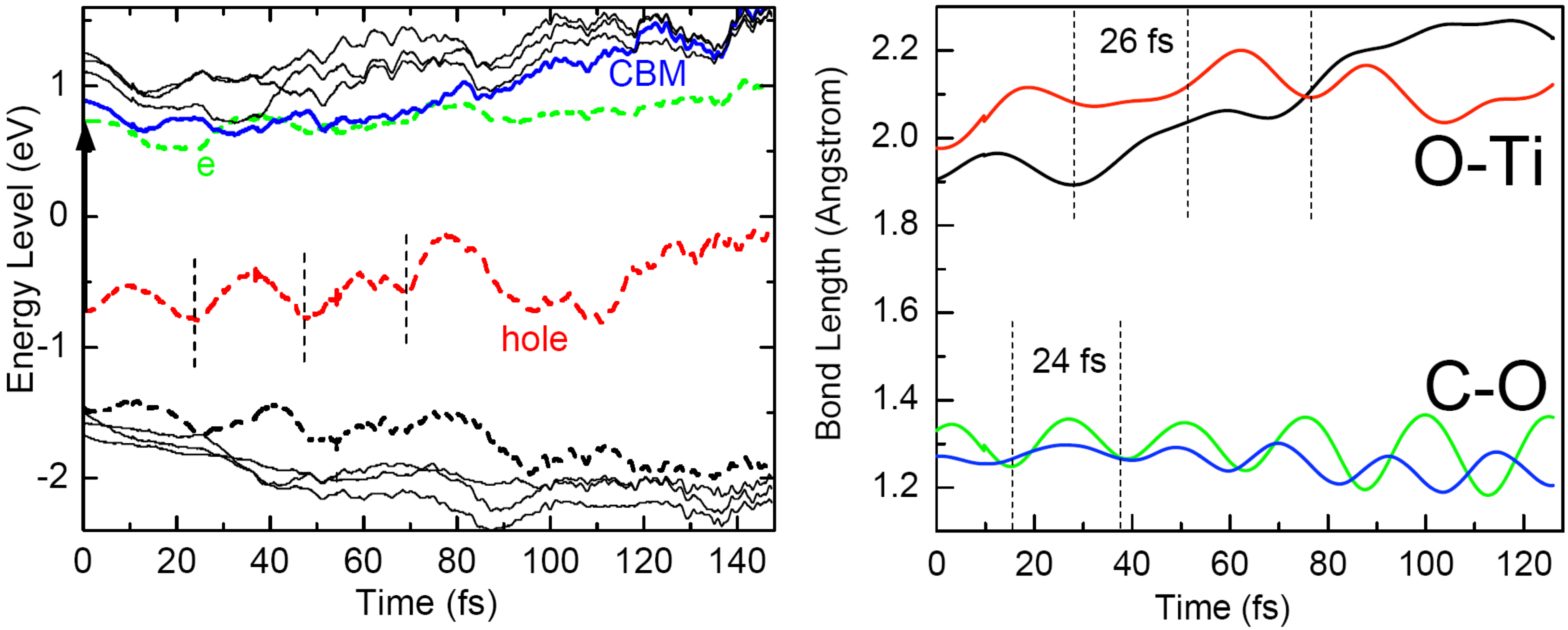


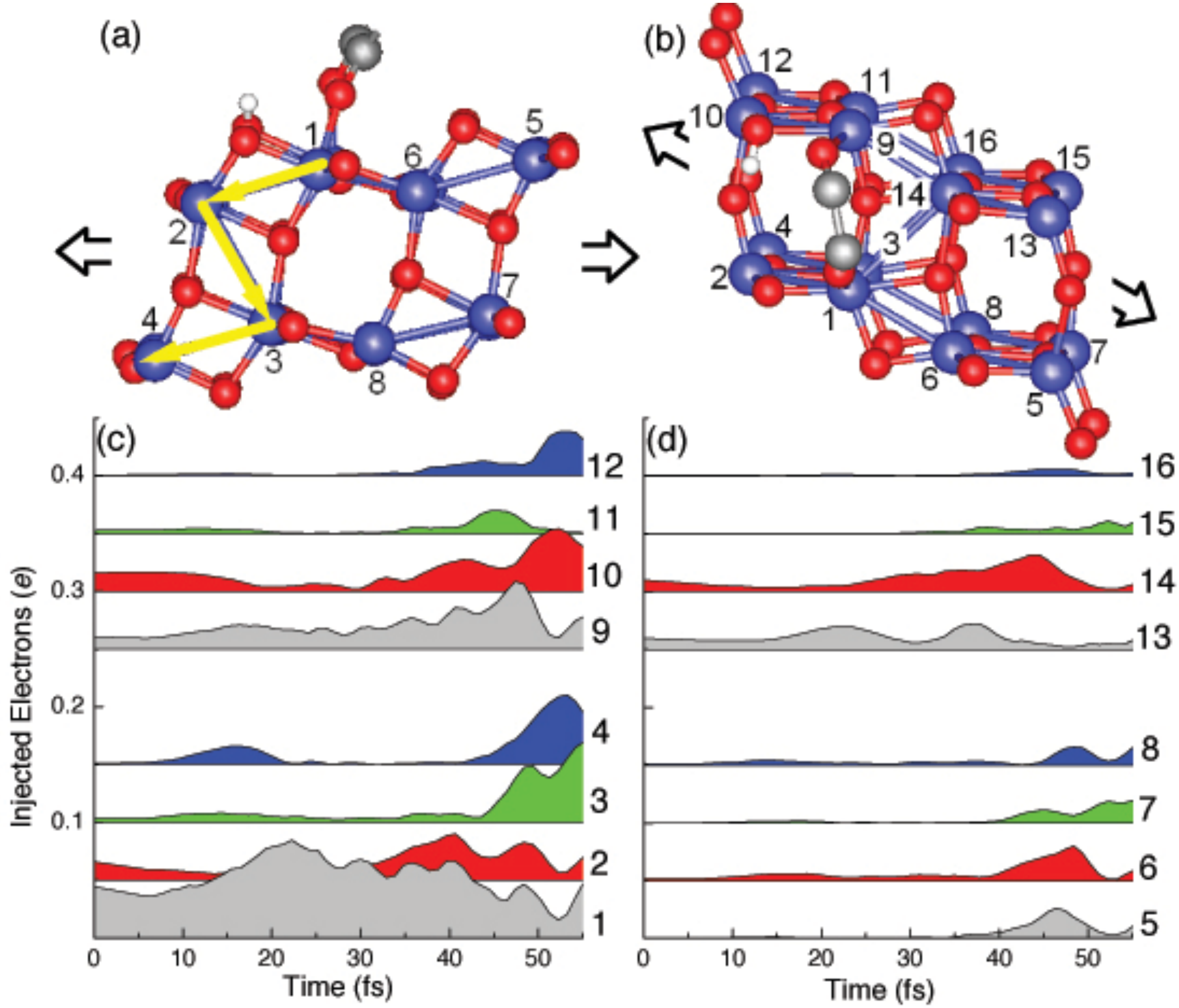
Exciton dynamics in OPV's: X. Zhang, Z. Li, Gang Lu, PRB 84 235208 (2011)

