Ab-initio of optical excitations in solids and molecules

With:

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Symposium on Physics of Complex Materials –
in Honor of Prof. Shi-Yu Wu
April 18, 2014, University of Louisville, KY

Collaboration with Shi-Yu involved lots of little piggies!

Szechuan style pork

Yunan shreded pork

Sweet and sour pork

Twice cooked pork (spicy!!)

PHYSICAL REVIEW B VOLUME 59, NUMBER 11 15 MARCH 1999-I

Linking chemical reactivity, magic numbers, and local electronic properties of clusters

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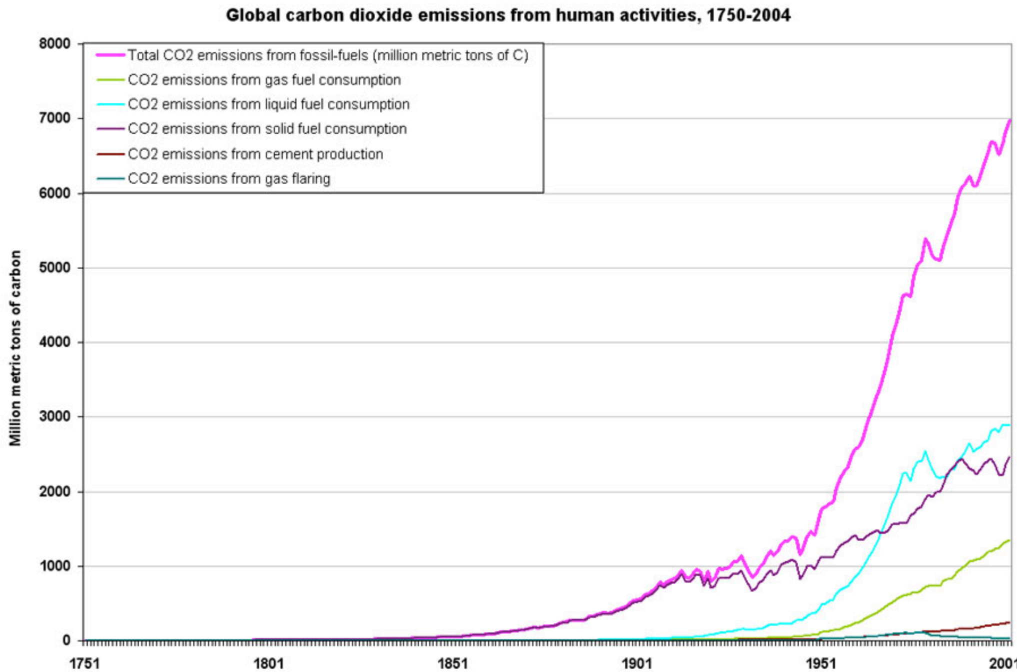
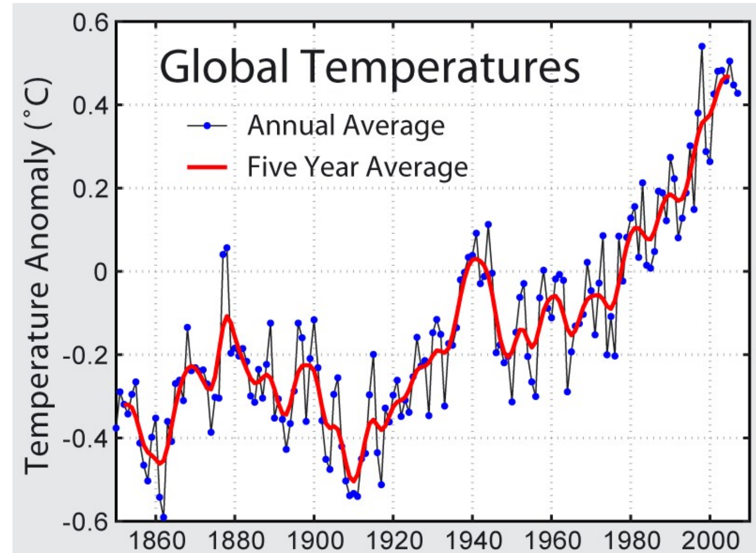
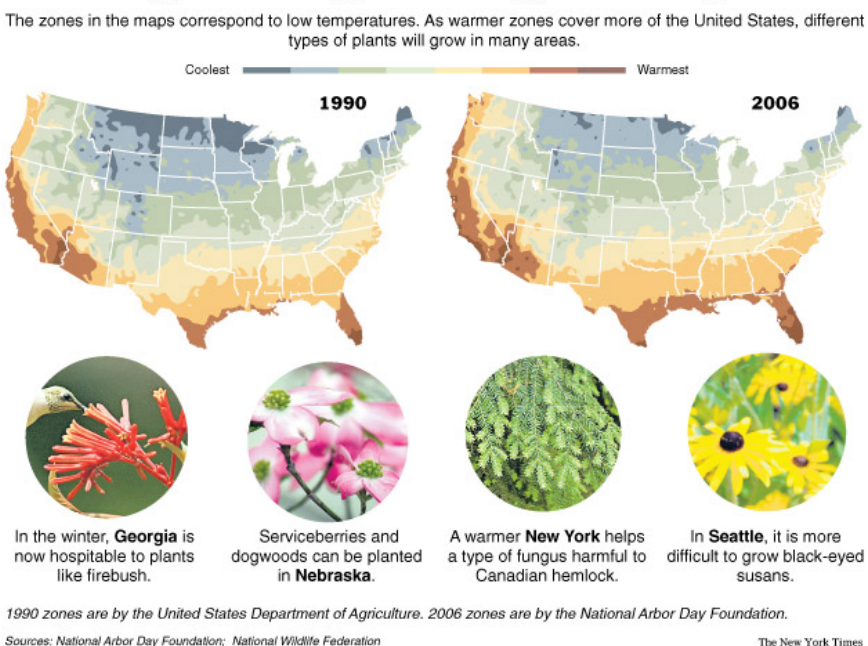
Received 24 August 1998

The interplay of local energetics, local electron occupancies, and local density of states is the key to the understanding of chemical reactivity. We define local measures, within a nonorthogonal tight-binding scheme, which clearly and unambiguously determine these local properties for an aggregate of atoms, such as a solid or a cluster. Using these measures, we identify the electronic level mechanisms responsible for the chemical reactivity of clusters of different sizes. A clear and concise picture of why Si33 is chemically inert while Si49*A* is reactive emerges from this analysis. A scheme for quantifying the dangling bonds is also presented in this work.

Motivation: The need for alternative energy sources

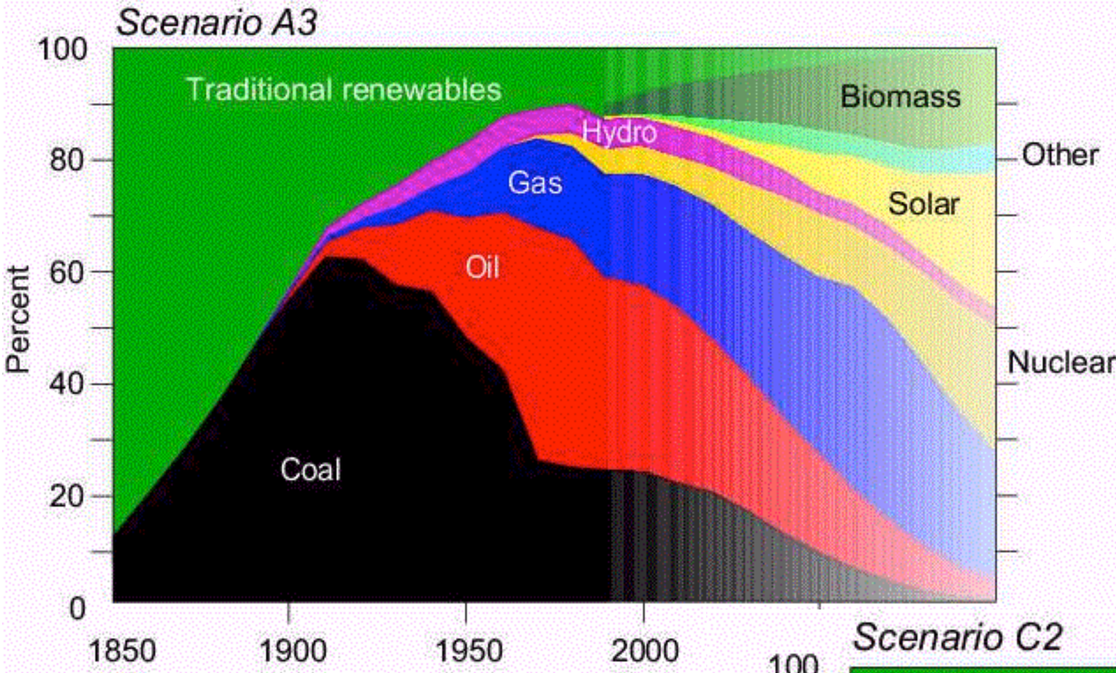




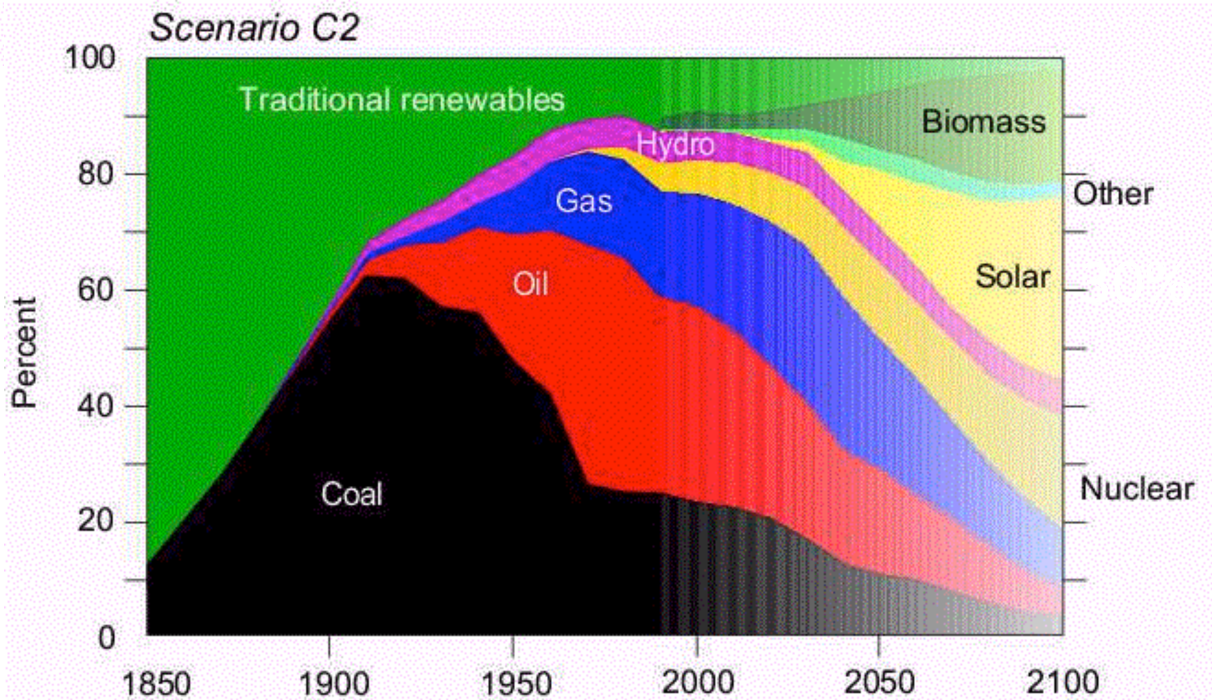


http://www.celsias.com/2007/03/20/channel-4-distances-itself-from-global-warming-documentary/

