Ab-initio studies of optical excitations in solids and molecules

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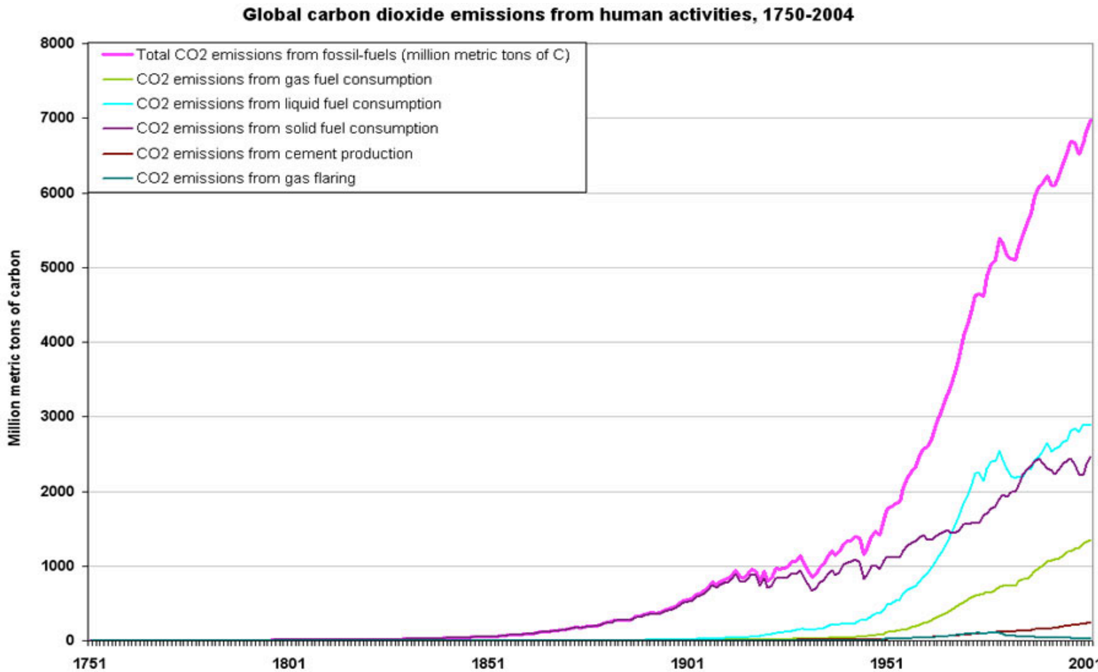
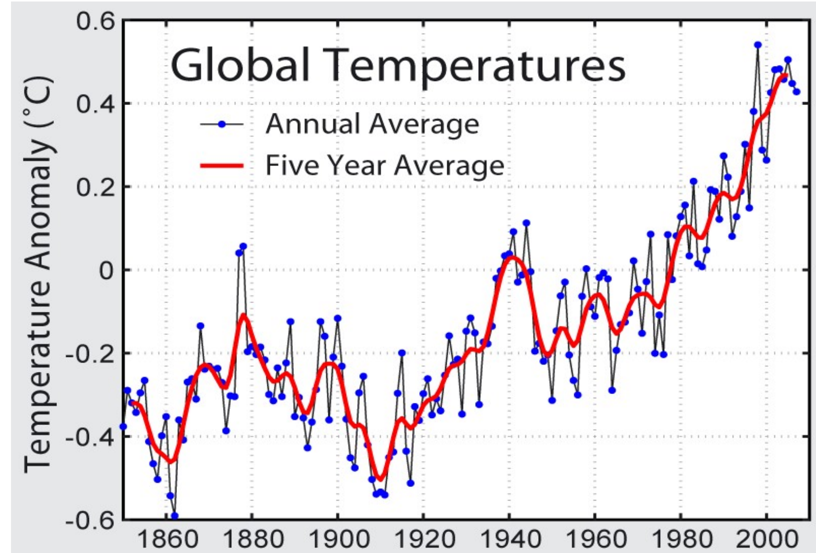
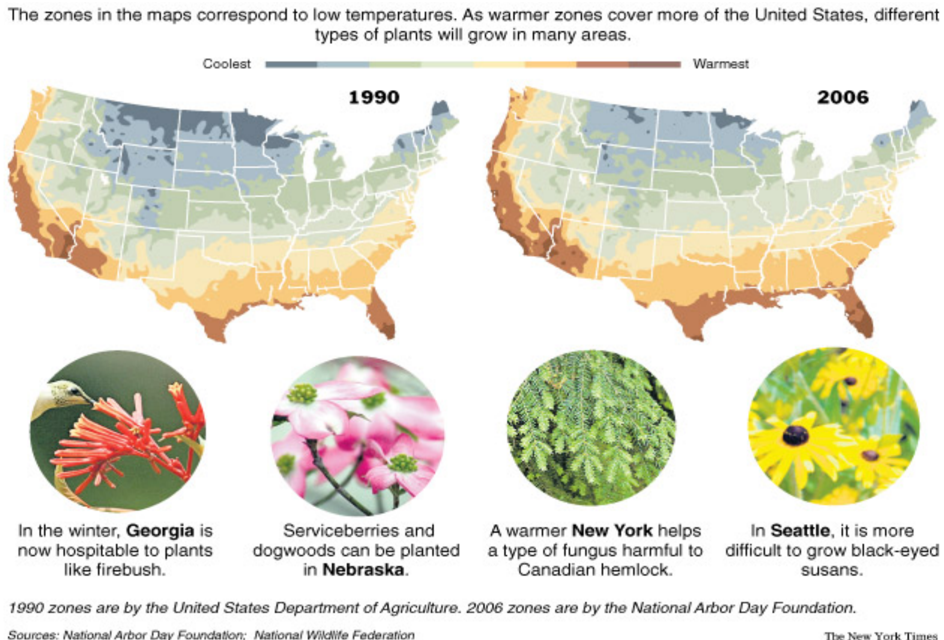
(earlier work: Sheng Meng, Jun Ren, Inst. of Phys., Ch. Acad. Sci.)

Sabanci University – May 8, 2014

The need for alternative energy sources

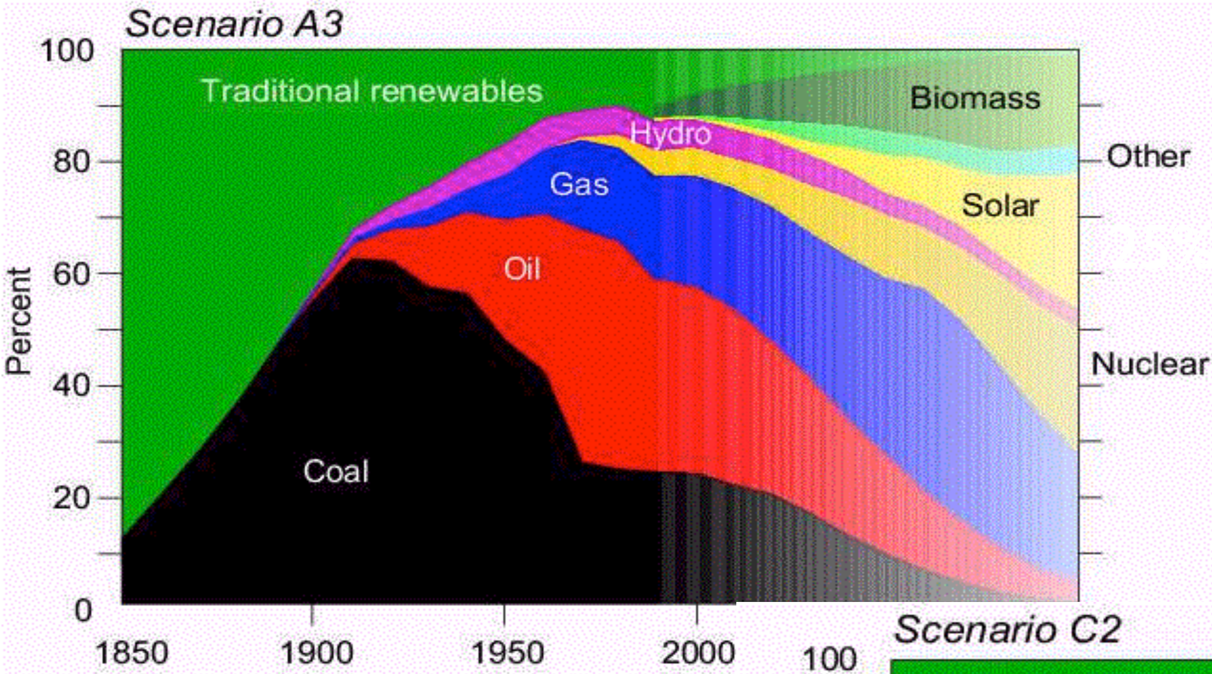




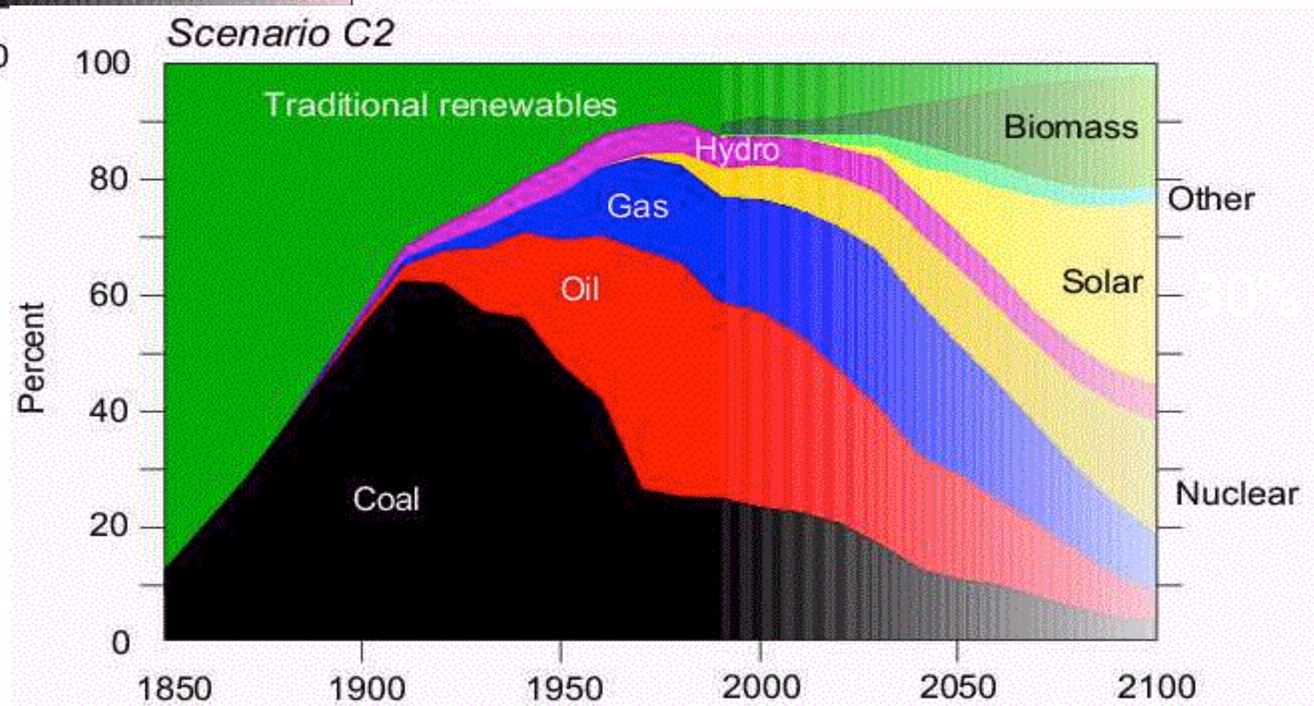


http://www.celsias.com/2007/03/20/channel-4-distances-itself-from-global-warming-documentary/

The challenge of sustainable energy

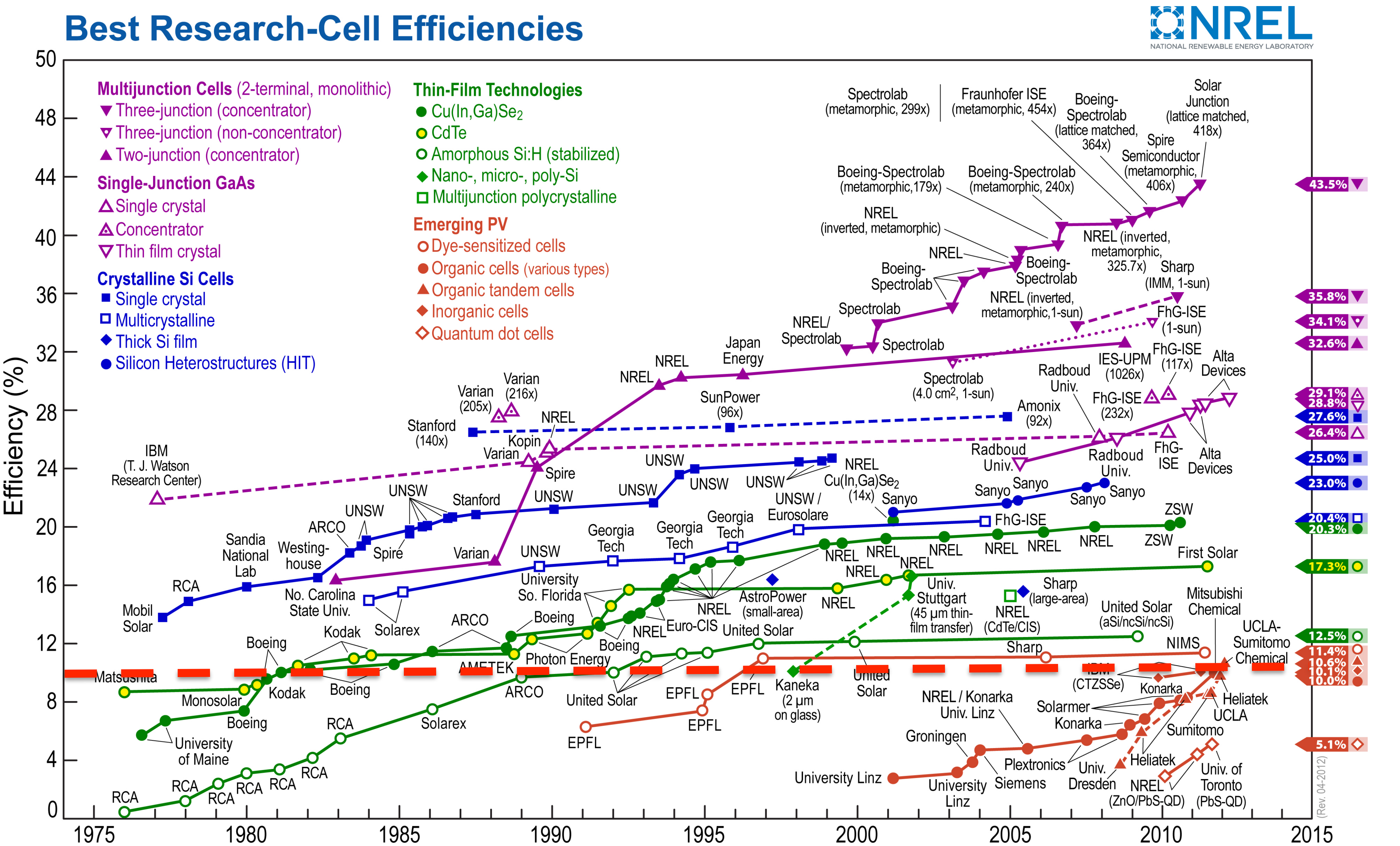


Time and resources running out



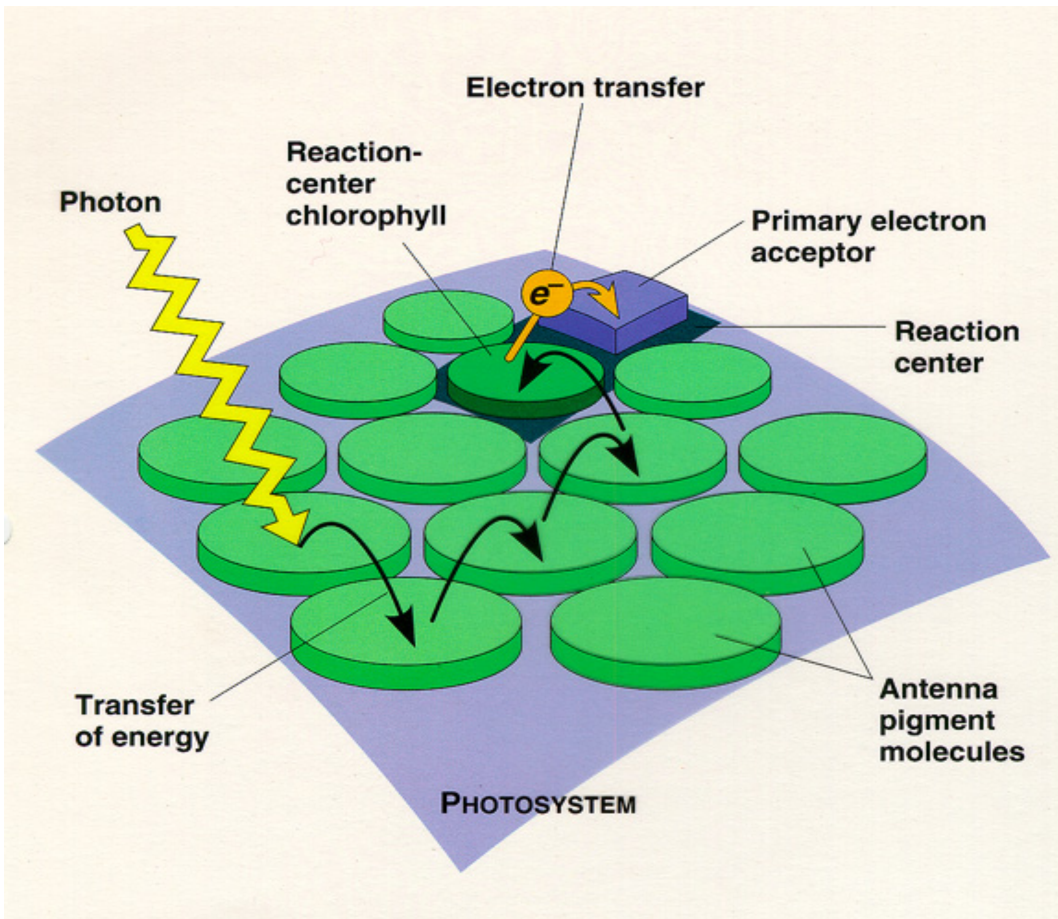
Report of Intergovernmental Panel on Climate Change