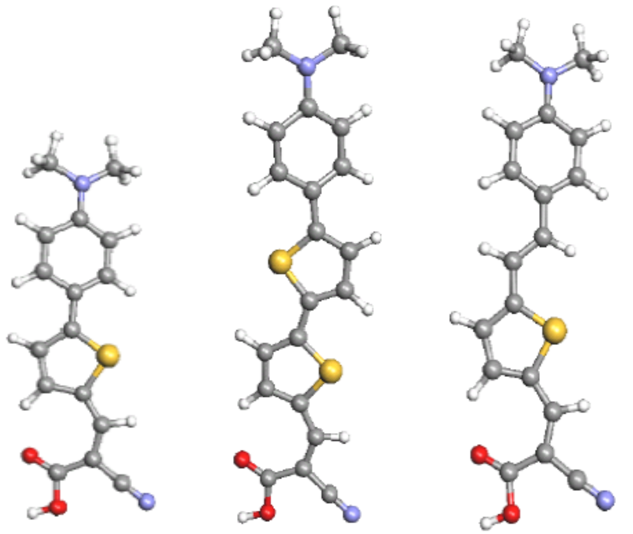
Importance of coupled e-ion dynamics



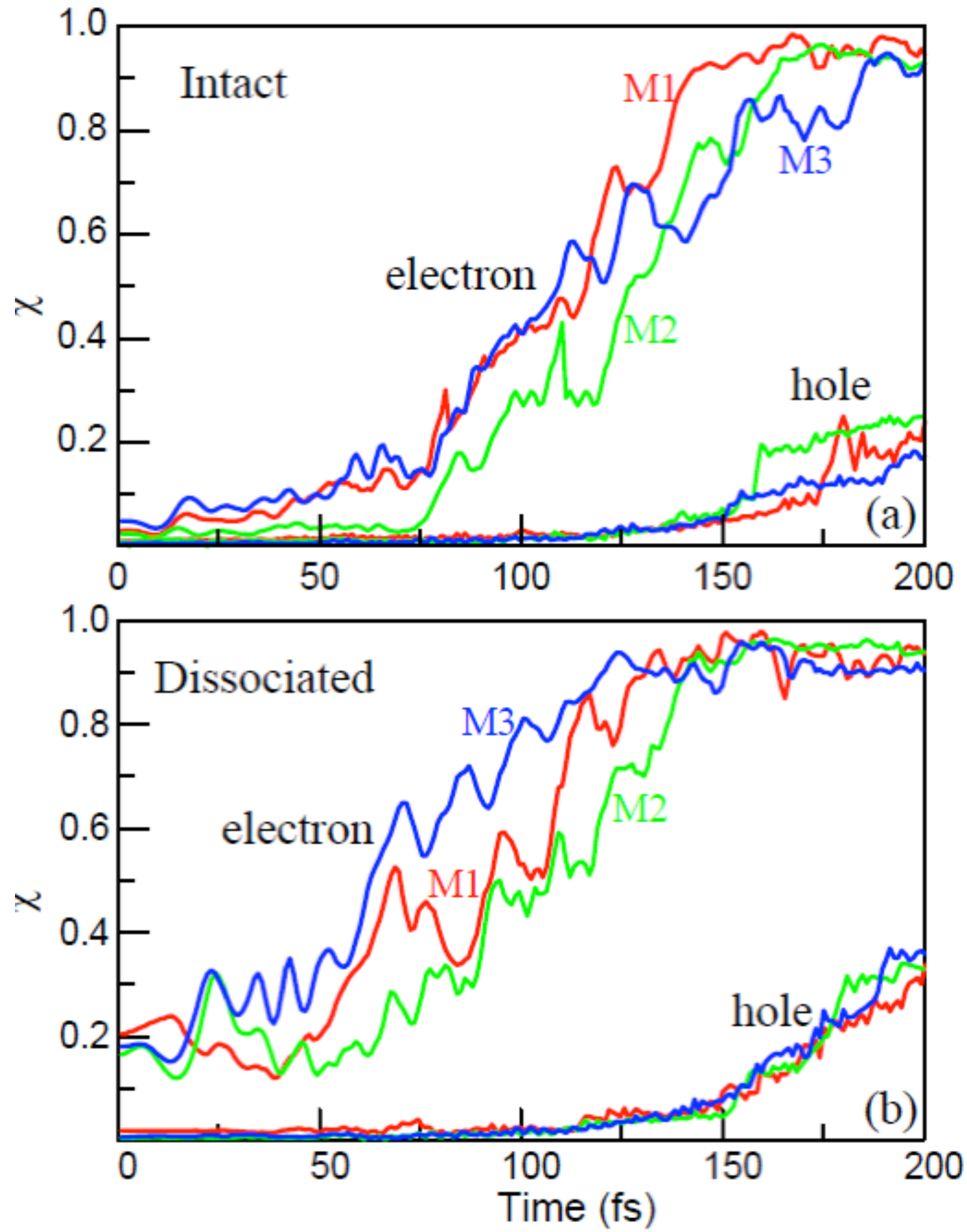
Coupling of electron-phonon motion




(a)
(b)
(c)
(d)
Injected Electrons (e)
Time (fs)
Time (fs)
0.1
0.2
0.3
0.4
0
10
20
30
40
50
12
11
10
9
4
3
2
1
16
15
14
13
8
7
6
5

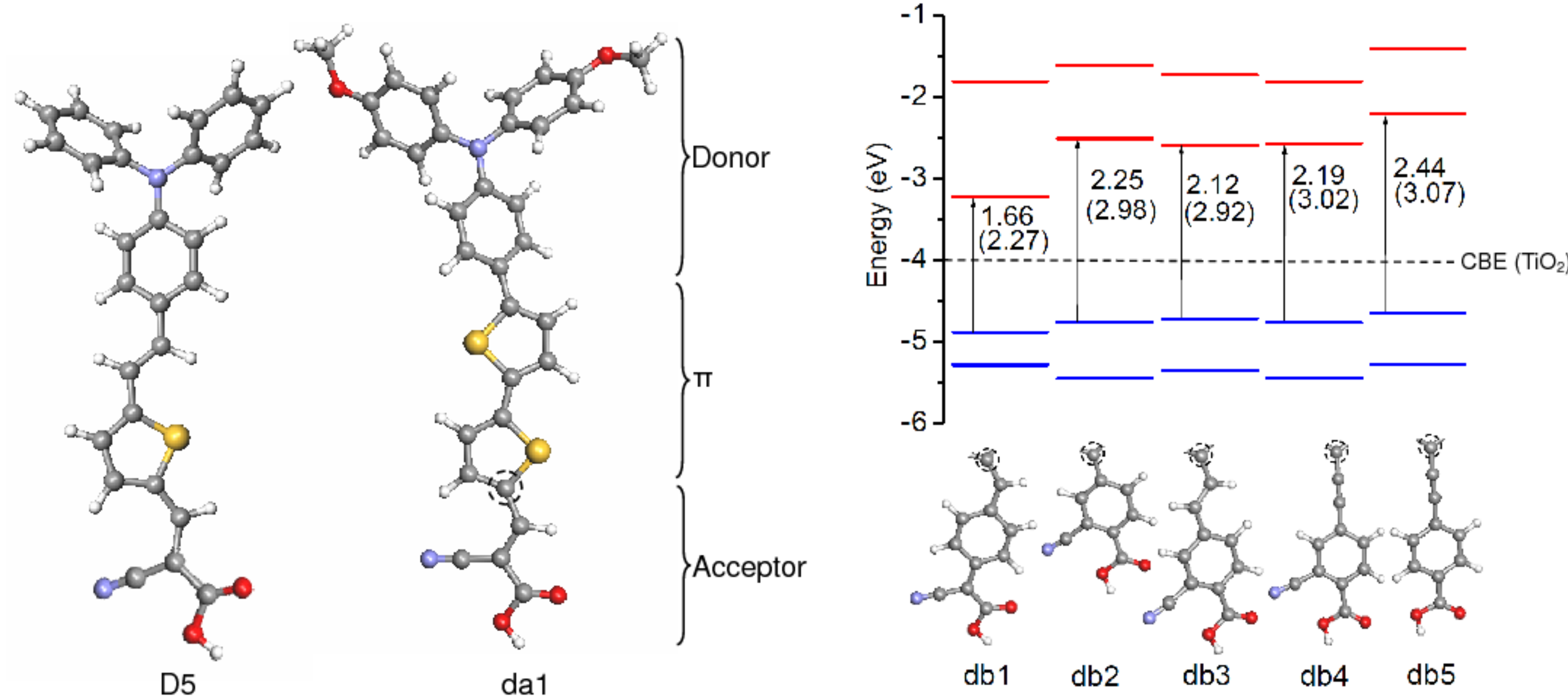


M1 M2 M3



- $t_{M1} < t_{M2} < t_{M3}$
- $t_{disso.} < t_{intact}$

Design of new dyes (not yet tried in experiments)