The challenge of sustainable energy sources

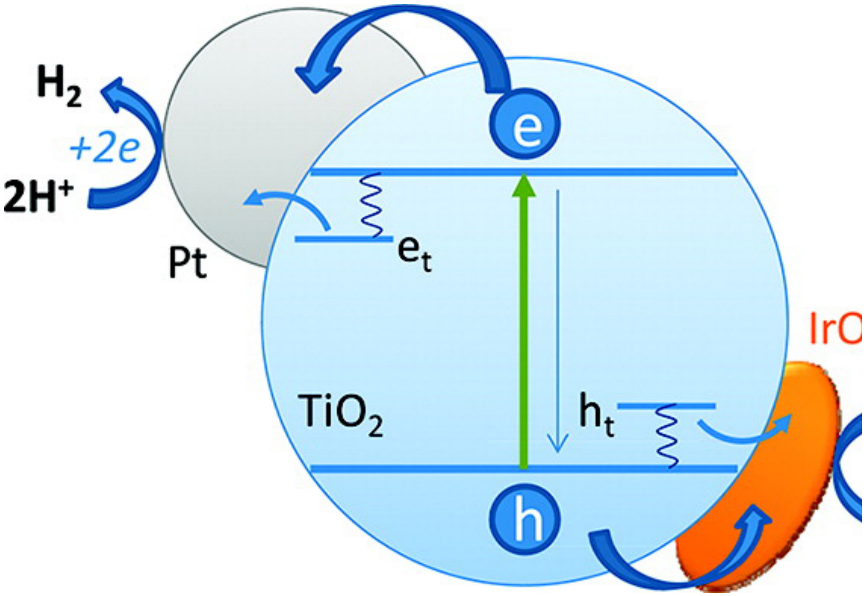


Time and resources running out – fundamental science can play key role in enabling technology

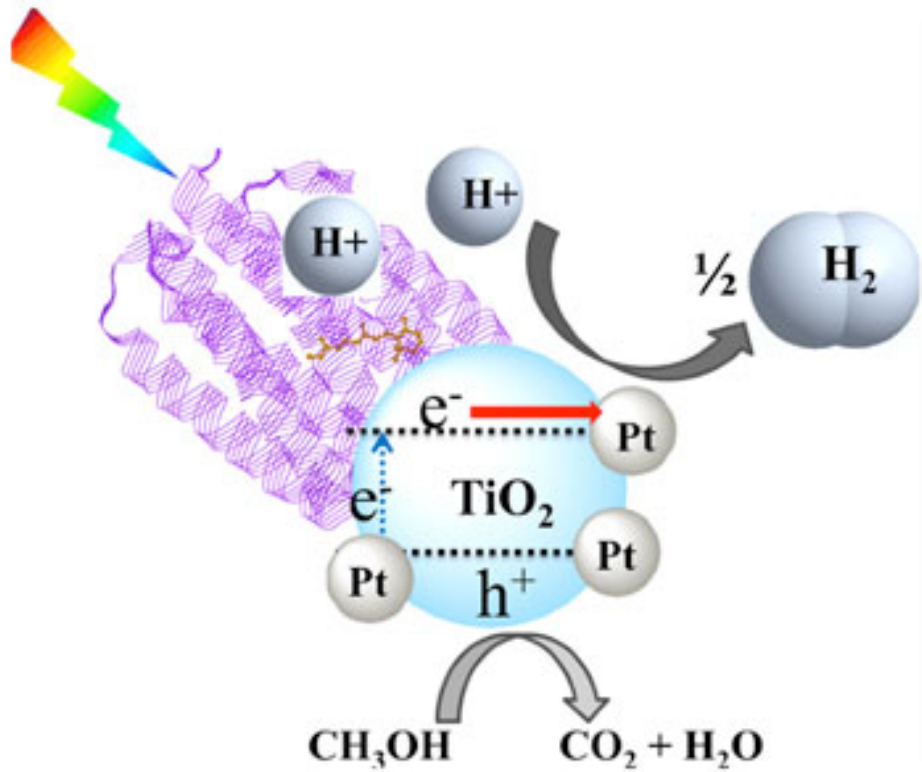


Report of Intergovernmental Panel on Climate Change

Water splitting

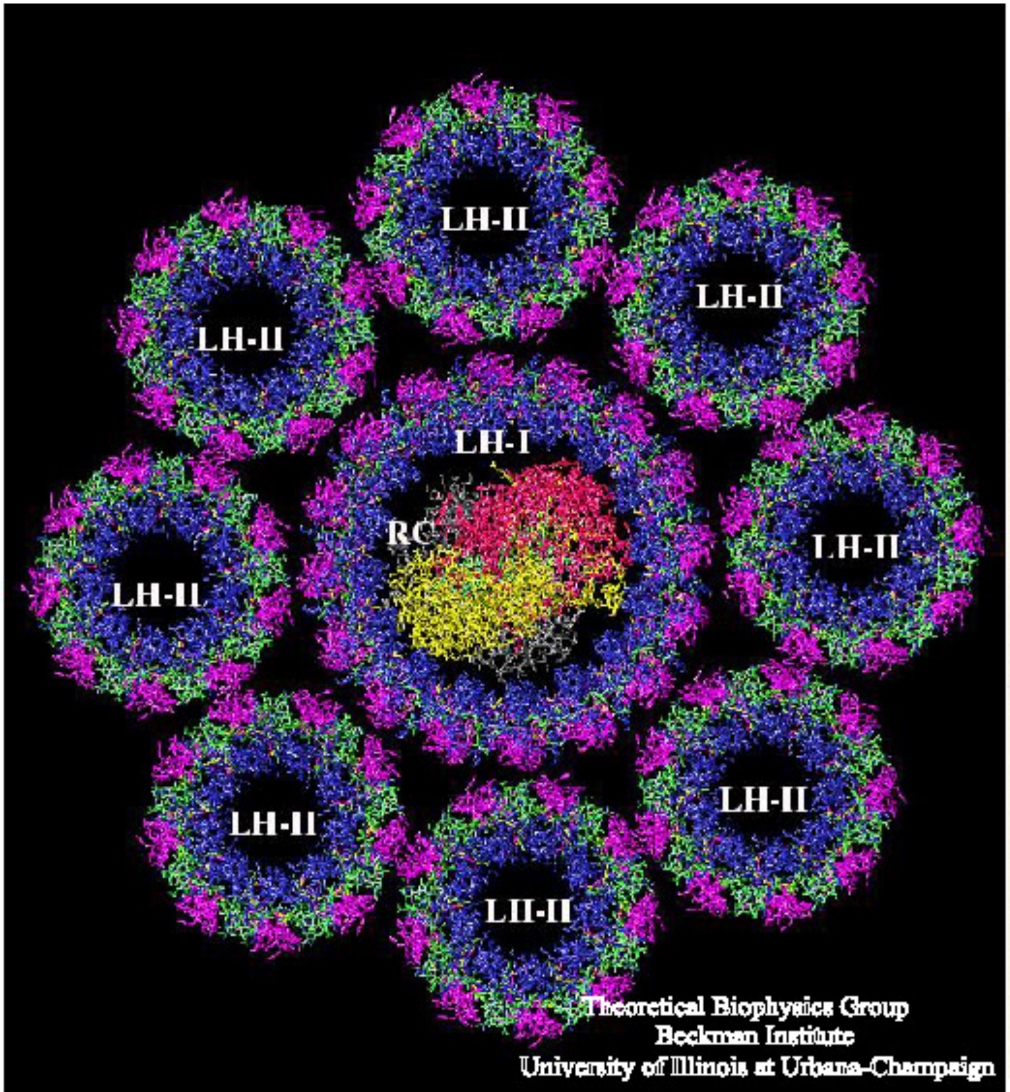


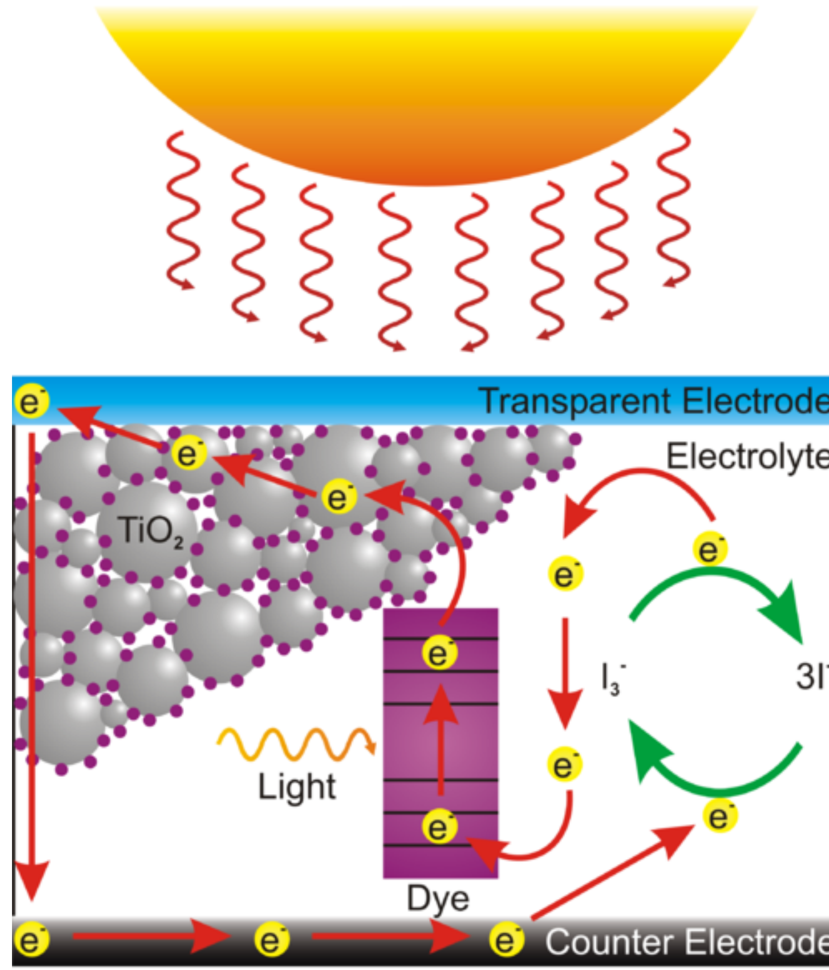
Photocatalytic water splitting system utilizing $Pt/TiO_2/IrO_2$:
TiO_2 is light absorber, Pt is the hydrogen evolution catalyst, and IrO_2 is the oxygen evolution catalyst.
(P. Kamat, U. Notre Dame)



