Multiscale Simulations of Materials: Exploring New Physics and Applications

With:
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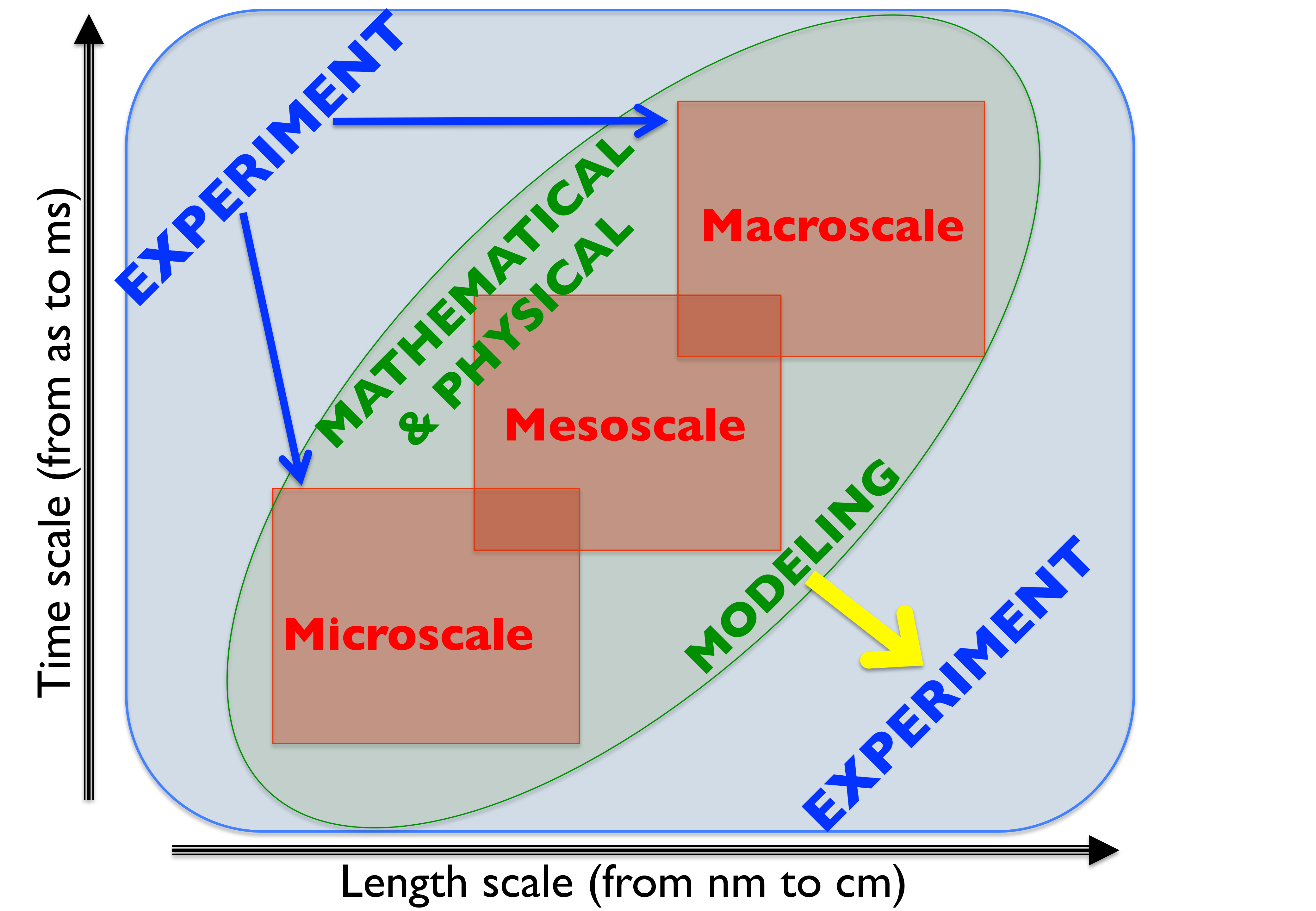
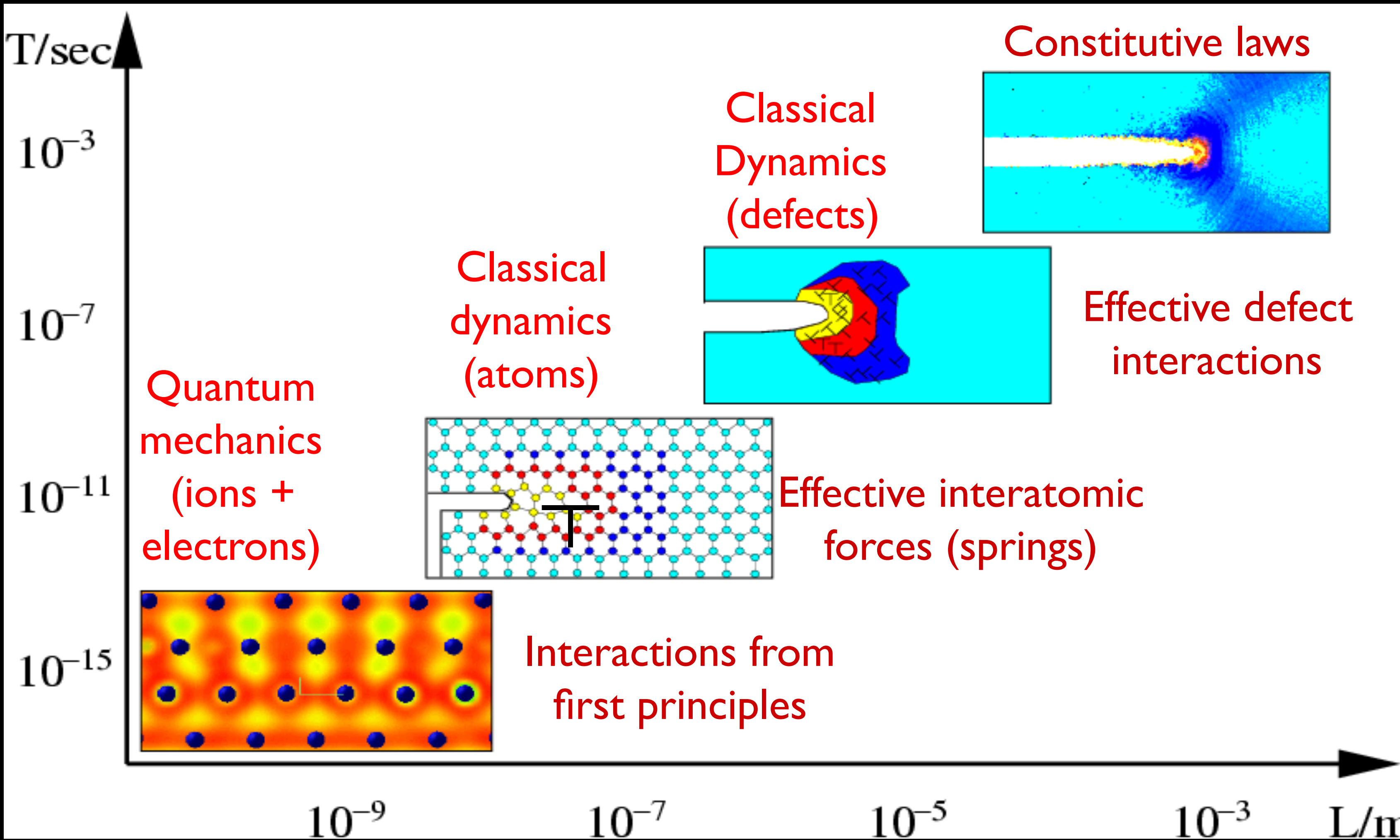
(earlier work: Sheng Meng, Jun Ren, Inst. of Phys., Ch. Acad. Sci.)

ICTP-ECAR Inaugural Symposium
Izmir – May 5-7, 2014



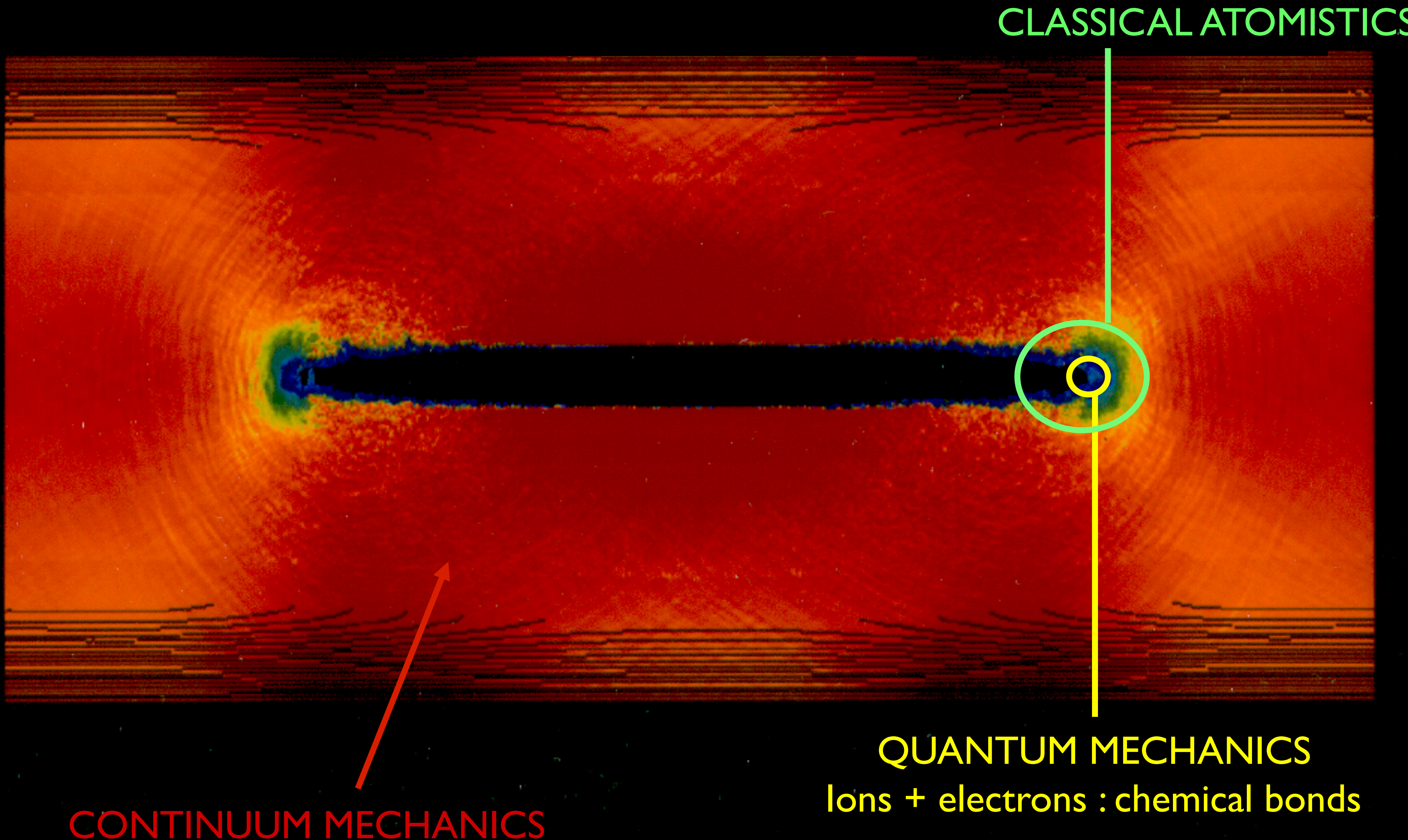
Time scale (from as to ms)
Length scale (from nm to cm)
EXPERIMENT
MATHEMATICAL & PHYSICAL
MODELING
Macroscale
Mesoscale
Microscale
EXPERIMENT

Multiple length/time scales: brittle fracture (corrosion)



Brittle fracture of silicon

Abraham, Broughton, Bernstein, Kaxiras, PRB (1998)



Density Functional Theory

Many-body:

$$\left(\hat{H} - E\right)\psi\left(\mathbf{r}_1\sigma_1, \mathbf{r}_2, \sigma_2, \ldots\right) = 0$$: Unsolvable

Hohenberg & Kohn (PRB, 1964):

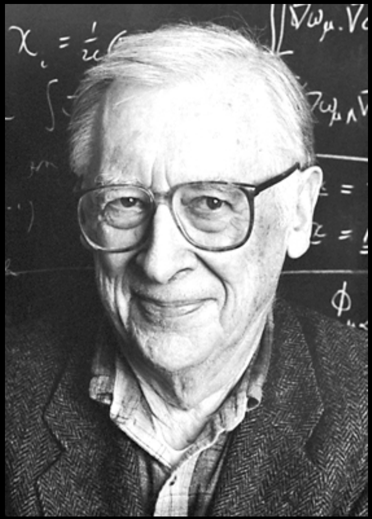
$$E\left[V(\mathbf{r})\right] = \min_{\rho(\mathbf{r})} E'\left[V(\mathbf{r}); \rho(\mathbf{r})\right]$$

Kohn & Sham (PRB, 1965):

$$E'\left[V(\mathbf{r}); \rho(\mathbf{r})\right] =$$

$$T_s[\rho] + E_{\mathrm{Hart}}[\rho] + \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r} + E_{\mathrm{xc}}[\rho]$$

$$\left(\hat{H}_{\mathrm{KS}} - \epsilon_i\right)\psi_i(\mathbf{r}) = 0$$



W. Kohn, J. Pople
Nobel Prize in
Chemistry, 1998

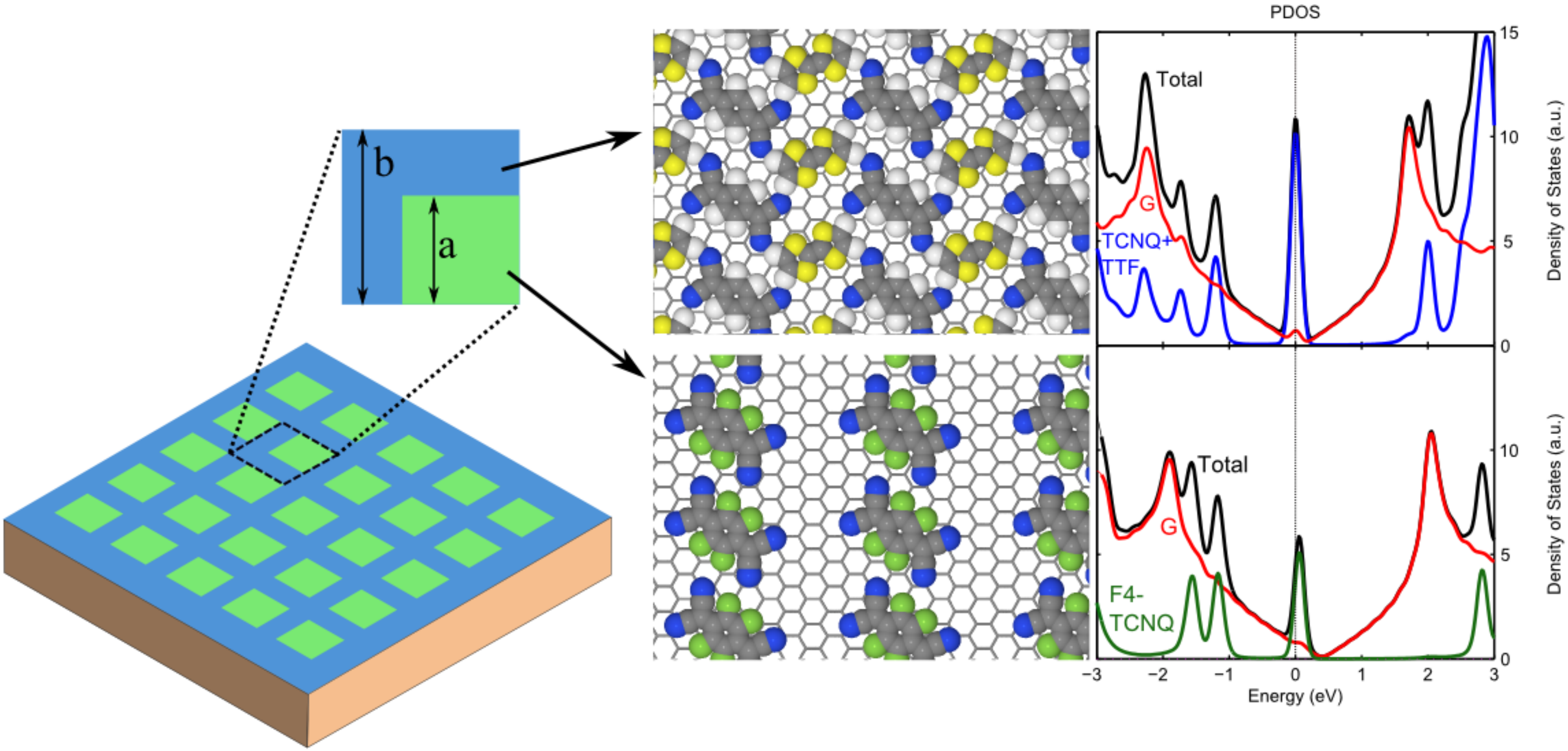
“Multiscale models for complex physical systems”

Nobel Prize in Chemistry 2013
Martin Karplus, Michael Levitt and Arieh Warshel

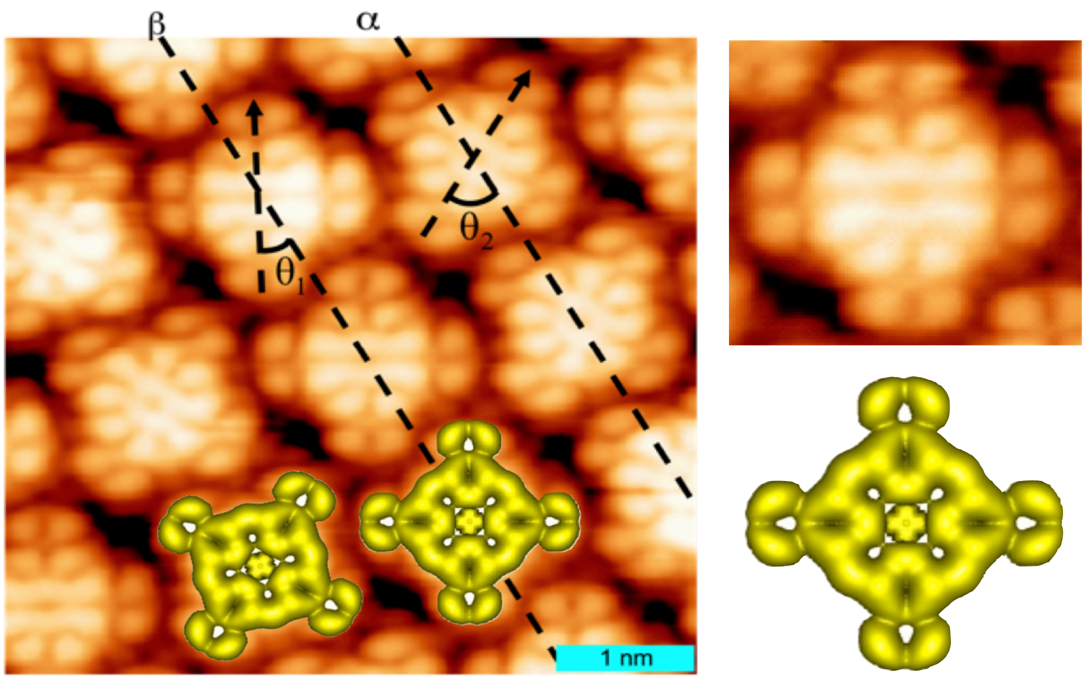
"for the development of multiscale models for complex chemical systems”
October 2013

Karplus: “I didn’t even know we were doing this!”

Proposal for a graphene-based plasmonic device



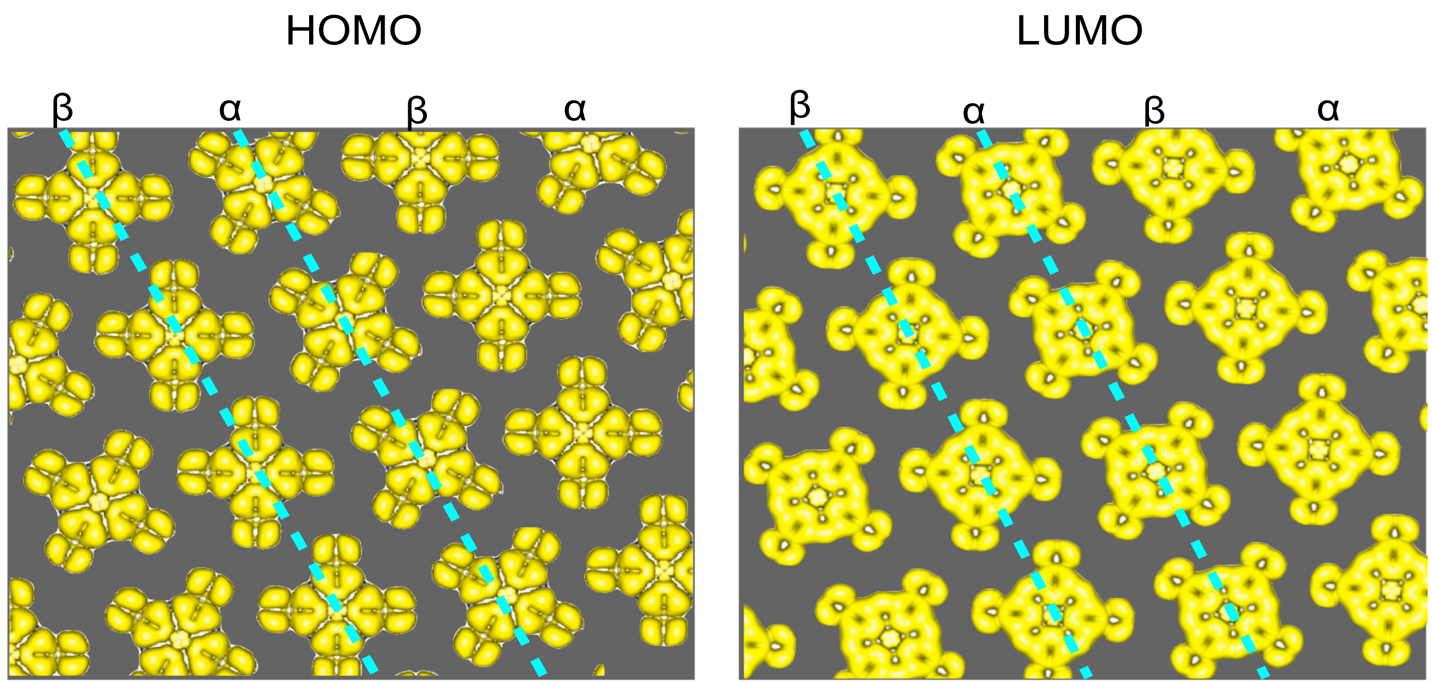
F4-TCNQ (blue area) and TCNQ+TTF (green area). Projected DOS shows effects of doping and the added molecular DOS signature to the total DOS due to the molecule-graphene interactions.