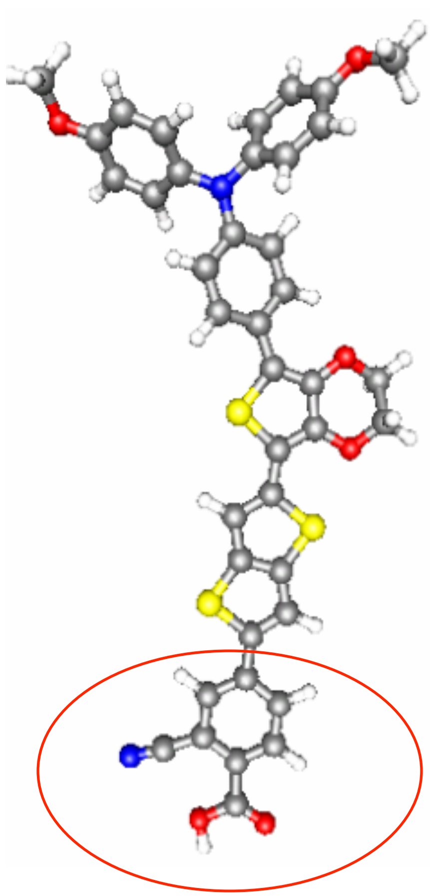


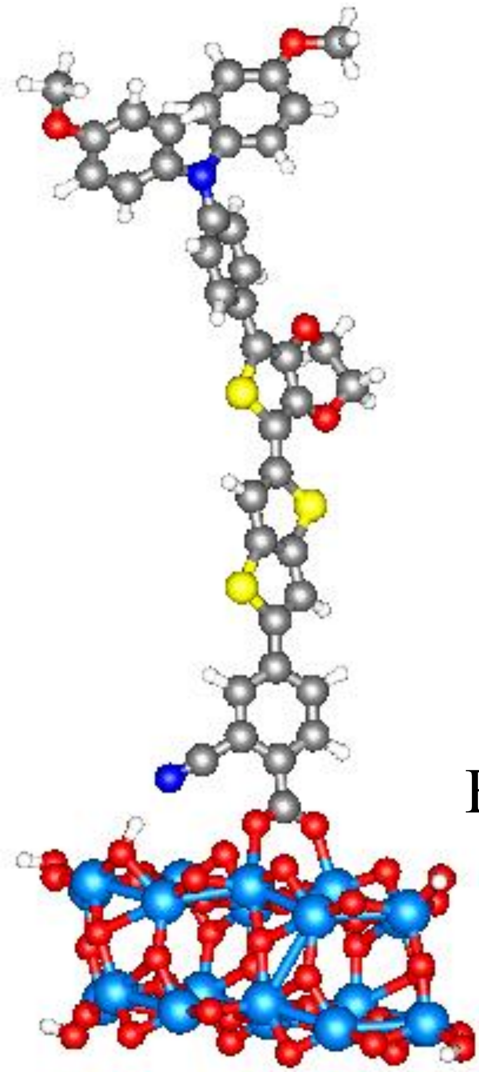
Design of Dye Acceptors for Photovoltaics from First-Principles Calculations

Sheng Meng, Efthimios Kaxiras, Md. K. Nazeeruddin, and Michael Gratzel

J. Phys. Chem. C 2011, **115**, 9276–9282

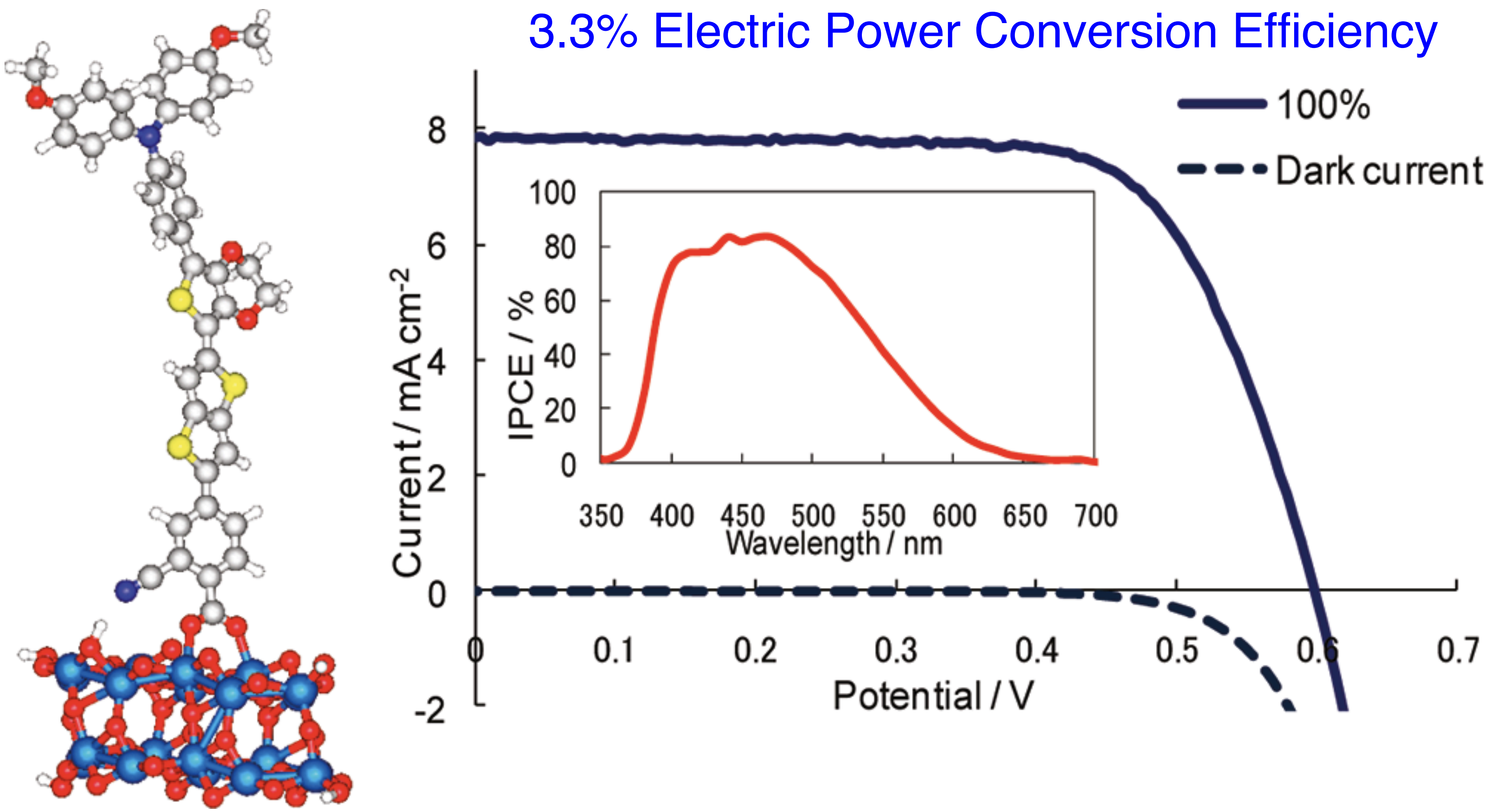
Enhanced dye binding to TiO_2





E_b=1.52 eV

84% Incident Photon to Current Efficiency,
3.3% Electric Power Conversion Efficiency