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

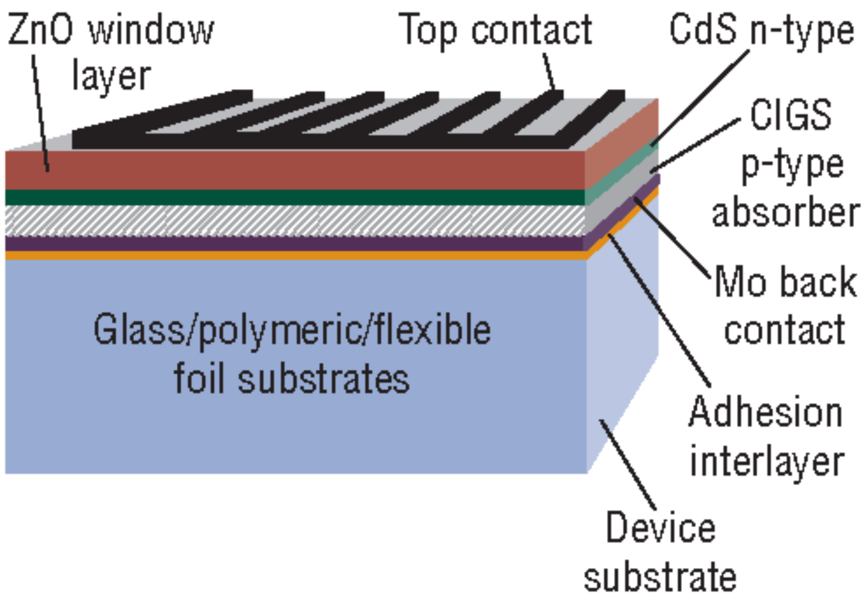
The Principle: separate light-absorption and charge collection processes





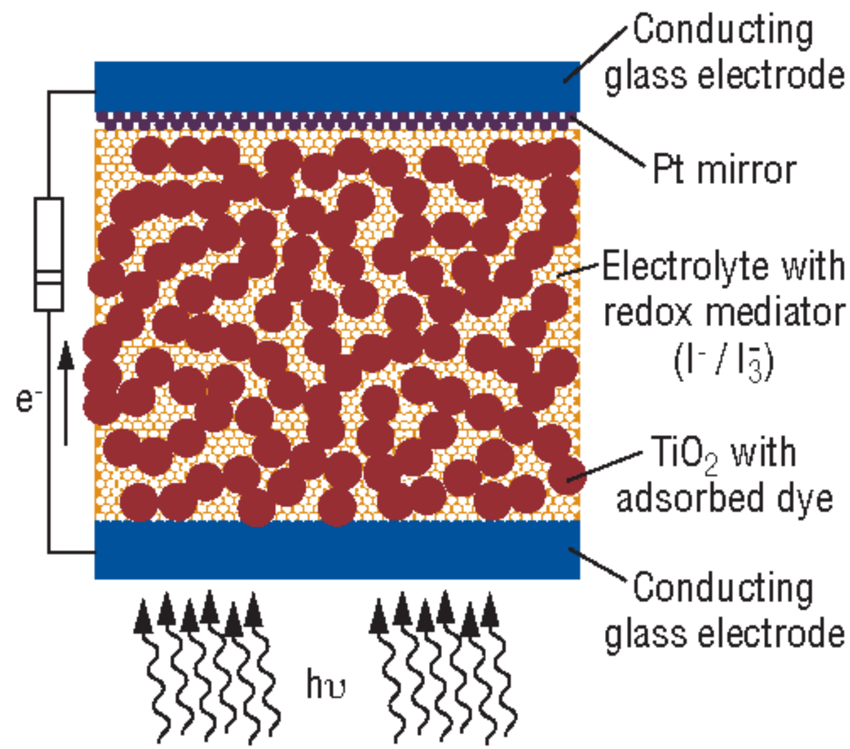
Major issues:
- stability
- efficiency (Inc.Ph.Cur.Eff.)

Copper-Indium-Gallium-Selenide cell



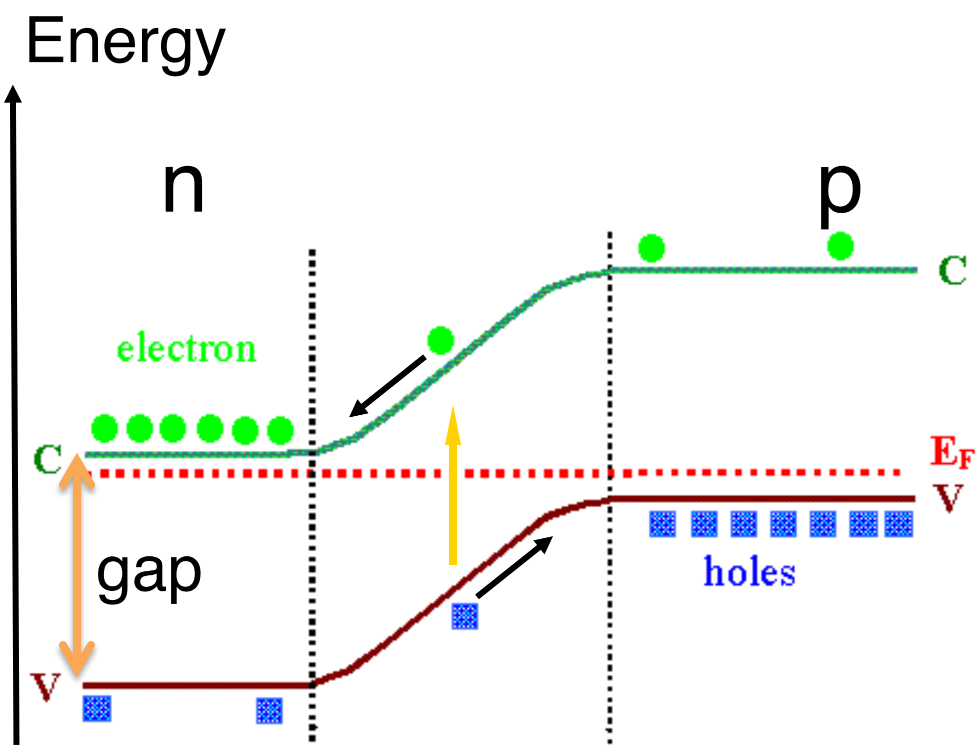
Conventional p-n junction cell
(inorganic)

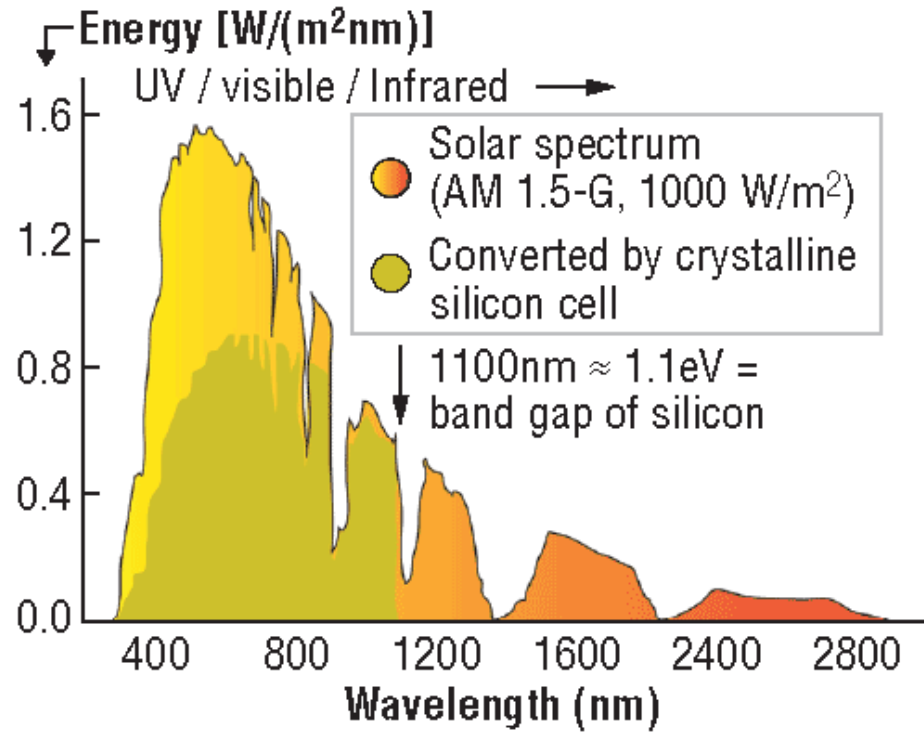
Dye-sensitized cell
(hybrid organic/inorganic)



O'Regan & Graetzel, Nature (1991)

Light absorption by solids: the pn-junction in semiconductors





Bulk semiconductor (inorganic)

-delocalized states (band structure)