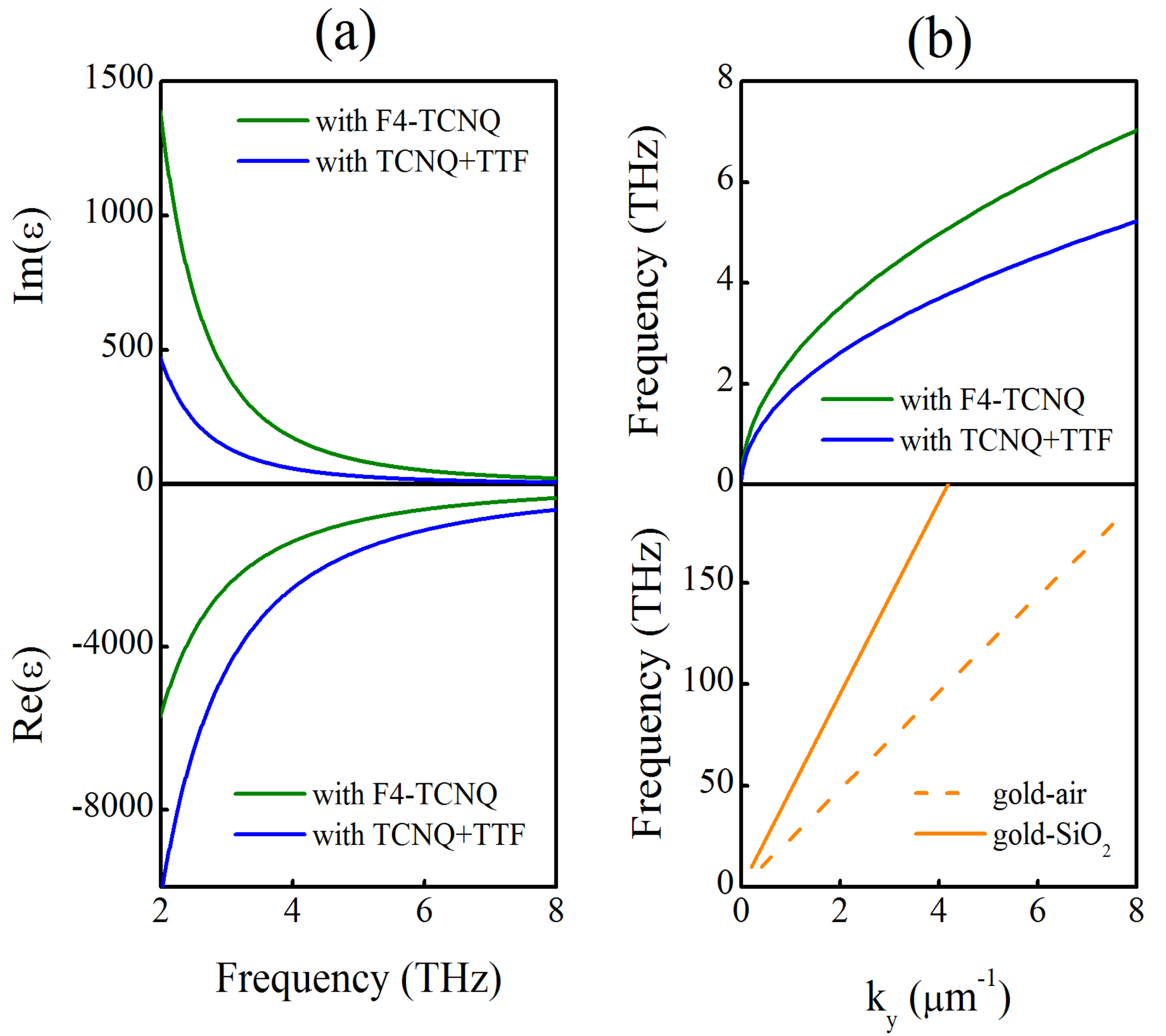
Properties of copper (fluoro-) phthalocyanine layers deposited on epitaxial graphene

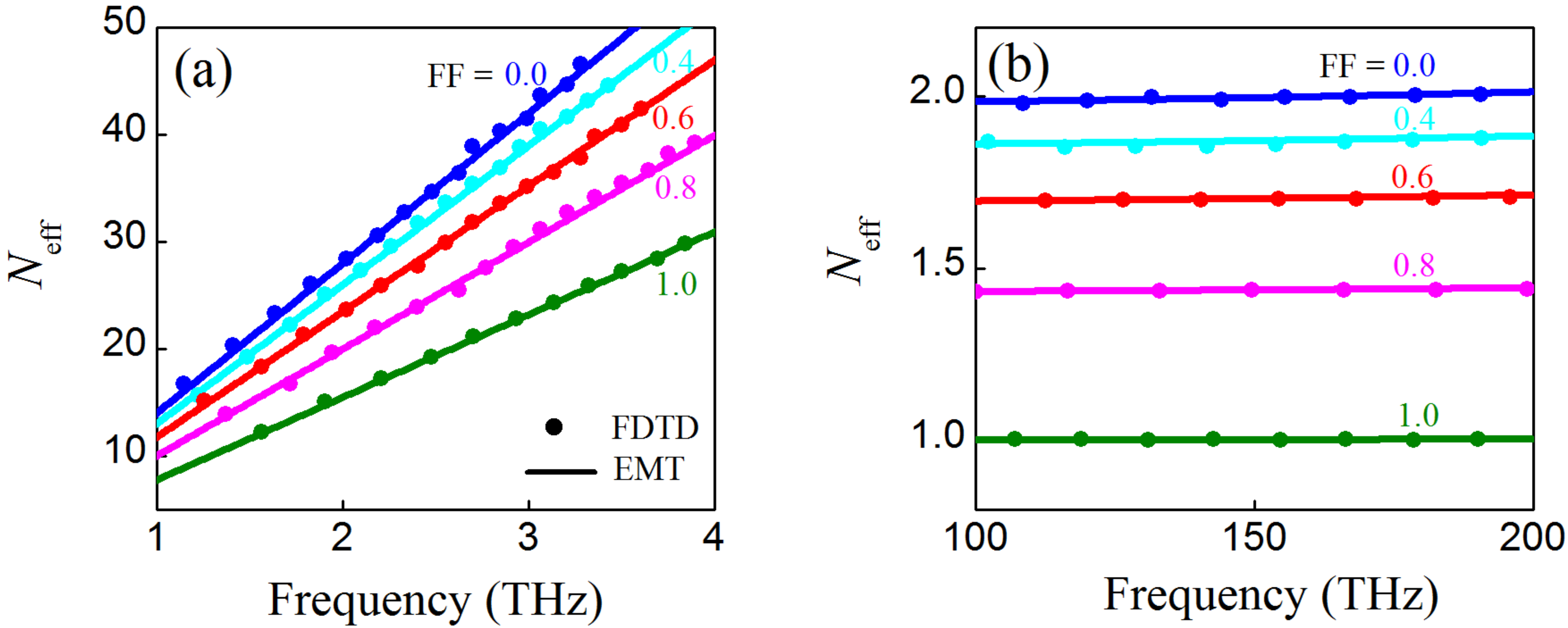
Ren, Sheng Meng, Yi-Lin Wang, Xu-Cun Ma, Qi-Kun Xue, and Efthimios Kaxiras

JOURNAL OF CHEMICAL PHYSICS **134**, 194706 (2011)



Spatially resolved dielectric function

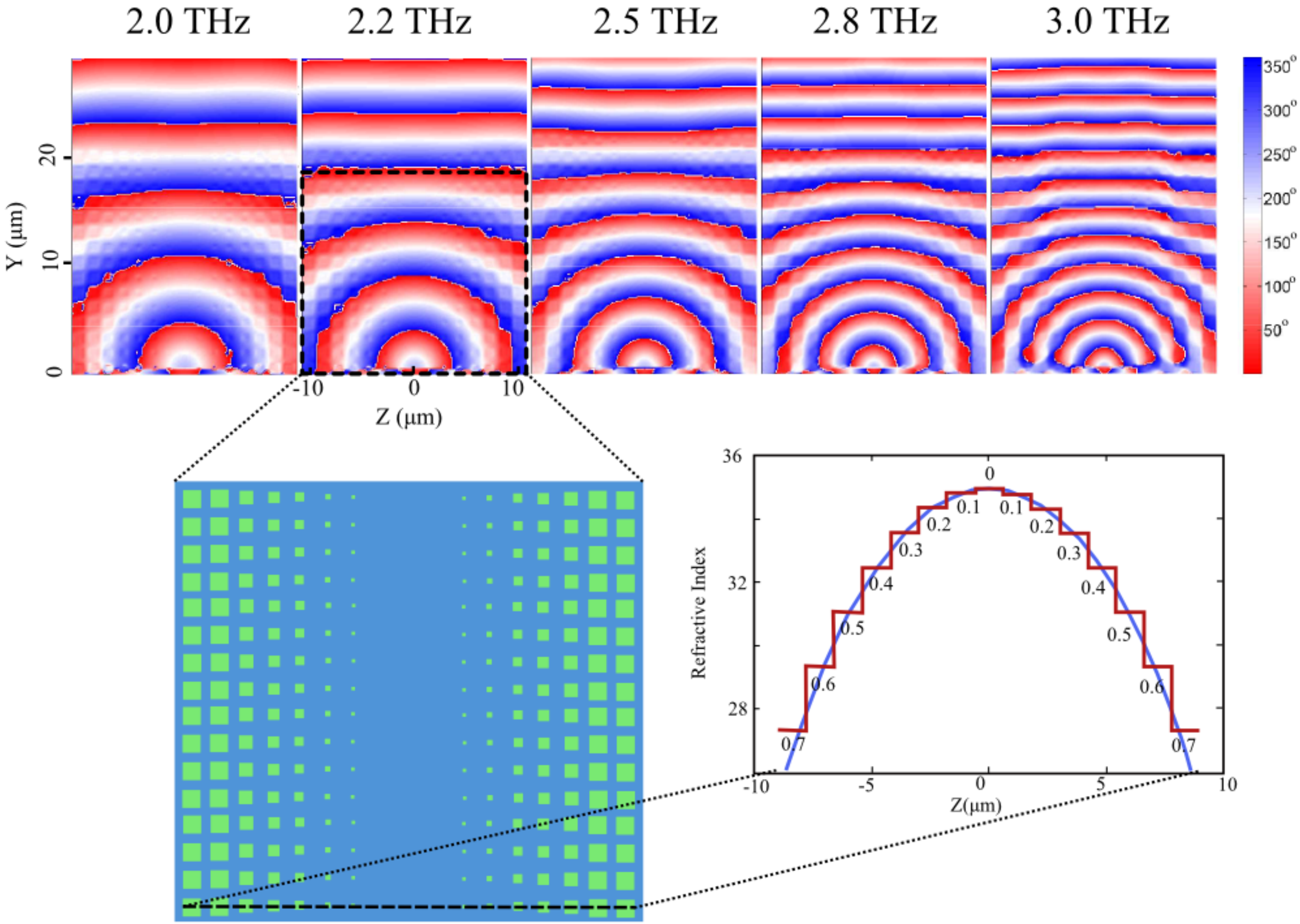




Refractive indices of metamaterials made of: (a) patterned graphene, (b) a gold film on top of Gradient Refractive Index dielectric substrate.

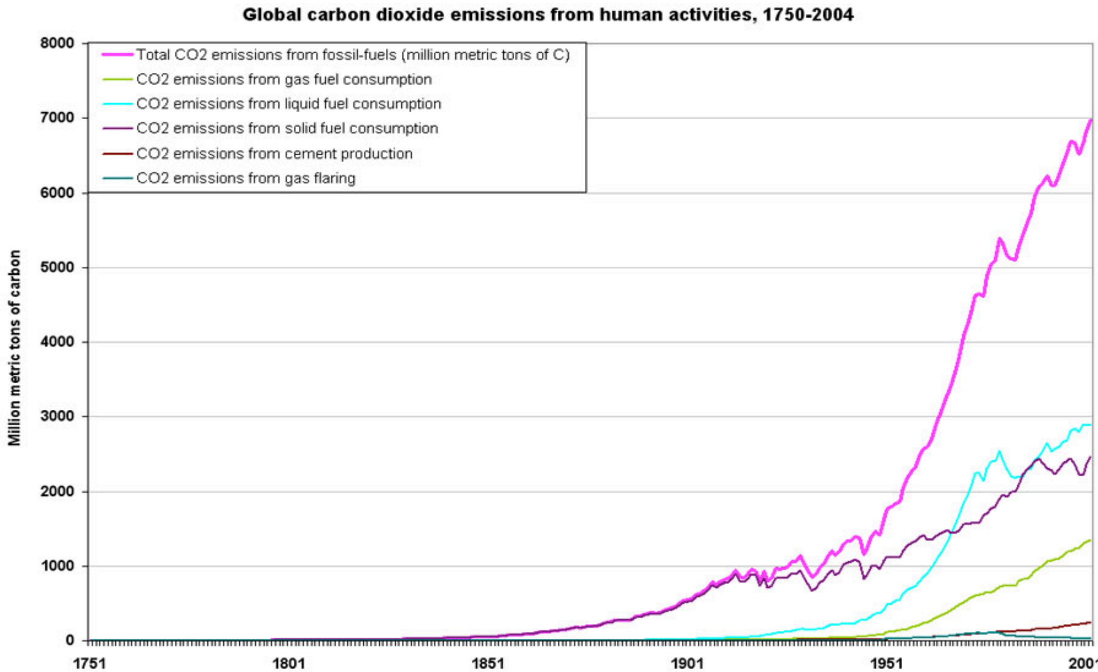
[dots: full-wave FDTD simulation; lines: EMT with filling factor (FF) ranging from 0.0 to 1.0]

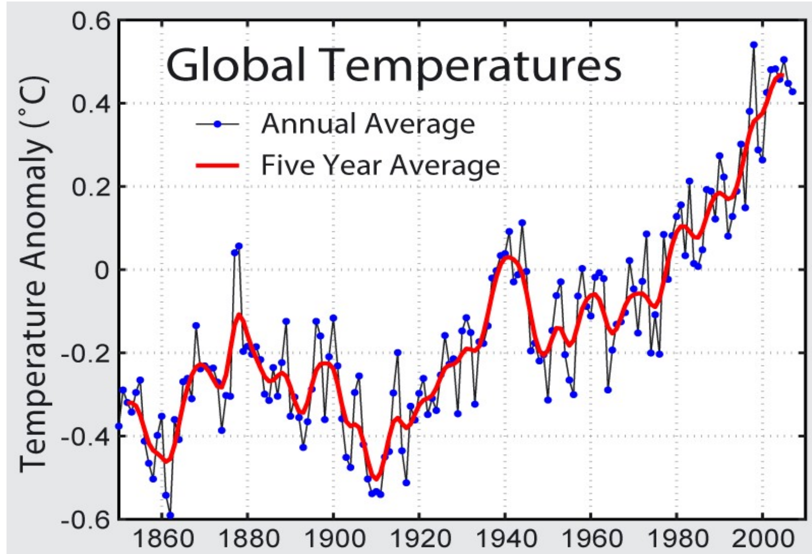
Selfoc lens: collimating EM waves

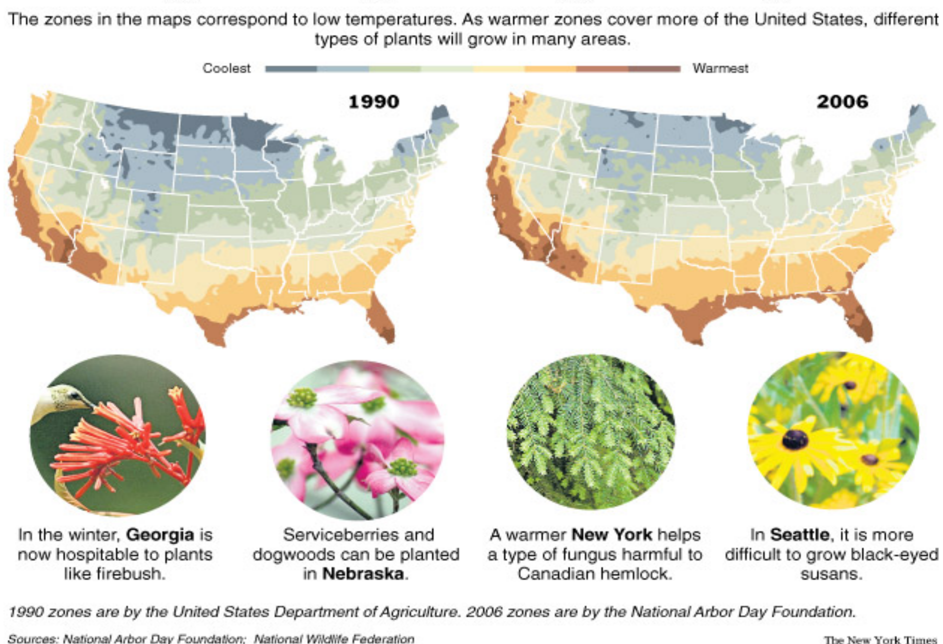


Waves propagate through the lens region (box) and turn into PW's.

The need for alternative energy sources

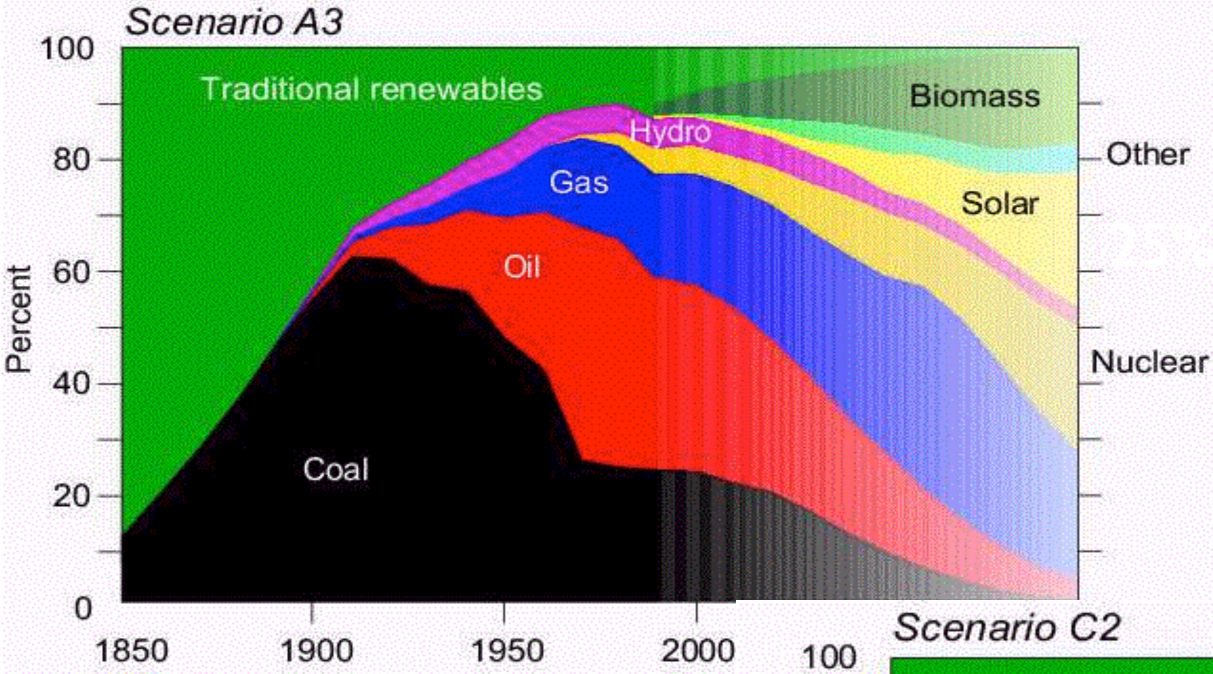






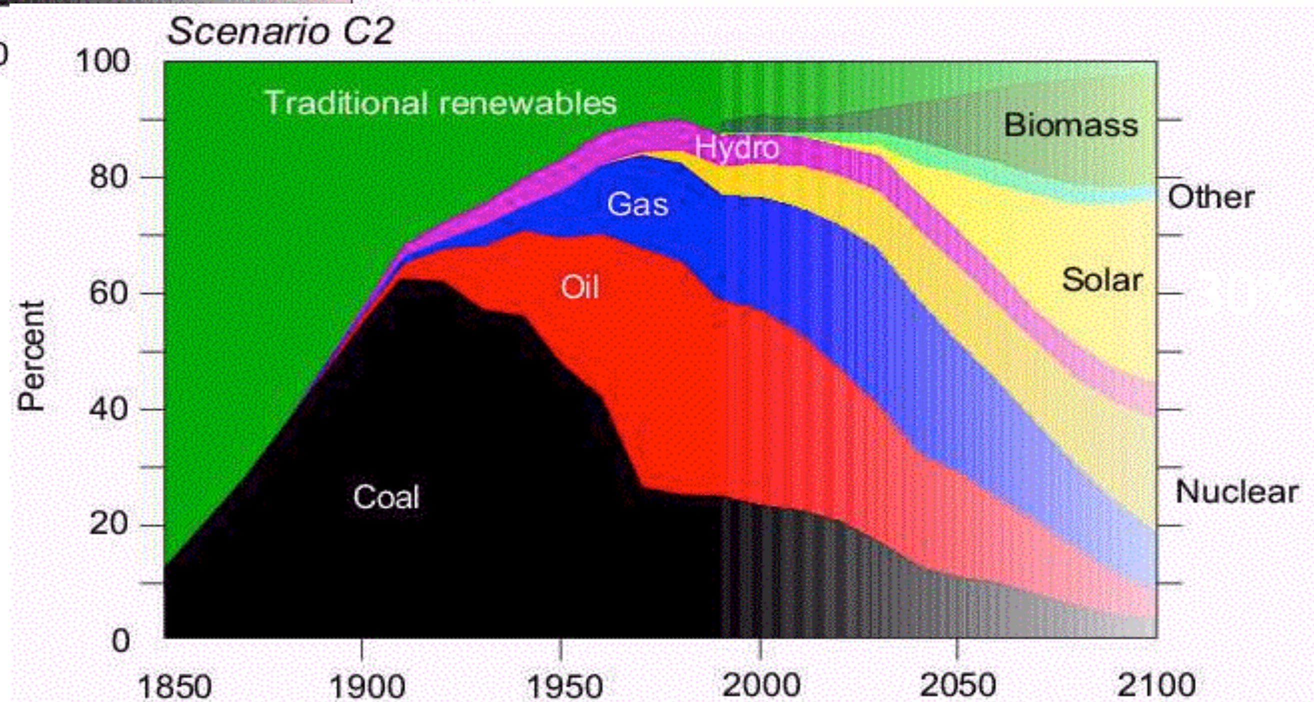
http://www.celsias.com/2007/03/20/channel-4-distances-itself-from-global-warming-documentary/