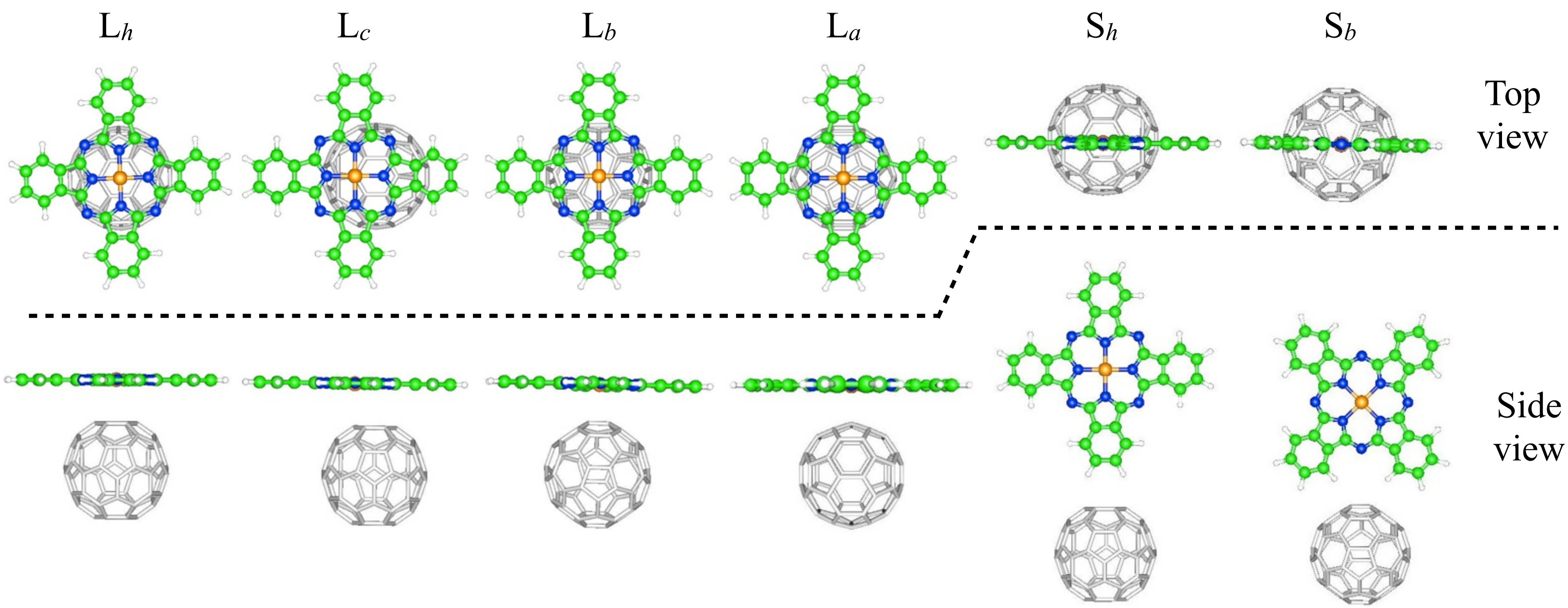
D-π-A Dye System Containing Cyano-Benzoic Acid as Anchoring Group for Dye-Sensitized Solar Cells

Masataka Katono, Takeru Bessho, Sheng Meng, Robin Humphry-Baker, Guido Rothenberger ,Shaik M. Zakeeruddin, Efthimios Kaxiras, and Michael Gratzel

Langmuir 2011, **27**, 14248–14252

Organic PV cells

The M-phthalocyanine / C_{60} system: prototypical OPV (M=Cu, Zn)

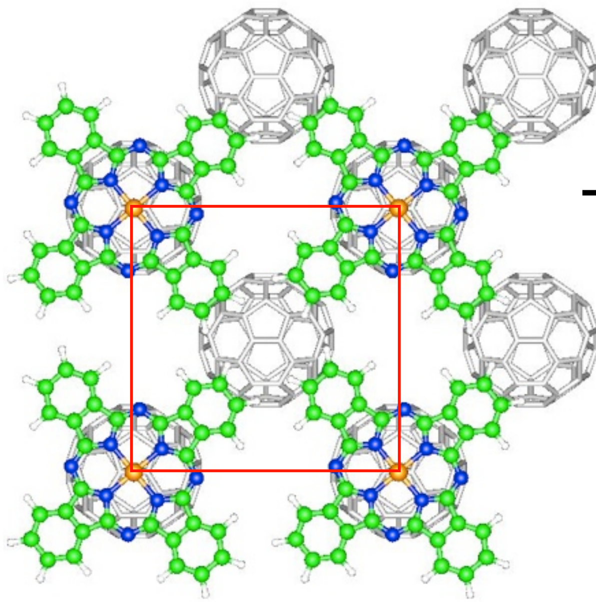


Lying down

Standing up

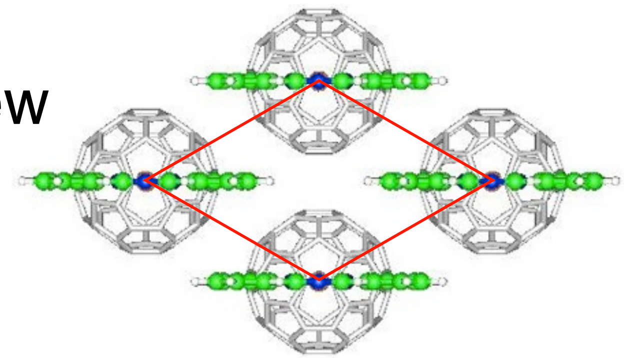
Periodic structures:

on (100) surface of C_{60} film



on (111) surface of C_{60} film

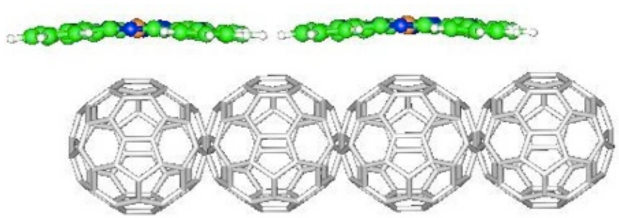
Top view

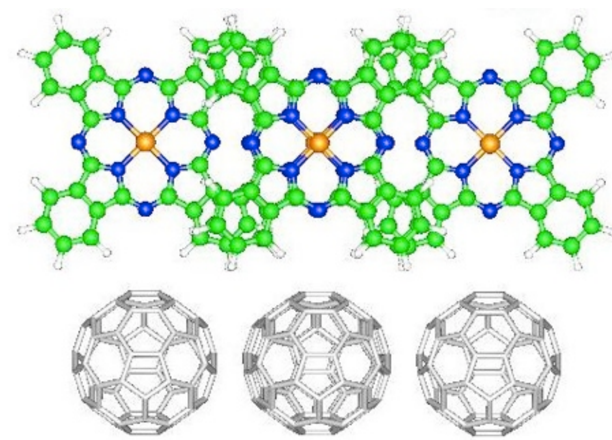


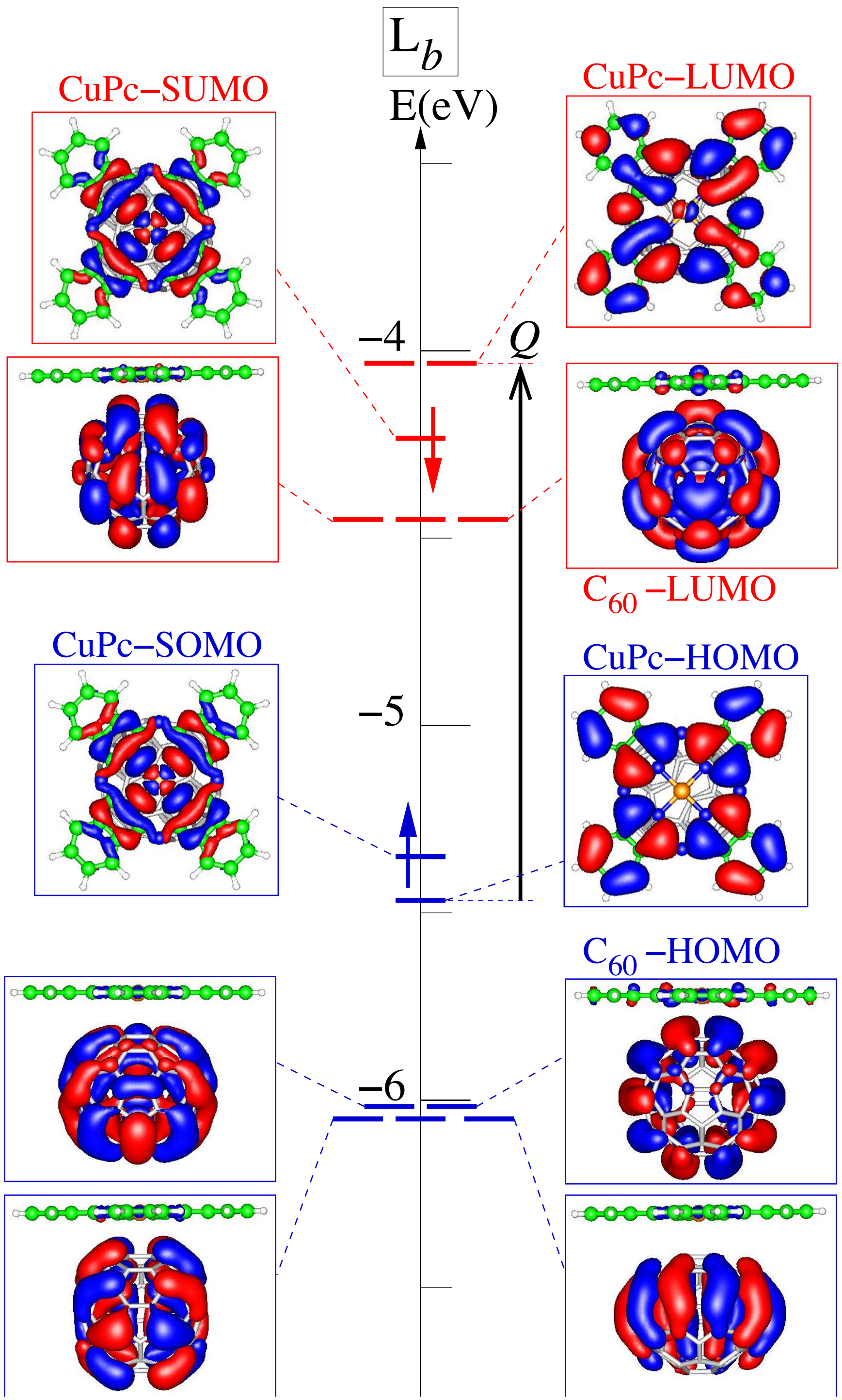
(b)

(a)