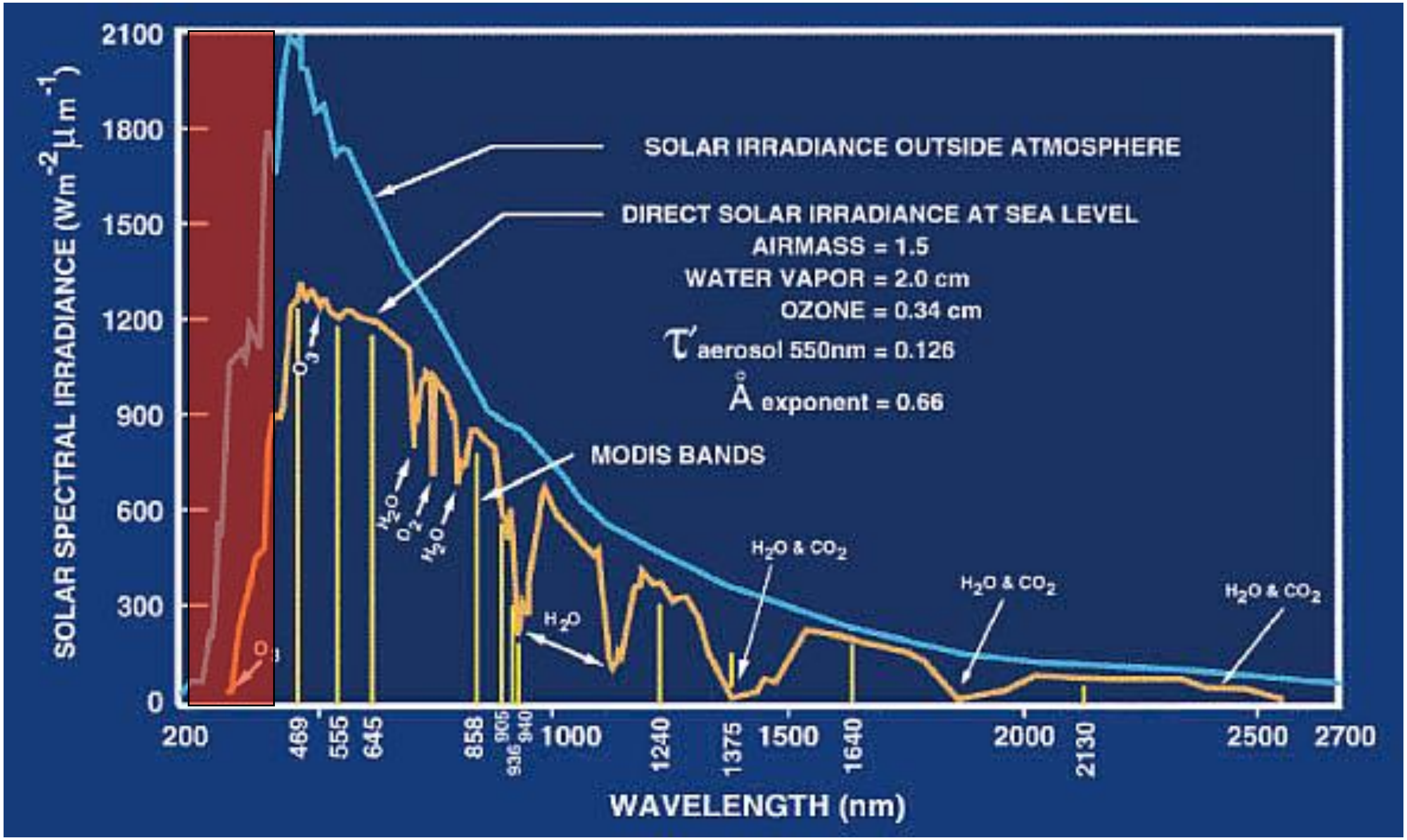
-nearly free electrons

-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

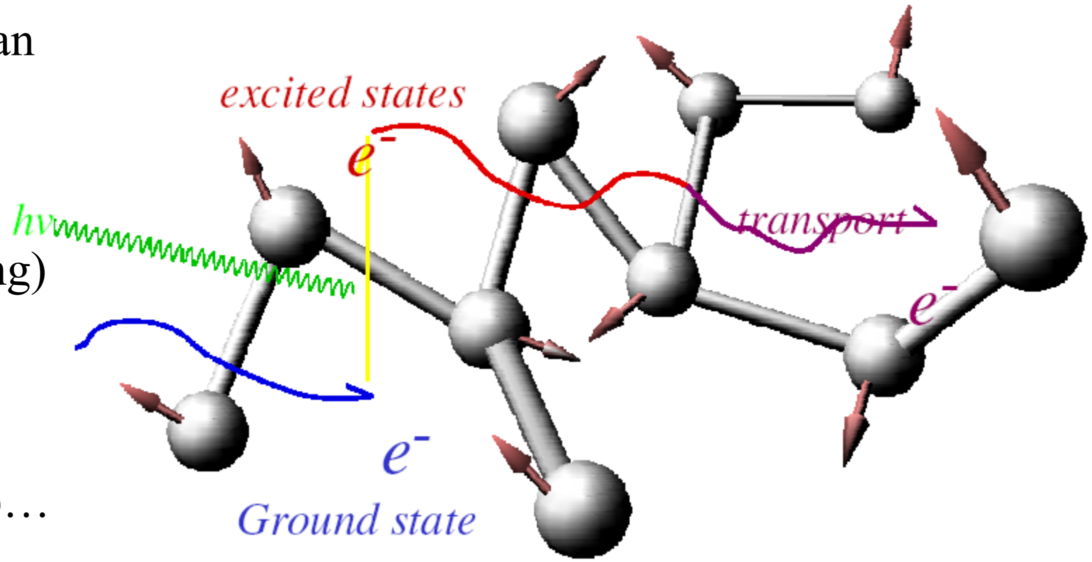
Main issue: coupled electron-ion dynamics

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)…



Our method:
TDAP: self-consistent TDDFT with atomic motion

Coupled electron-ion dynamics without empirical parameters

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

TDAP: improved TDDFT (computationally efficient) + Ehrenfest dynamics

Electrons are propagated according to time-dependent Kohn-Sham equations

$$i\hbar\frac{\partial\phi_j(\mathbf{r},t)}{\partial t}=\hat{H}_{KS}\phi_j \qquad \rho(\mathbf{r},t)=\sum_j|\phi_j(\mathbf{r},t)|^2$$

Nuclei are propagated classically

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

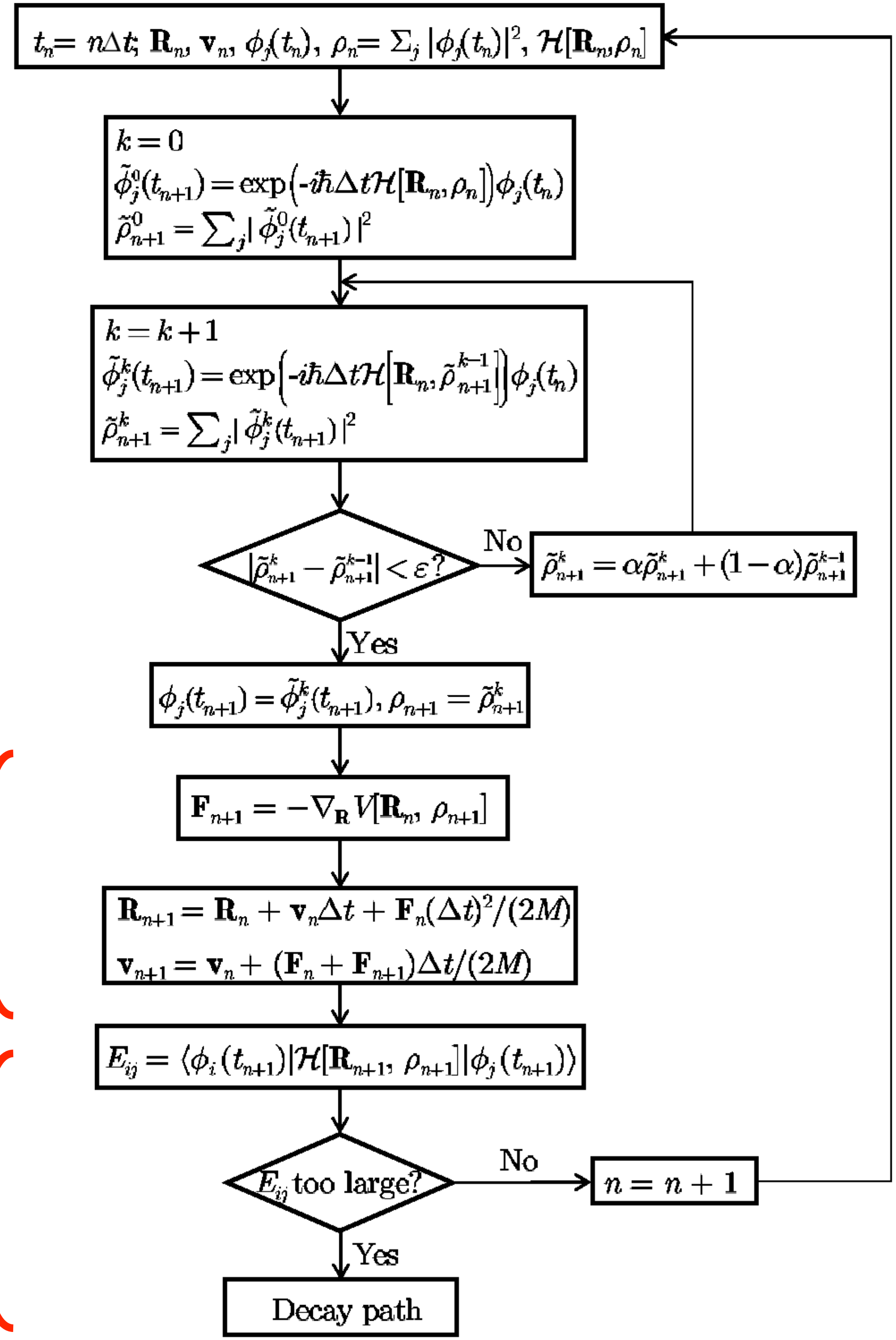
$$\rho_J(\mathbf{R},t)=|\psi_J(\mathbf{R},t)|^2=\delta\left(\mathbf{R}-\mathbf{R}_J^{cl}\right)$$

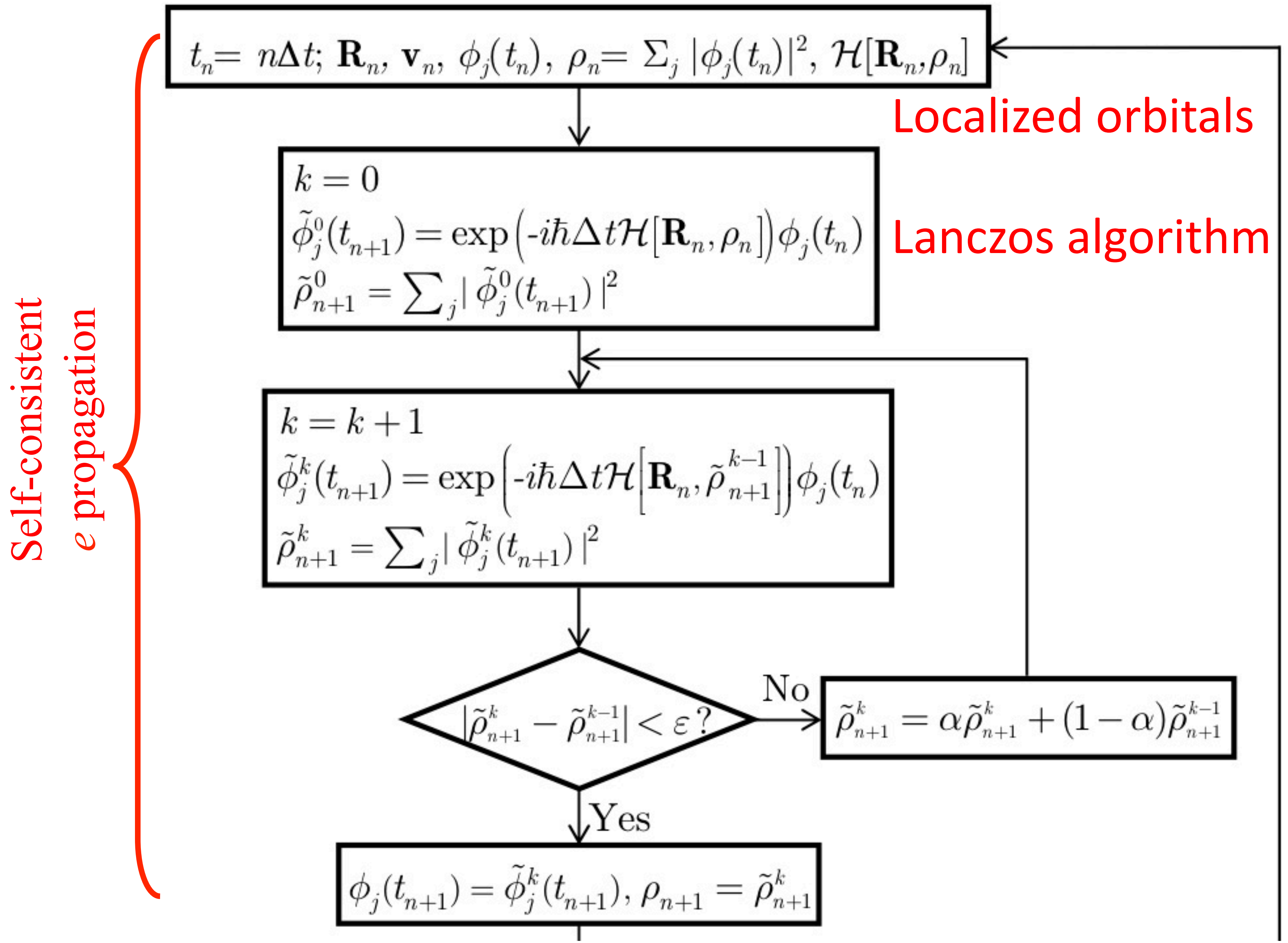
<u>TDAP: an improved TDDFT scheme (computationally efficient) w/ Ehrenfest dynamics</u>