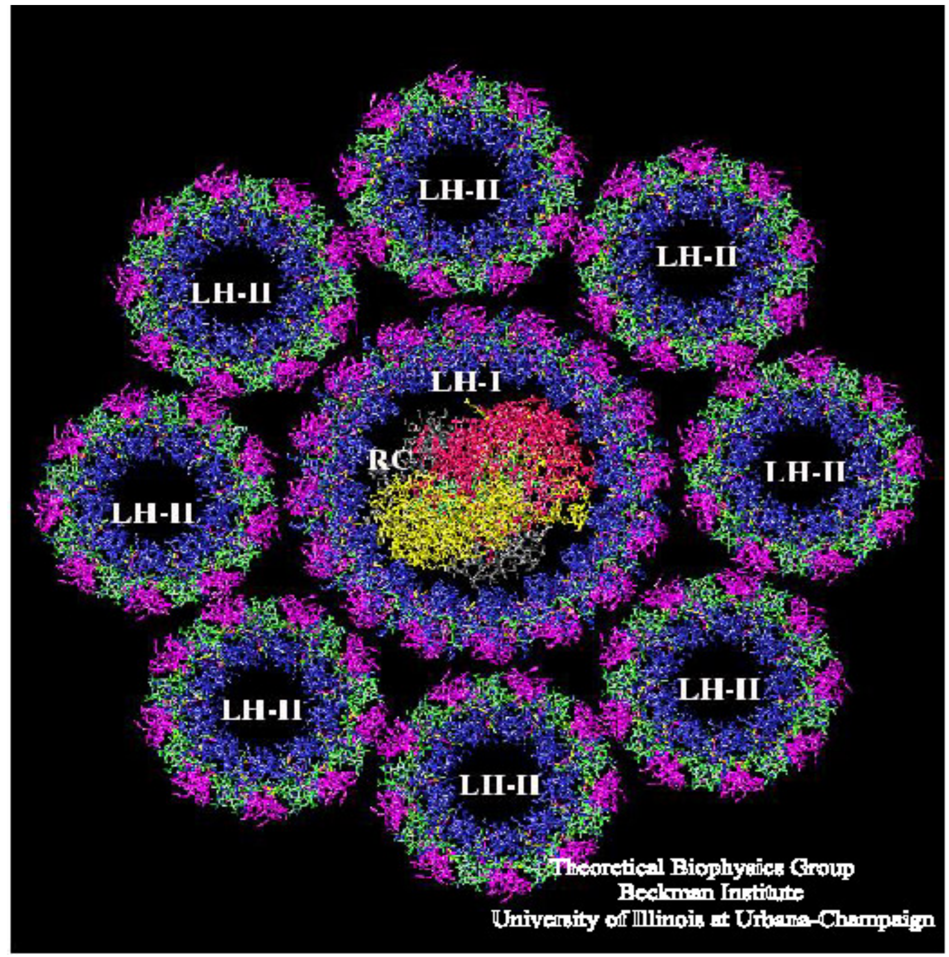
Best Research-Cell Efficiencies



The dye-sensitized (3rd generation) solar cell

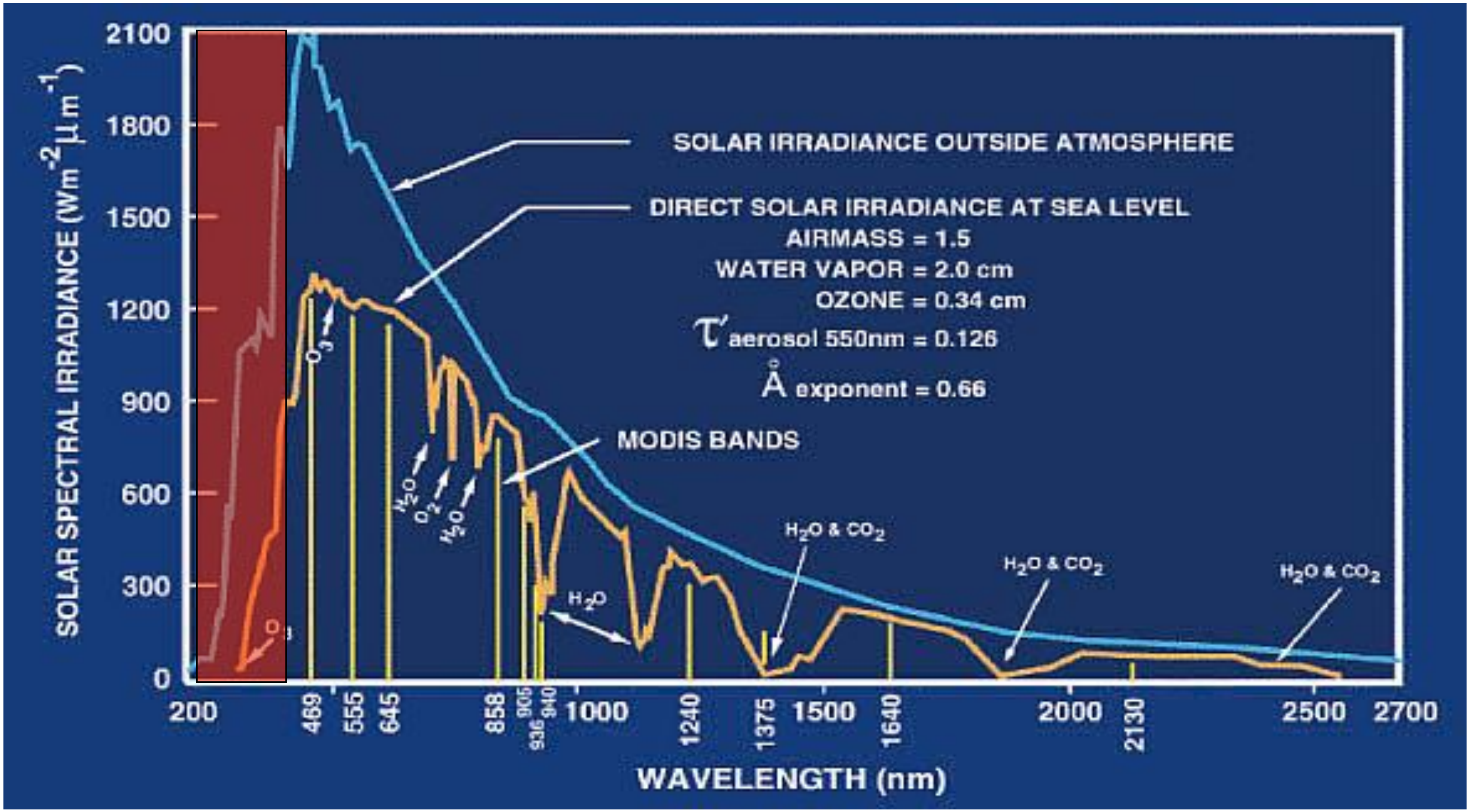
The Principle: Separate light-absorption and charge collection processes





Light absorption by hybrid cells

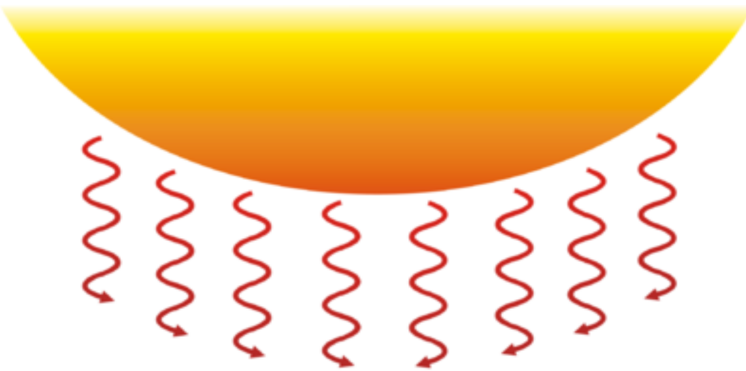
TiO_2 gap = 3.2 eV (200 nm < λ < 400 nm)



solar spectrum

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

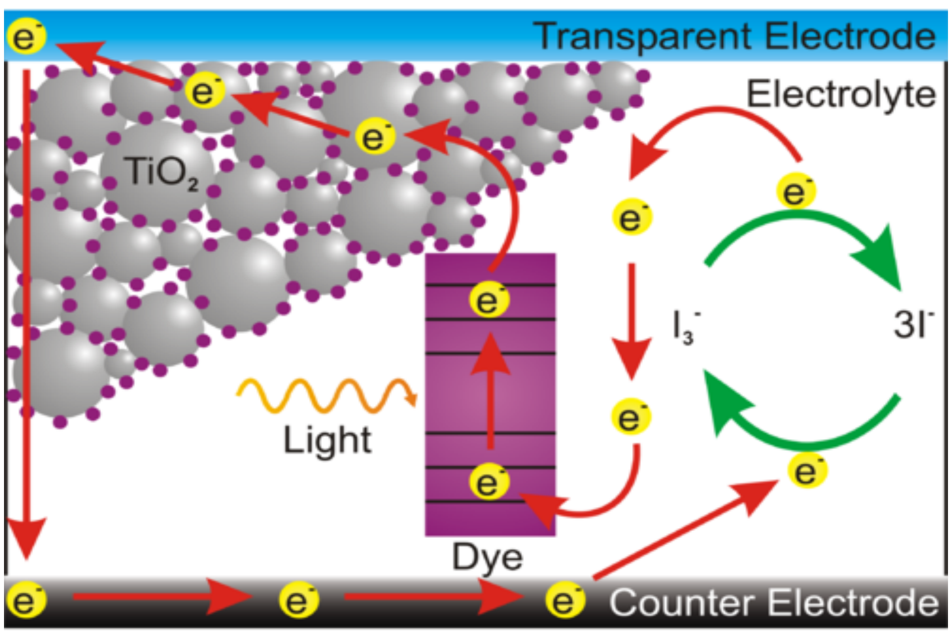
Simple device, complex physics



Major issues:

- stability
- efficiency

  Incident Photon to Current Efficiency



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

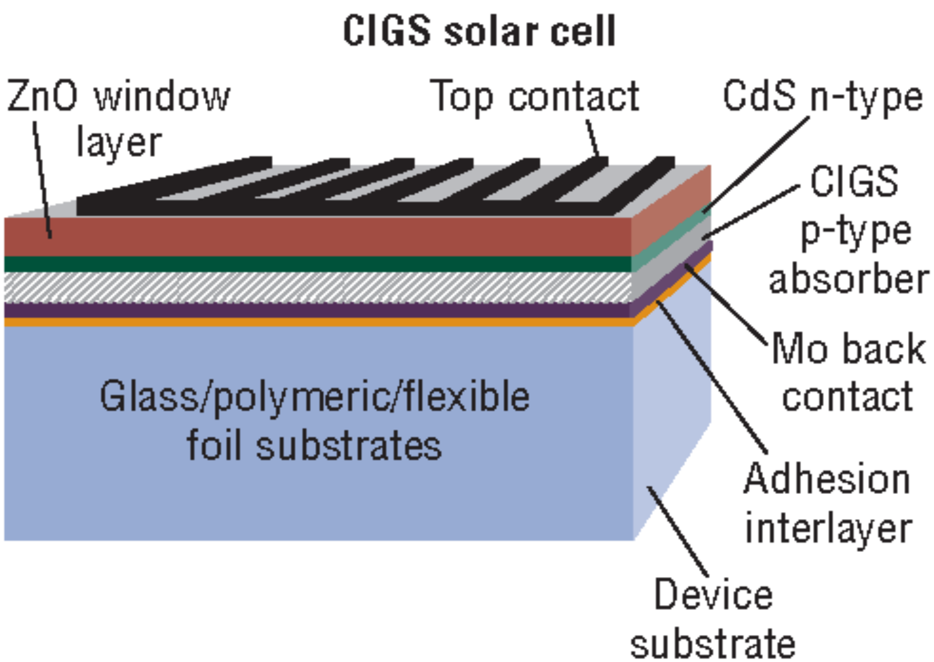
LHE = Light Harvesting Efficiency

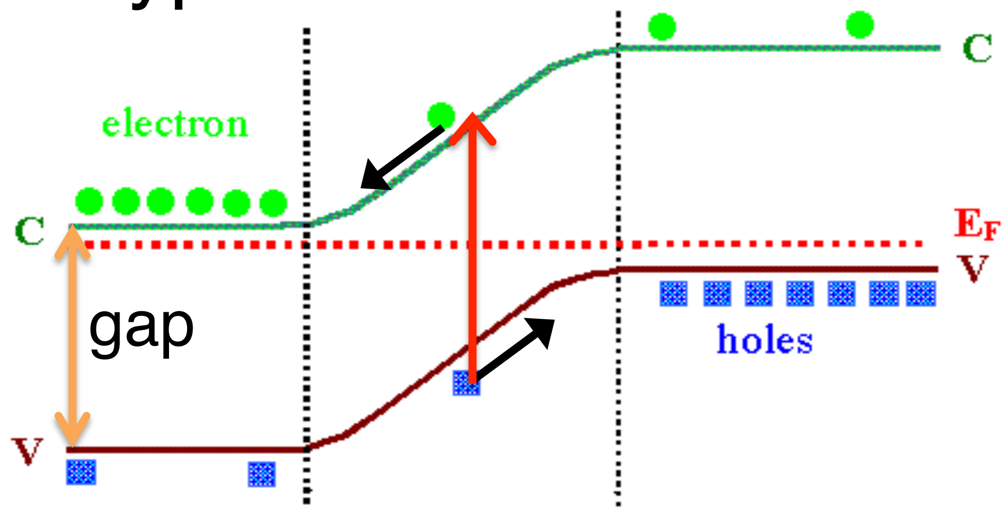
Φ(inj) = electron injection efficiency

η (c) = charge collection efficiency

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

Copper-Indium-Gallium-Selenide cell



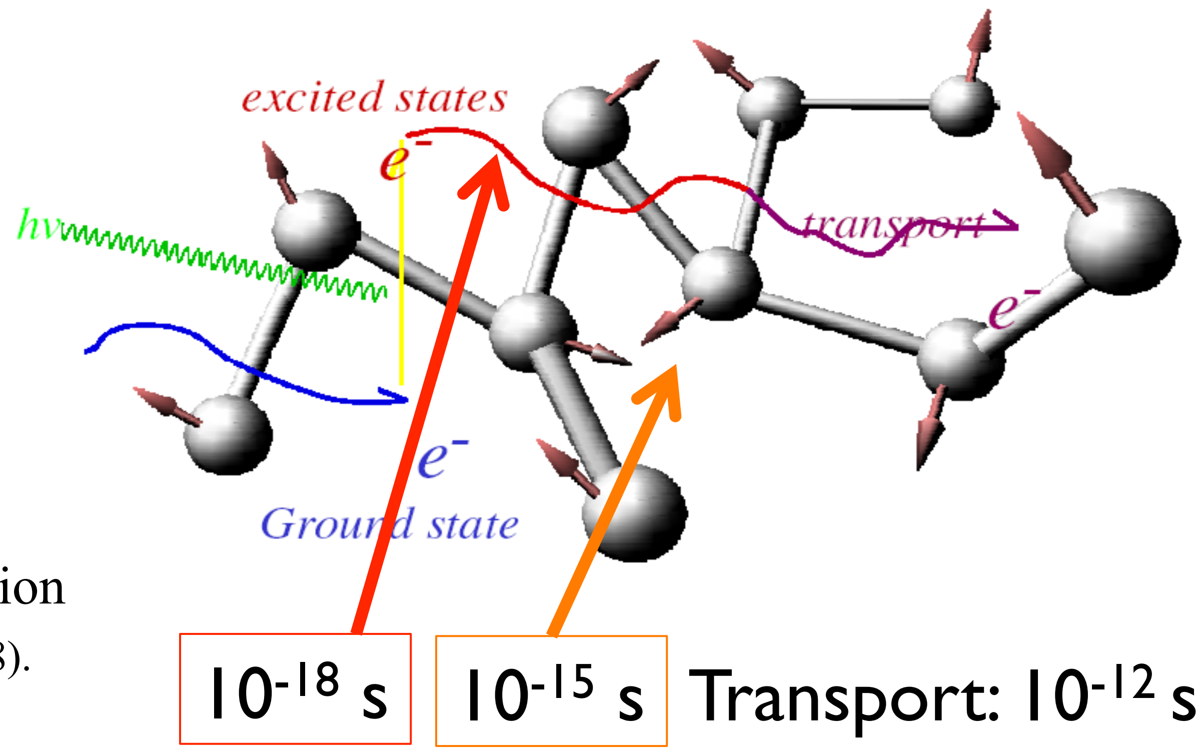


Bulk semiconductor (inorganic)
- delocalized states (band structure)
- nearly free electrons
- single band-gap

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).

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

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

Density Functional Theory

Many-body:

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

Hohenberg & Kohn (PRB, 1964):

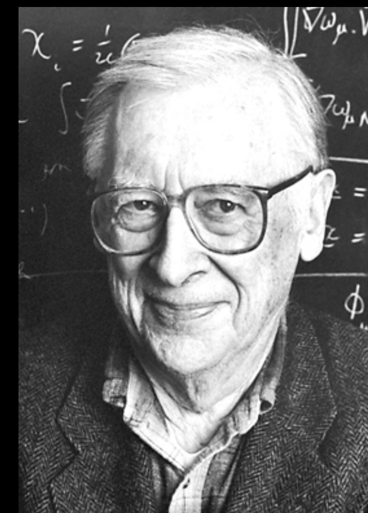
$$E\left[V(\mathbf{r})\right] = \min_{\rho(\mathbf{r})} E'\left[V(\mathbf{r}); \rho(\mathbf{r})\right]$$

Kohn & Sham (PRB, 1965):

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

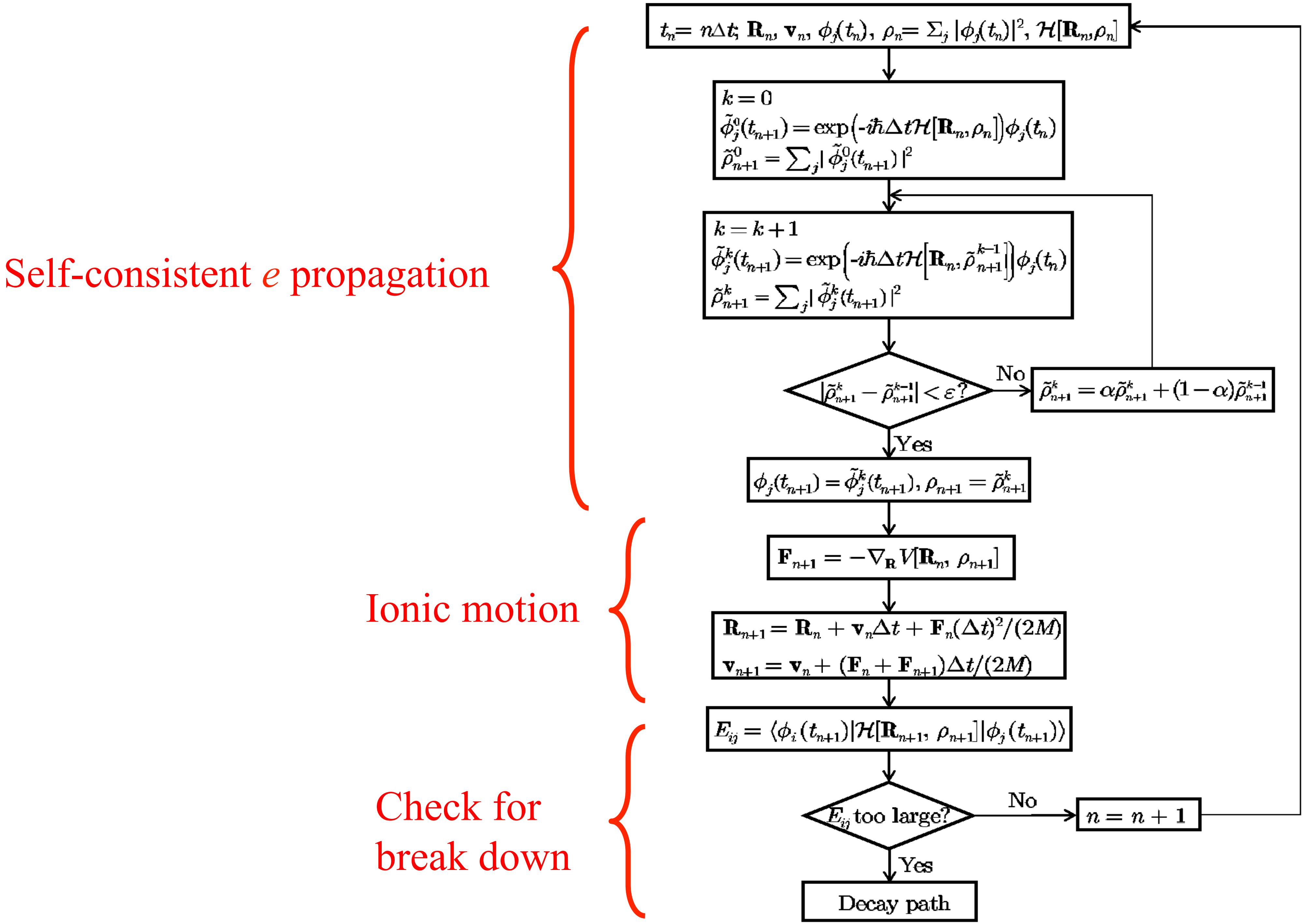
$$T_s[\rho] + E_{\mathrm{Hart}}[\rho] + \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r} + E_{\mathrm{xc}}[\rho]$$