The challenge of sustainable energy

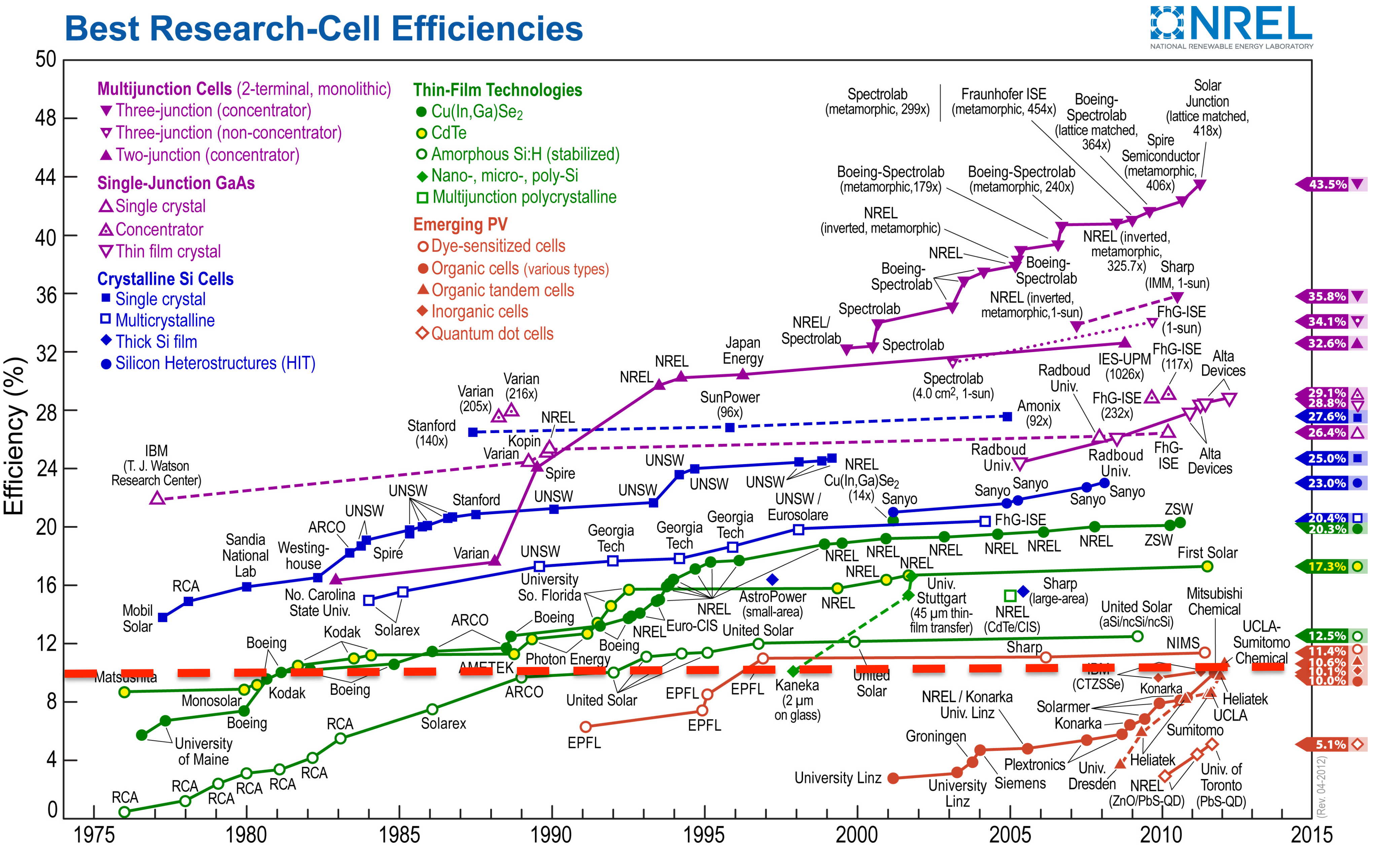


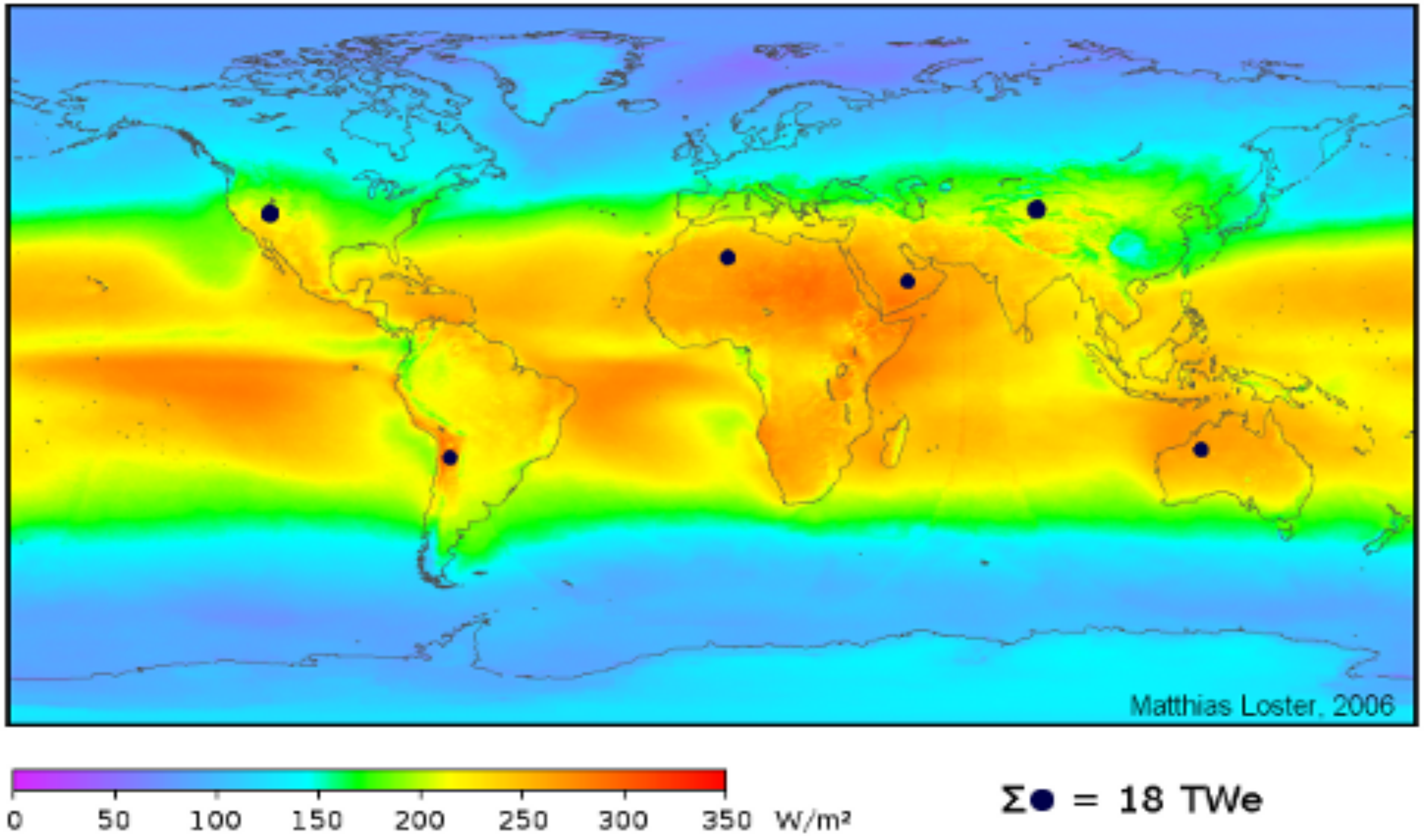
Time and resources running out

Report of Intergovernmental Panel on Climate Change



Best Research-Cell Efficiencies

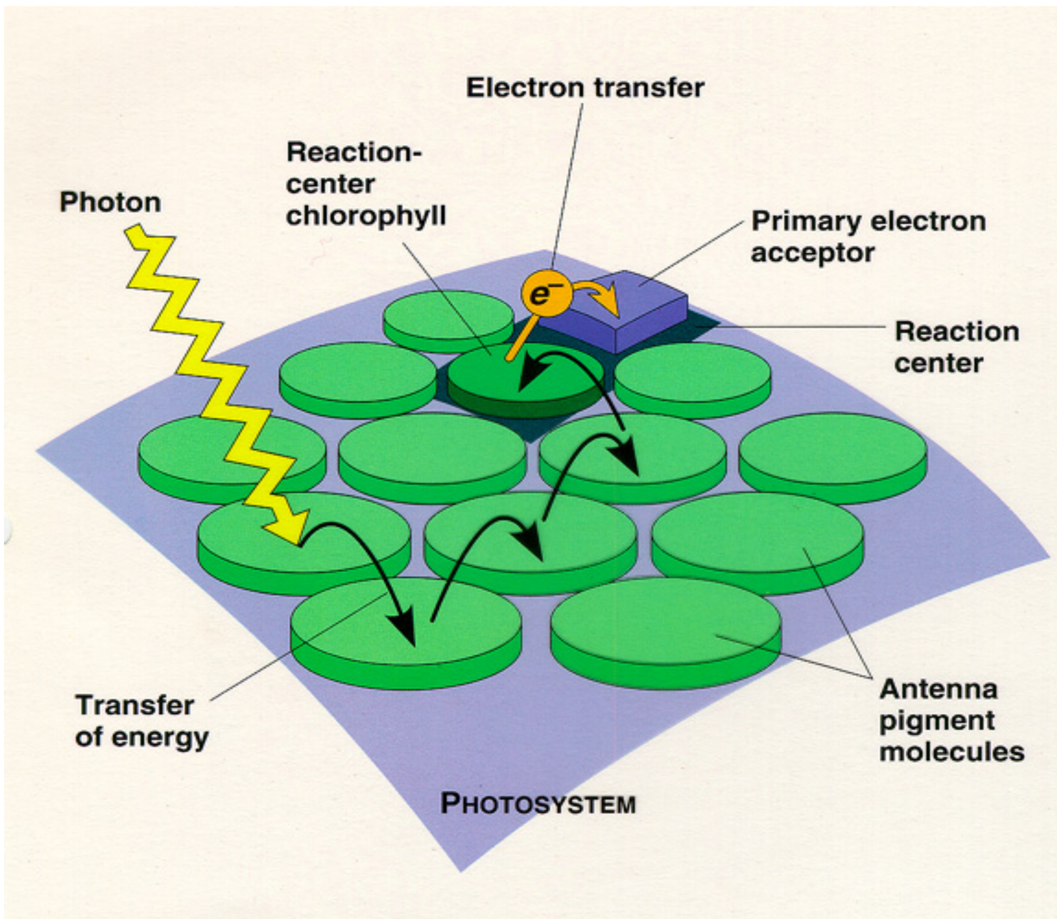


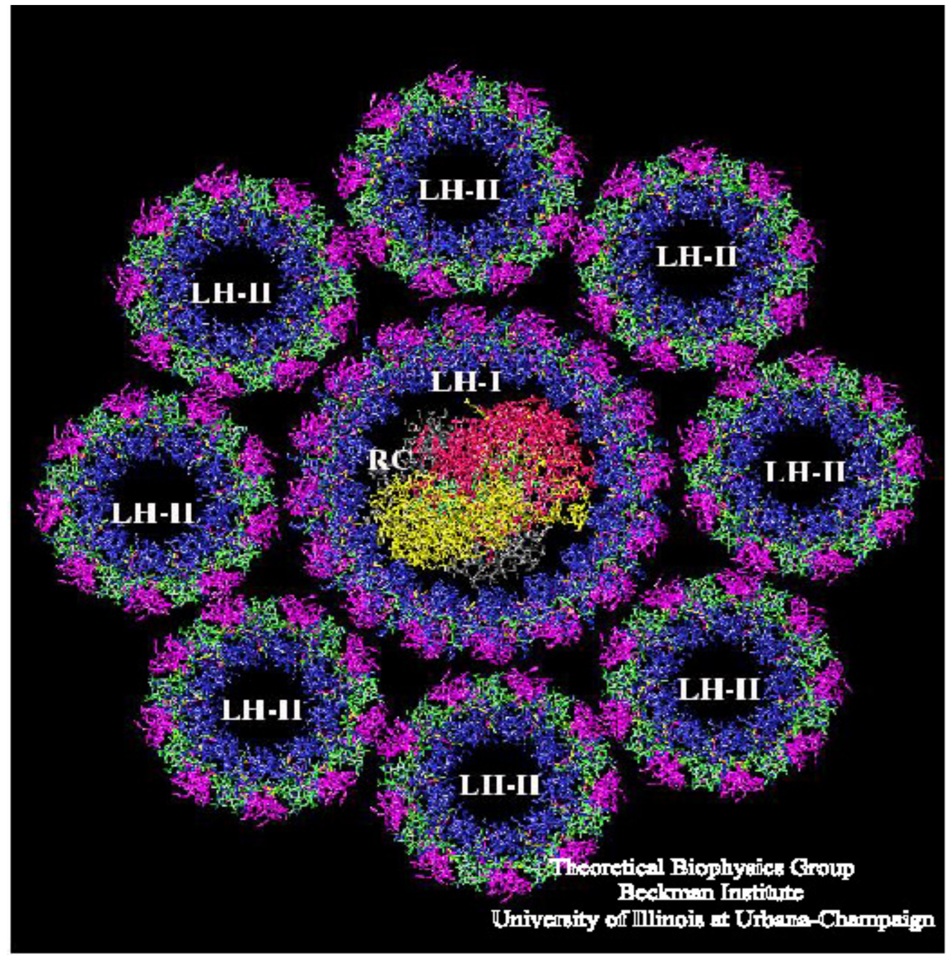


Sunlight hitting the dark discs could power the whole world: solar cells with a conversion efficiency of only 8% would produce 18 TW (current use ~14 TW).

The dye-sensitized (3rd generation) solar cell

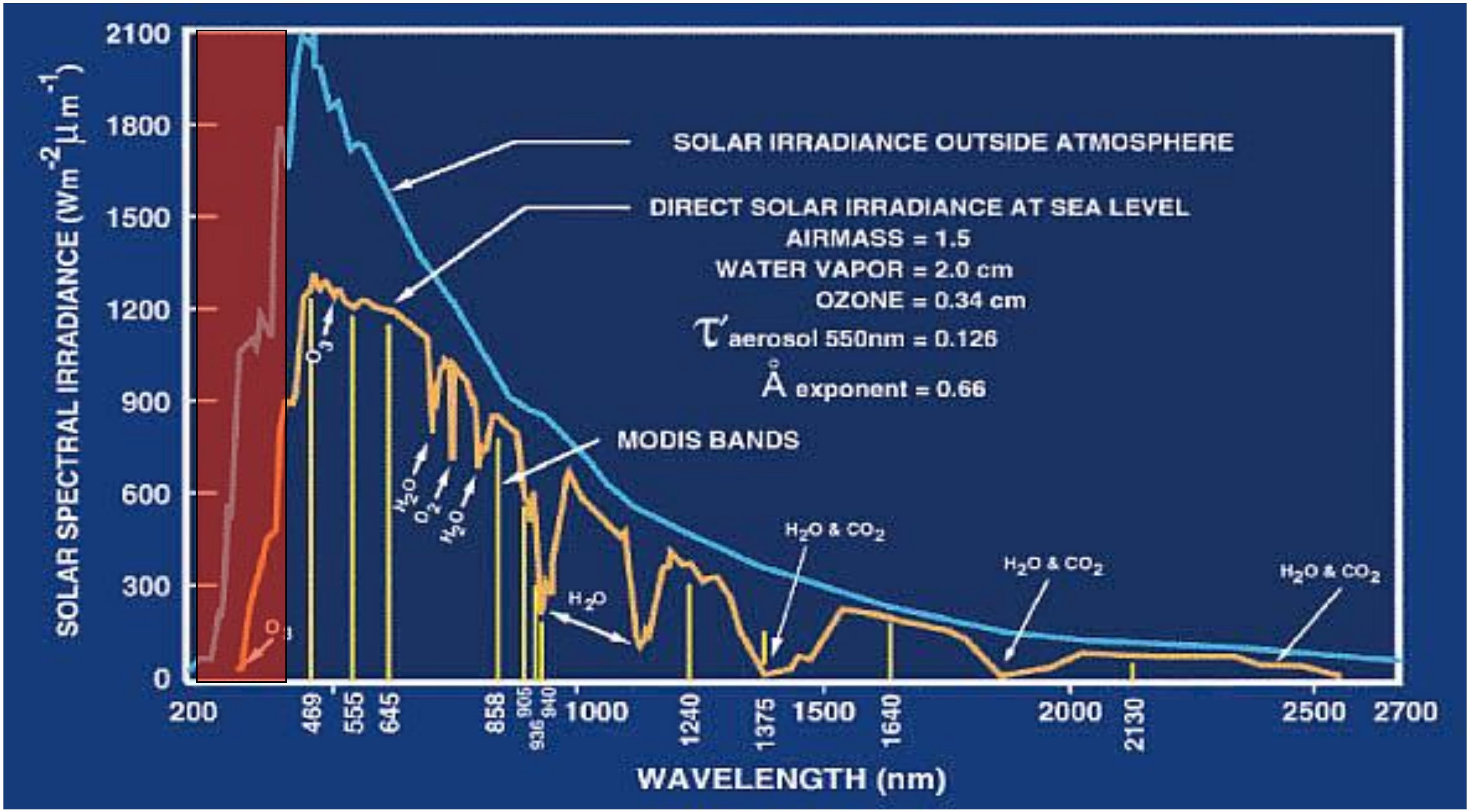
The Principle: Separate light-absorption and charge collection processes





Light absorption by hybrid cells

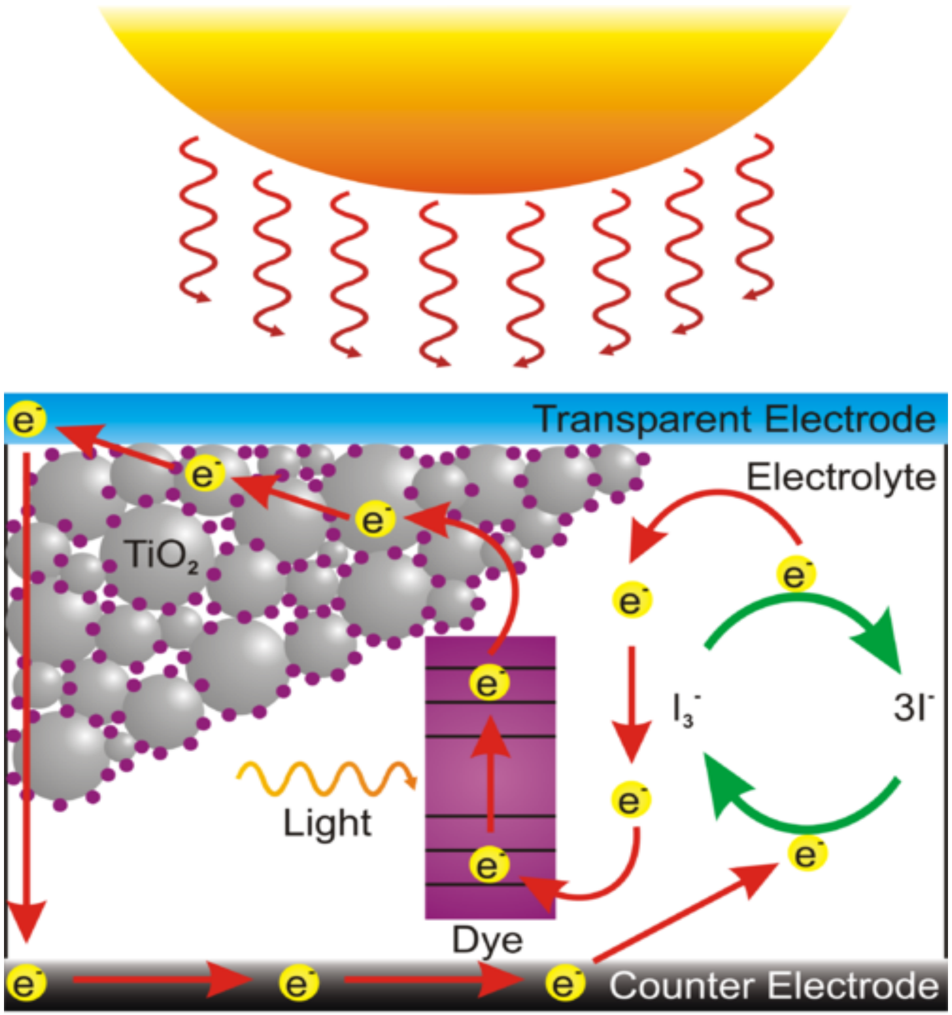
TiO_2 gap = 3.2 eV (200 nm < λ < 400 nm)



solar spectrum

The dye-sensitized solar cell (DSSC)
O'Regan & Graetzel, Nature (1991)