Side view

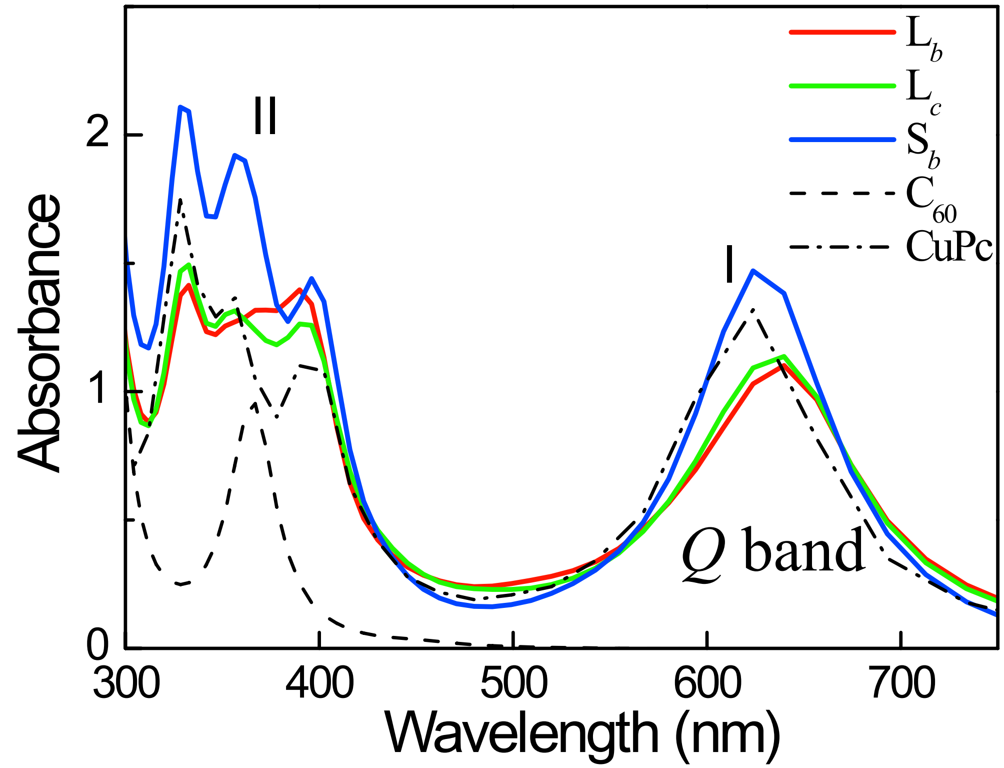






<u>C_{60} spectrum</u>

Expt. :	330	270	235	212
The. :	365	288	230	210



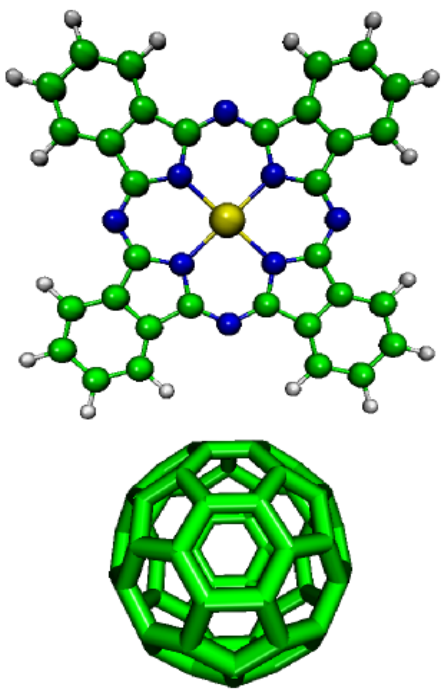
<u>M-Pc (M=Zn, Cu, …) spectrum</u>

Expt.: Q band ~650 nm

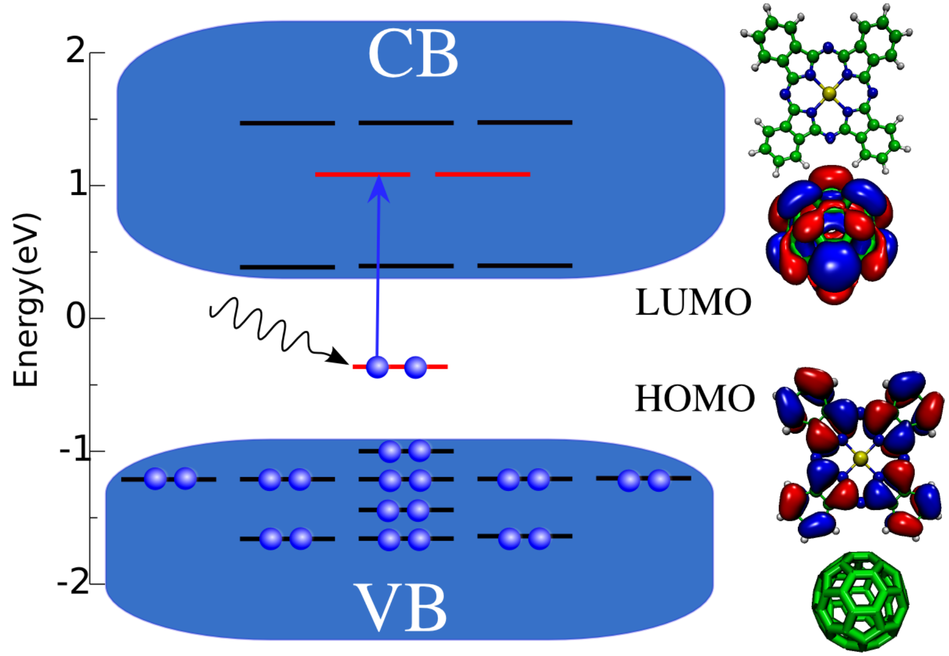
B band ~350 nm

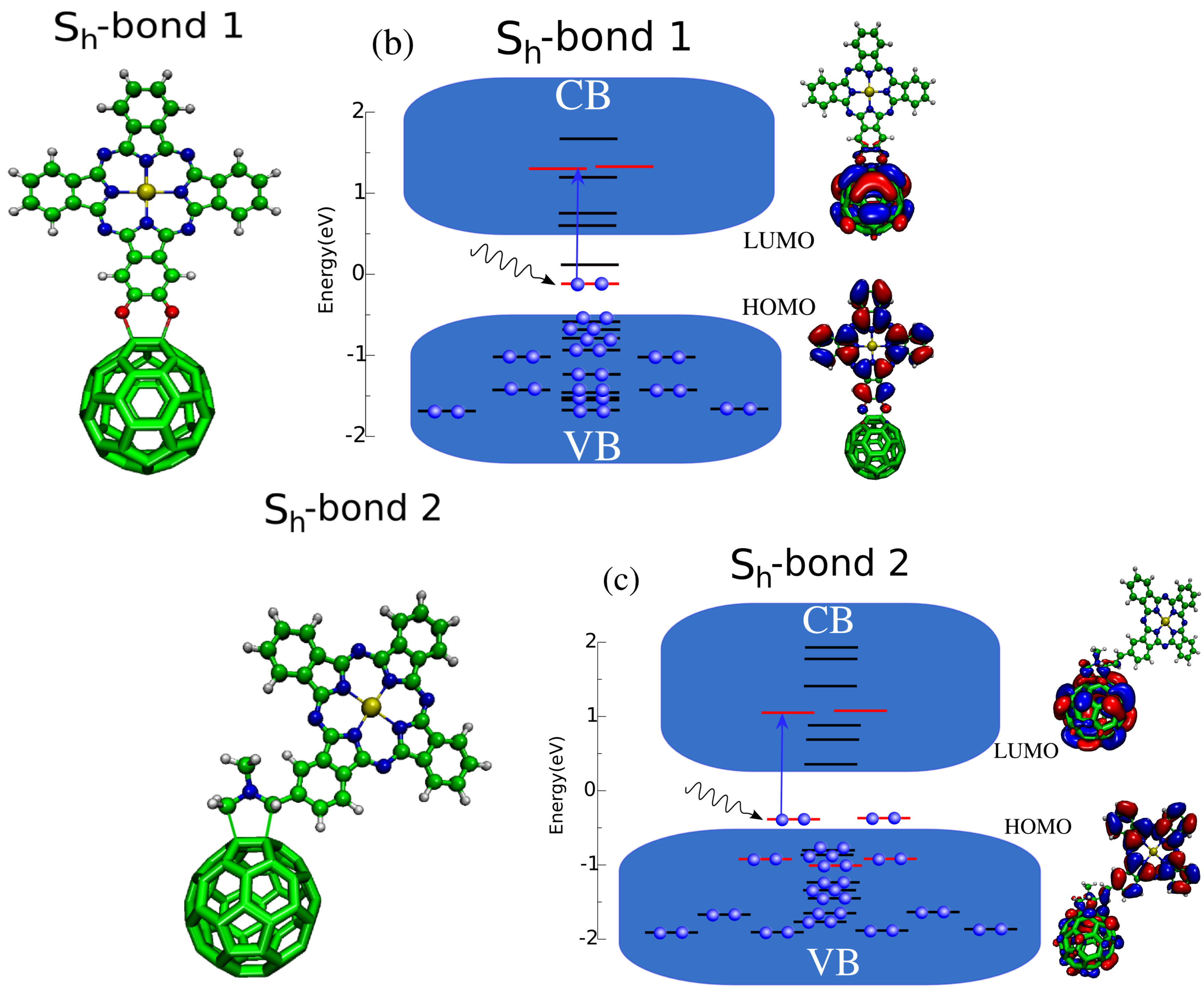
Edwards and Couterman, *J. Mol. Spectr.* (1970)