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

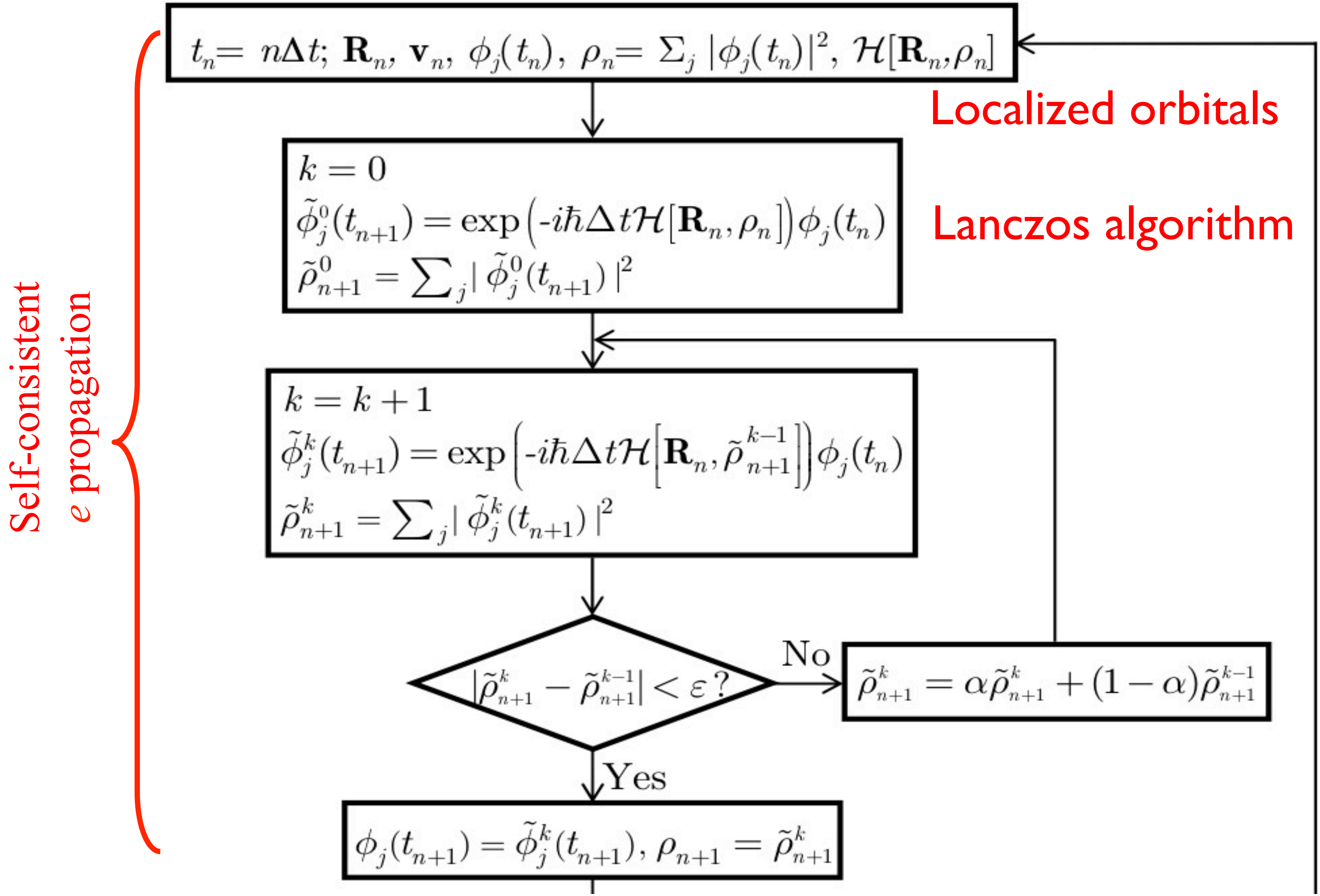


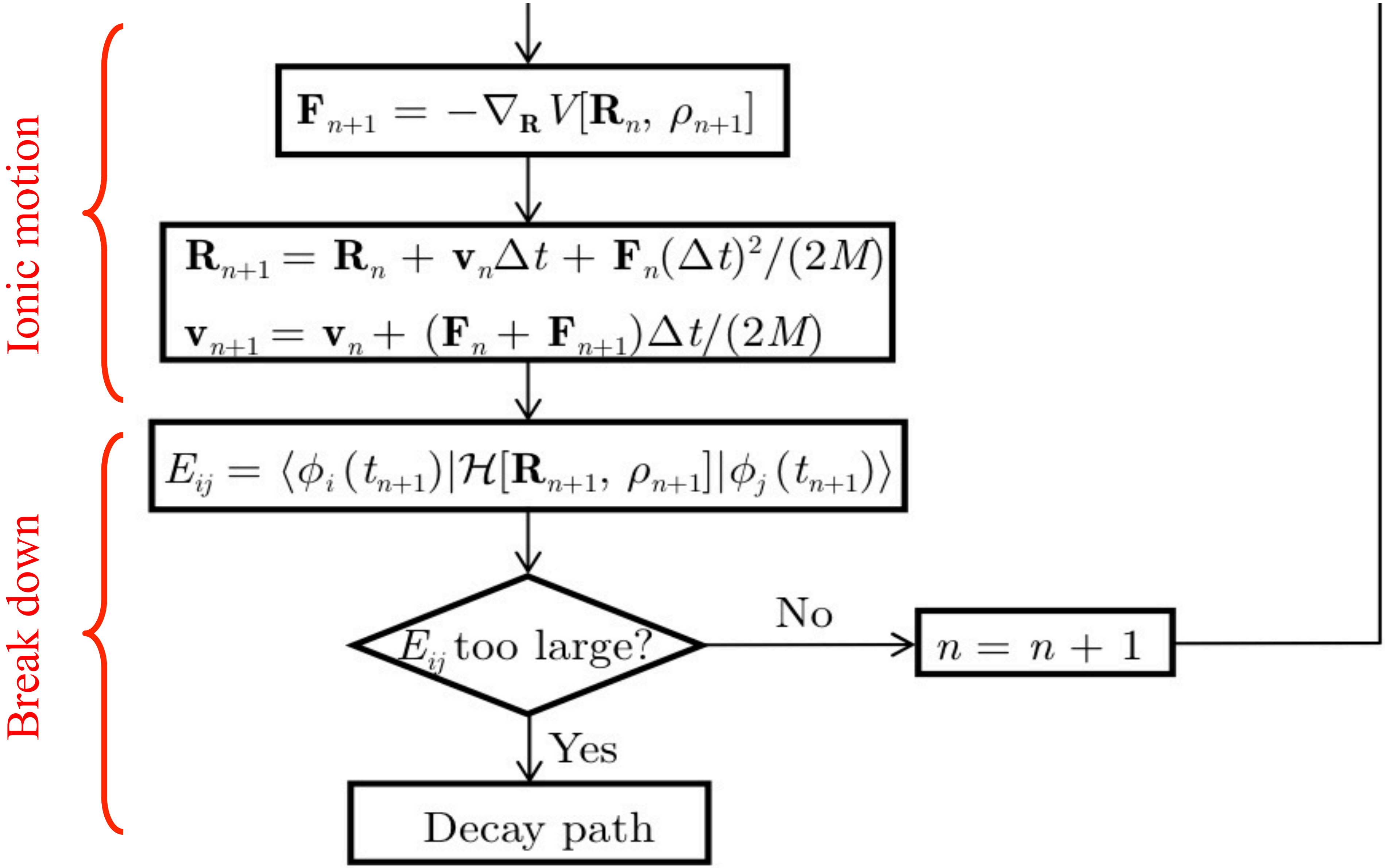
W. Kohn, J. Pople
Nobel Prize in
Chemistry, 1998

Runge-Gross theorem for TD-DFT



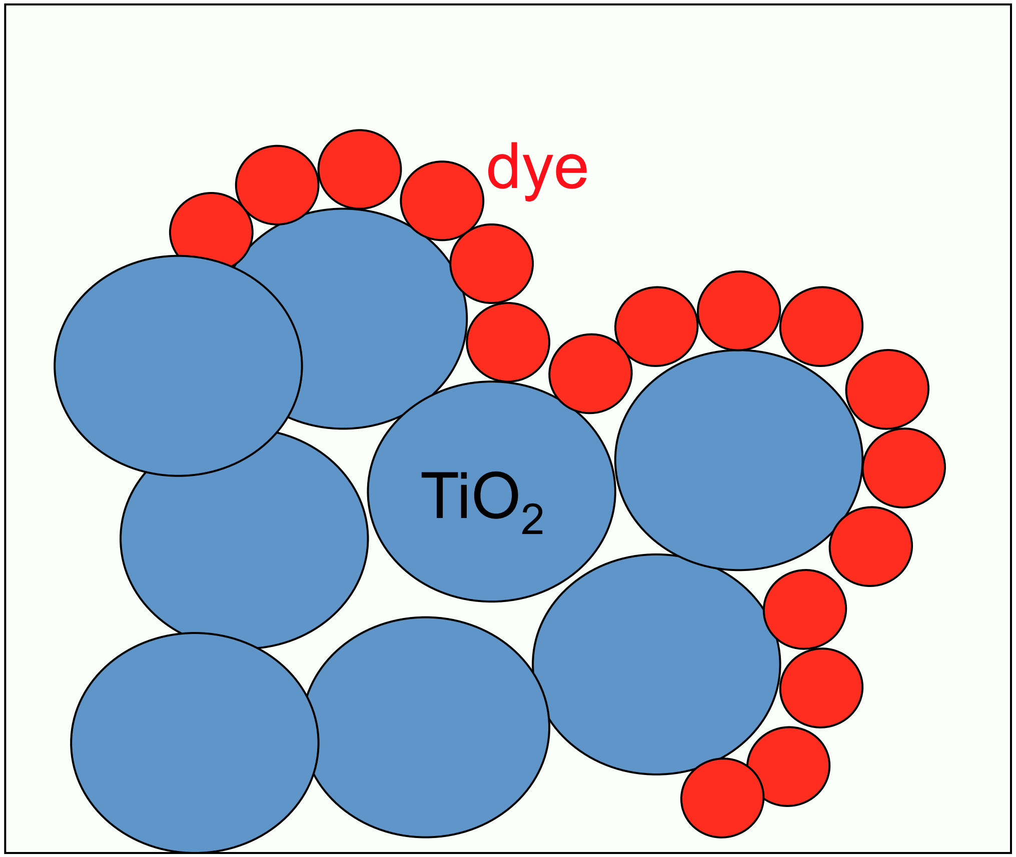
Self-consistent e propagation
Ionic motion
Check for
break down
$t_n = n\Delta t$; $\mathbf{R}_n$, $\mathbf{v}_n$, $\phi_j(t_n)$, $\rho_n = \Sigma_j |\phi_j(t_n)|^2$, $\mathcal{H}[\mathbf{R}_n, \rho_n]$
$k = 0$
$\tilde{\phi}_j^0(t_{n+1}) = \exp\left(-i\hbar\Delta t\mathcal{H}[\mathbf{R}_n, \rho_n]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^0 = \sum_j |\tilde{\phi}_j^0(t_{n+1})|^2$
$k = k+1$
$\tilde{\phi}_j^k(t_{n+1}) = \exp\left(-i\hbar\Delta t\mathcal{H}\left[\mathbf{R}_n, \tilde{\rho}_{n+1}^{k-1}\right]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^k = \sum_j |\tilde{\phi}_j^k(t_{n+1})|^2$
$|\tilde{\rho}_{n+1}^k - \tilde{\rho}_{n+1}^{k-1}| < \varepsilon$?
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

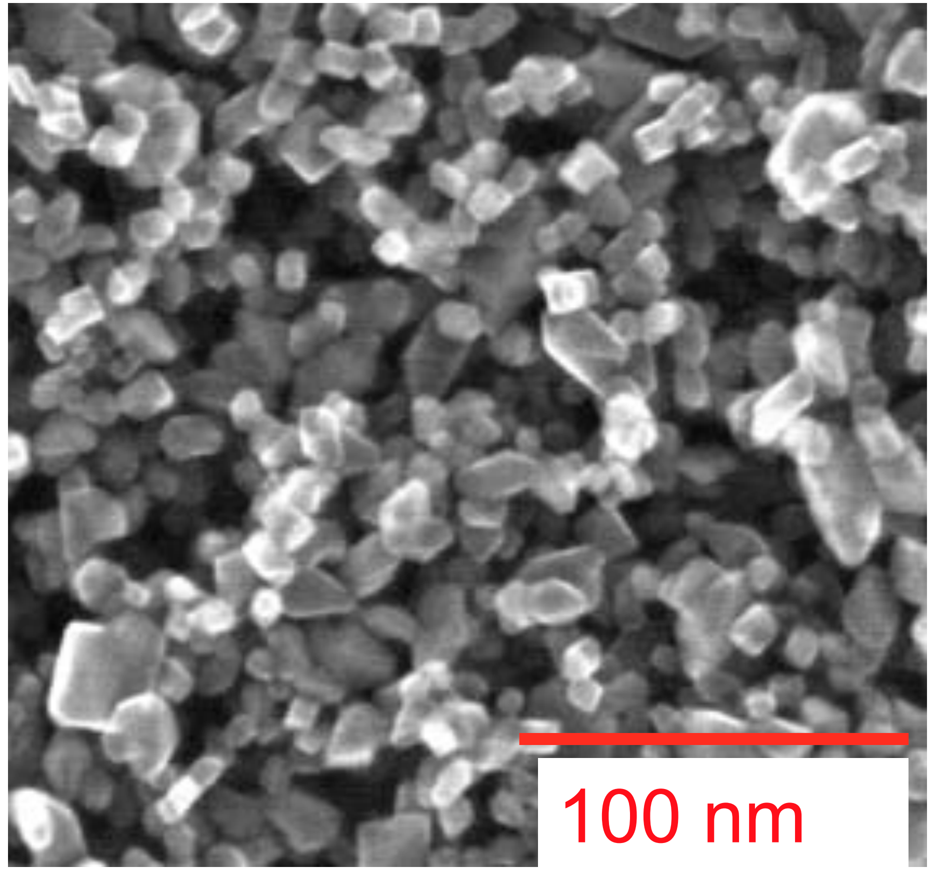

$t_n = n\Delta t;\ \mathbf{R}_n,\ \mathbf{v}_n,\ \phi_j(t_n),\ \rho_n = \Sigma_j\ |\phi_j(t_n)|^2,\ \mathcal{H}[\mathbf{R}_n,\rho_n]$
Localized orbitals
$k = 0$
$\tilde{\phi}_j^0(t_{n+1}) = \exp\left(-i\hbar\Delta t\mathcal{H}[\mathbf{R}_n,\rho_n]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^0 = \sum_j |\tilde{\phi}_j^0(t_{n+1})|^2$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

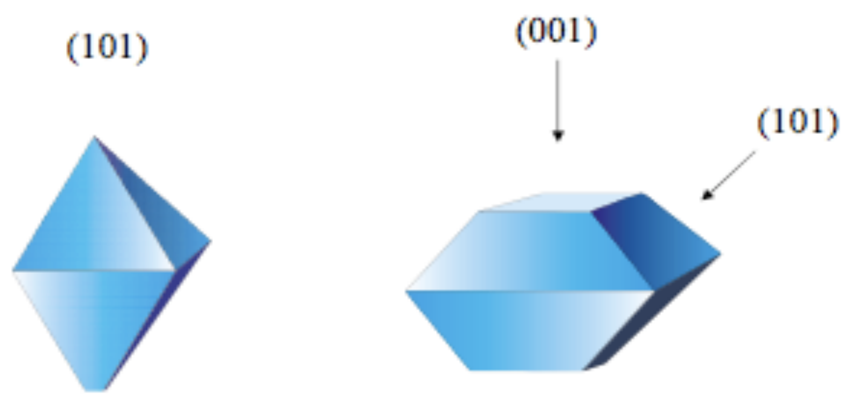


Ionic motion
$\mathbf{F}_{n+1} = -\nabla_{\mathbf{R}} V[\mathbf{R}_n, \rho_{n+1}]$
$\mathbf{R}_{n+1} = \mathbf{R}_n + \mathbf{v}_n \Delta t + \mathbf{F}_n (\Delta t)^2/(2M)$
$\mathbf{v}_{n+1} = \mathbf{v}_n + (\mathbf{F}_n + \mathbf{F}_{n+1})\Delta t/(2M)$
Break down
$E_{ij} = \langle \phi_i(t_{n+1})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

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

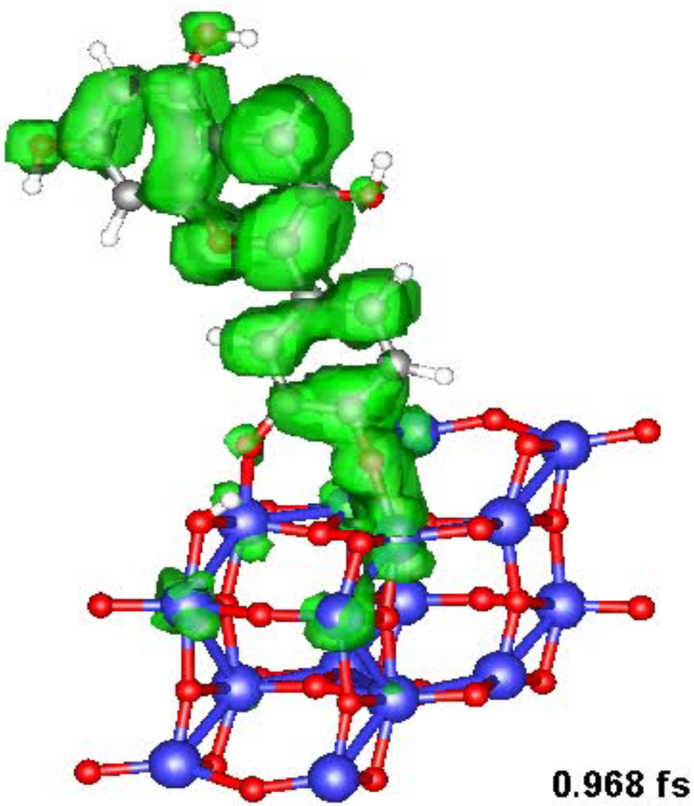


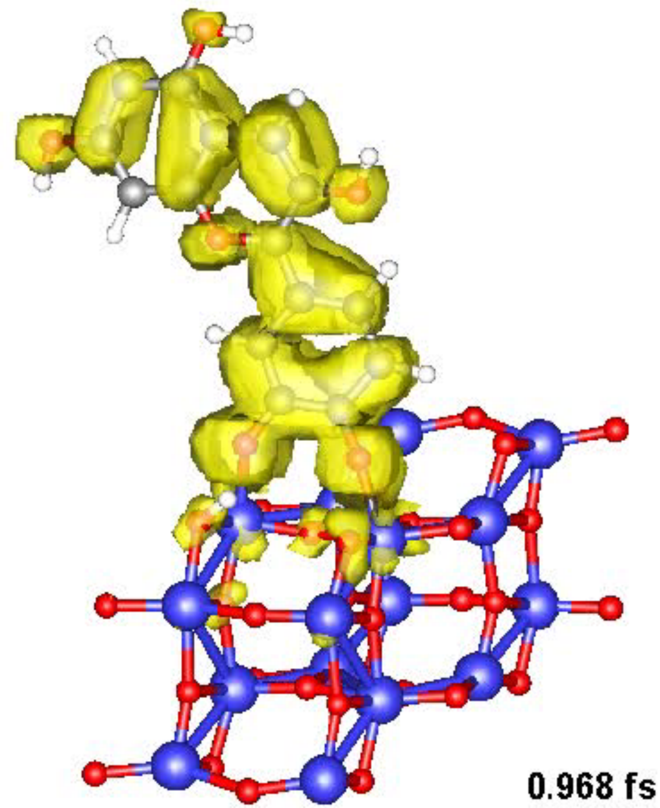




Nano-size: helps in many aspects (e.g. efficiency, transparency, transport, …)