Simple device, complex physics



Major issues:

- stability
- efficiency

  Incident Photon to Current Efficiency

$$IPCE(\lambda) = LHE(\lambda) \times \Phi(inj) \times \eta(c)$$

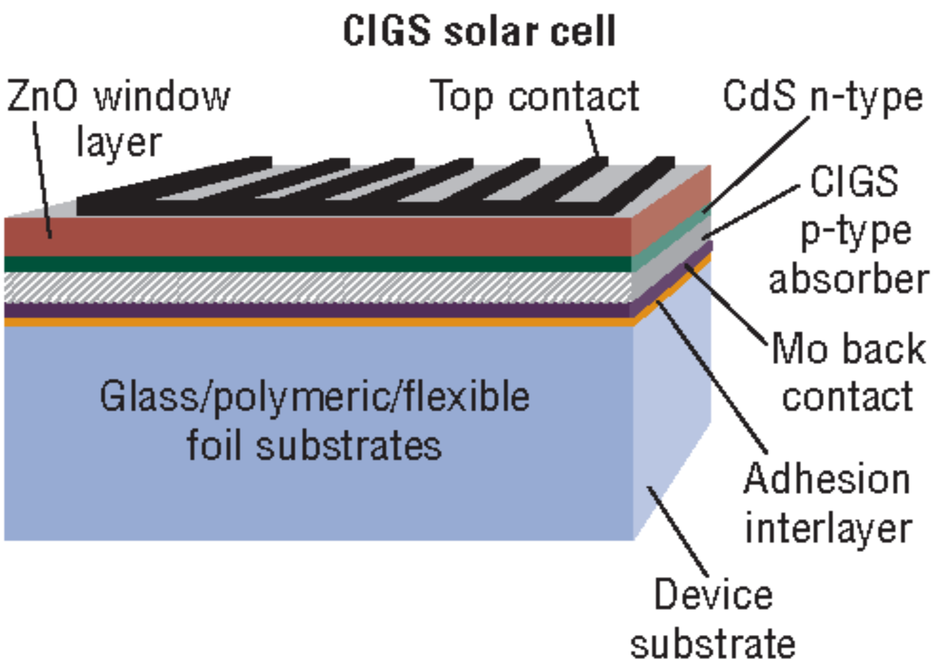
LHE = Light Harvesting Efficiency

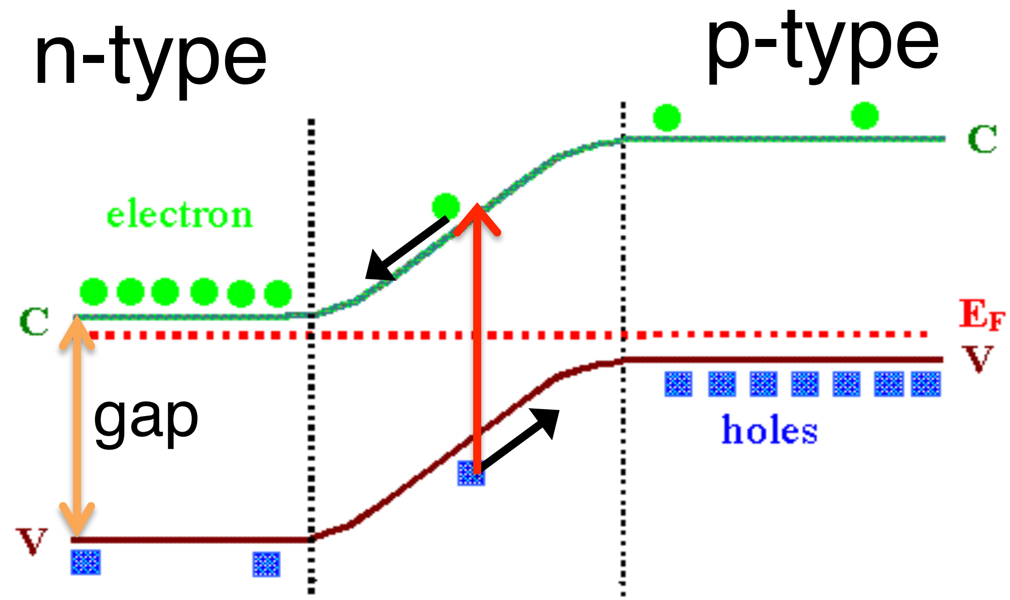
$\Phi(inj)$ = electron injection efficiency

$\eta(c)$ = charge collection efficiency

Conventional p-n junction cell
(inorganic)
Complex device, simple physics

Copper-Indium-Gallium-Selenide cell



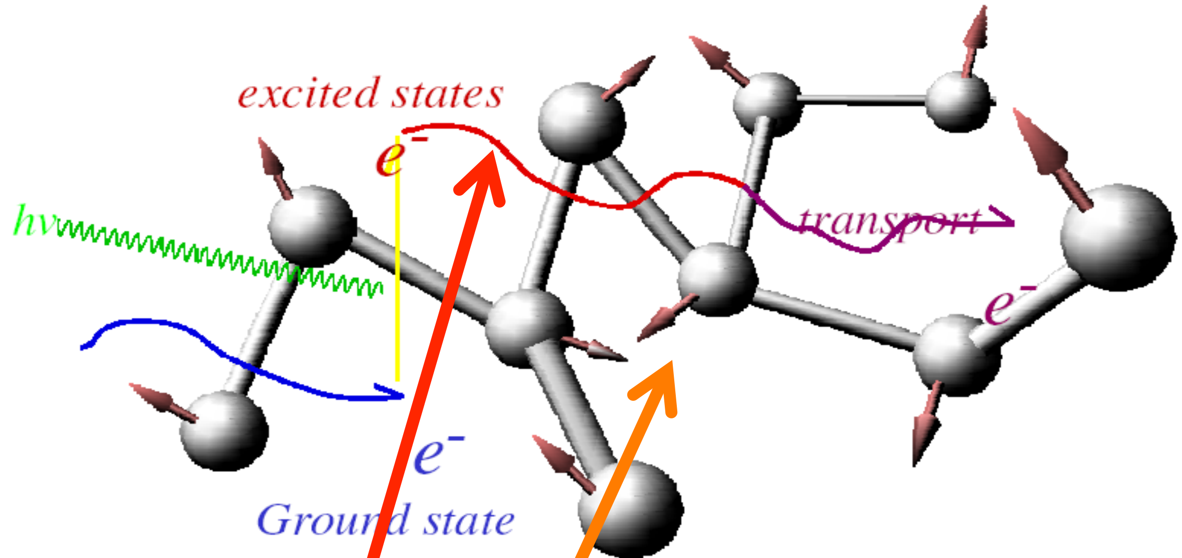


Bulk semiconductor (inorganic)
- delocalized states (band structure)
- nearly free electrons
- single band-gap

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)…



self-consistent TDDFT with atomic motion

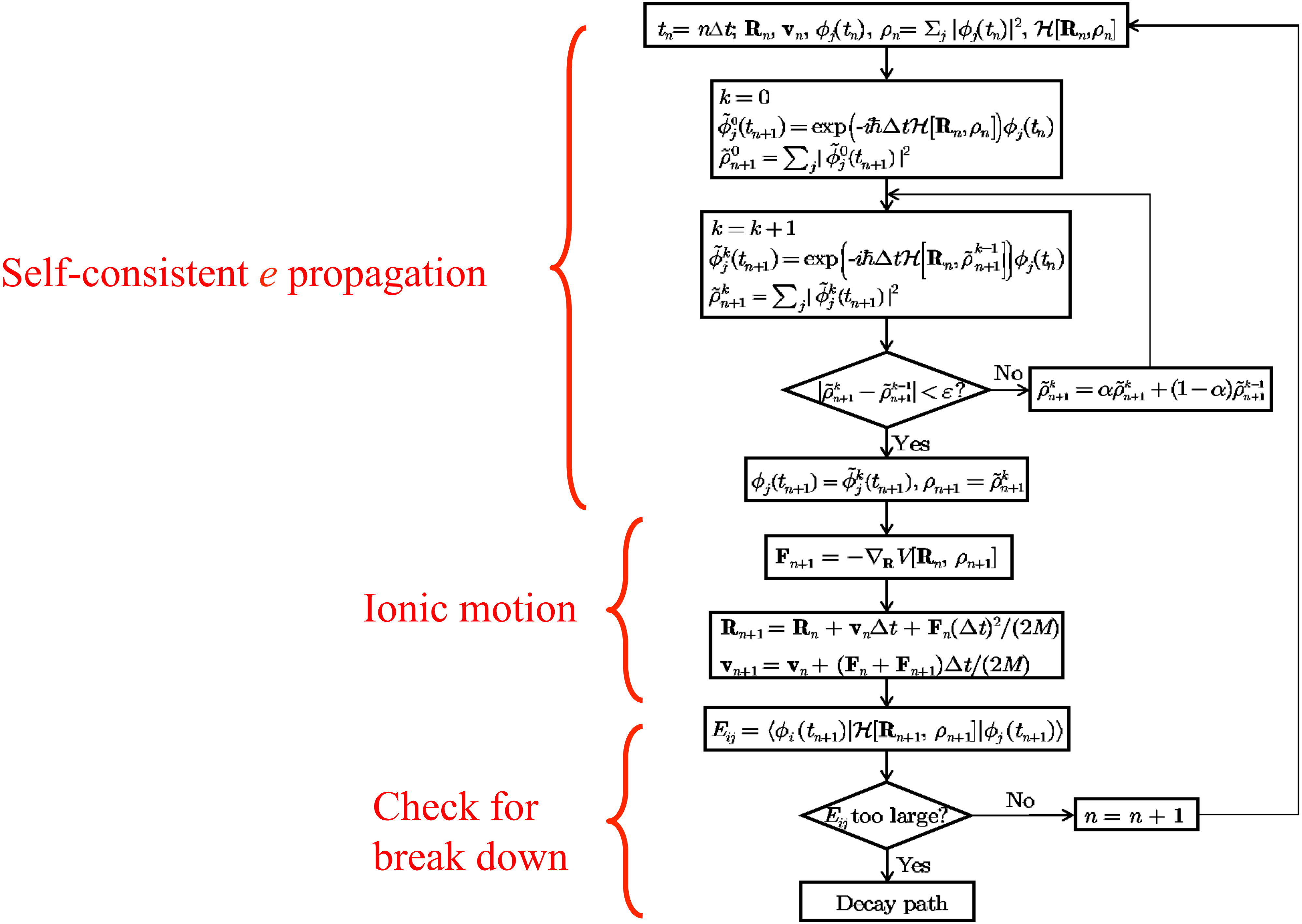
Meng & Kaxiras, J. Chem. Phys. (2008).

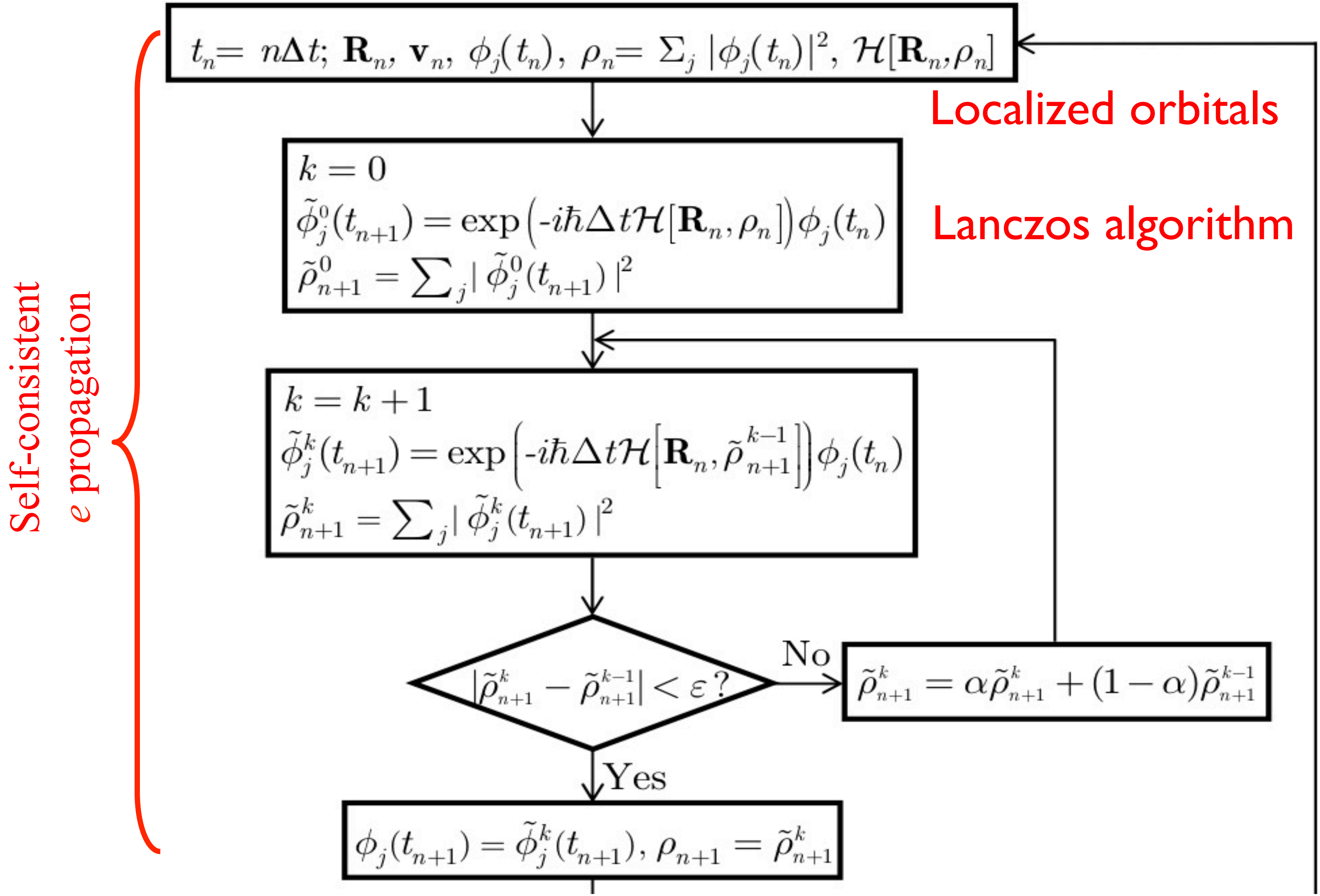
10^{-18} s | 10^{-15} s | Transport: 10^{-12} s

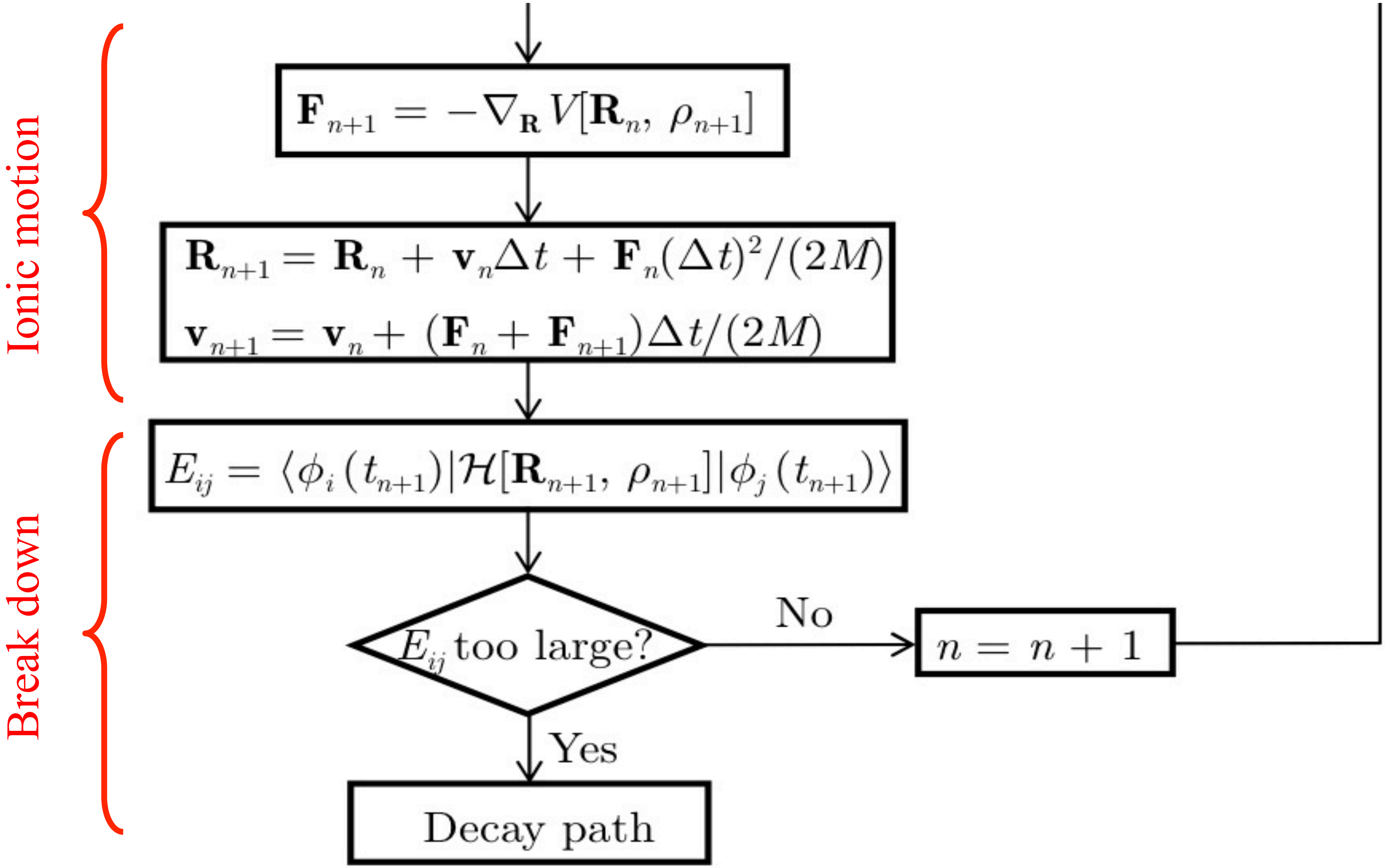
Coupled electron-ion dynamics

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

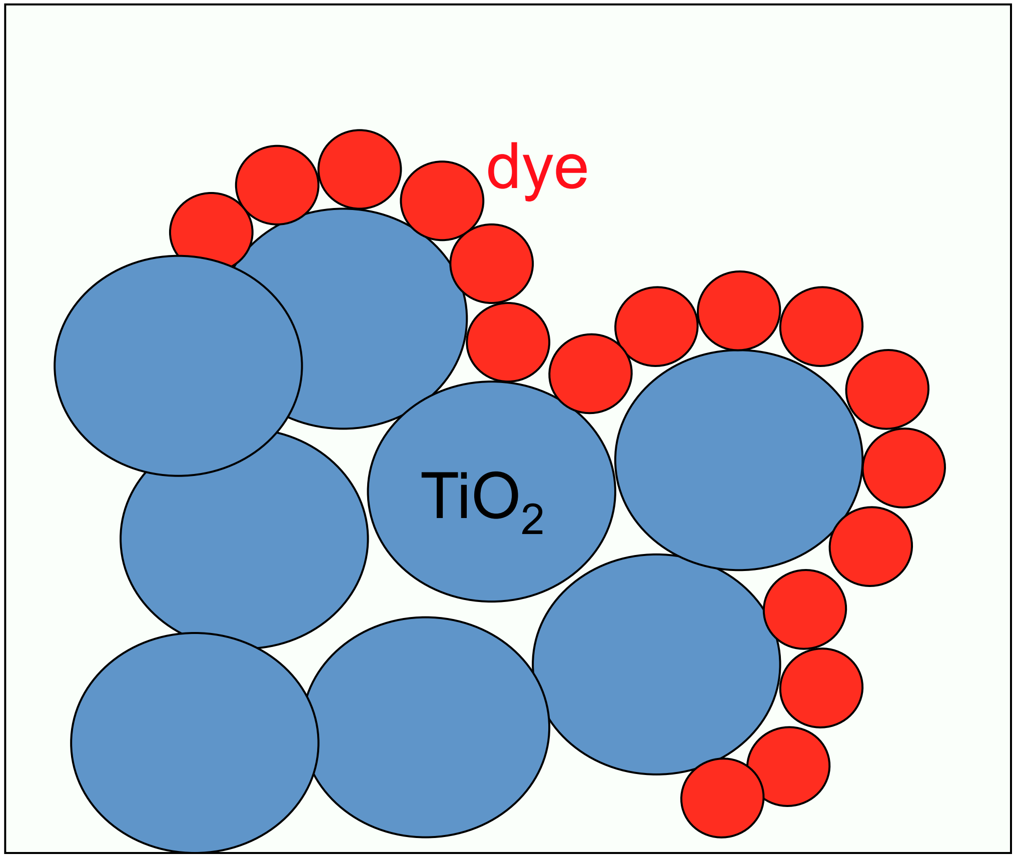
Propagation of electrons in time (TDSE) + Ehrenfest dynamics for ions