S_b

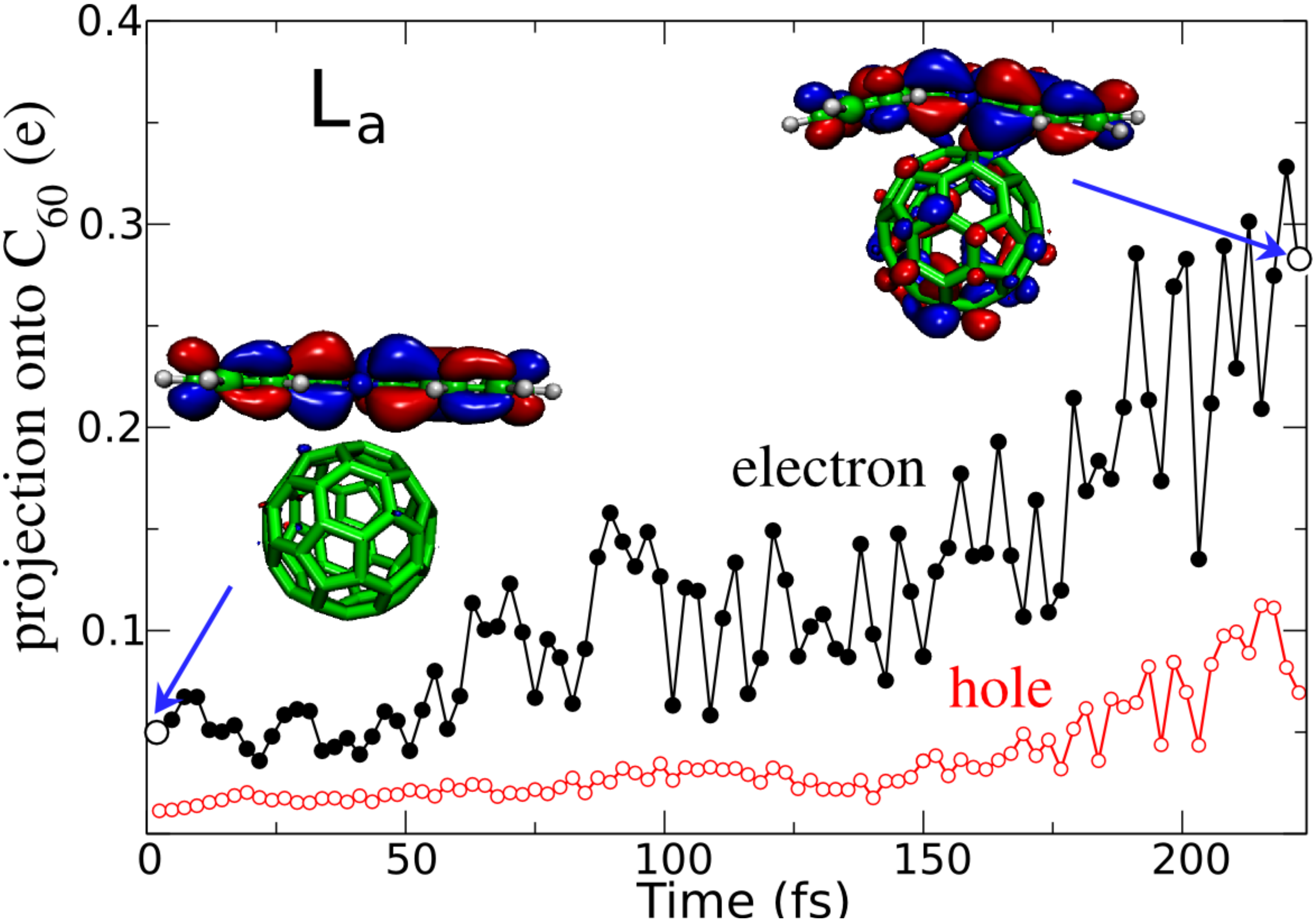


(a) S_b

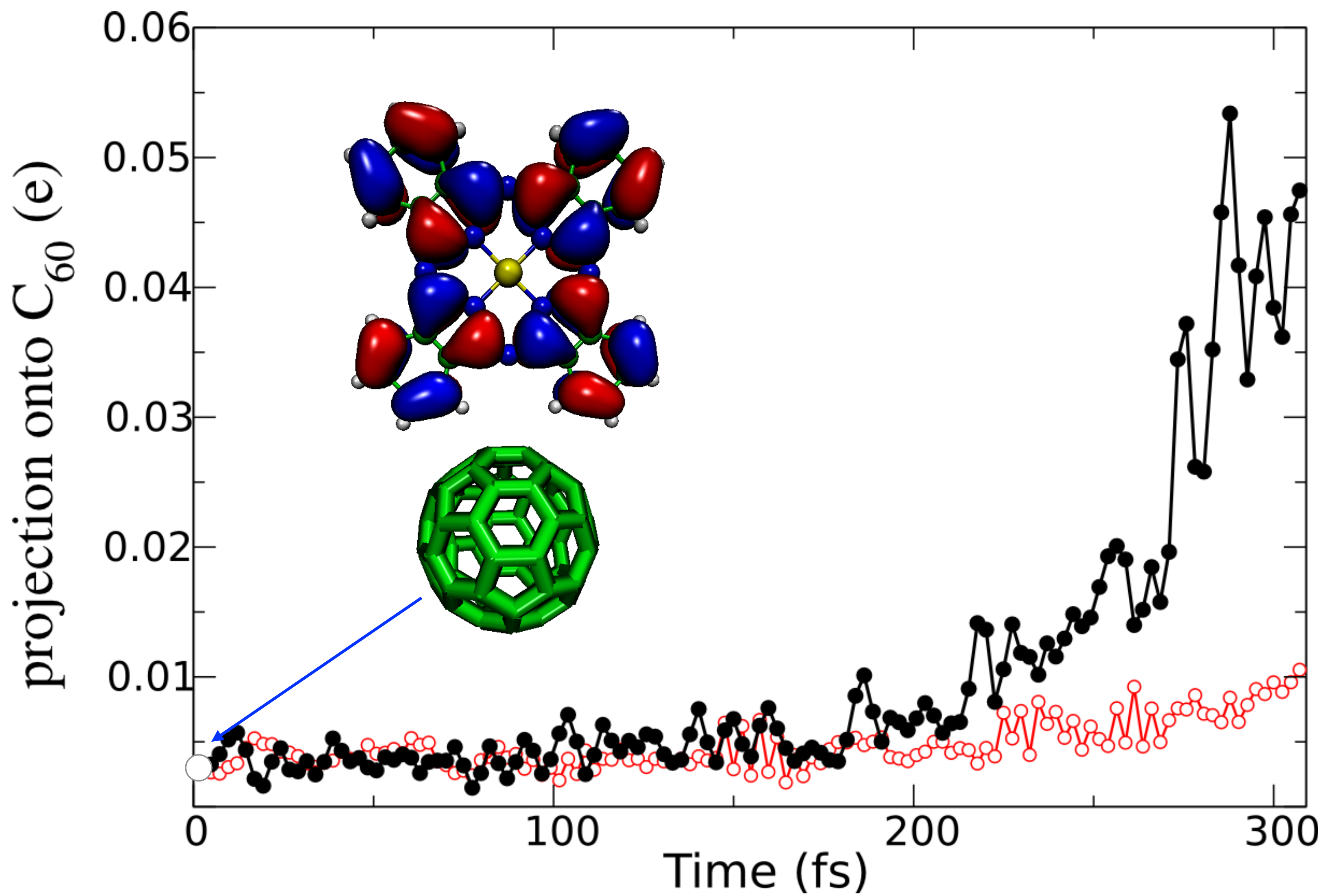




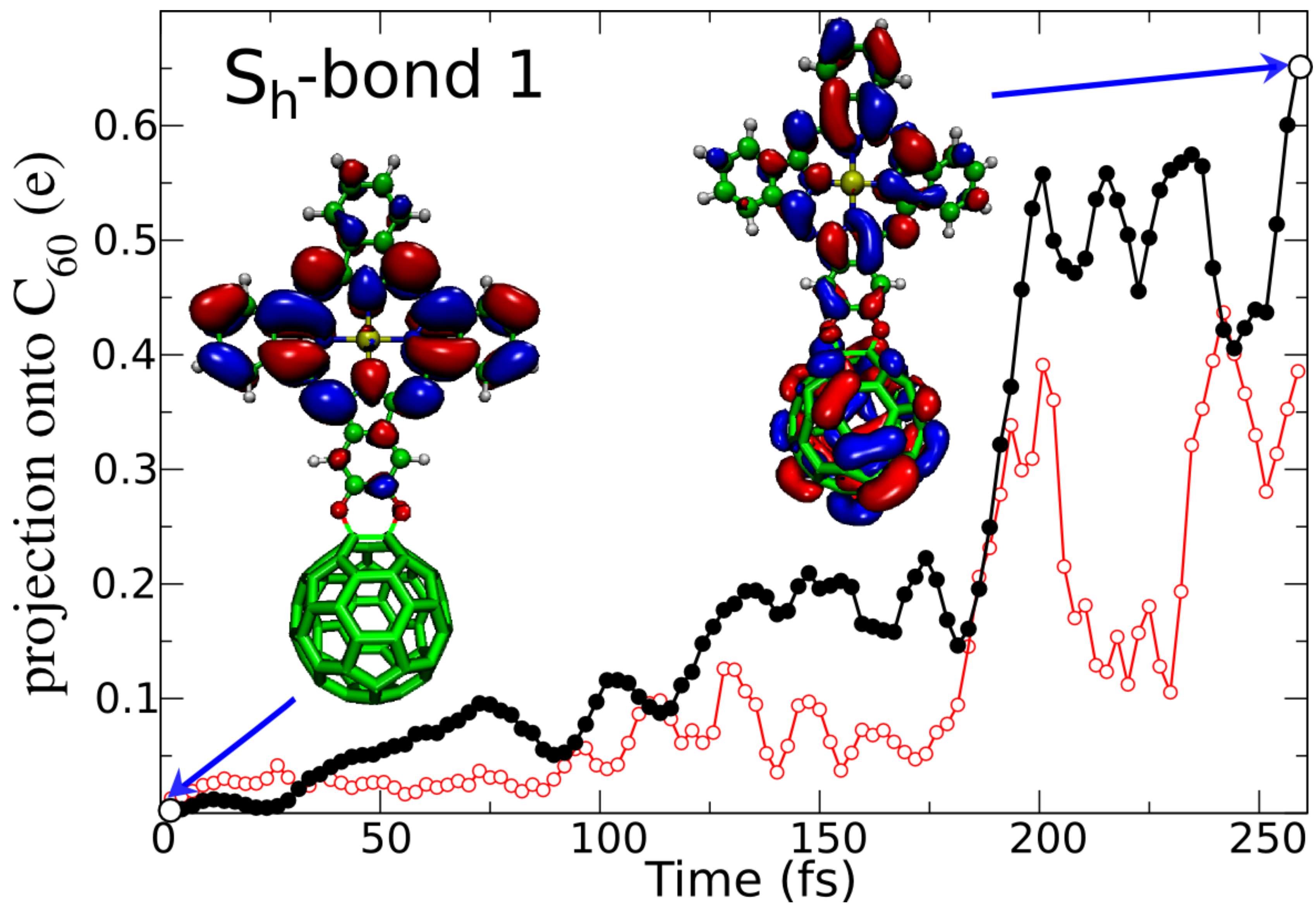
S_h-bond 1
(b)
S_h-bond 1
CB
VB
Energy(eV)
2
1
0
-1
-2
LUMO
HOMO
S_h-bond 2
(c)
S_h-bond 2
CB
VB
Energy(eV)
2
1
0
-1
-2
LUMO
HOMO



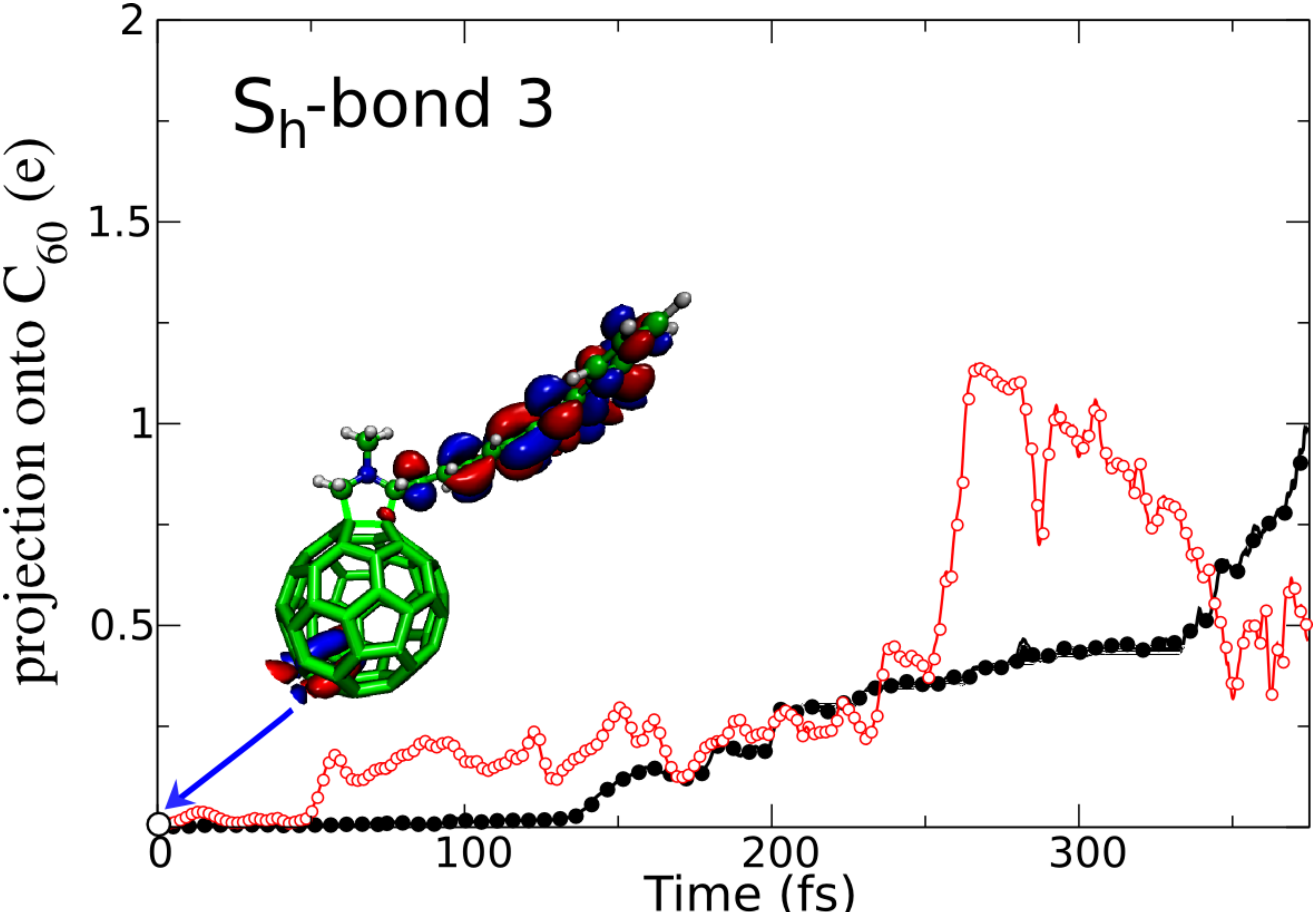
L_a
electron
hole
projection onto C_60 (e)
Time (fs)
0.4
0.3
0.2
0.1
0
50
100
150
200



0.06
0.05
0.04
0.03
0.02
0.01
projection onto C_{60} (e)
0
100
200
300
Time (fs)



S$_h$-bond 1
projection onto C$_{60}$ (e)
Time (fs)
0
50
100
150
200
250
0.1
0.2
0.3
0.4
0.5
0.6



S_h-bond 3
projection onto C_{60} (e)
2
1.5
1
0.5
0
0
100
200
300
Time (fs)

Highlights:

- Efficient theoretical tool for modeling **trends** in hybrid systems
- Insights and predictions for charge transfer in DSSC's
- Insights into M-Pc/C_{60} system (excitation, charge transfer)
- Predictions for specific molecular/substrate arrangements

Issues:

- "Band alignment" – band gaps, eigenvalues
- Exciton dynamics – e-h coupling
- Long range transport

Saving grace(s):

- Eigenvalue corrections: similar (?)
- Rates not affected by small changes (?)
- Trends in behavior more robust (?)