Self-consistent *e* propagation

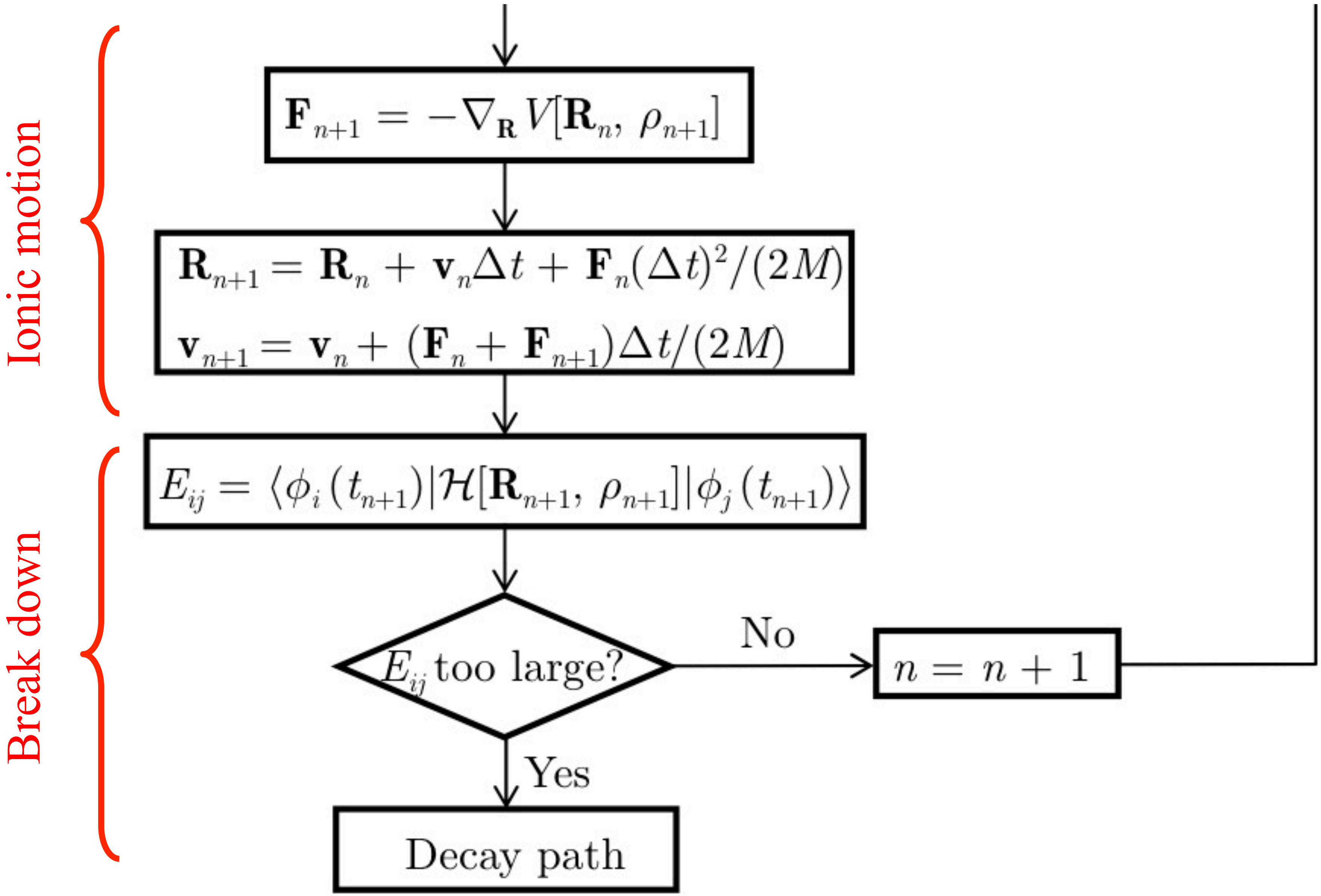
Ionic motion

Break down



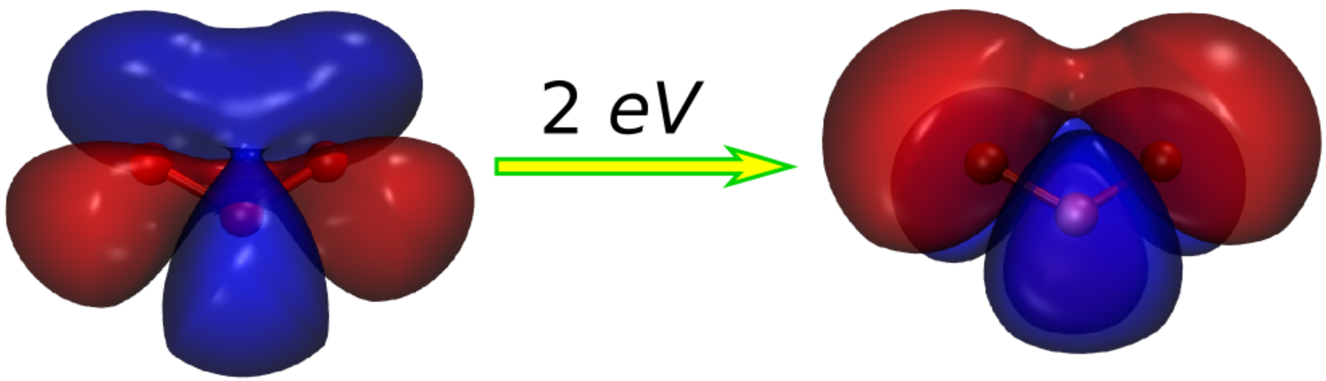


$t_n = n\Delta t$; $\mathbf{R}_n$, $\mathbf{v}_n$, $\phi_j(t_n)$, $\rho_n = \Sigma_j |\phi_j(t_n)|^2$, $\mathcal{H}[\mathbf{R}_n, \rho_n]$
Localized orbitals
$k = 0$
$\tilde{\phi}_j^0(t_{n+1}) = \exp\left(-i\hbar\Delta t \mathcal{H}[\mathbf{R}_n, \rho_n]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^0 = \sum_j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