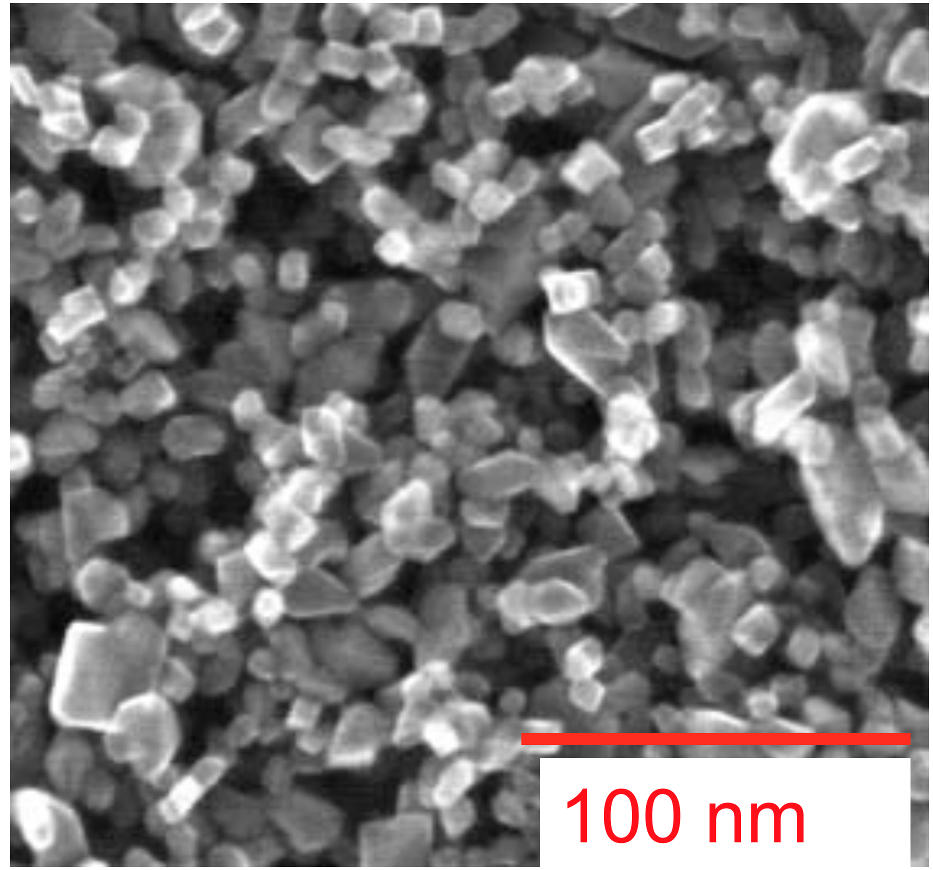

Self-consistent e propagation
Ionic motion
Check for
break down
$t_n = n\Delta t$; $\mathbf{R}_n$, $\mathbf{v}_n$, $\phi_j(t_n)$, $\rho_n = \Sigma_j |\phi_j(t_n)|^2$, $\mathcal{H}[\mathbf{R}_n, \rho_n]$
$k = 0$
$\tilde{\phi}_j^0(t_{n+1}) = \exp\left(-i\hbar\Delta t\mathcal{H}[\mathbf{R}_n, \rho_n]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^0 = \sum_j |\tilde{\phi}_j^0(t_{n+1})|^2$
$k = k+1$
$\tilde{\phi}_j^k(t_{n+1}) = \exp\left(-i\hbar\Delta t\mathcal{H}\left[\mathbf{R}_n, \tilde{\rho}_{n+1}^{k-1}\right]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^k = \sum_j |\tilde{\phi}_j^k(t_{n+1})|^2$
$|\tilde{\rho}_{n+1}^k - \tilde{\rho}_{n+1}^{k-1}| < \varepsilon$?
No
$\tilde{\rho}_{n+1}^k = \alpha\tilde{\rho}_{n+1}^k + (1-\alpha)\tilde{\rho}_{n+1}^{k-1}$
Yes
$\phi_j(t_{n+1}) = \tilde{\phi}_j^k(t_{n+1})$, $\rho_{n+1} = \tilde{\rho}_{n+1}^k$
$\mathbf{F}_{n+1} = -\nabla_{\mathbf{R}} V[\mathbf{R}_n, \rho_{n+1}]$
$\mathbf{R}_{n+1} = \mathbf{R}_n + \mathbf{v}_n\Delta t + \mathbf{F}_n(\Delta t)^2/(2M)$
$\mathbf{v}_{n+1} = \mathbf{v}_n + (\mathbf{F}_n + \mathbf{F}_{n+1})\Delta t/(2M)$
$E_{ij} = \langle\phi_i(t_{n+1})|\mathcal{H}[\mathbf{R}_{n+1}, \rho_{n+1}]|\phi_j(t_{n+1})\rangle$
E_{ij} too large?
No
$n = n + 1$
Yes
Decay path

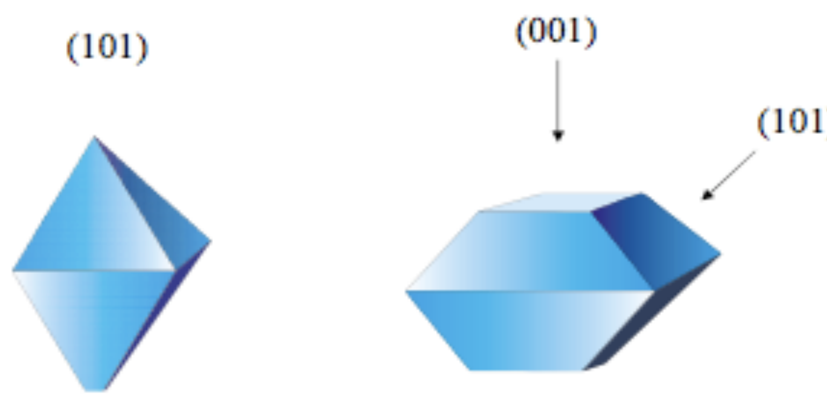

$t_n = n\Delta t$; $\mathbf{R}_n$, $\mathbf{v}_n$, $\phi_j(t_n)$, $\rho_n = \Sigma_j |\phi_j(t_n)|^2$, $\mathcal{H}[\mathbf{R}_n, \rho_n]$
Localized orbitals
$k = 0$
$\tilde{\phi}_j^0(t_{n+1}) = \exp\left(-i\hbar\Delta t \mathcal{H}[\mathbf{R}_n, \rho_n]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^0 = \sum_j |\tilde{\phi}_j^0(t_{n+1})|^2$
Lanczos algorithm
$k = k + 1$
$\tilde{\phi}_j^k(t_{n+1}) = \exp\left(-i\hbar\Delta t \mathcal{H}\left[\mathbf{R}_n, \tilde{\rho}_{n+1}^{k-1}\right]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^k = \sum_j |\tilde{\phi}_j^k(t_{n+1})|^2$
$|\tilde{\rho}_{n+1}^k - \tilde{\rho}_{n+1}^{k-1}| < \varepsilon$?
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

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

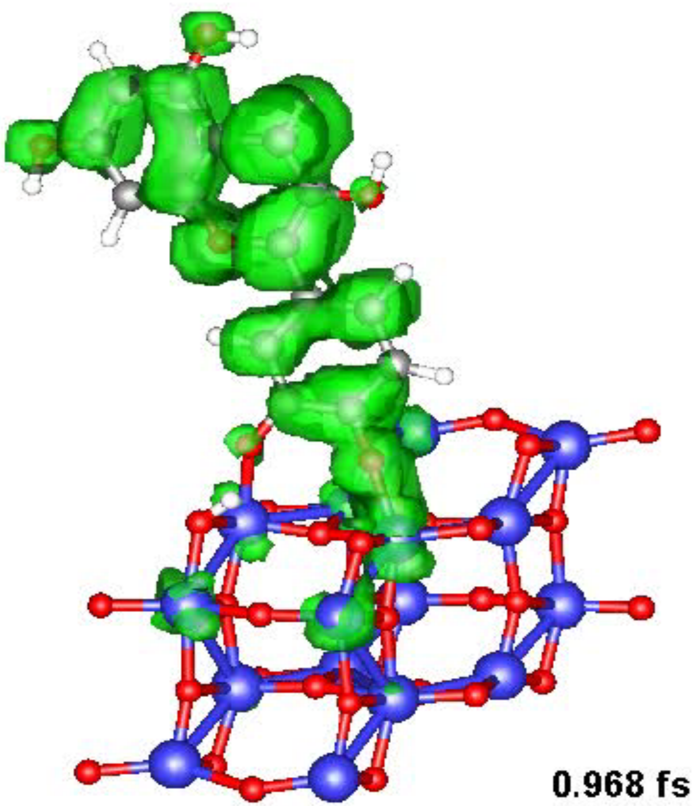


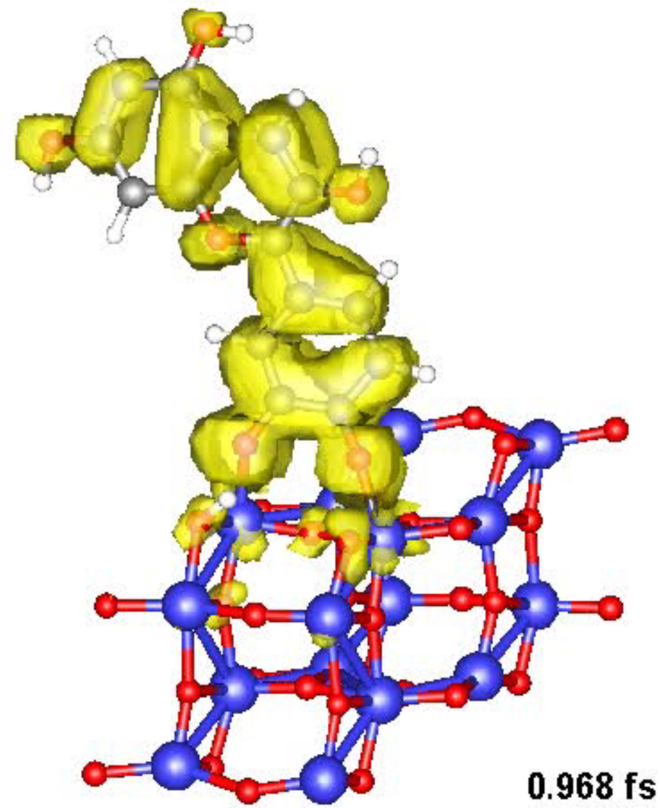




Nano-size: helps in many aspects (e.g. efficiency, transparency, transport, …)

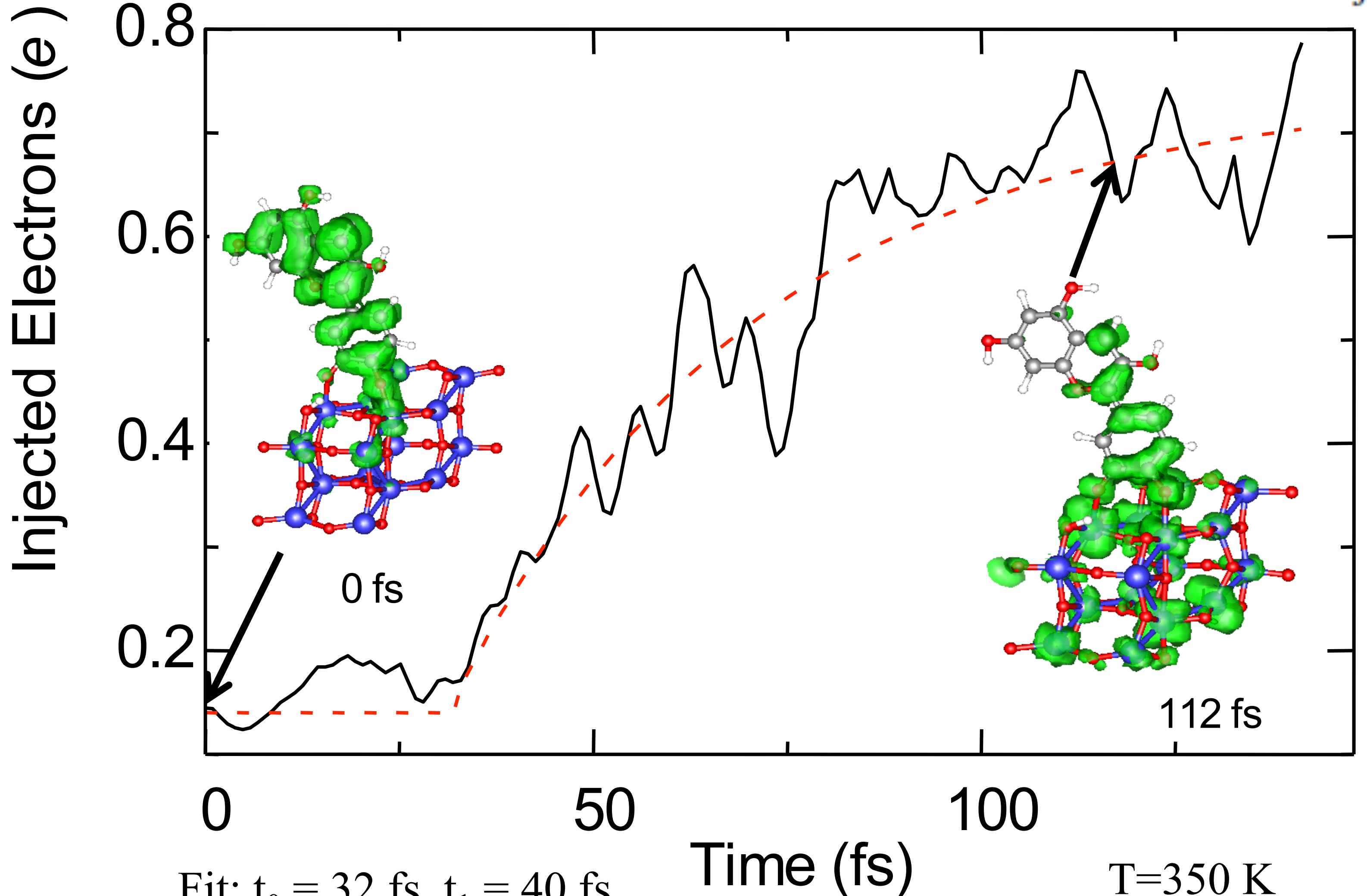
Electron and hole motion in DSSC





Charge injection dynamics:

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



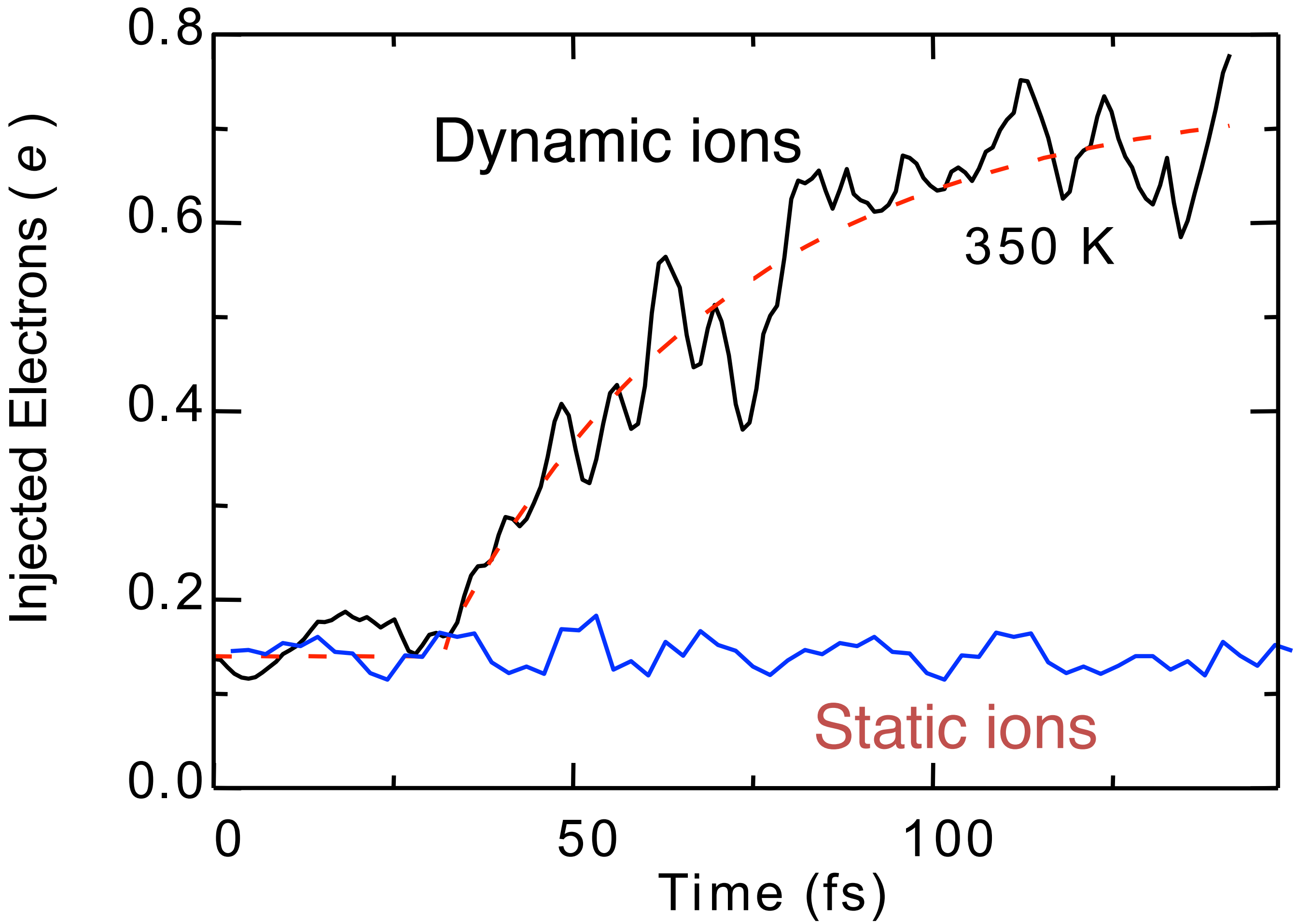
Fit: t_0 = 32 fs, t_1 = 40 fs

Expt.[a)] : <100 fs

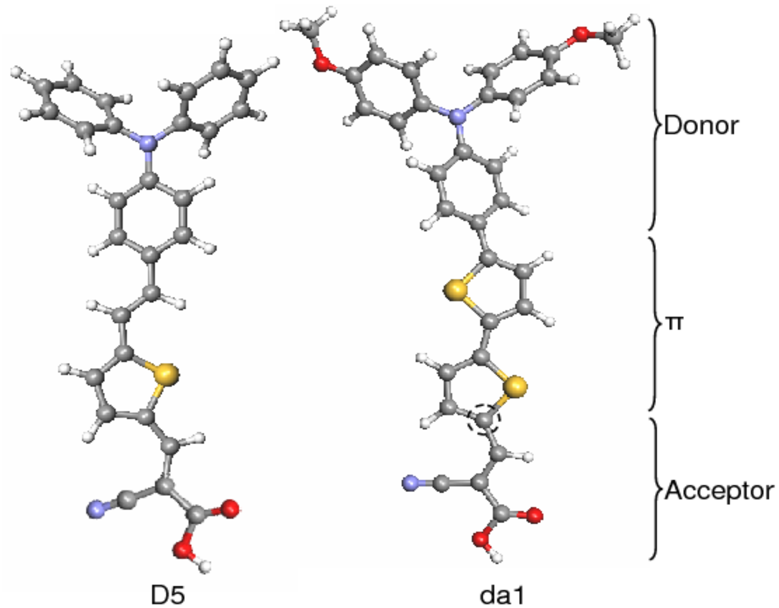
T=350 K

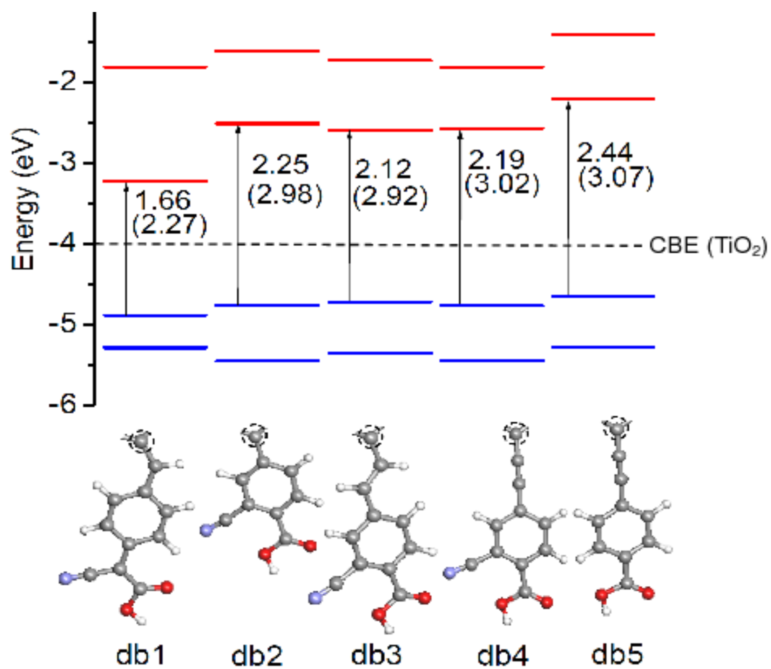
δt=0.02419 fs

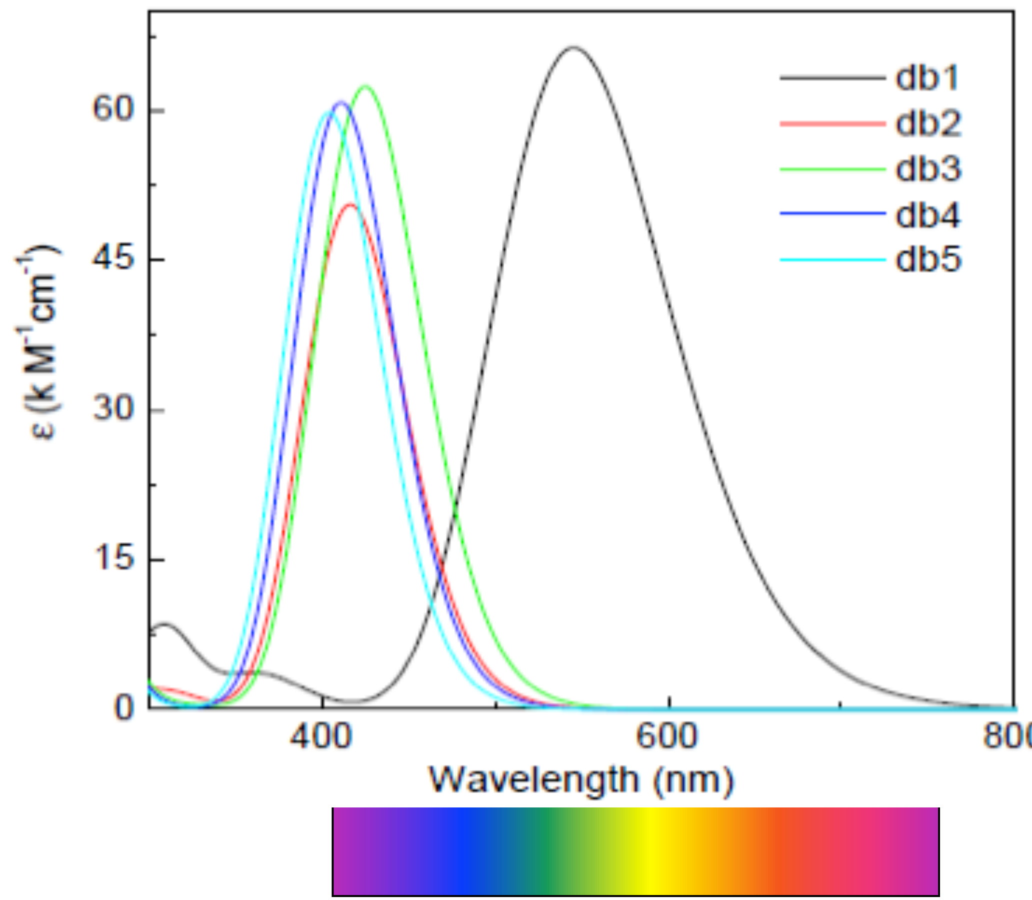
Importance of coupled e-ion dynamics



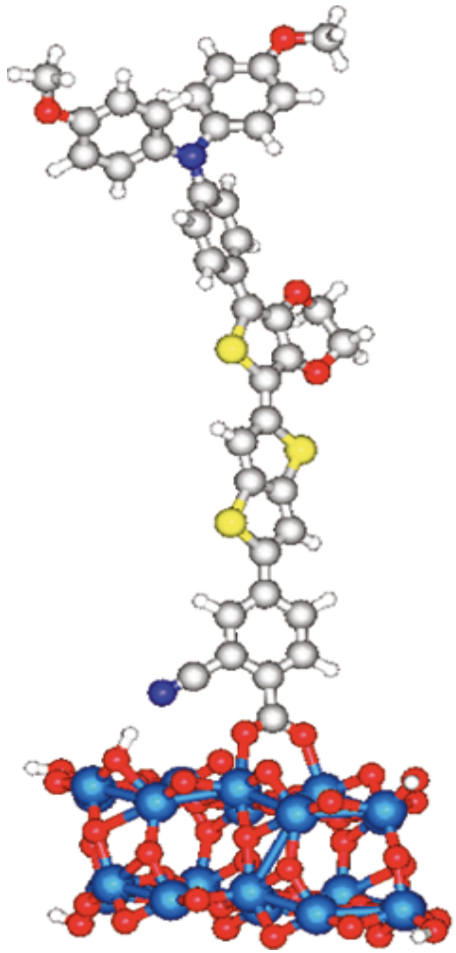
"Designer" dyes: Predict properties of new dyes (not yet tried in experiments))

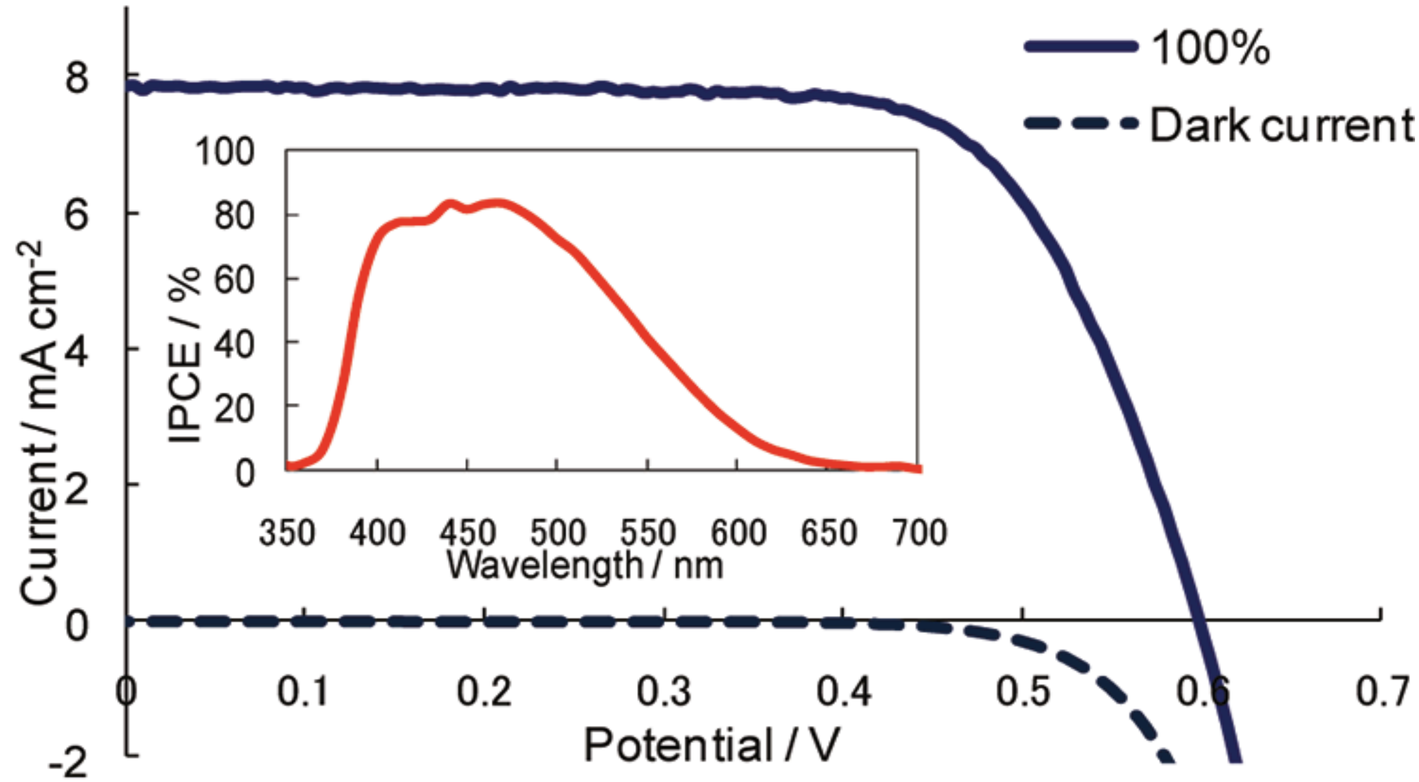






84% Incident Photon to Current Efficiency,
3.3% Electric Power Conversion Efficiency



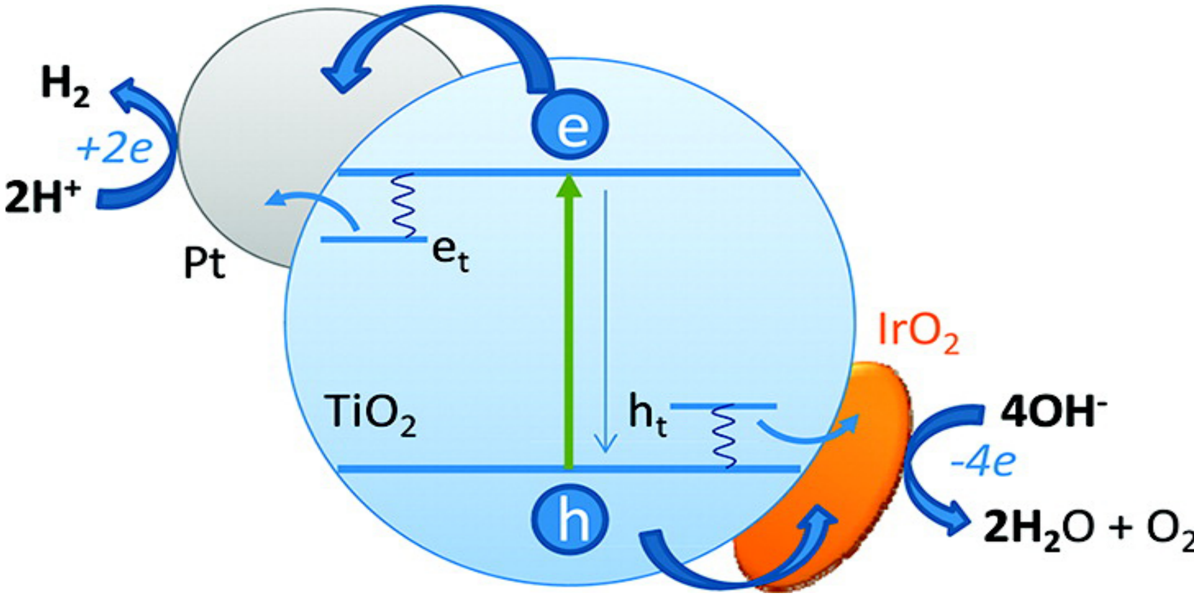


D-π-A Dye System Containing Cyano-Benzoic Acid as Anchoring Group for Dye-Sensitized Solar Cells

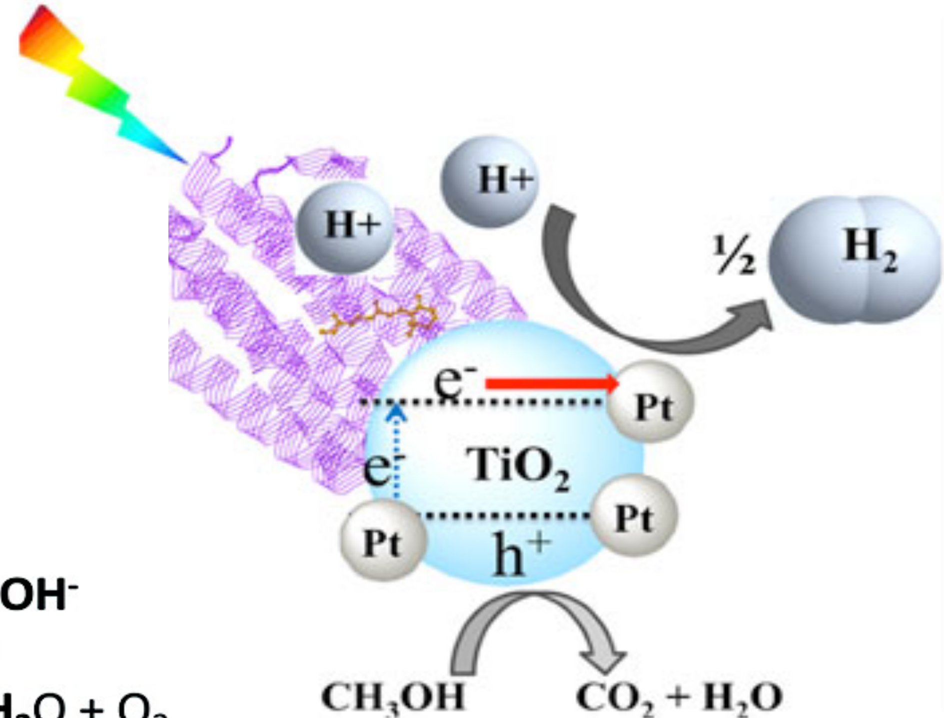
Masataka Katono, Takeru Bessho, Sheng Meng, Robin Humphry-Baker, Guido Rothenberger ,Shaik M. Zakeeruddin, Efthimios Kaxiras, and Michael Gratzel

Langmuir 2011, **27**, 14248–14252

Photo-catalysts



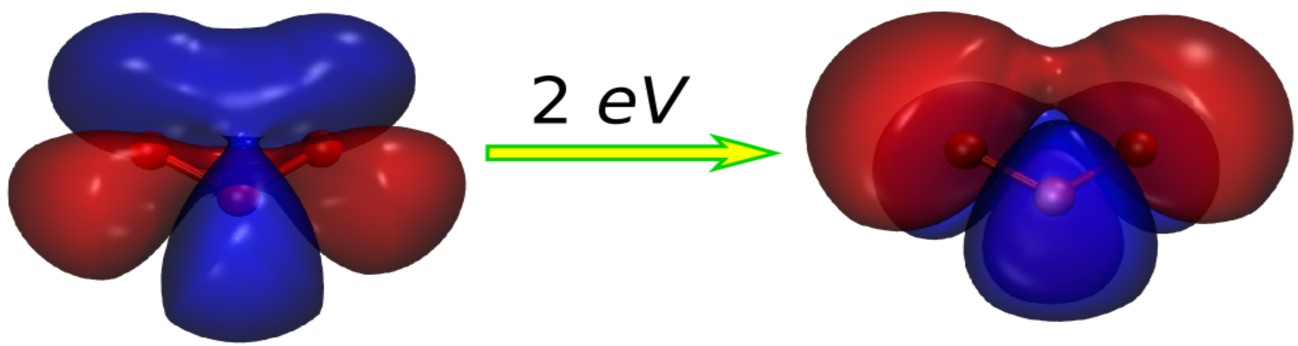
Photocatalytic water splitting system utilizing Pt/TiO_2/IrO_2:
TiO_2 is light absorber, Pt is the hydrogen evolution catalyst, and IrO_2 is the oxygen evolution catalyst.
(P. Kamat, U. Notre Dame)



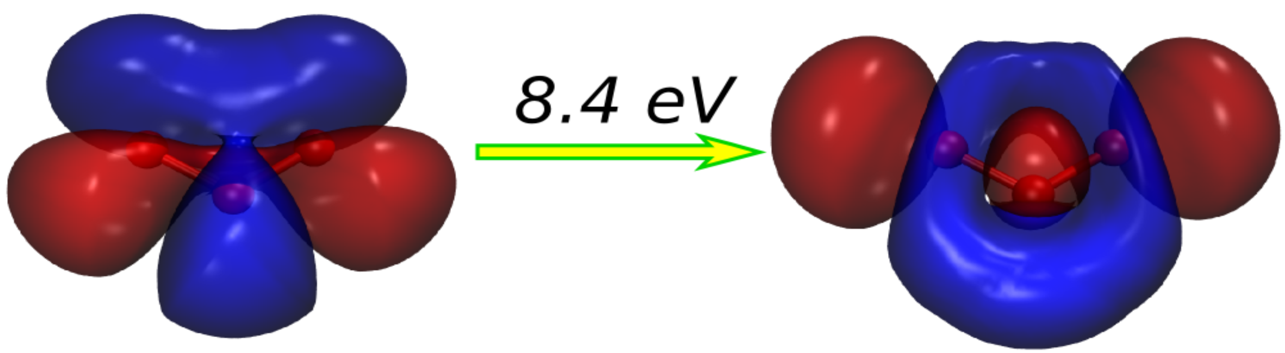
H_2 production from organic molecules using TiO_2 nano-particles as photo-catalysts
(Argonne National Lab)

Example: ozone photolysis

- Excitation HOMO to LUMO: slow dissociation

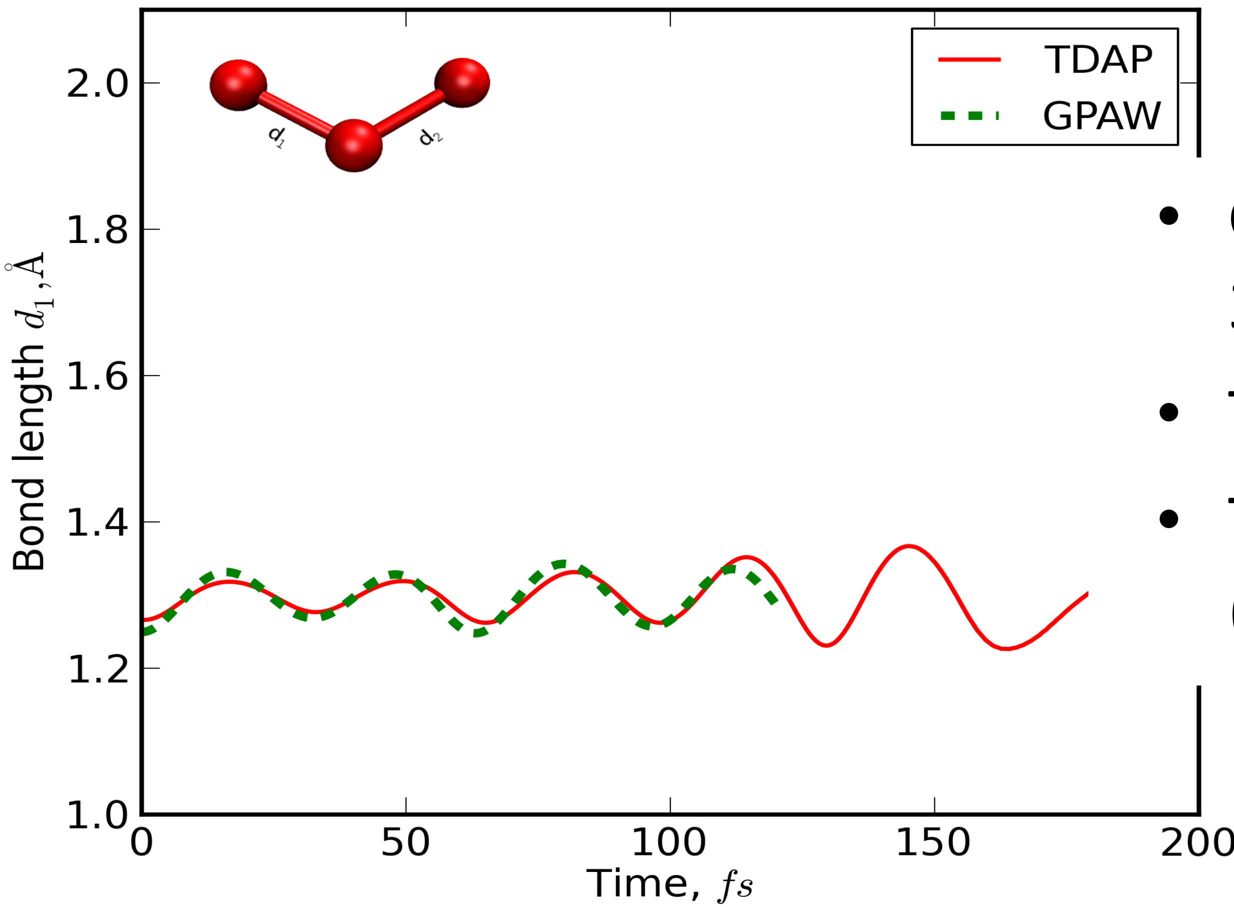


- Excitation HOMO to LUMO+1: quick dissociation



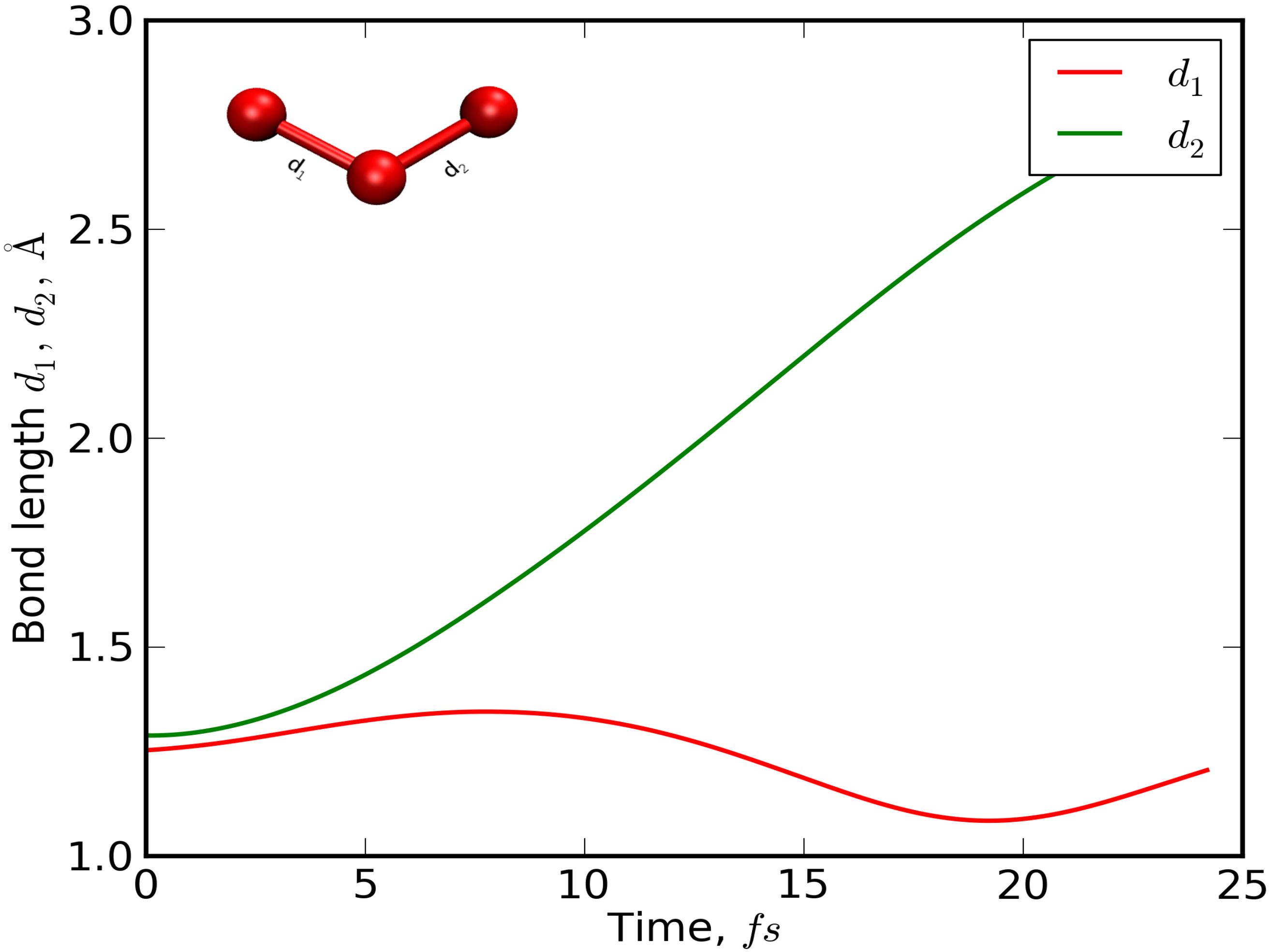
Matsumi, Y. & Kawasaki, M. Photolysis of atmospheric ozone in the ultraviolet region. *Chemical reviews* **103**, 4767–4782 (2003).