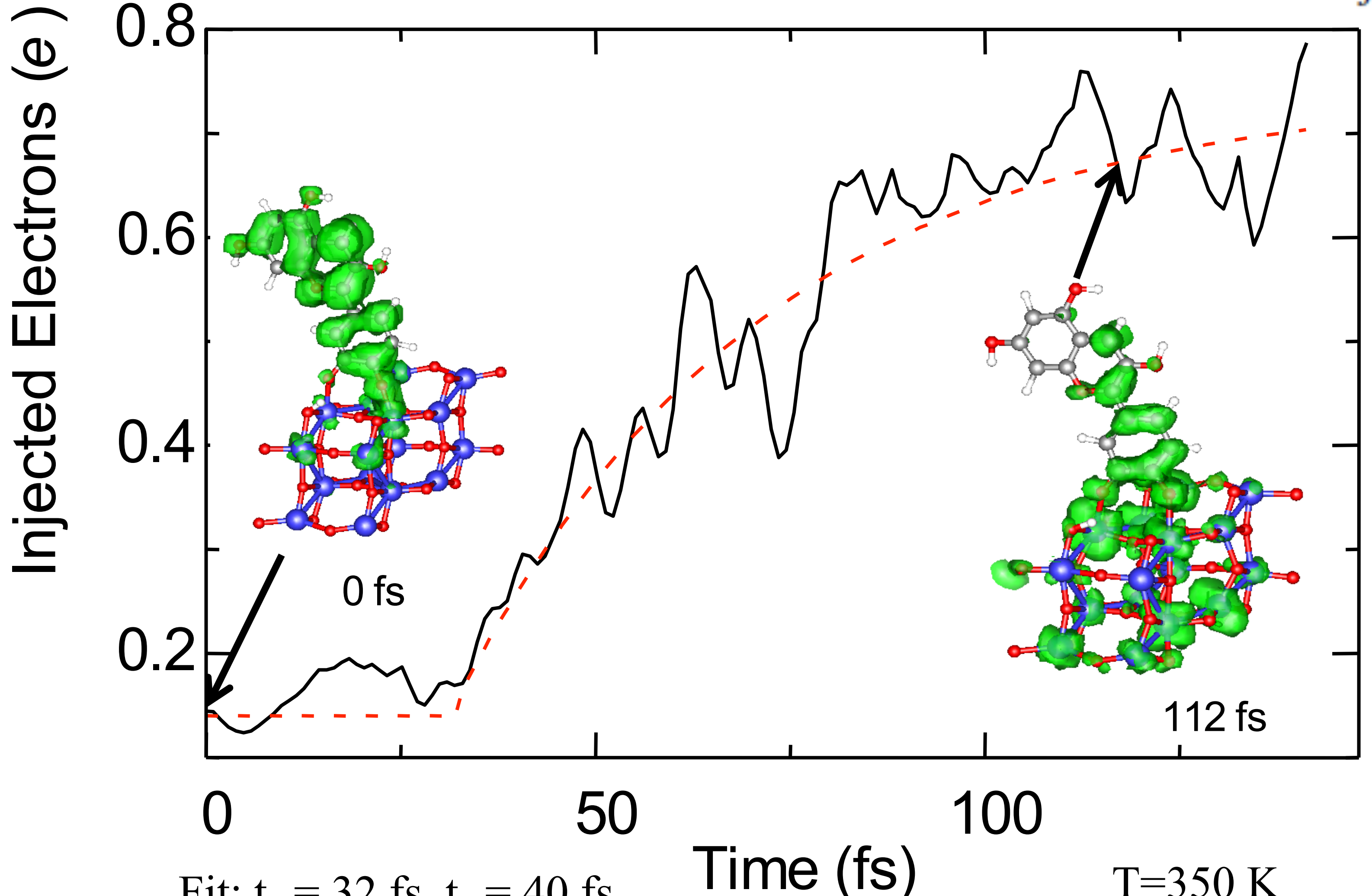
Electron and hole motion in DSSC





Charge injection dynamics:

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



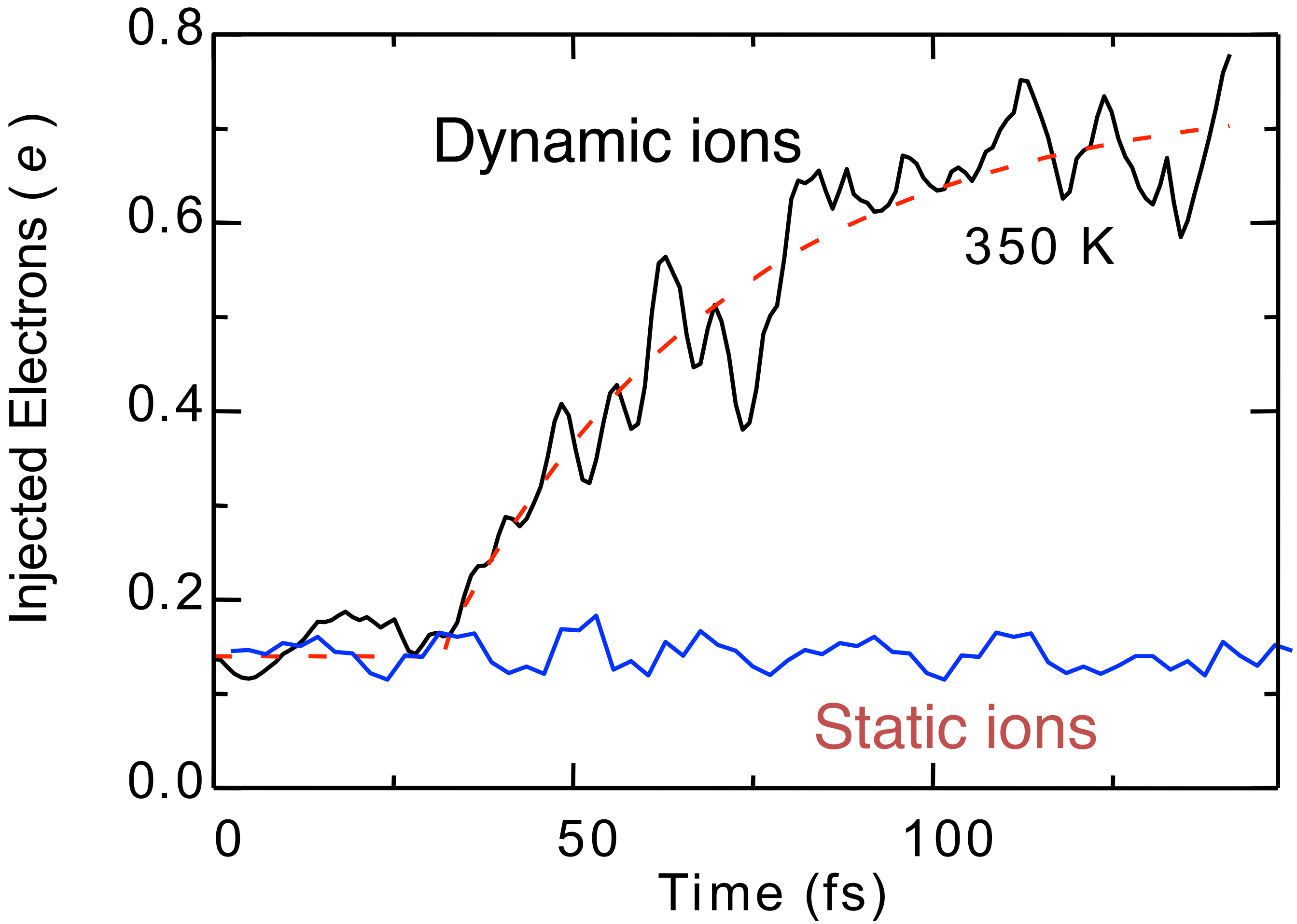
Fit: t_0 = 32 fs, t_1 = 40 fs

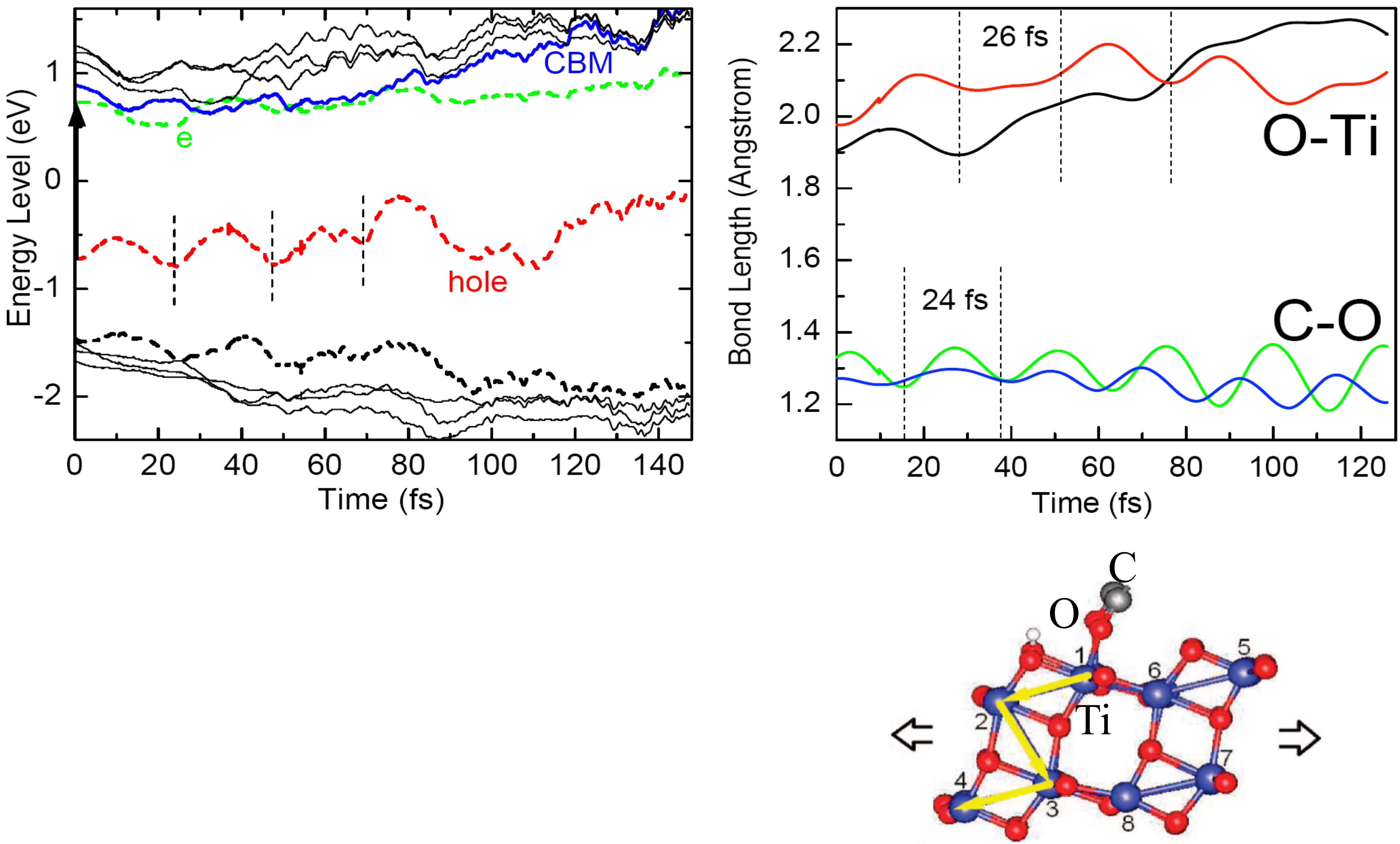
Expt.[a)] : <100 fs

T=350 K

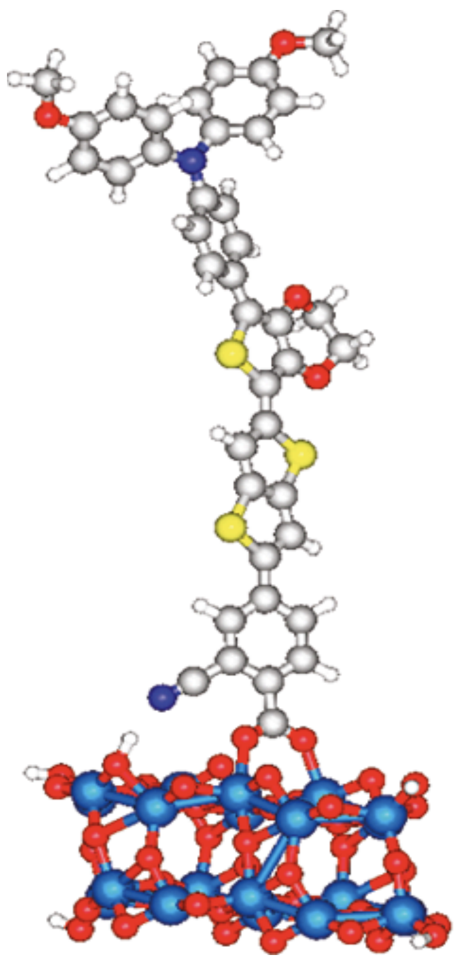
δt=0.02419 fs

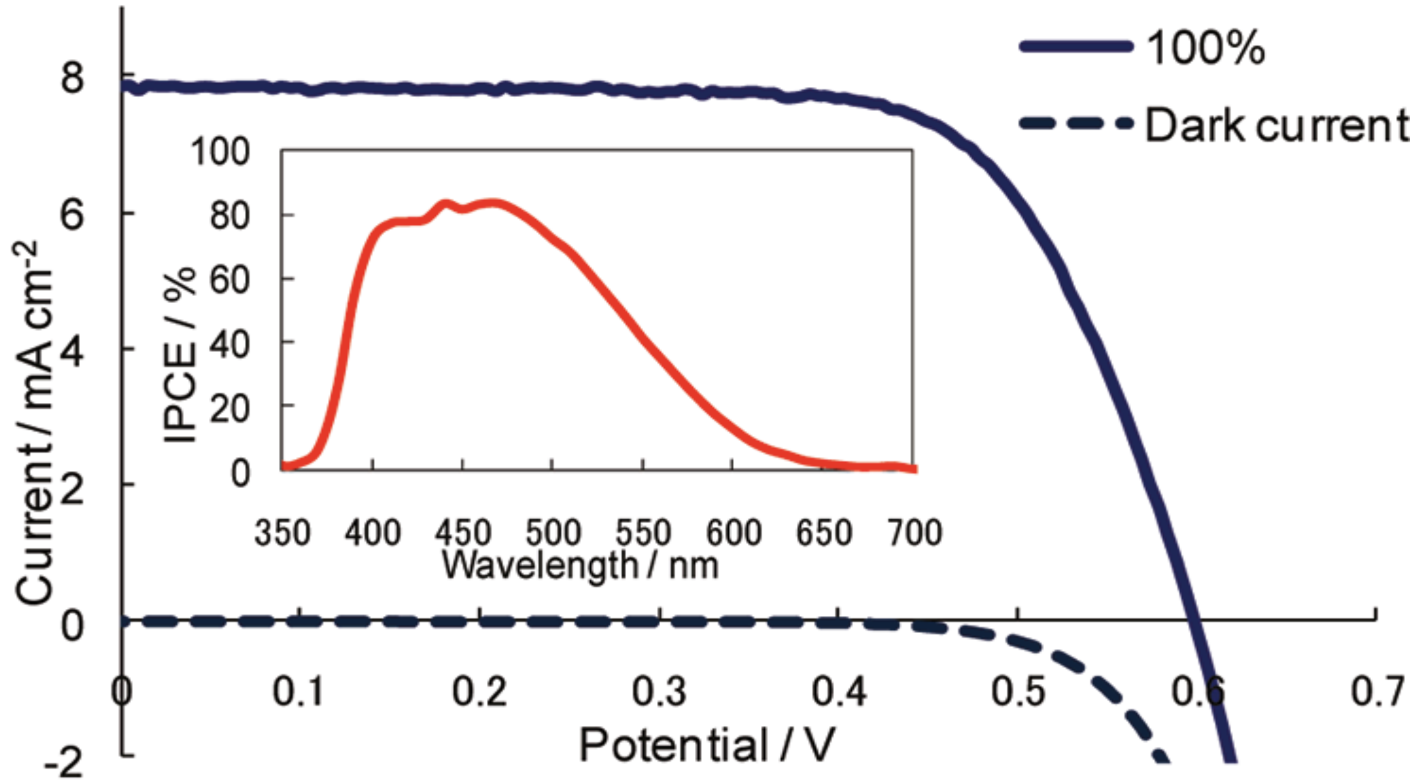
Importance of coupled e-ion dynamics




Energy Level (eV)
Time (fs)
CBM
e
hole
Bond Length (Angstrom)
Time (fs)
26 fs
24 fs
O-Ti
C-O
C
O
Ti
1
2
3
4
5
6
7
8

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



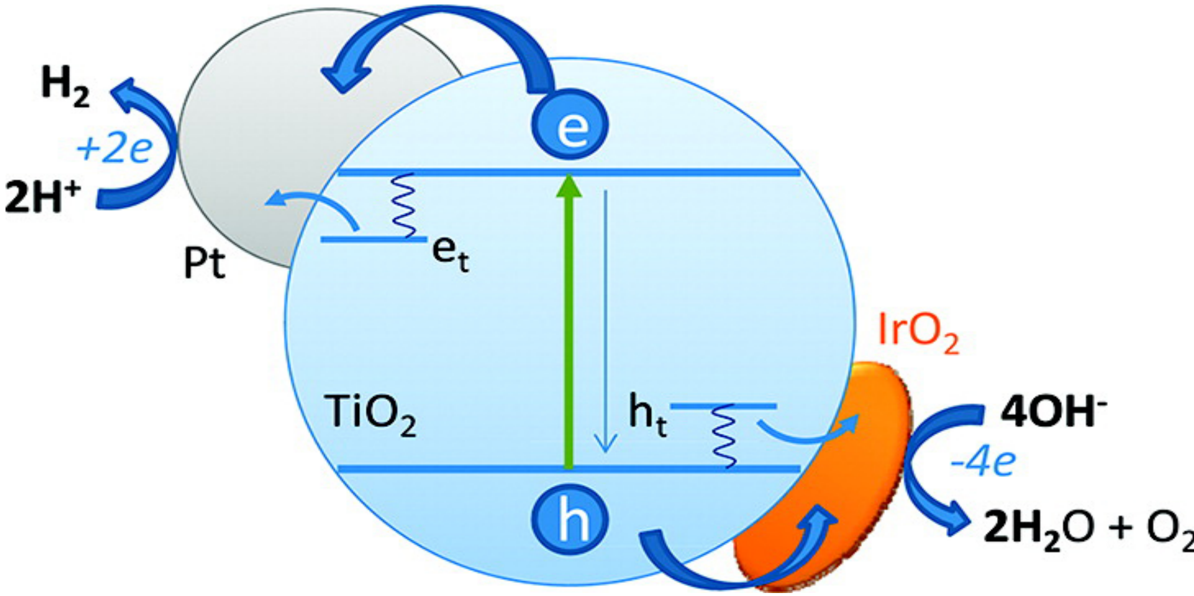


D-π-A Dye System Containing Cyano-Benzoic Acid as Anchoring Group for Dye-Sensitized Solar Cells