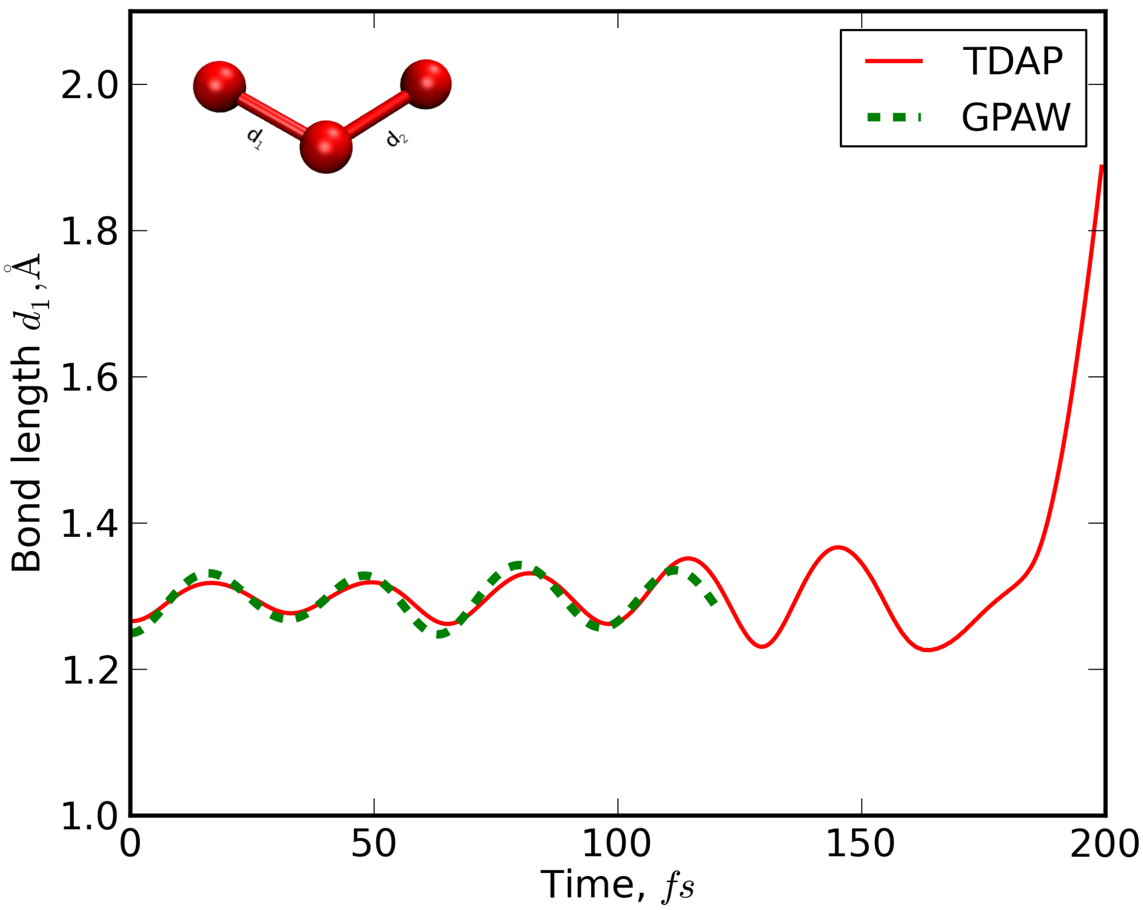
Example: ozone photolysis

- Excitation HOMO to LUMO: slow dissociation



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

1^{st} excited state trajectory



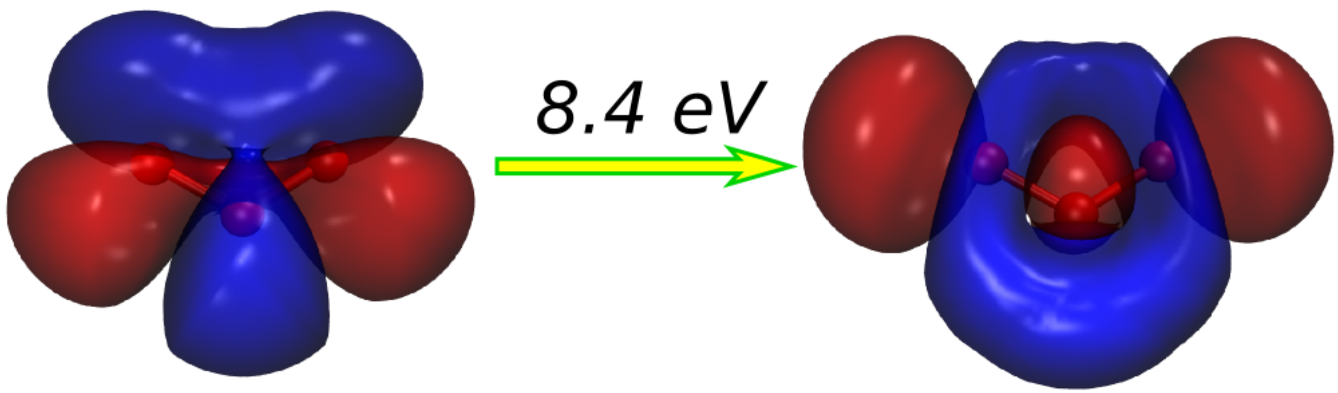
GPAW computation time 37 days (4 cores)

TDAP: 1 hour

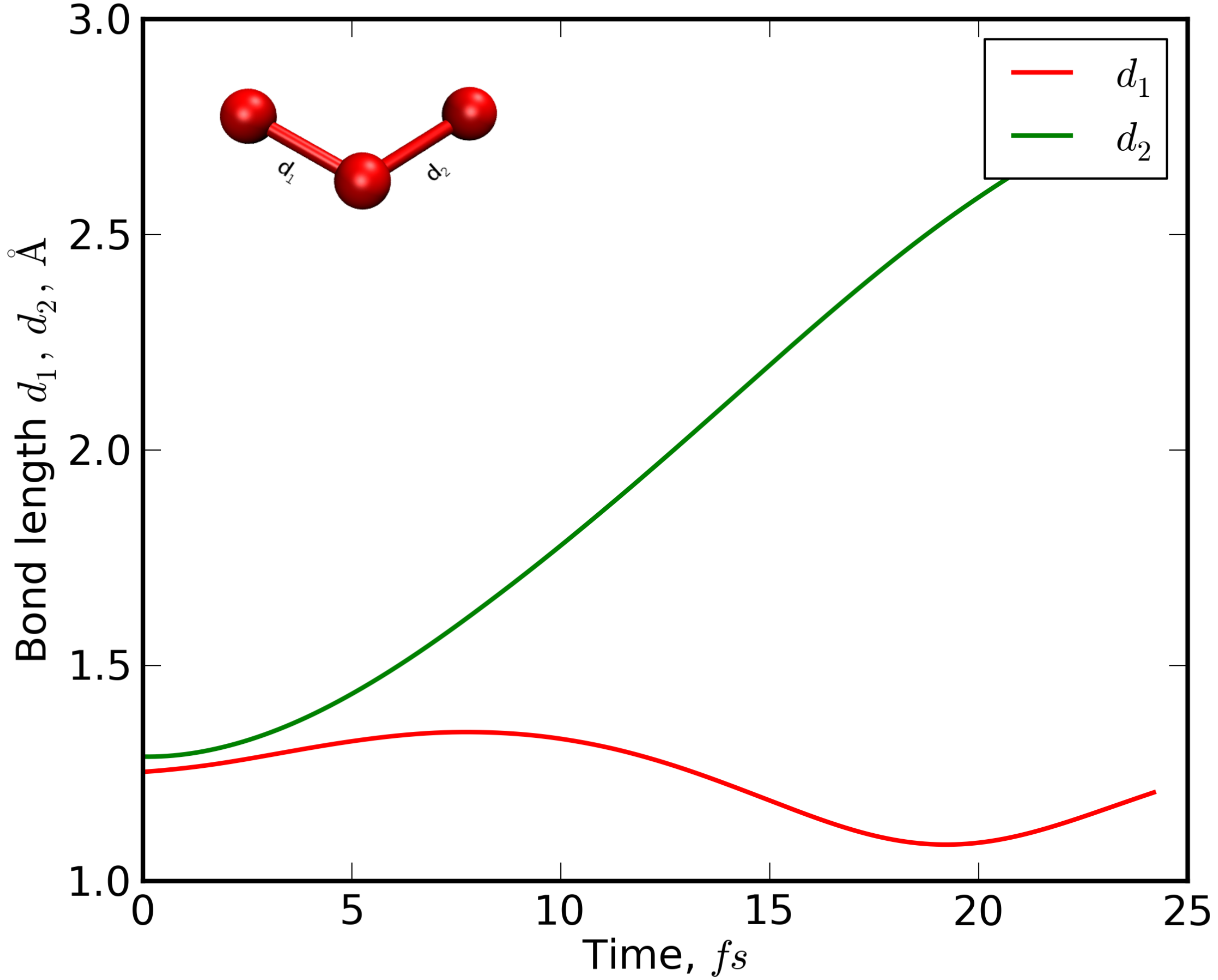
Time step: 5 attosec (both)

Example: ozone photolysis

- Excitation HOMO to LUMO+1: quick dissociation



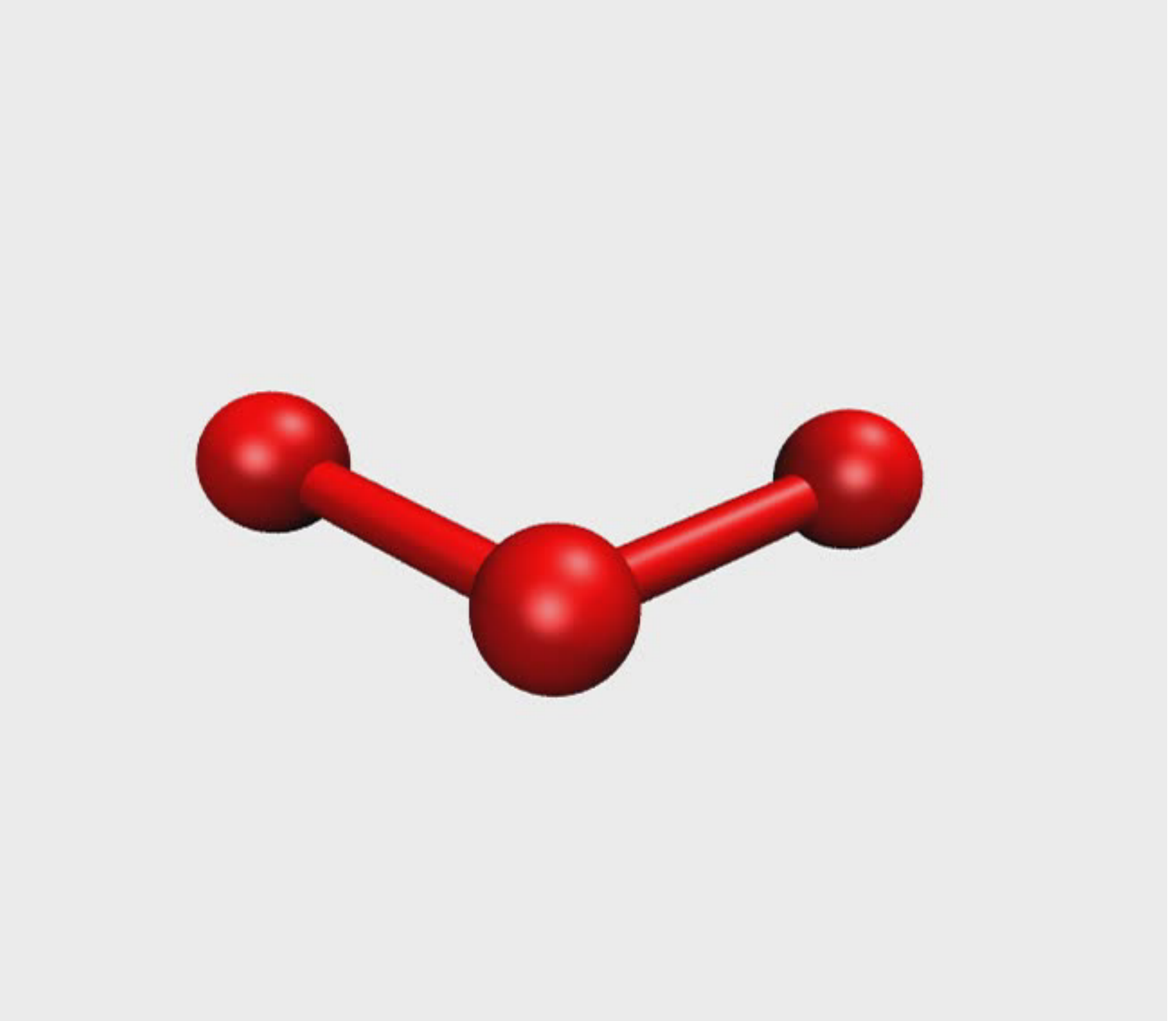
2^{nd} excited state trajectory



2^{nd} excited state trajectory

- Movie:

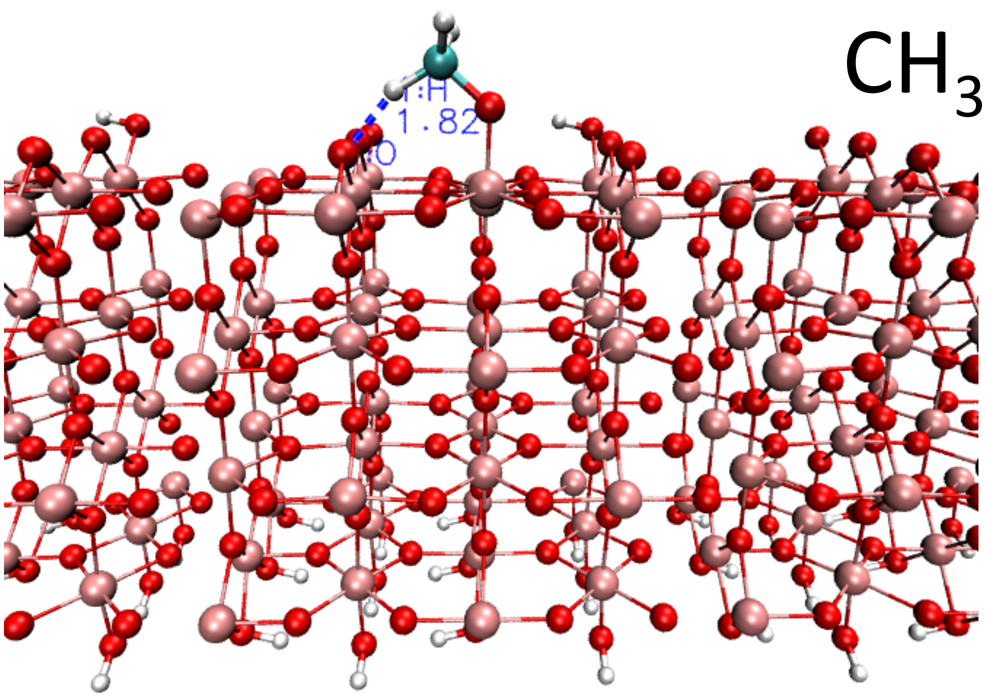
o3split.mov



Methoxy splitting on TiO_2 surface

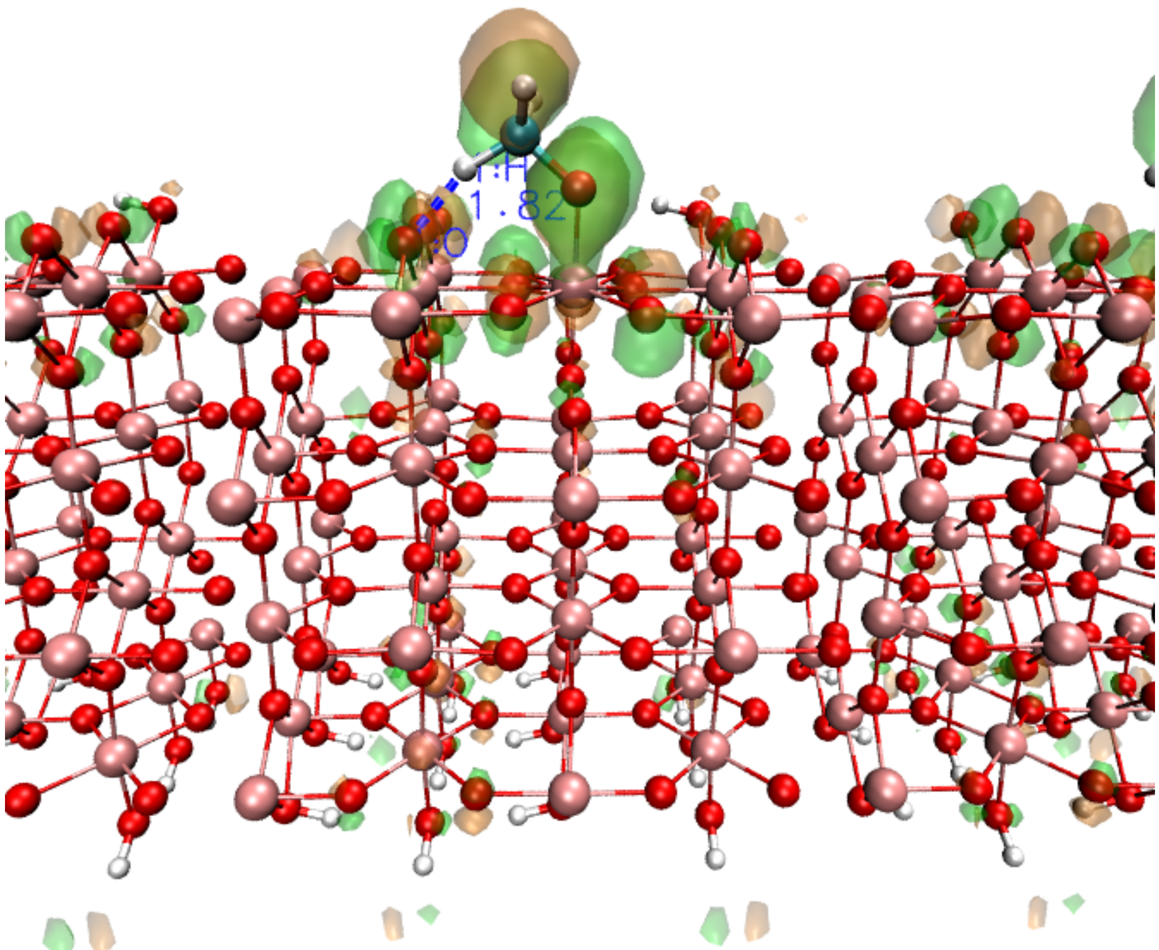
- Formaldehyde was photochemically produced from methoxy on TiO_2 (110) surface

$$CH_3OH+h\nu \rightarrow CH_2O+H_2$$

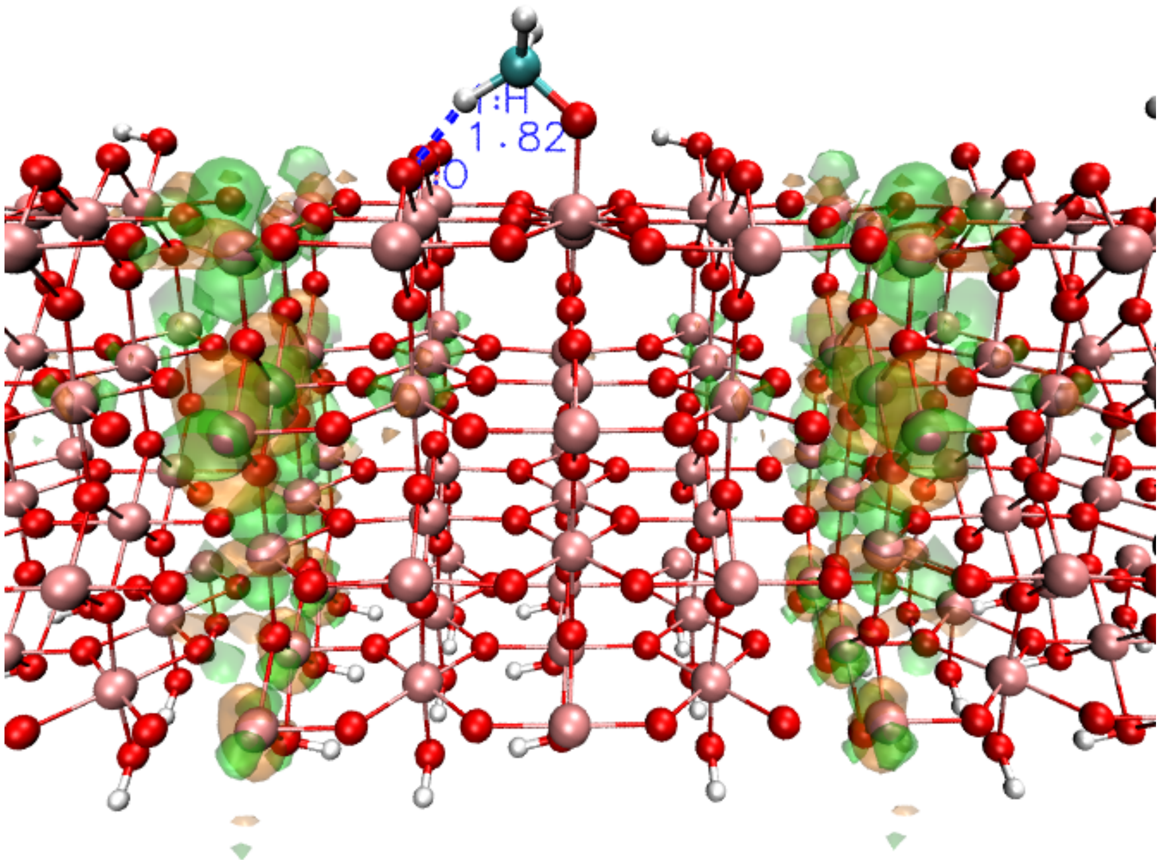


Phillips, K. R., Jensen, S. C., Baron, M., Li, S.-C. & Friend, C. M. Sequential photo-oxidation of methanol to methyl formate on TiO2 (110). *Journal of the American Chemical Society* **135**, 574–577 (2013).