1^{st} excited state trajectory



- GPAW computation time 37 days (4 cores)
- TDAP: 1 hour
- Time step: 5 attosec (both)

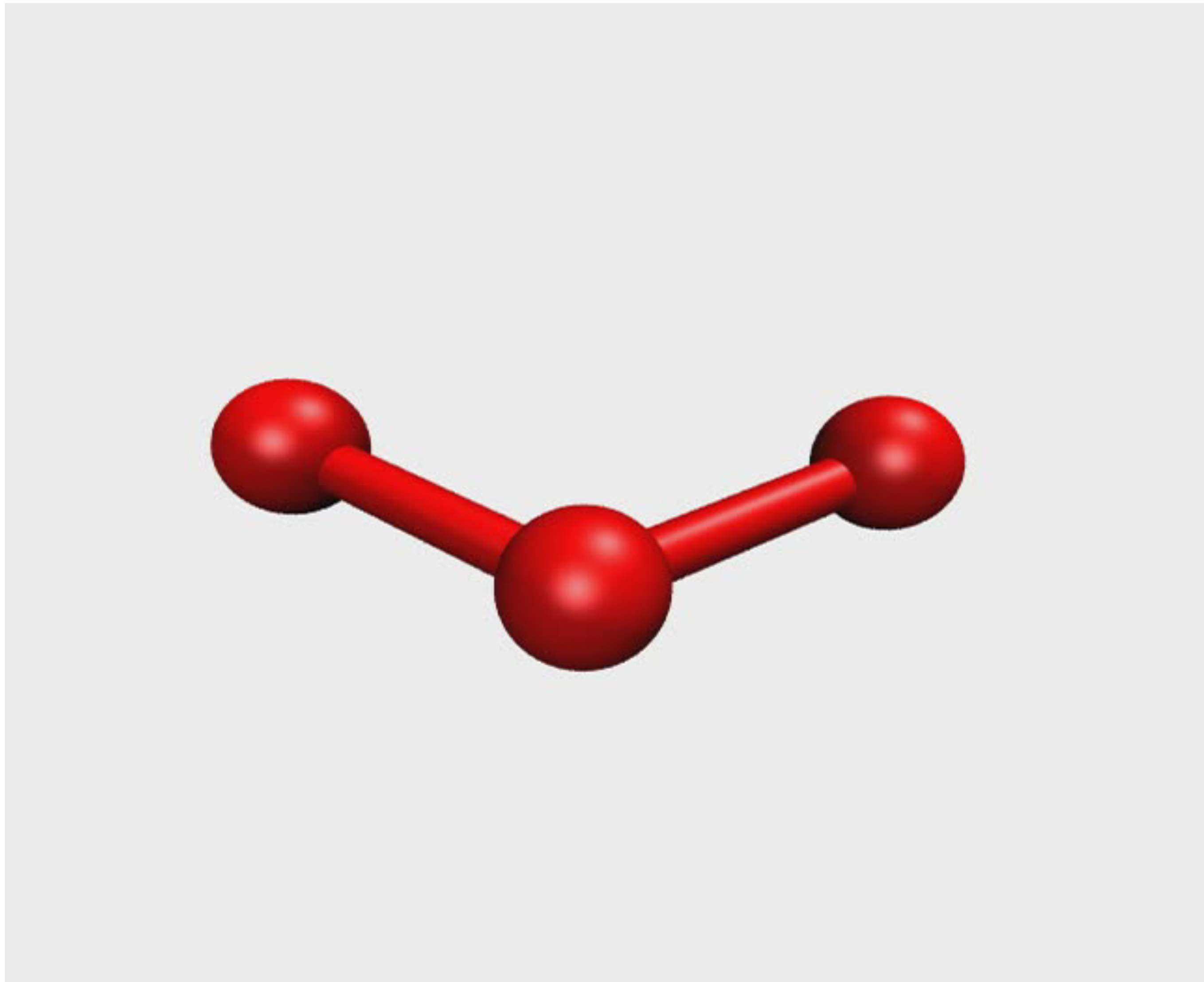
2nd excited state trajectory



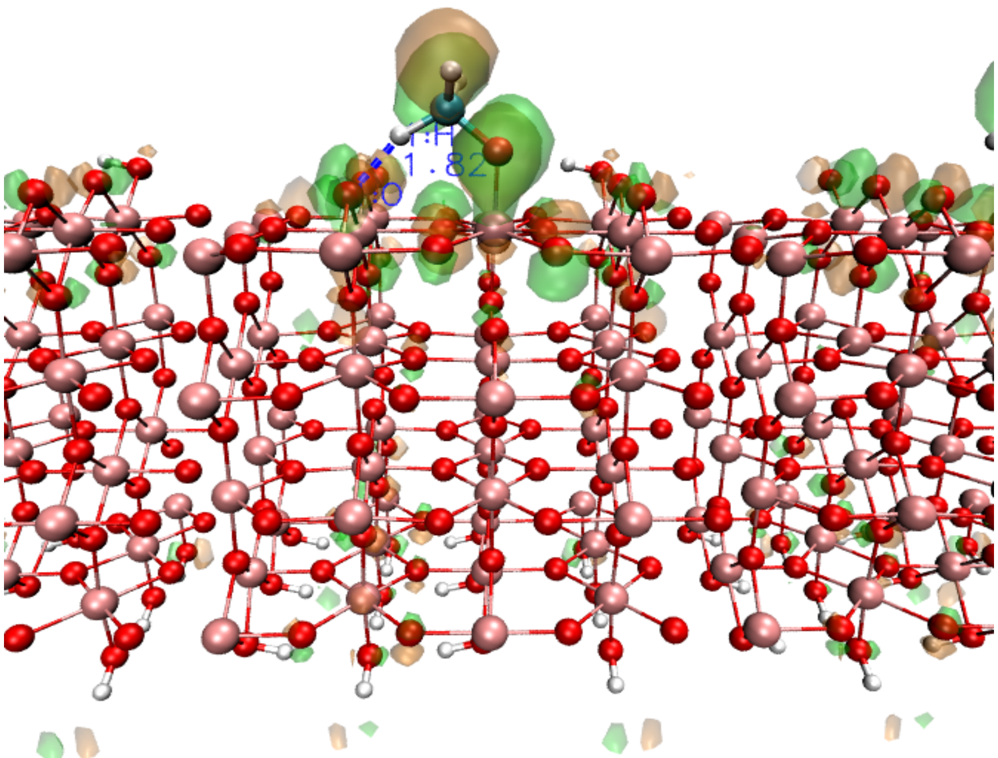
2nd excited state trajectory

- Movie:

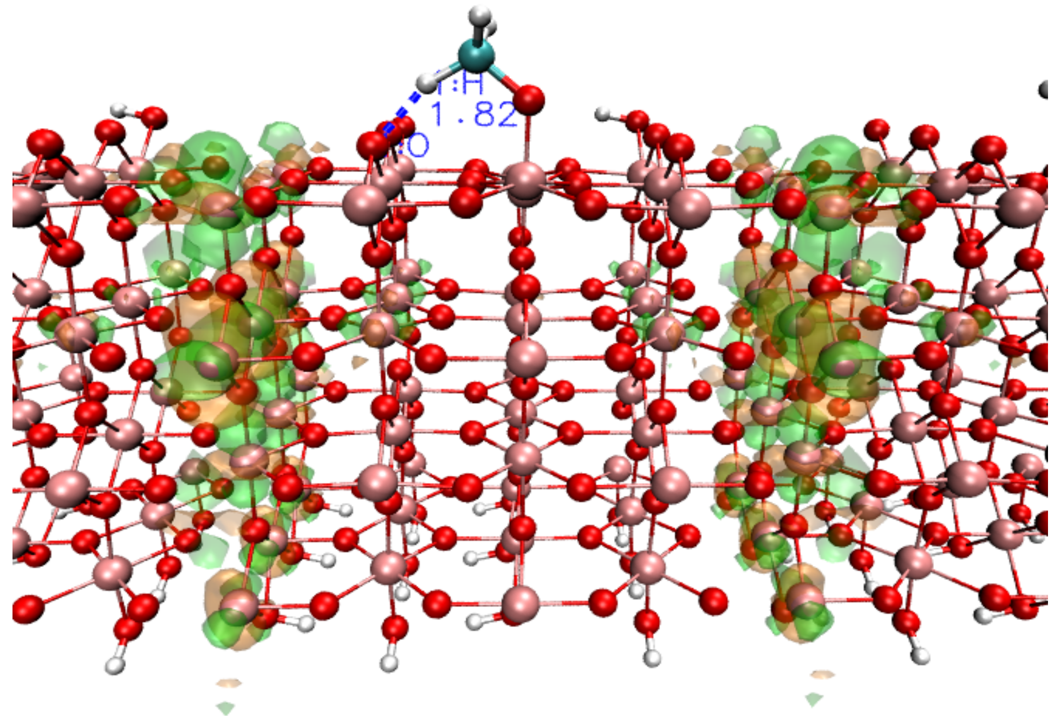
o3split.mov



Hole: HOMO-4 State



Electron: LUMO state



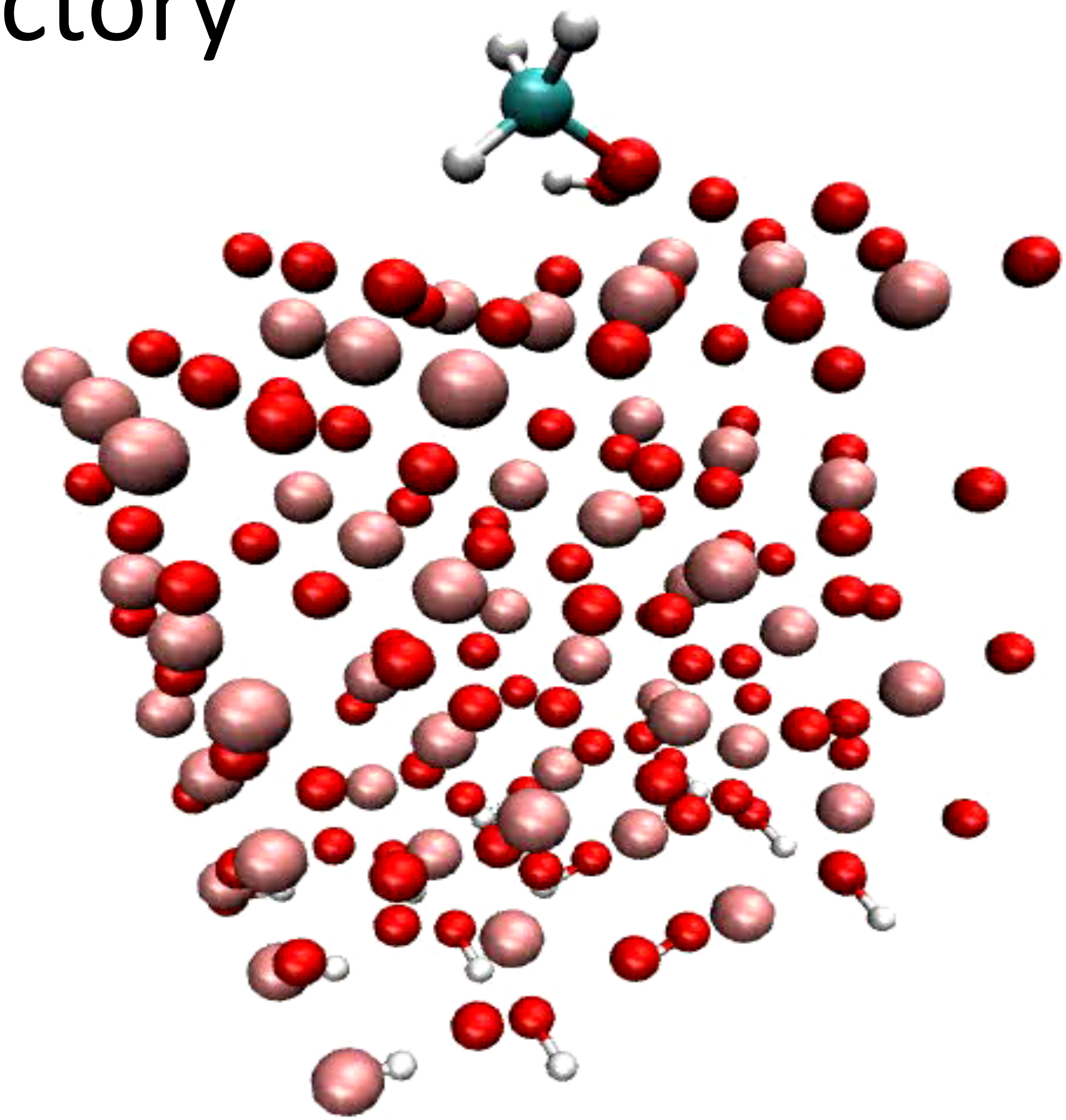
- Formaldehyde was photochemically produced from methoxy on TiO_2 (110) surface

Phillips, K. R., Jensen, S. C., Baron, M., Li, S.-C. & Friend, C. M. Sequential photo-oxidation of methanol to methyl formate on TiO2 (110). *Journal of the American Chemical Society* **135**, 574–577 (2013).

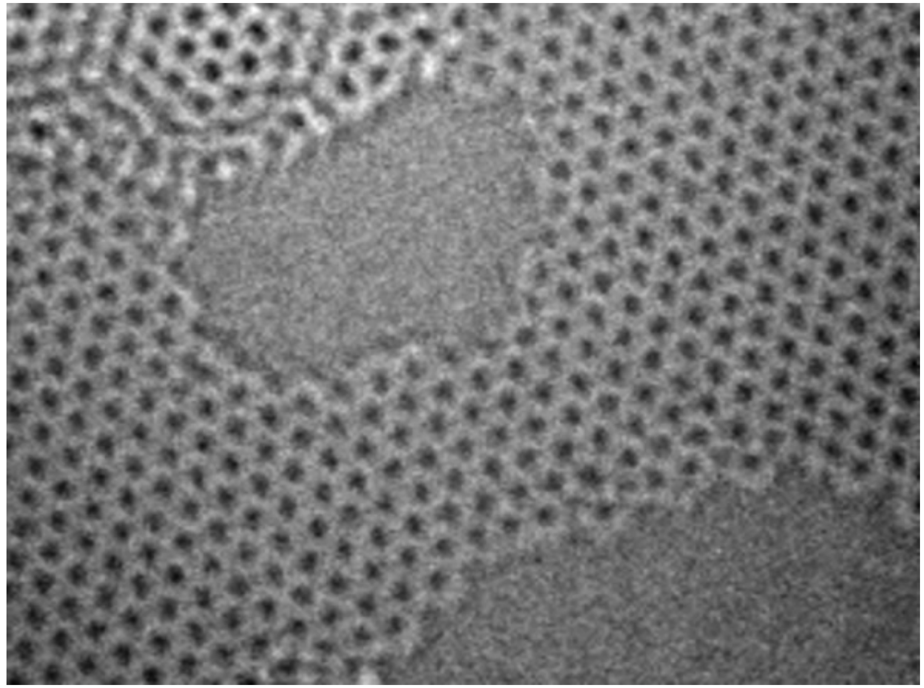
TDDFT trajectory

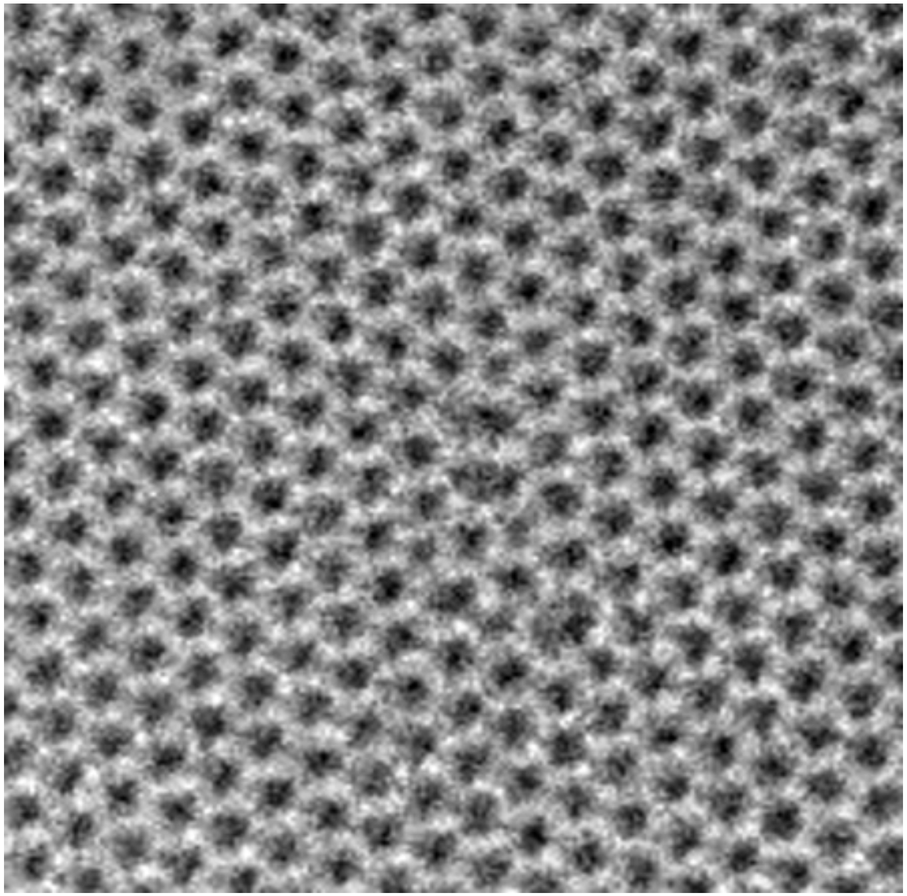
- Movie:

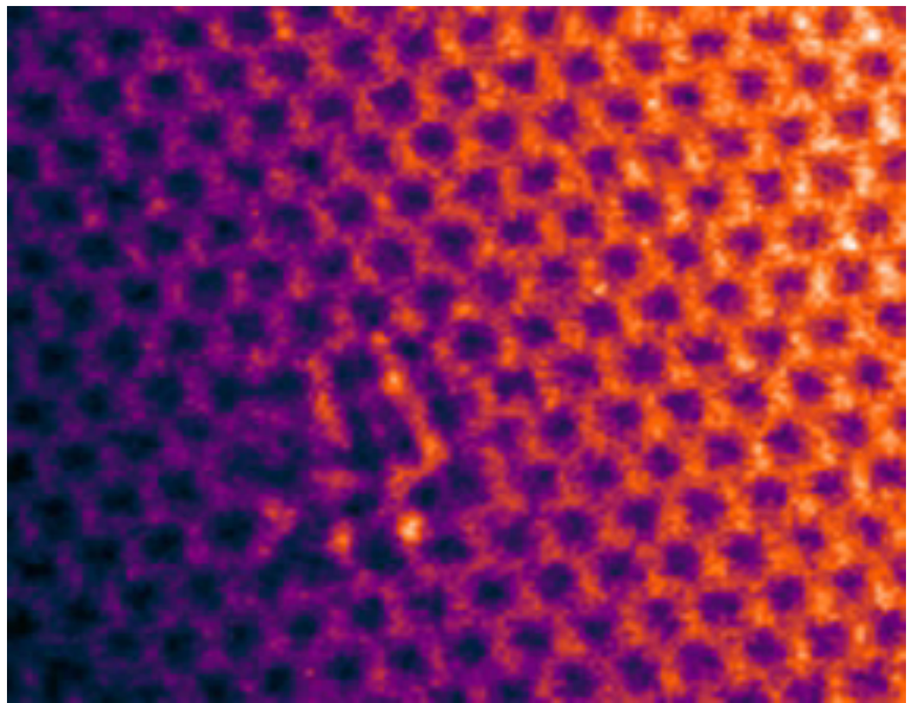
mxsplit.mpg

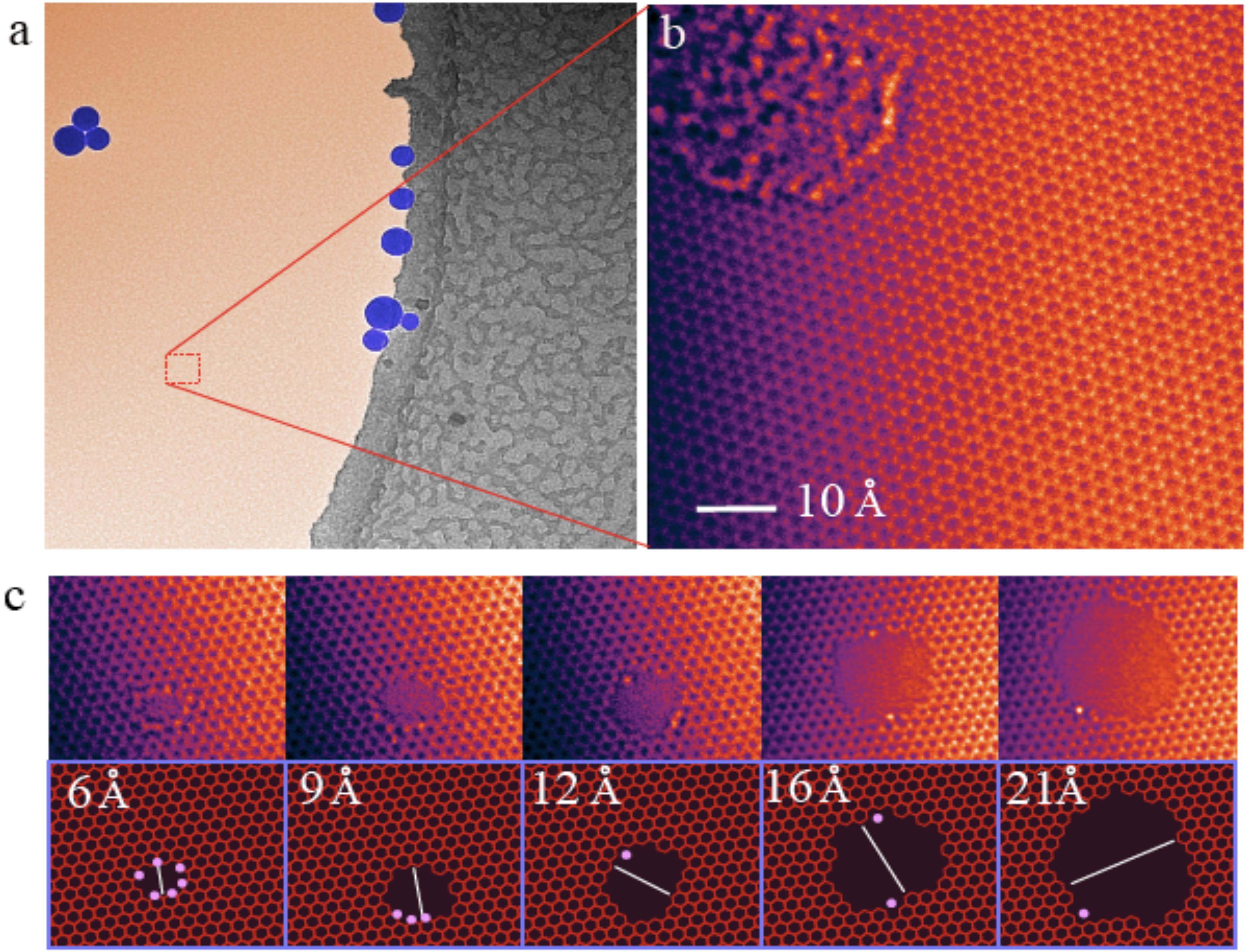


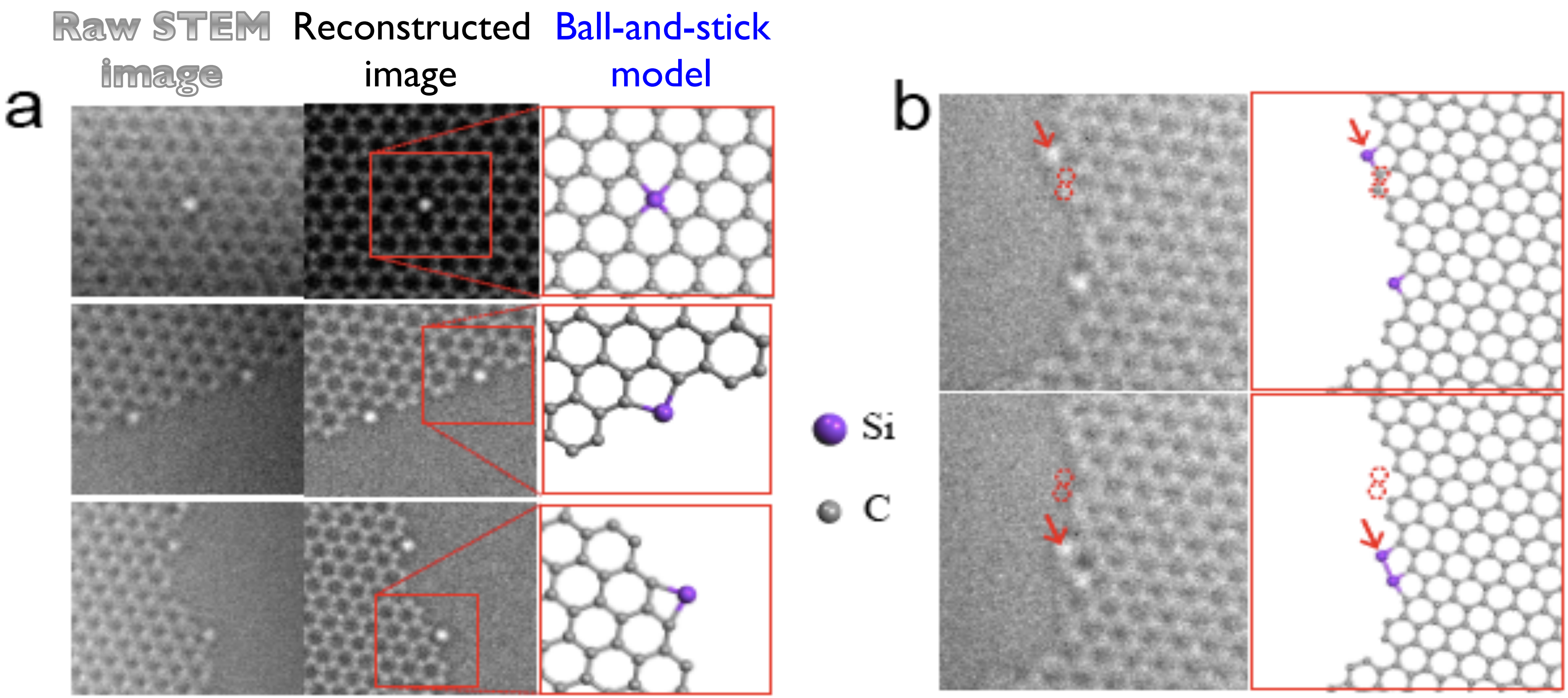
An atomic-scale chisel for sculpting graphene

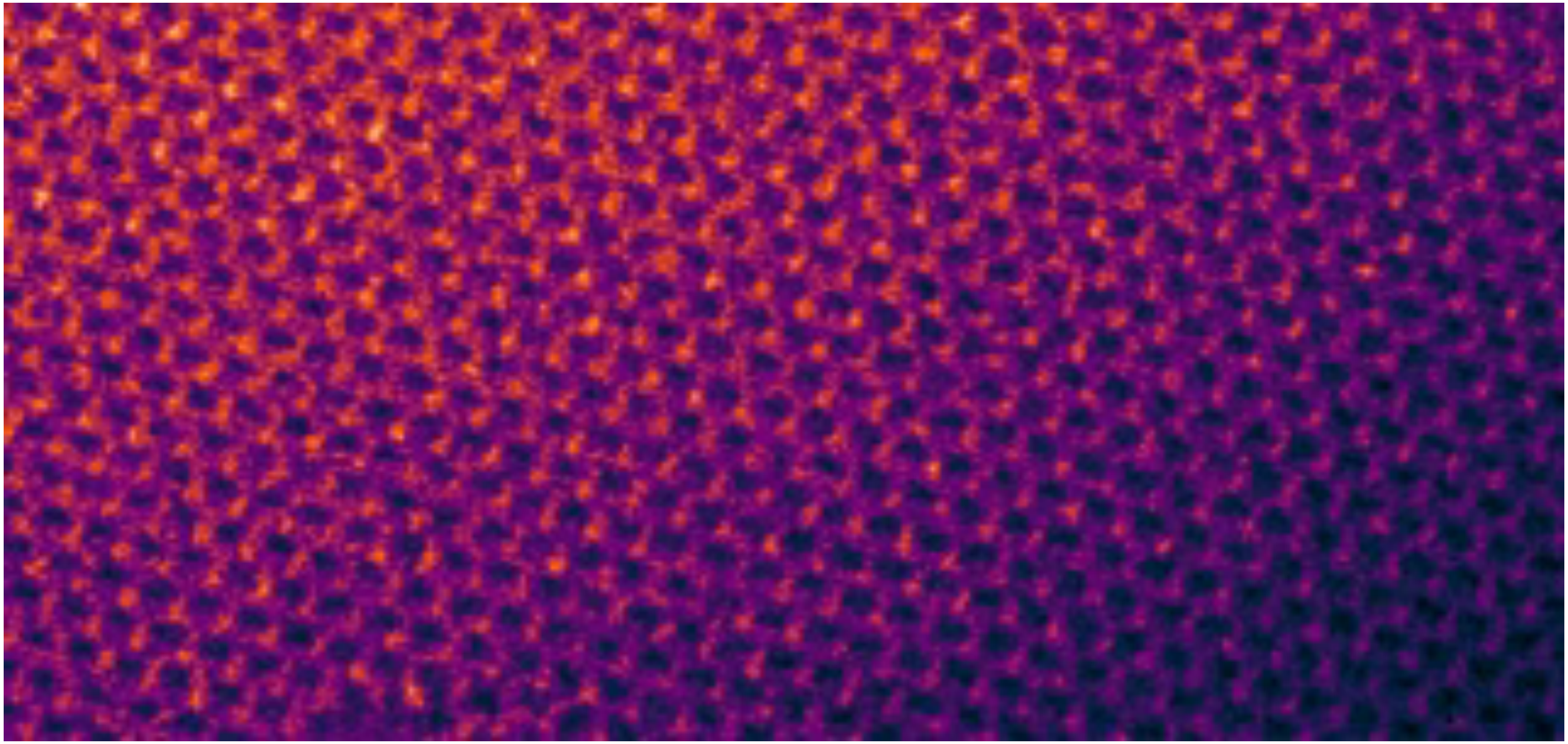


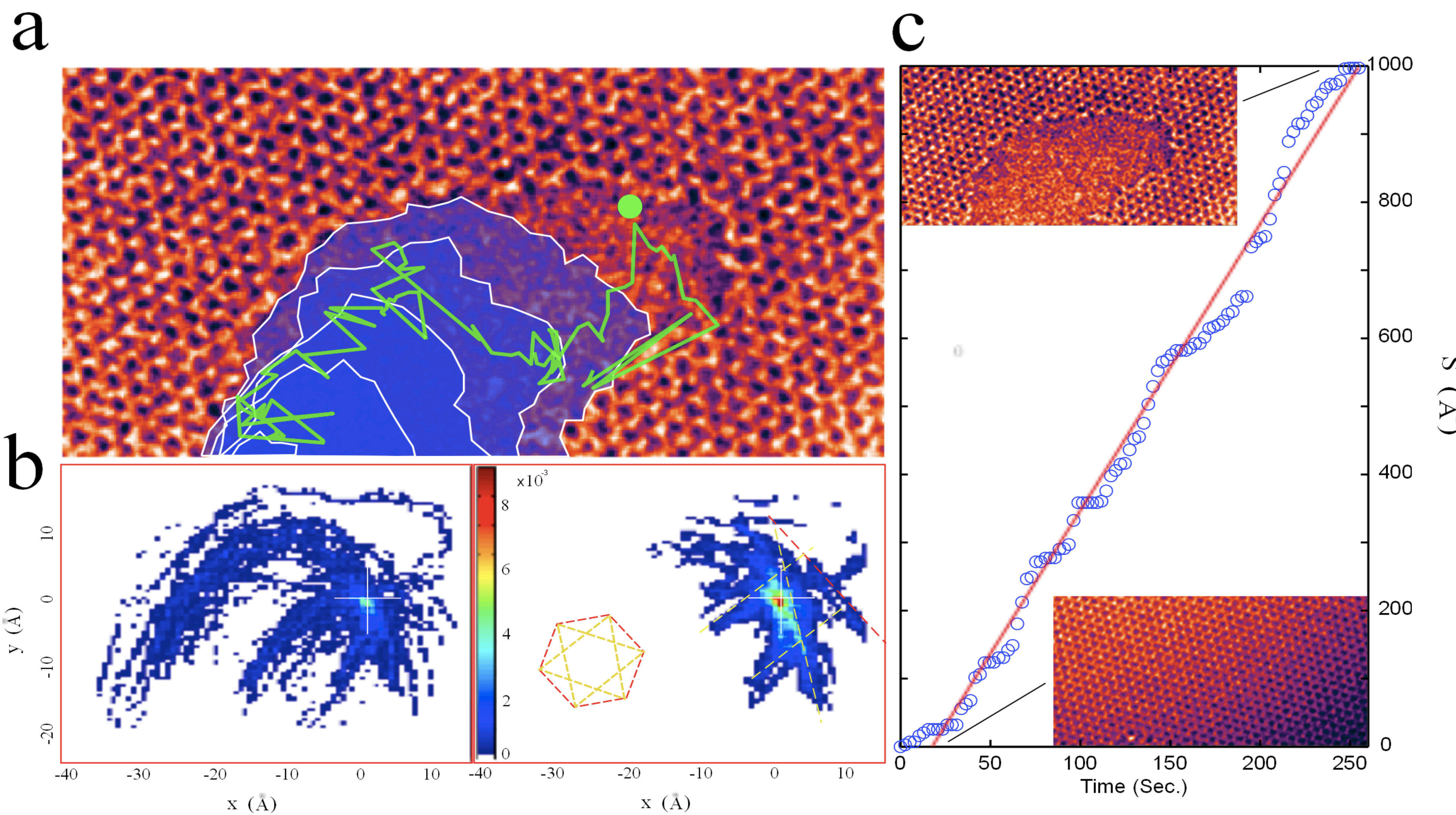




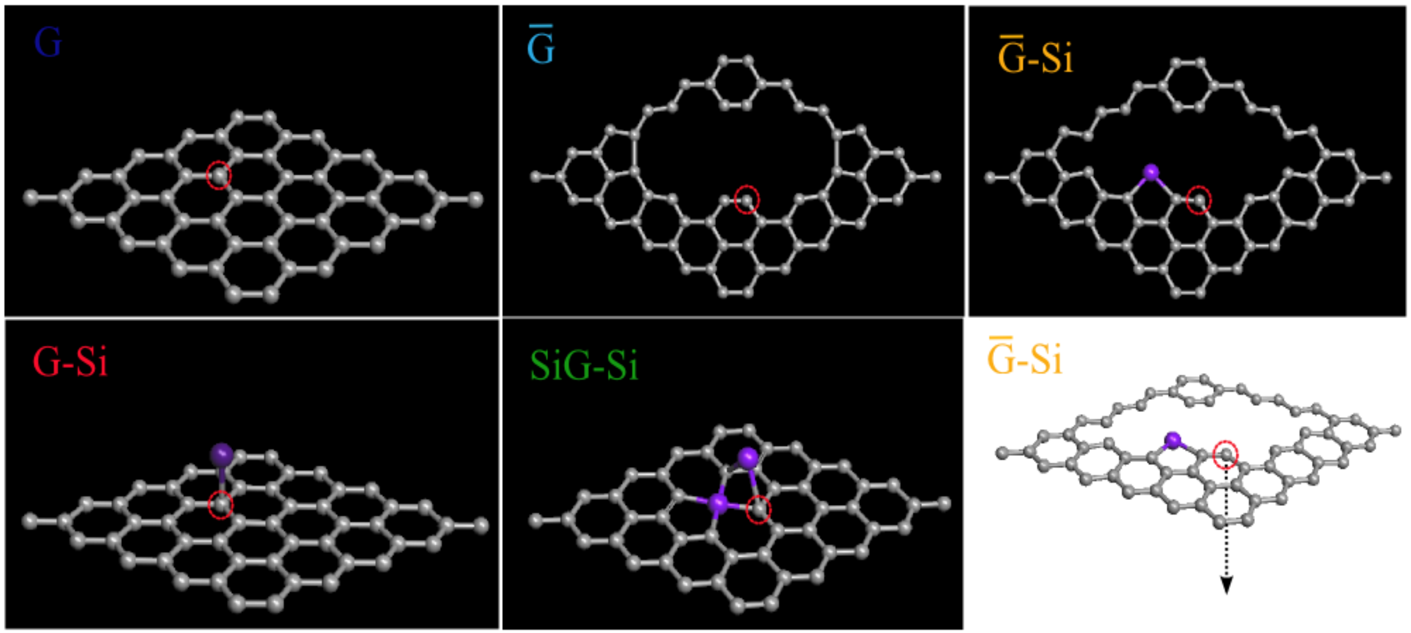

a
b
10 Å
c
6 Å
9 Å
12 Å
16 Å
21Å


Raw STEM image
Reconstructed image
Ball-and-stick model
a
b
Si
C

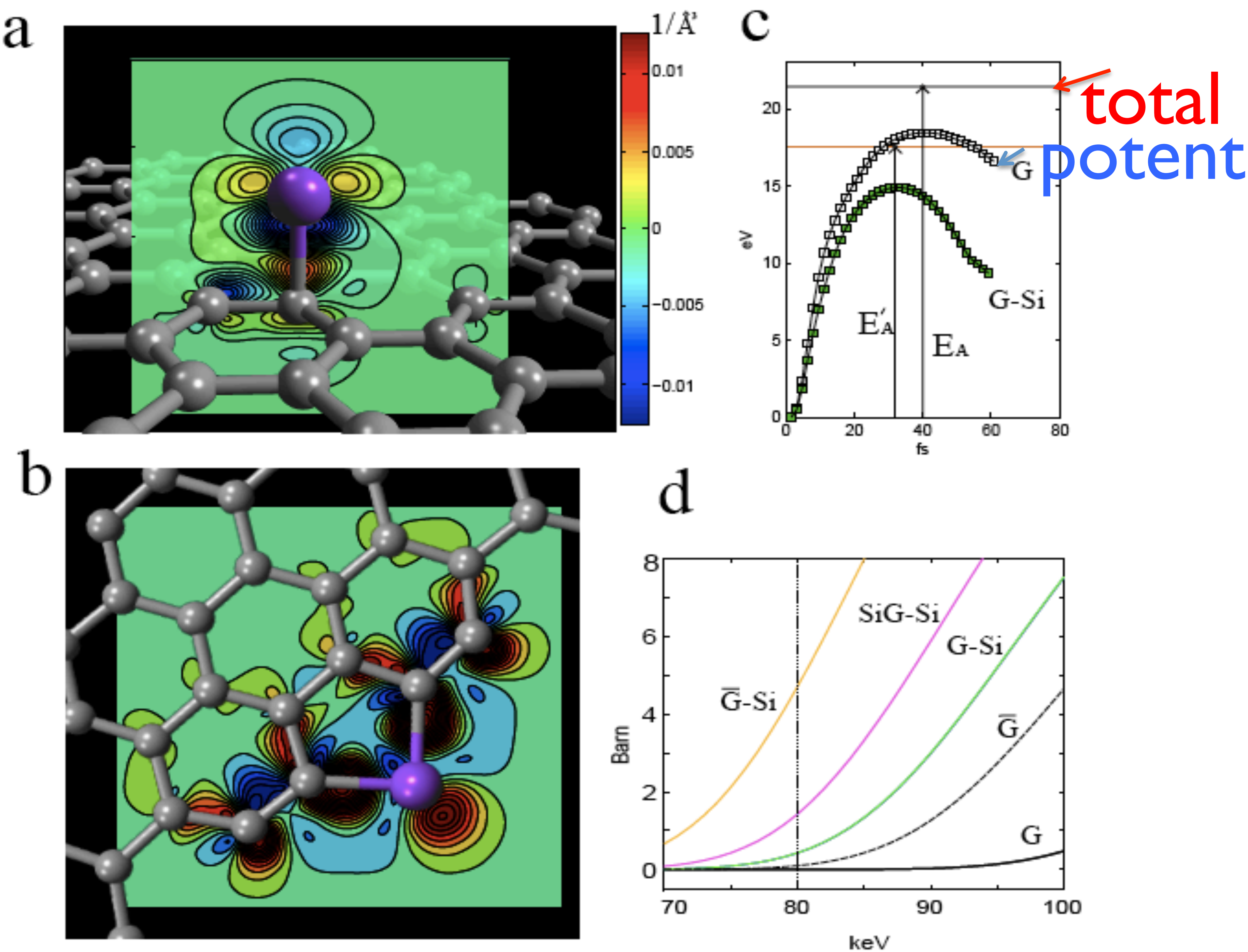




a
b
c
y (Å)
x (Å)
x (Å)
x10^-3
Time (Sec.)
S (Å^2)



G
G̅
G̅-Si
G-Si
SiG-Si
G̅-Si



a
1/Å³
0.01
0.005
0
−0.005
−0.01
b
c
eV
fs
E′A
EA
G
G-Si
total
potent
d
Barn
keV
$\bar{G}$-Si
SiG-Si
G-Si
$\bar{G}$
G

Summary: by combining

- fundamental physics (TDSE)
- methodologies for coupling of scales
- computational tools

can address complex phenomena of intrinsic interest and potential for useful applications.

TDAP: improved TDDFT (computationally efficient) + Ehrenfest dynamics

$$i\hbar \frac{\partial \phi_j(\mathbf{r},t)}{\partial t} = \hat{H}_{KS}\phi_j$$

$$\rho(\mathbf{r},t) = \sum_j |\phi_j(\mathbf{r},t)|^2$$

$$M_J \frac{d^2\mathbf{R}_J^{cl}(t)}{dt^2} = -\nabla_{\mathbf{R}_J^{cl}} \left[V_{ext}^J(\mathbf{R}_J^{cl},t) - \int \frac{Z_J \rho(\mathbf{r},t)}{|\mathbf{R}_J^{cl} - \mathbf{r}|} d\mathbf{r} + \sum_{I \neq J} \frac{Z_J Z_I}{|\mathbf{R}_J^{cl} - \mathbf{R}_I^{cl}|} \right]$$

$$\rho_J(\mathbf{R},t) = |\psi_J(\mathbf{R},t)|^2 = \delta\left(\mathbf{R} - \mathbf{R}_J^{cl}\right)$$