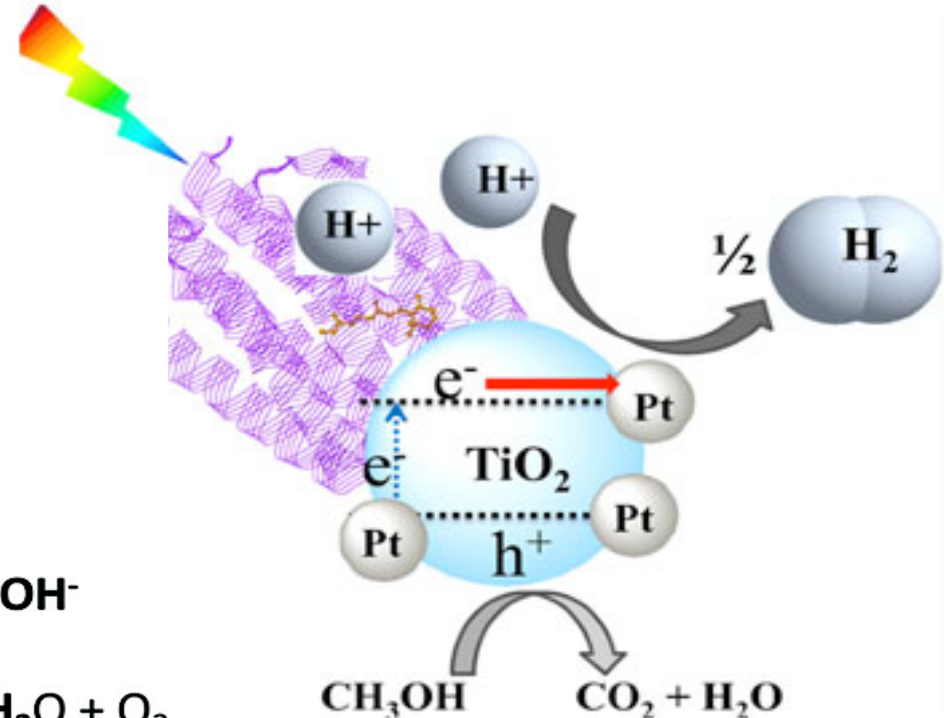
Masataka Katono, Takeru Bessho, Sheng Meng, Robin Humphry-Baker, Guido Rothenberger ,Shaik M. Zakeeruddin, Efthimios Kaxiras, and Michael Gratzel

Langmuir 2011, **27**, 14248–14252

Photo-catalysts



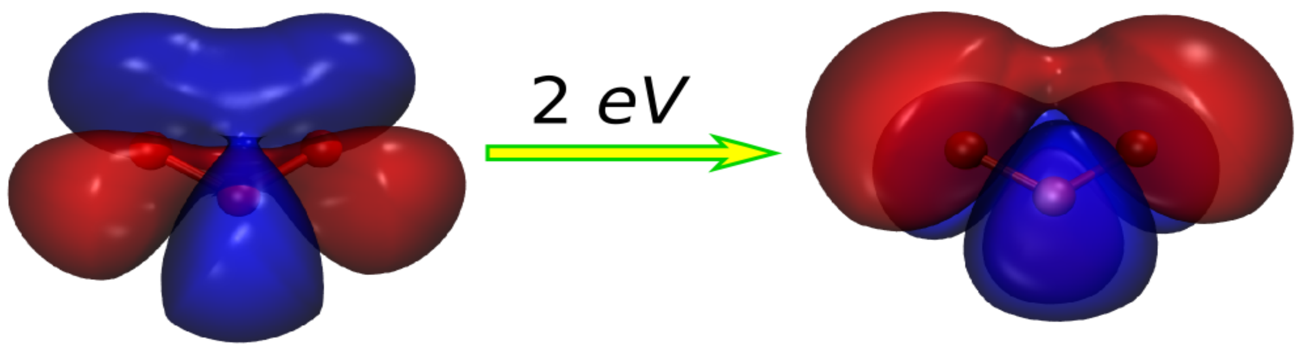
Photocatalytic water splitting system utilizing Pt/TiO_2/IrO_2:
TiO_2 is light absorber, Pt is the hydrogen evolution catalyst, and IrO_2 is the oxygen evolution catalyst.
(P. Kamat, U. Notre Dame)



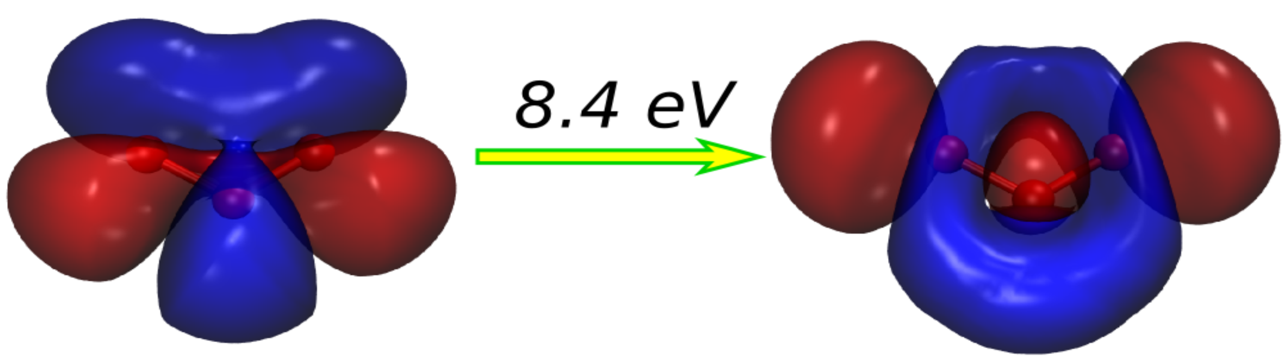
H_2 production from organic molecules using TiO_2 nano-particles as photo-catalysts
(Argonne National Lab)

Example: ozone photolysis

- Excitation HOMO to LUMO: slow dissociation

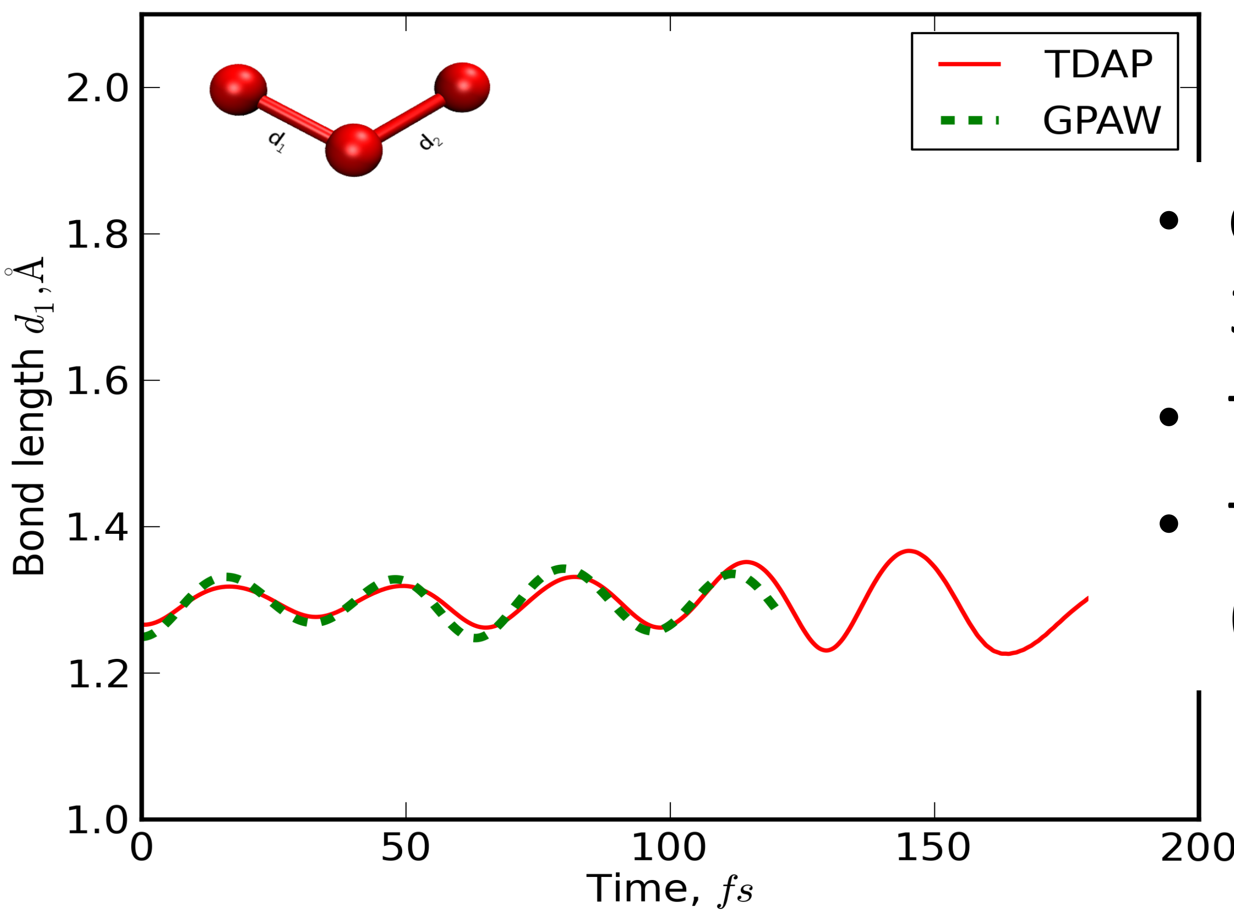


- Excitation HOMO to LUMO+1: quick dissociation



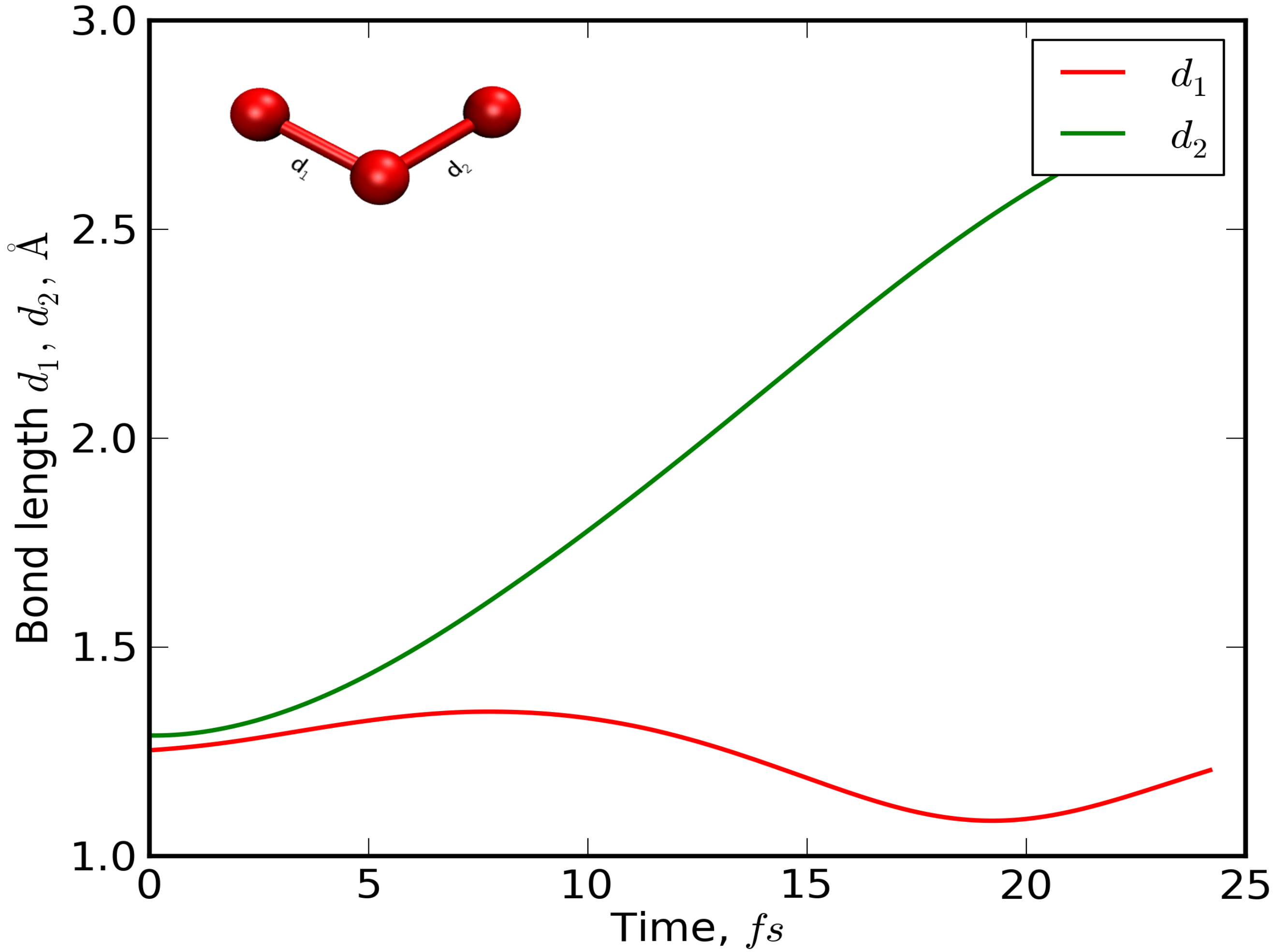
Matsumi, Y. & Kawasaki, M. Photolysis of atmospheric ozone in the ultraviolet region. *Chemical reviews* **103**, 4767–4782 (2003).

1st excited state trajectory



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

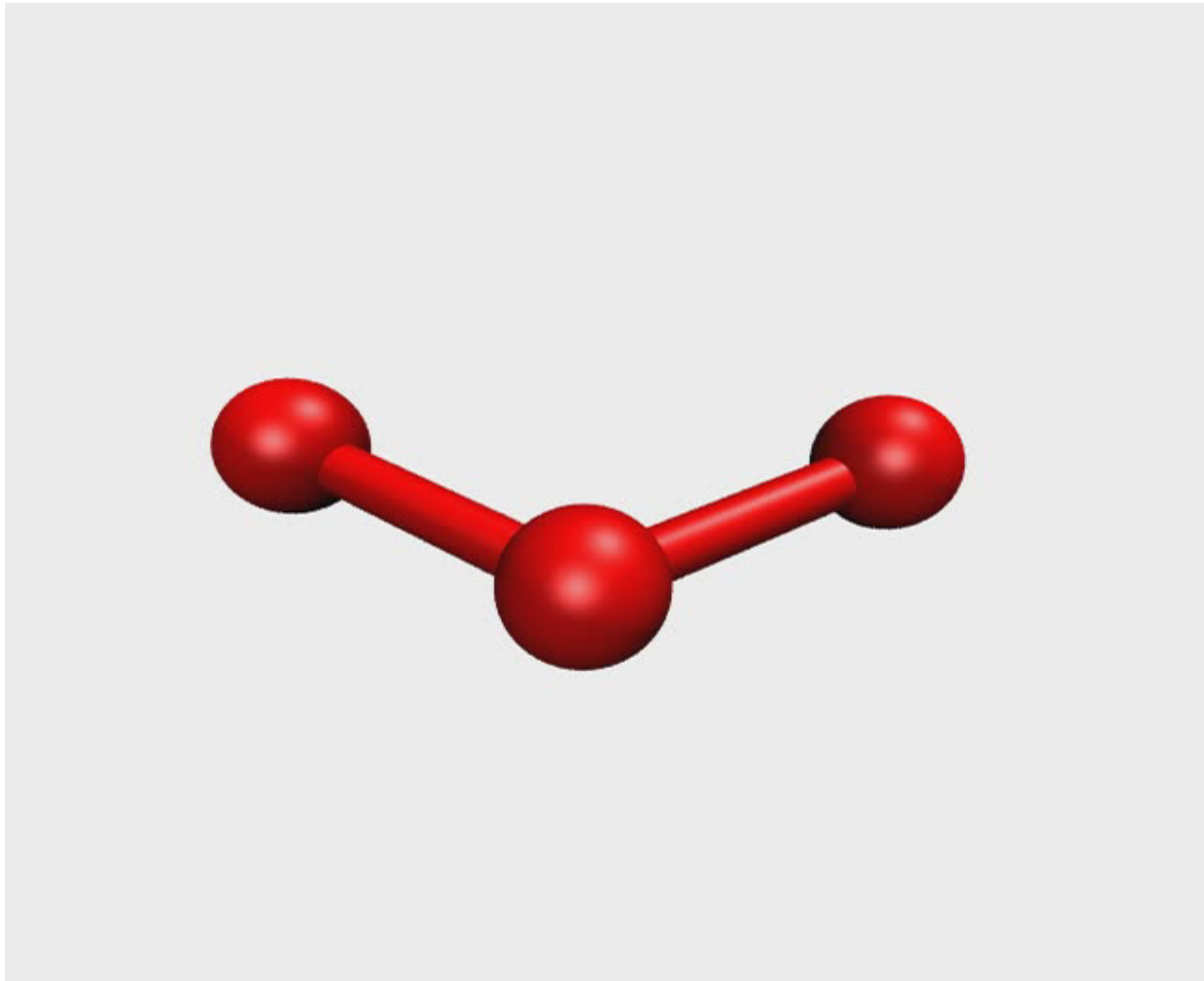
2nd excited state trajectory



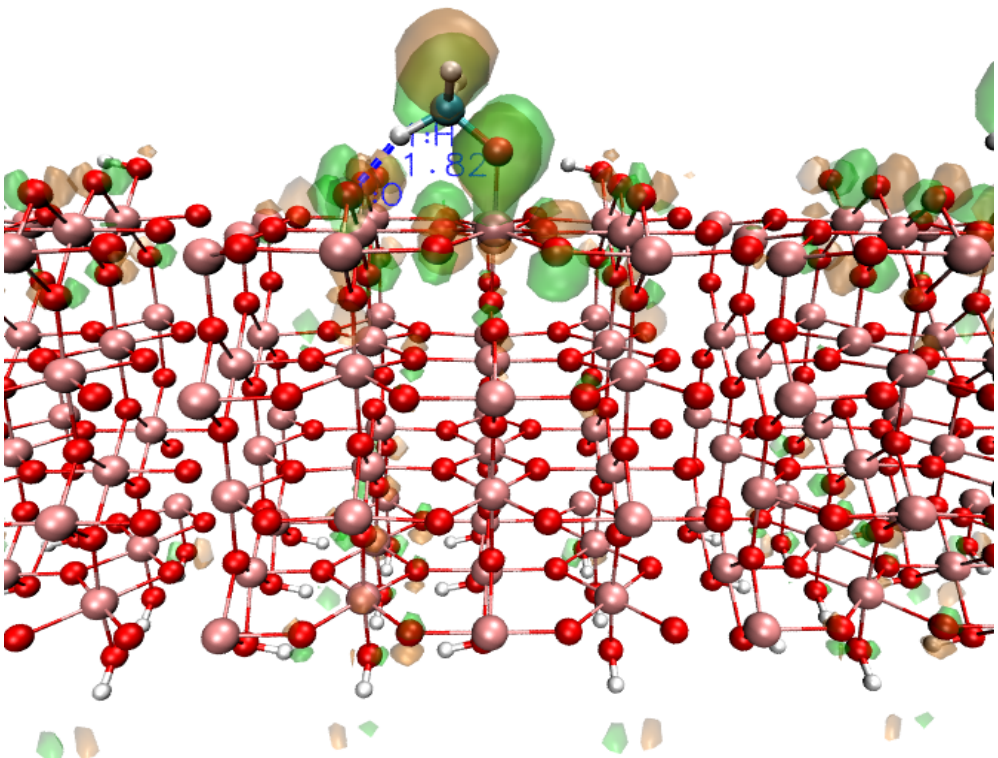
2nd excited state trajectory

- Movie:

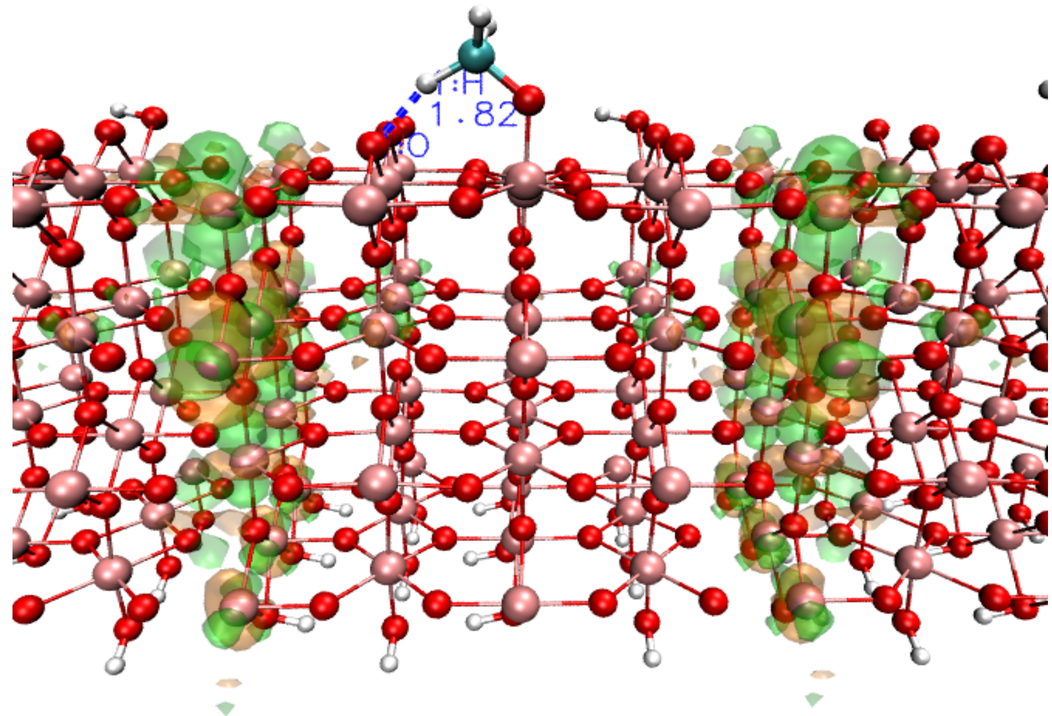
o3split.mov



Hole: HOMO-4 State



Electron: LUMO state



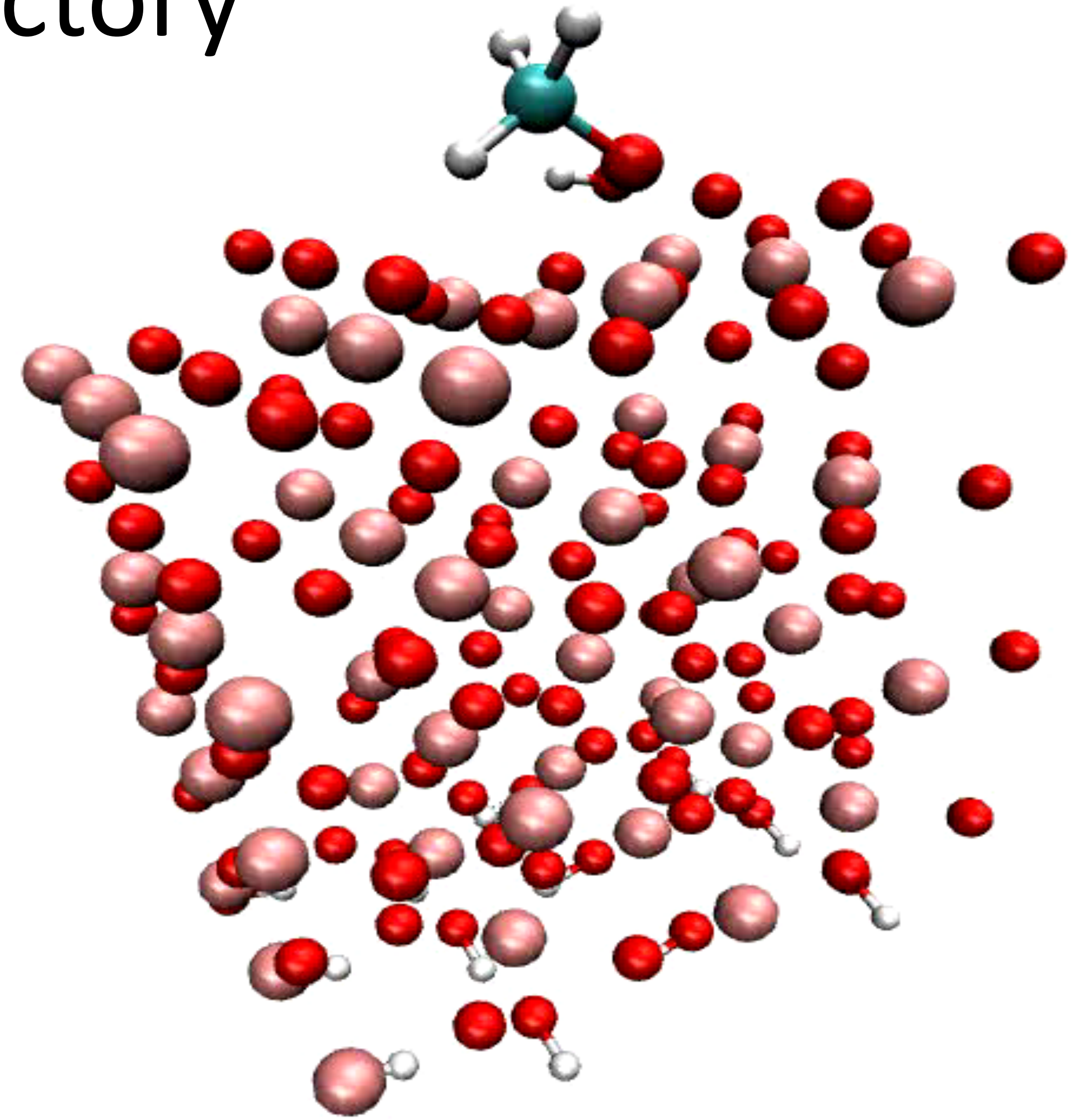
- Formaldehyde was photochemically produced from methoxy on TiO_2 (110) surface

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:

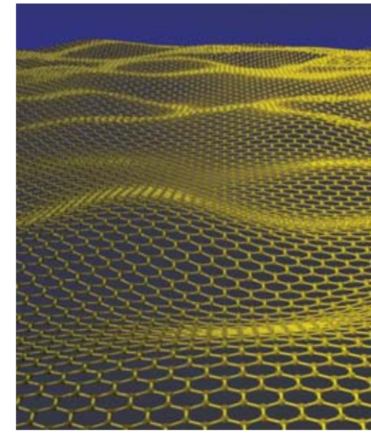
mxsplit.mpg

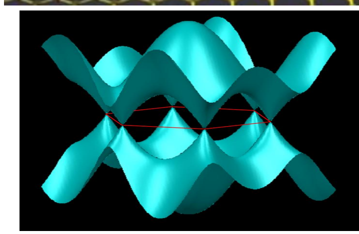


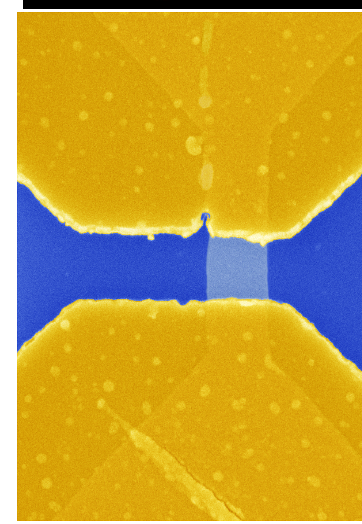
Manipulating the properties of graphene

Graphene

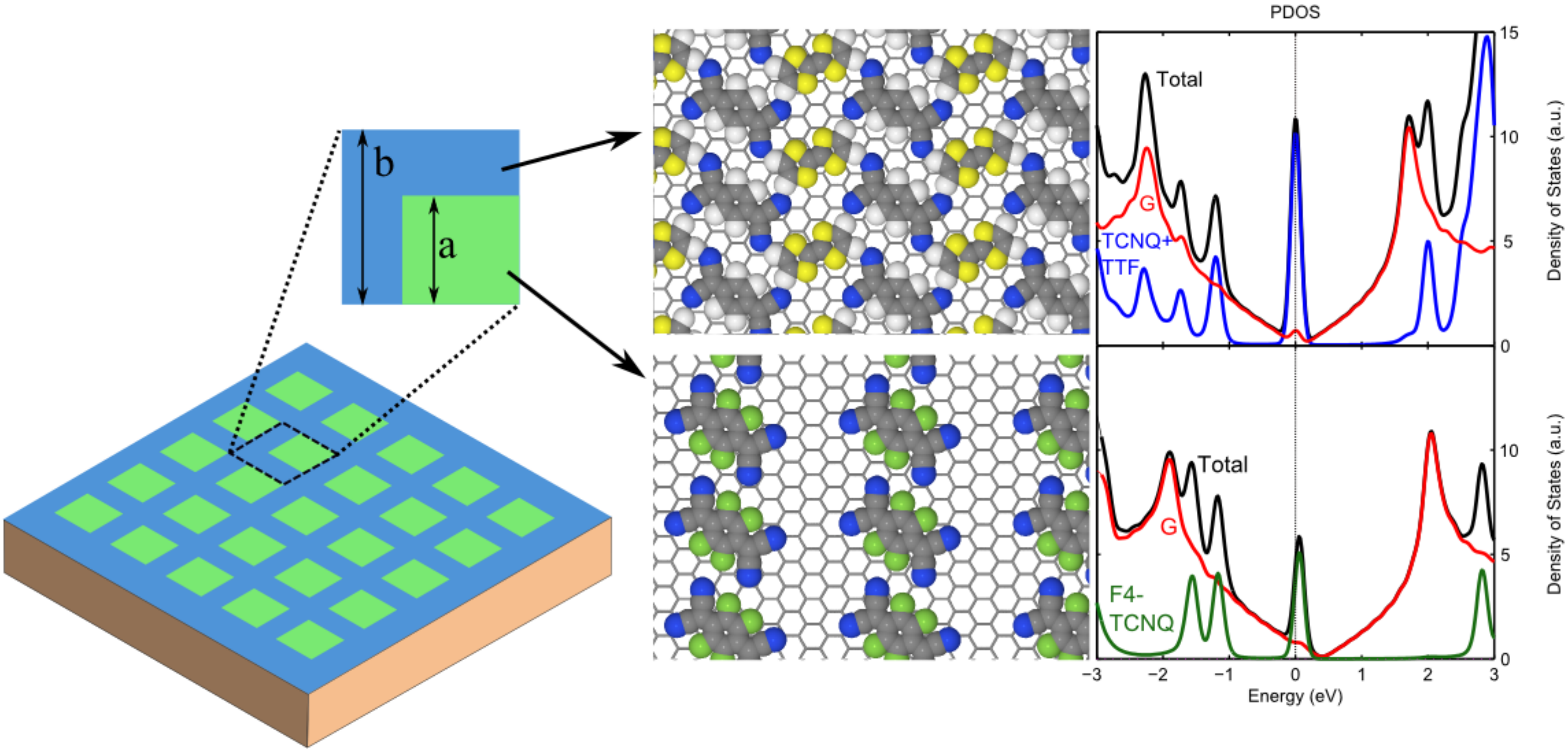
- Quasi-2D crystal: strongest material recorded E=1 TP
- High mobility: as high as $2x10^5$ $cm^2V^{-1}s^{-1}$
- Low spin-orbit coupling and hyperfine interaction (1% C^{13})
- Unique band structure: massless quasi-particle
- Other properties: room temperature quantum hall effect, Klein paradox, etc.



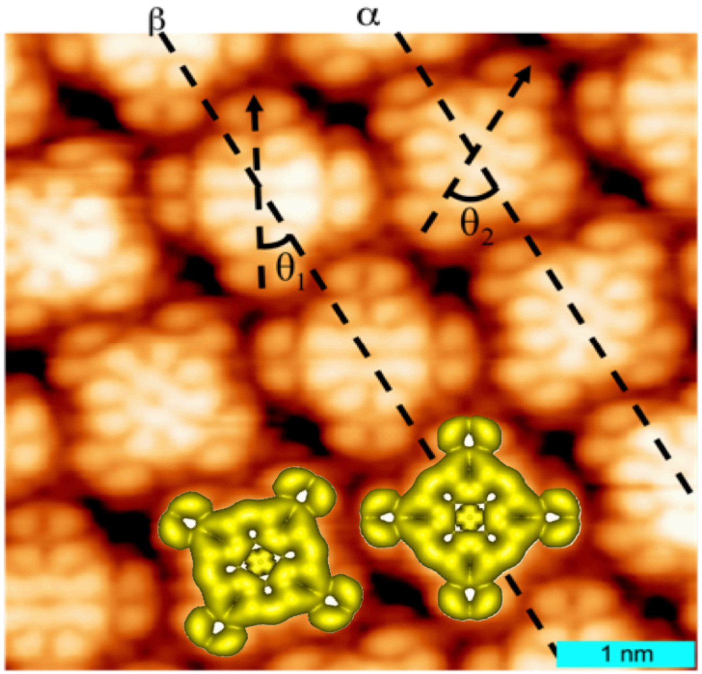


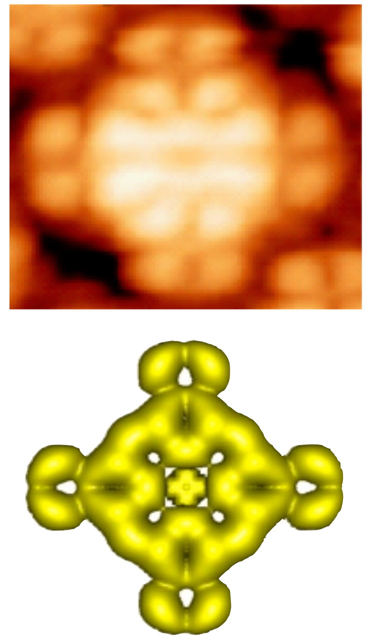


Proposal for a graphene-based plasmonic device



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.



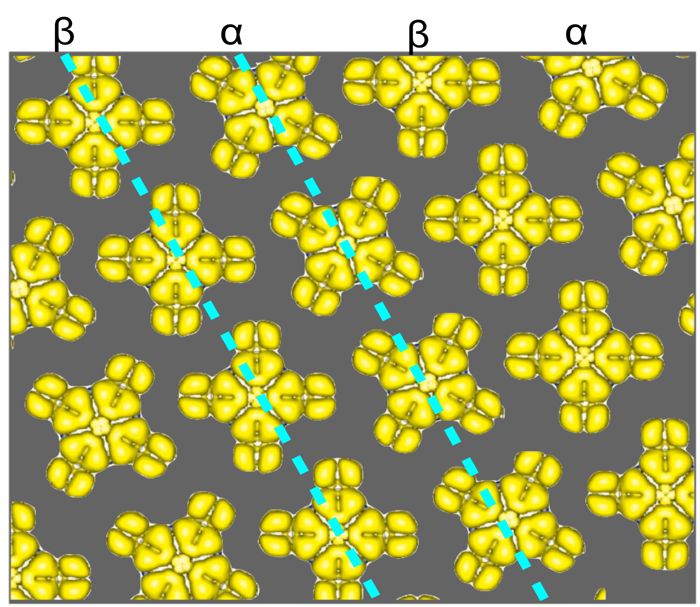


Properties of copper (fluoro-) phthalocyanine layers deposited on epitaxial graphene

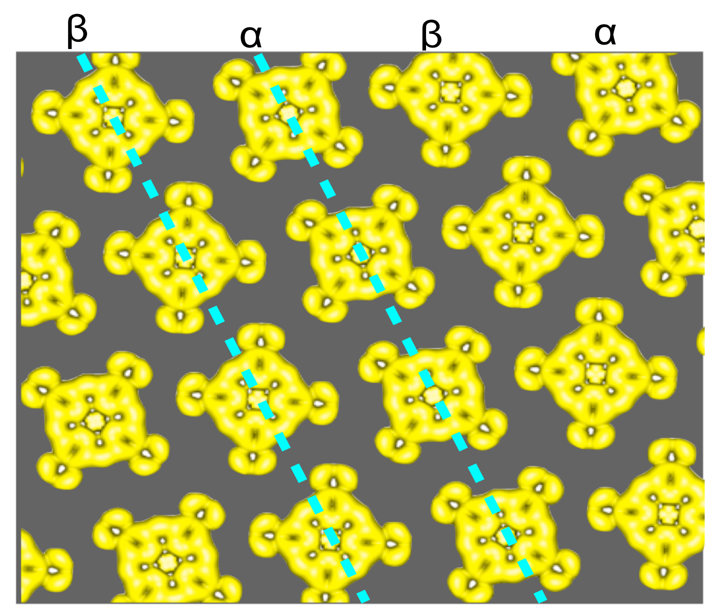
Ren, Sheng Meng, Yi-Lin Wang, Xu-Cun Ma, Qi-Kun Xue, and Efthimios Kaxiras

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

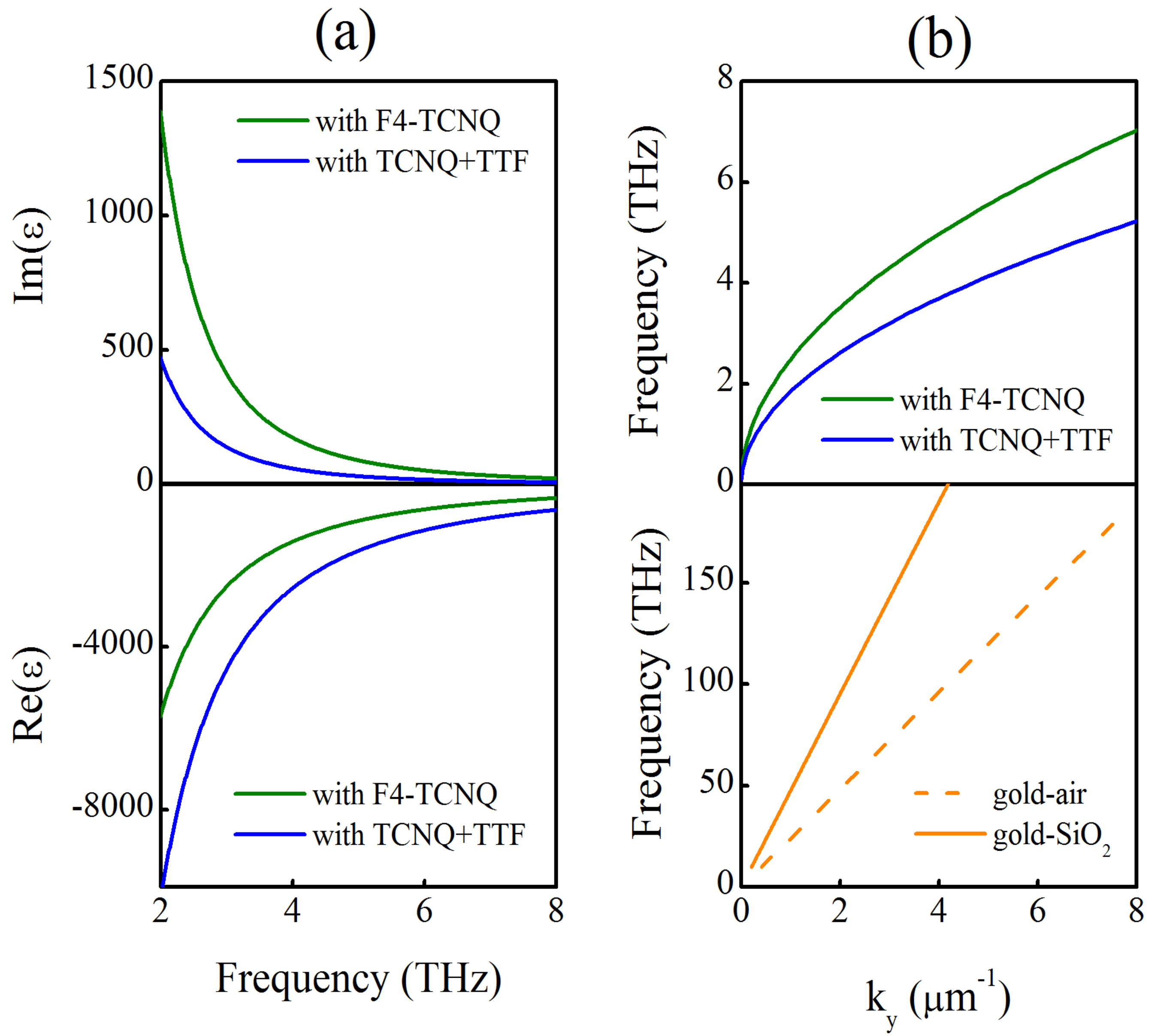
HOMO

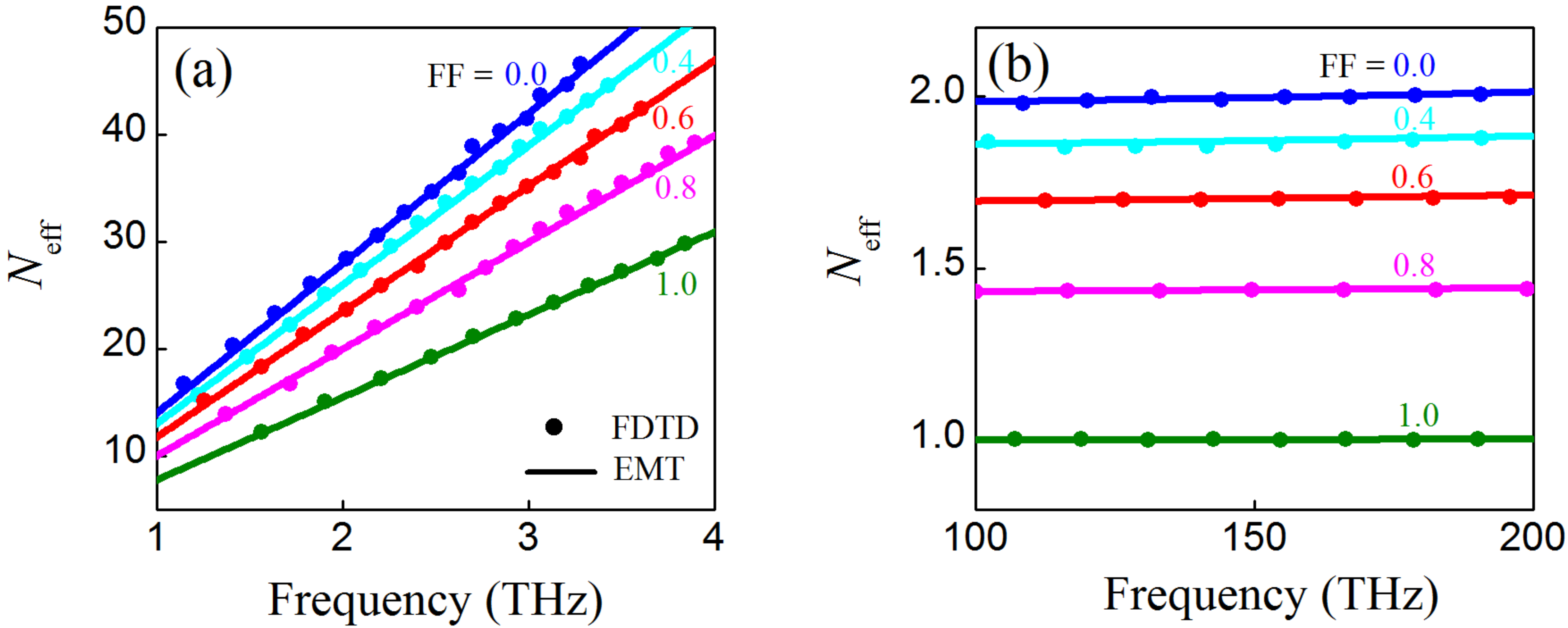


LUMO



Spatially resolved dielectric function

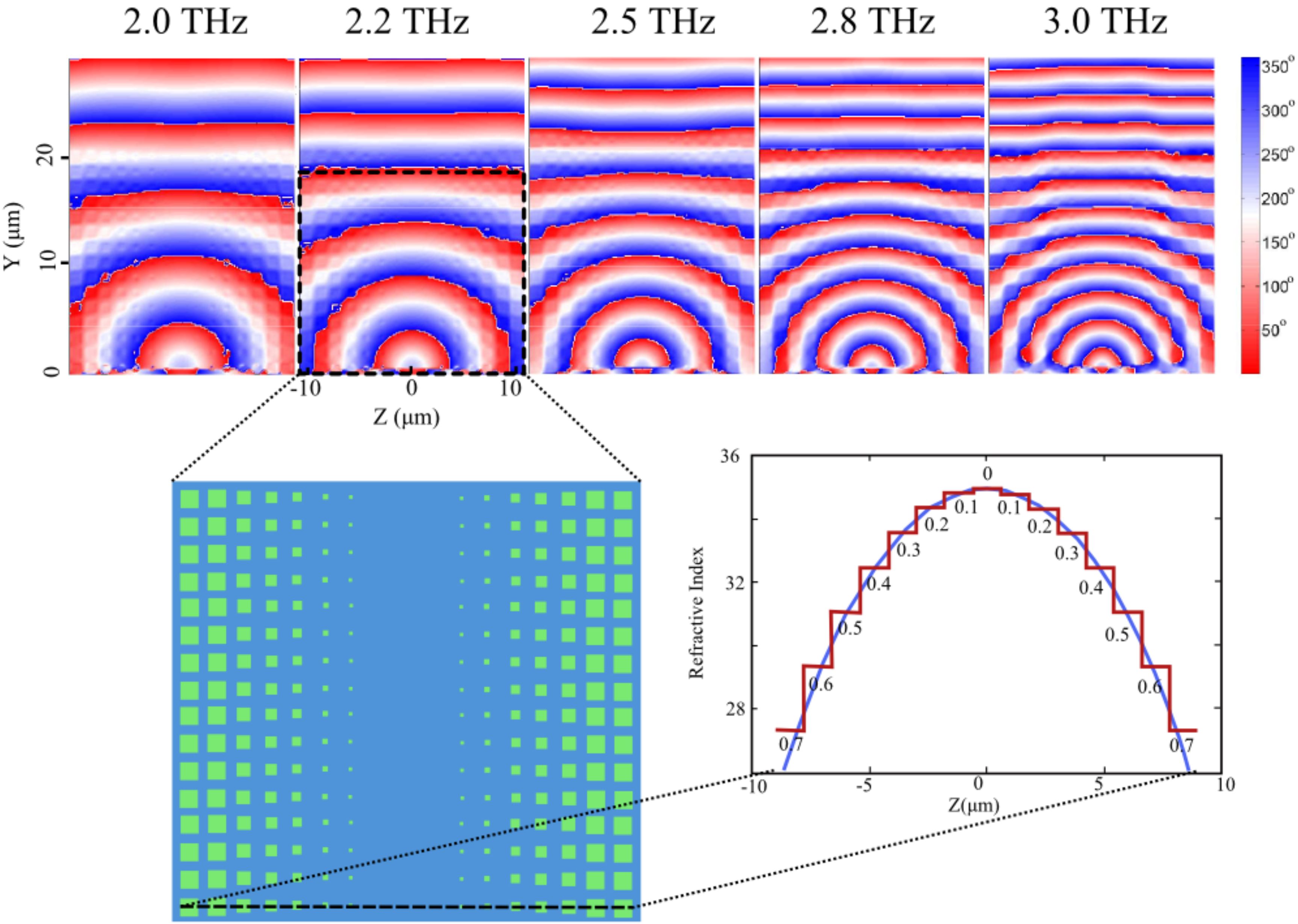




Refractive indices of metamaterials made of: (a) patterned graphene, (b) a gold film on top of Gradient Refractive Index dielectric substrate.

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

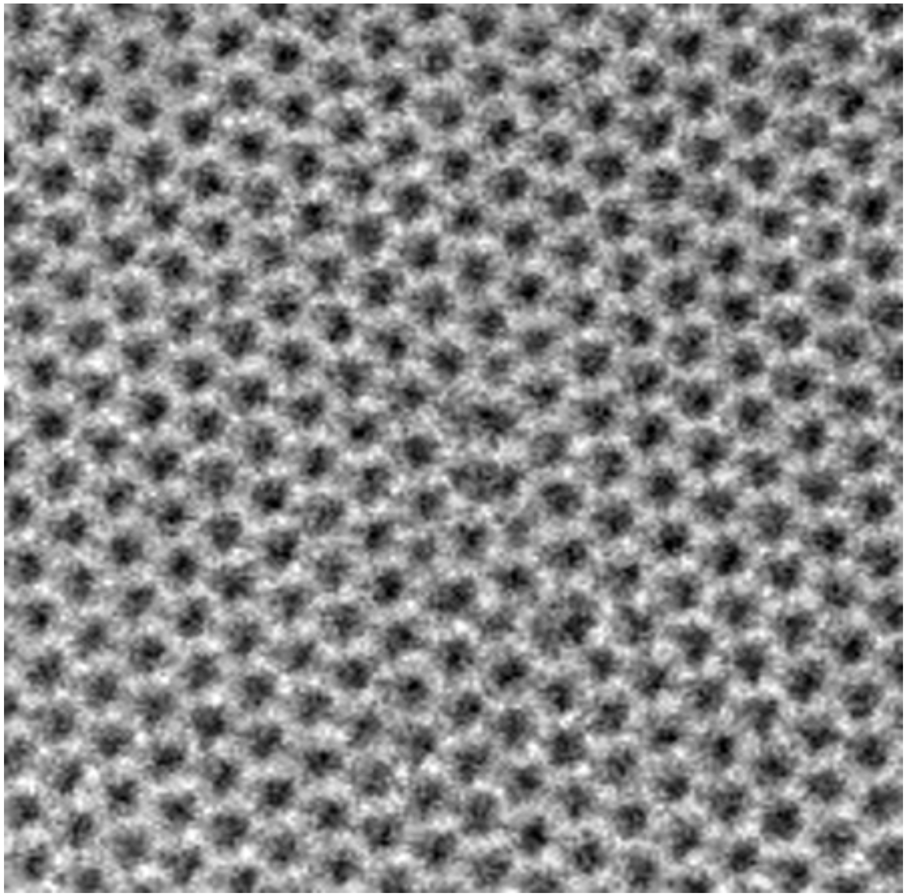
Selfoc lens: collimating EM waves

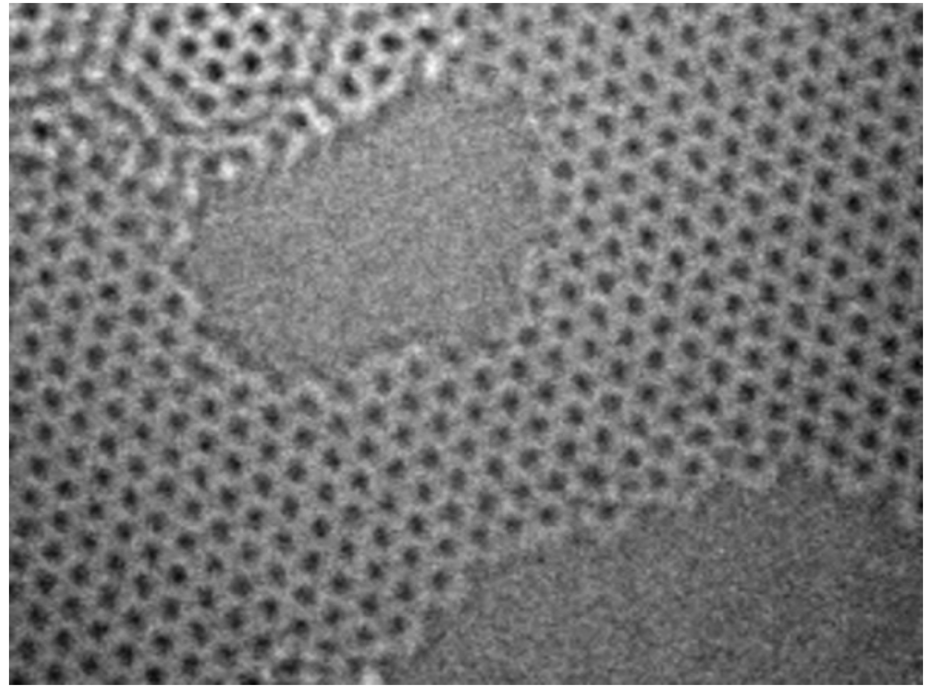


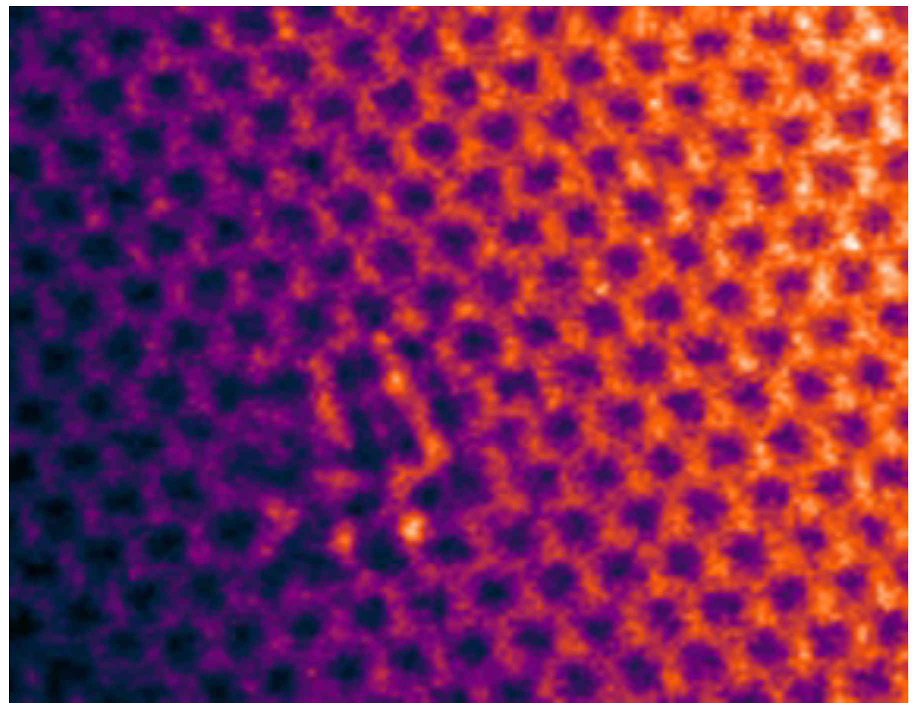
Waves propagate through the lens region (box) and turn into PW's.

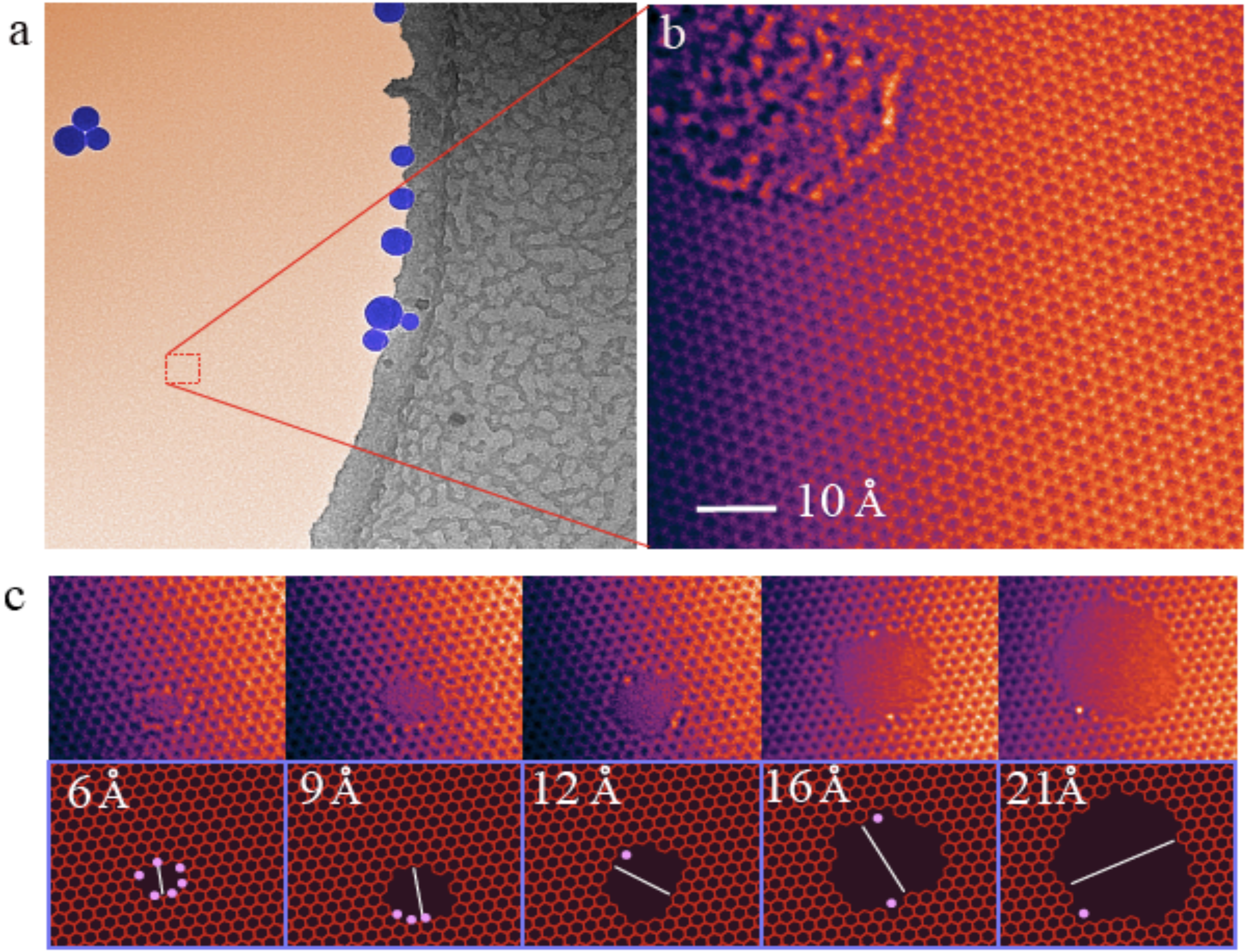
An atomic-scale chisel for sculpting graphene

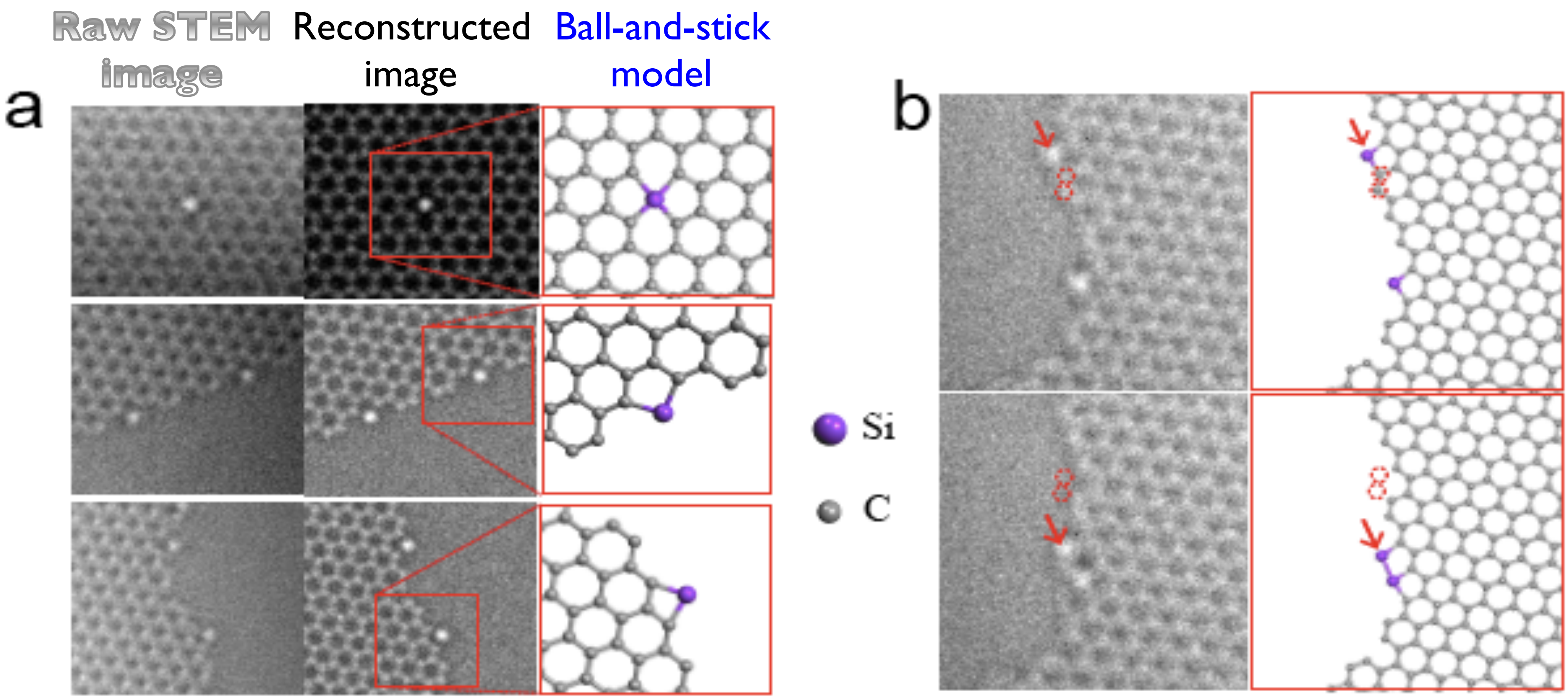
By Wei Li Wang
Expts. carried out at LBNL's NCEM



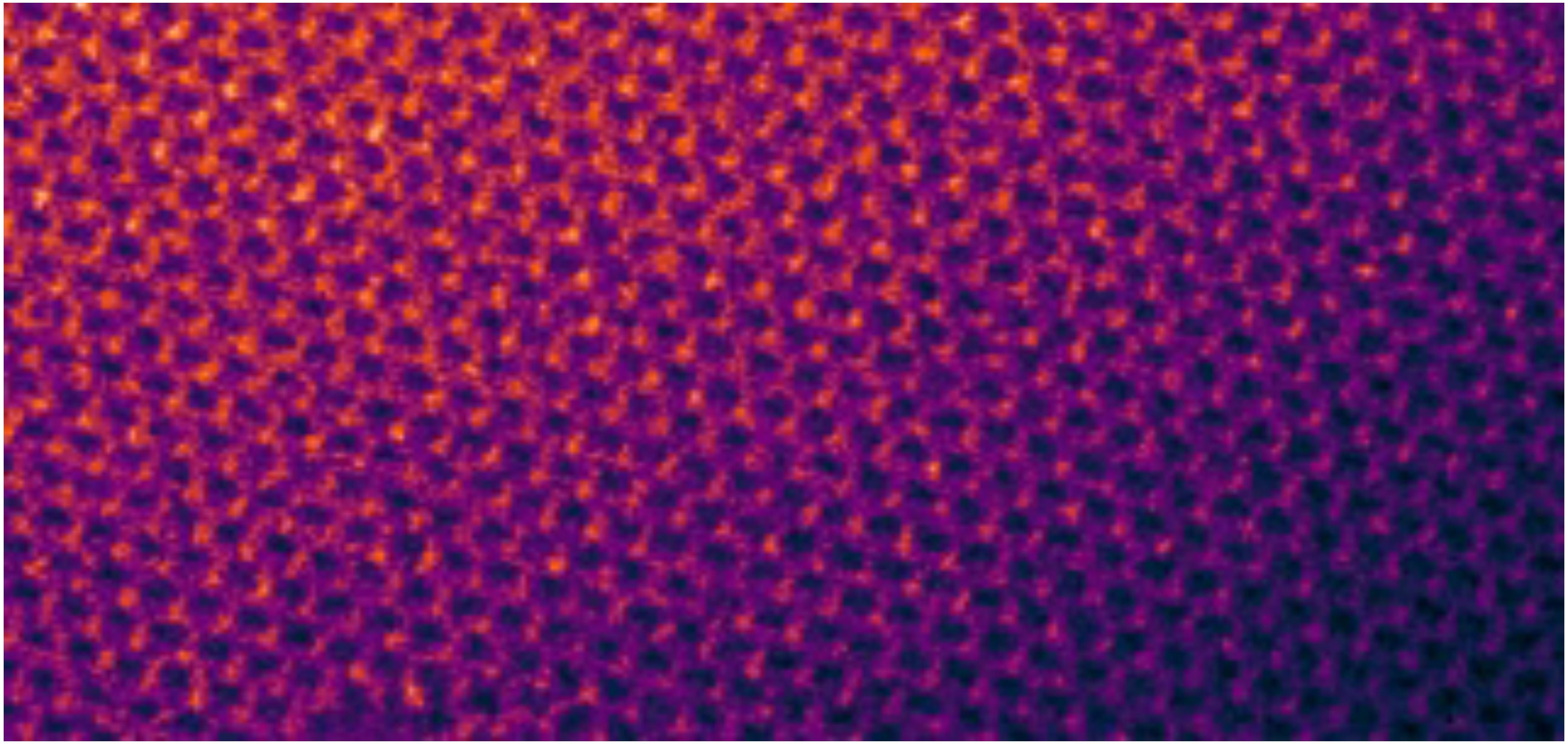


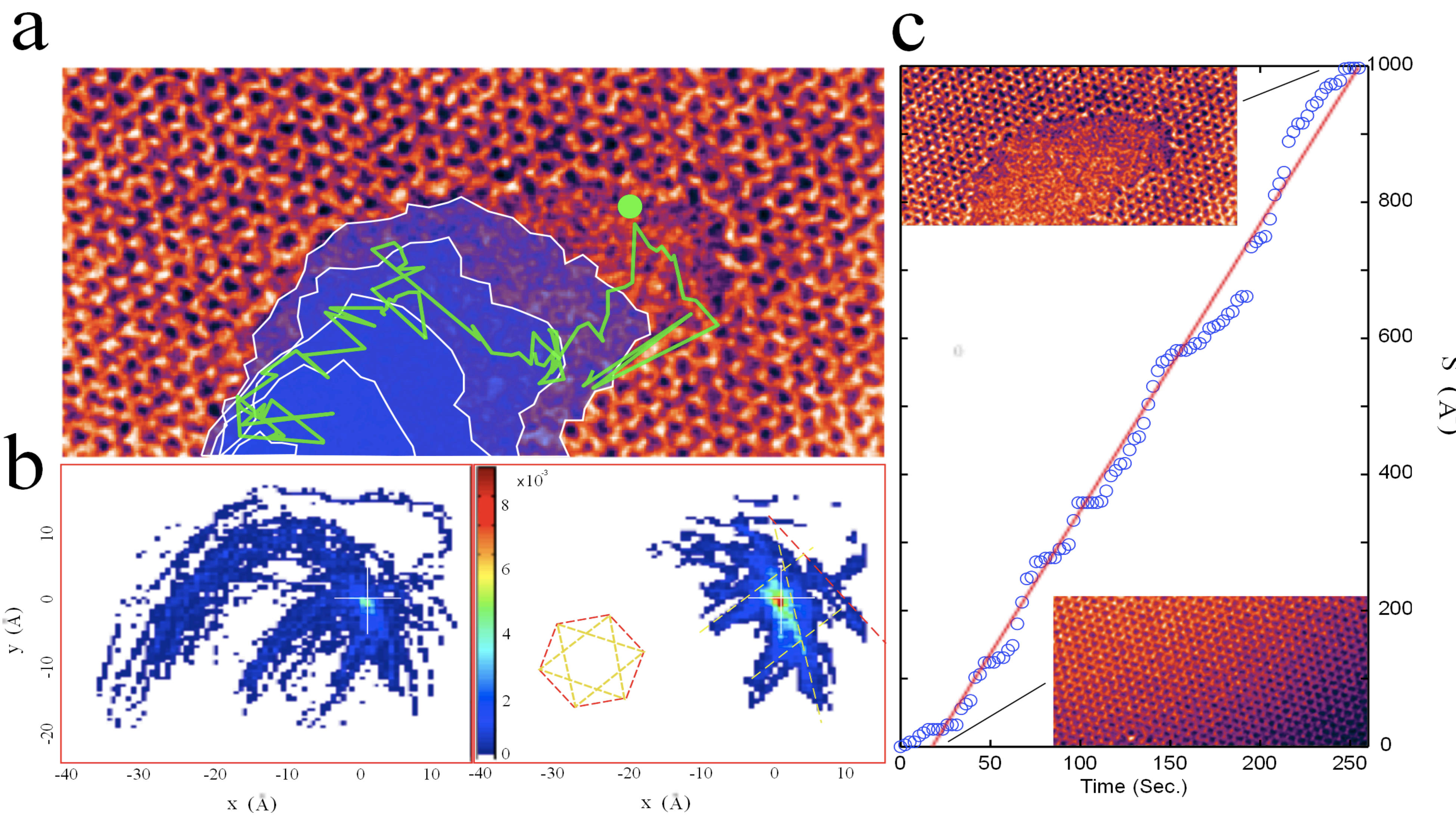



a
b
10 Å
c
6 Å
9 Å
12 Å
16 Å
21Å

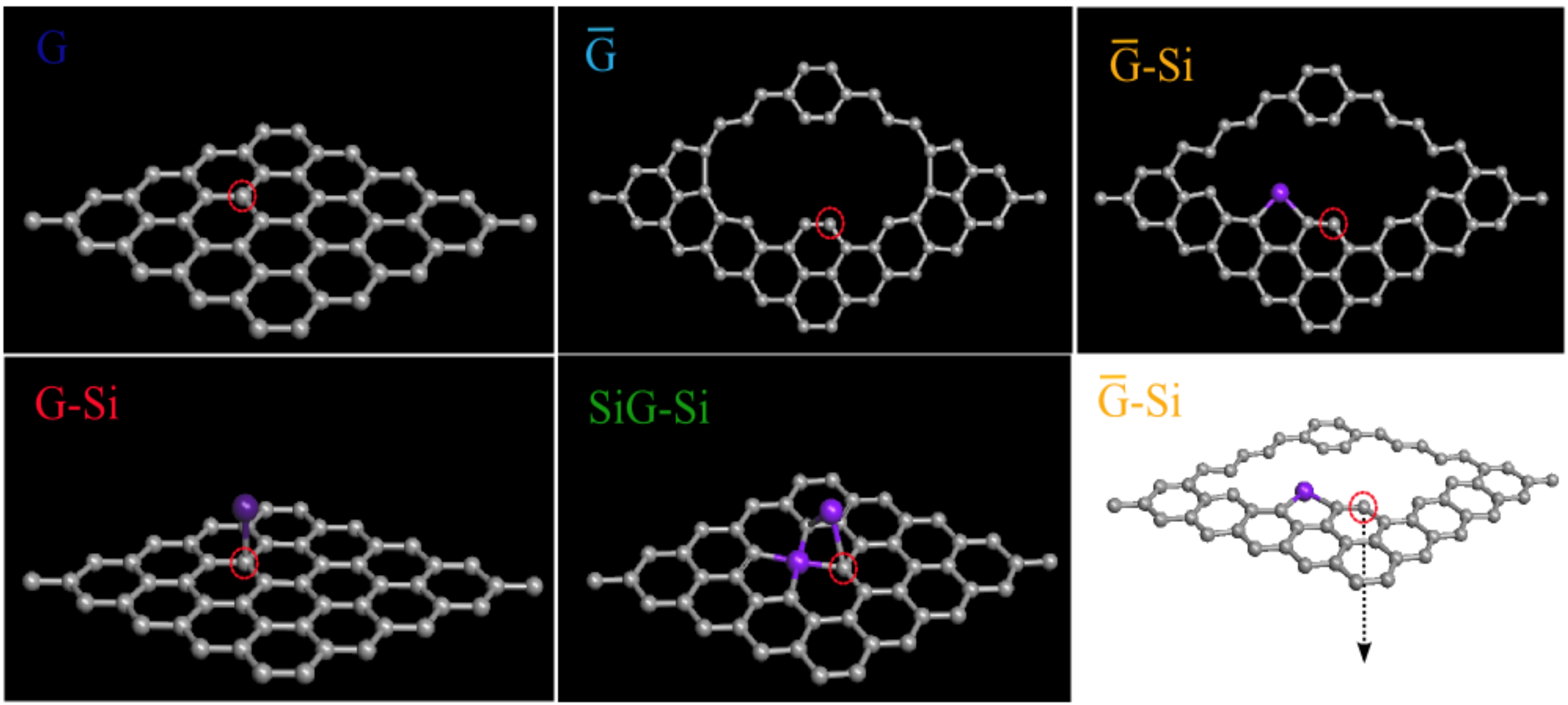


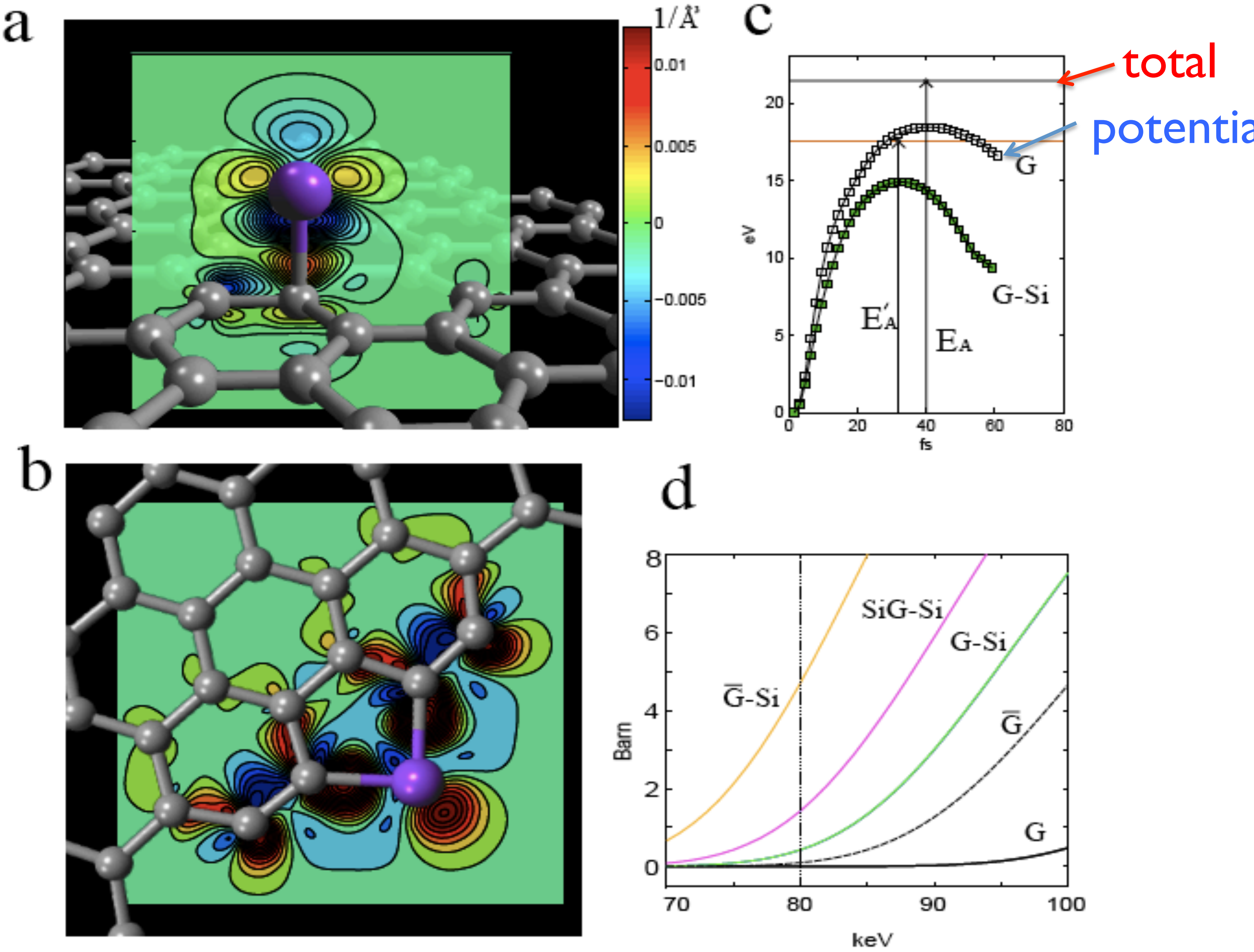
Raw STEM image
Reconstructed image
Ball-and-stick model
a
b
Si
C





a
b
c
y (Å)
x (Å)
x (Å)
x10⁻³
Time (Sec.)
S (Å²)


G
G̅
G̅-Si
G-Si
SiG-Si
G̅-Si


a
1/Å³
0.01
0.005
0
−0.005
−0.01
b
c
total
potentia
20
15
10
5
0
eV
0
20
40
60
80
fs
G
G-Si
E′A
EA
d
8
6
4
2
0
Barn
70
80
90
100
keV
SiG-Si
G-Si
Ḡ-Si
Ḡ
G

Summary: by combining

- fundamental physics (TDSE)
- methodologies for extending time-scale
- computational tools

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