Hole: HOMO-4 State



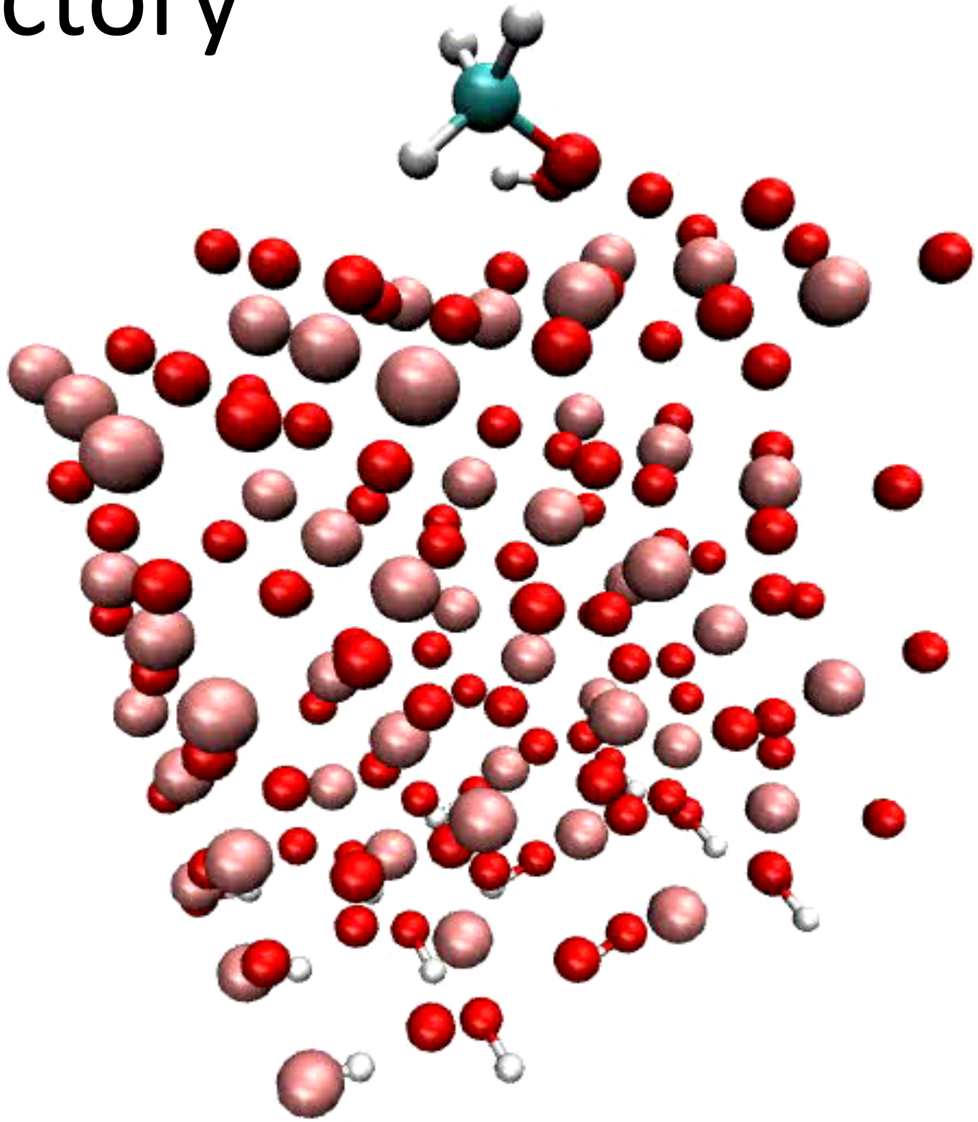
Electron: LUMO state



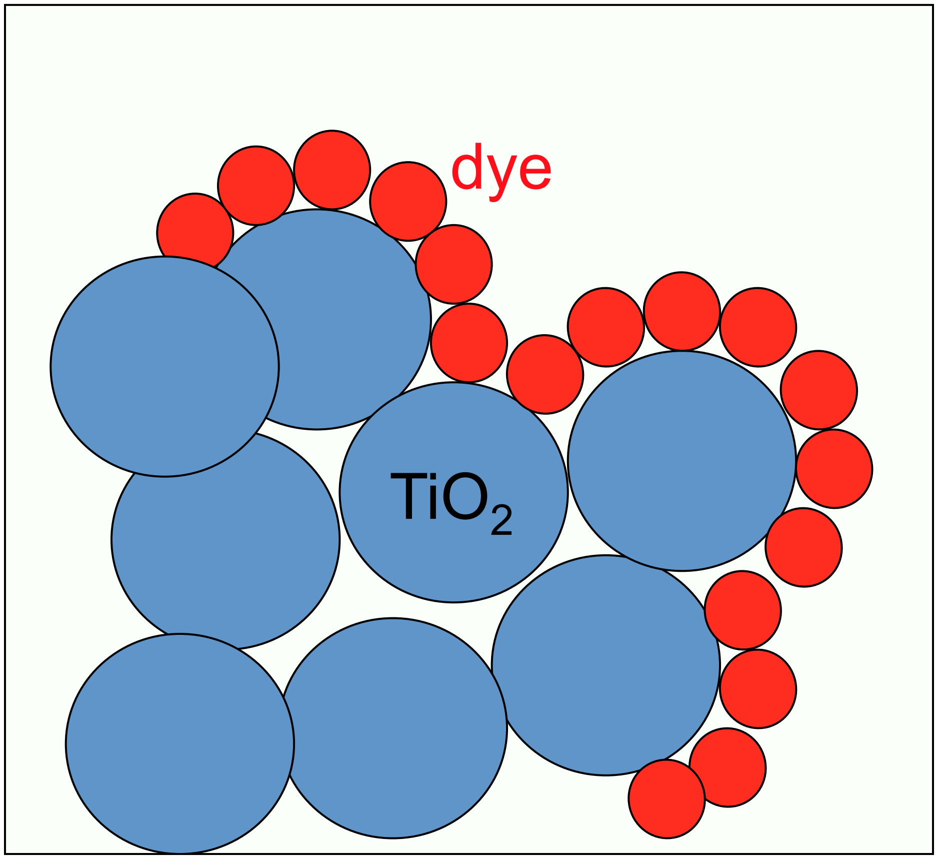
TDDFT trajectory

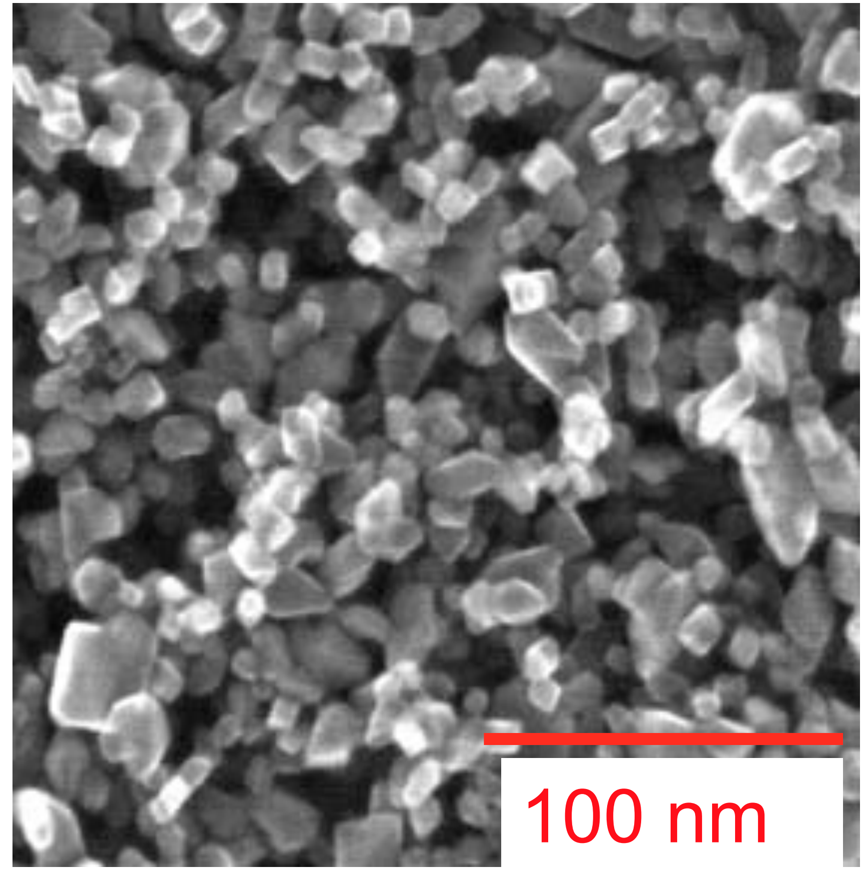
- Movie:

mxsplit.mpg

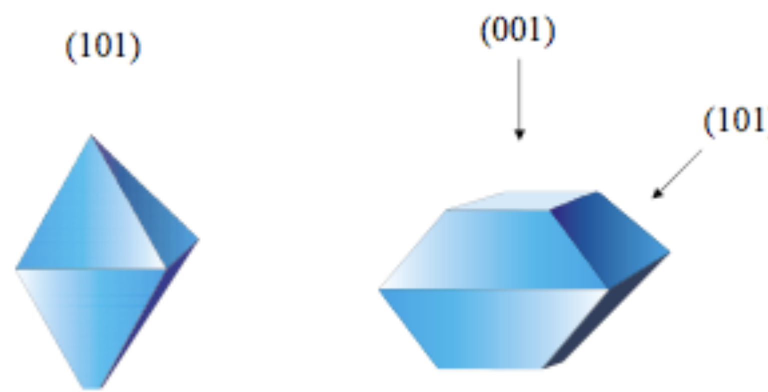


Approximately complete surface coverage (i.e. densest possible packing of dye molecules)





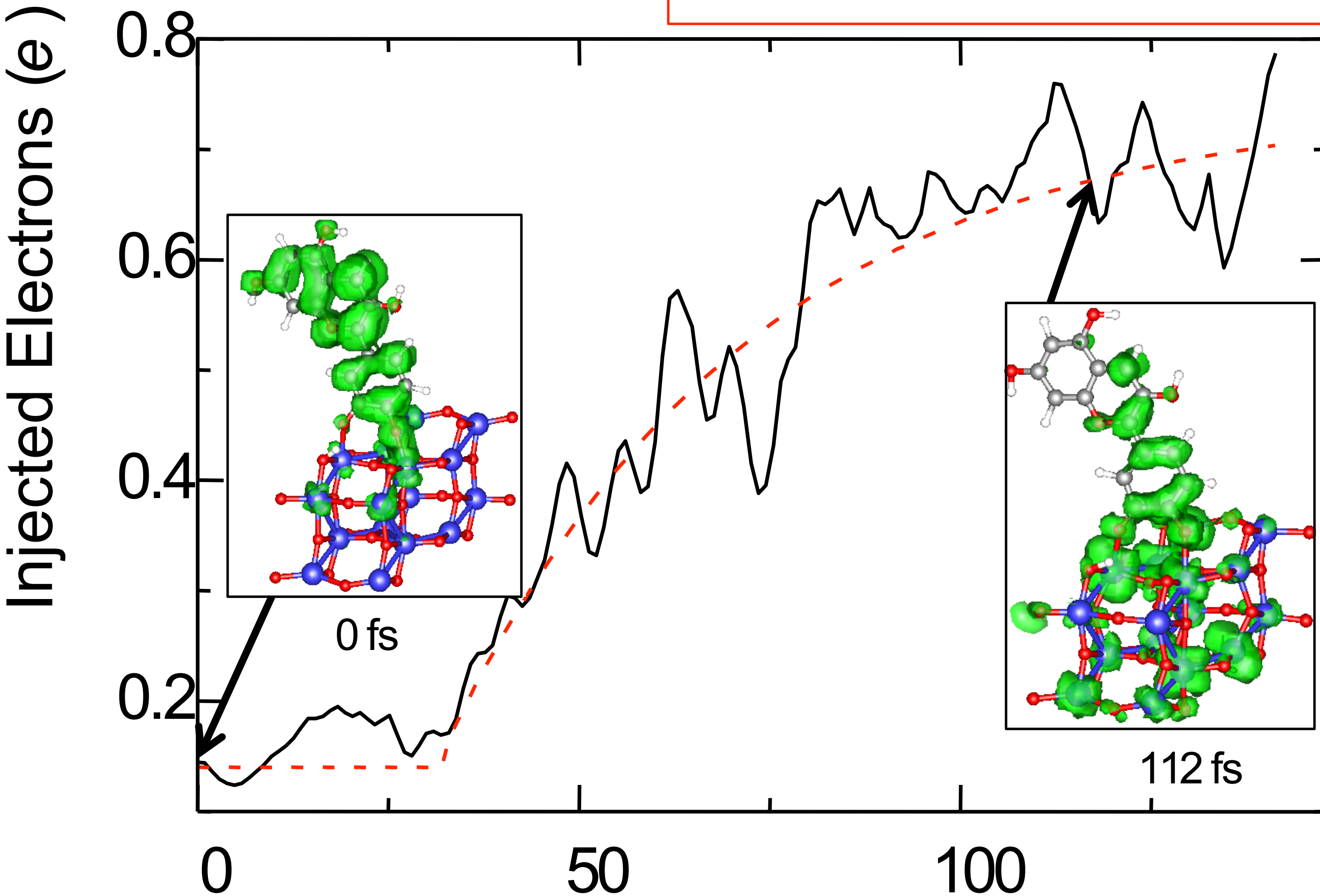
~20 nm sized faccetted anatase nanoparticles



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

Charge injection dynamics:

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



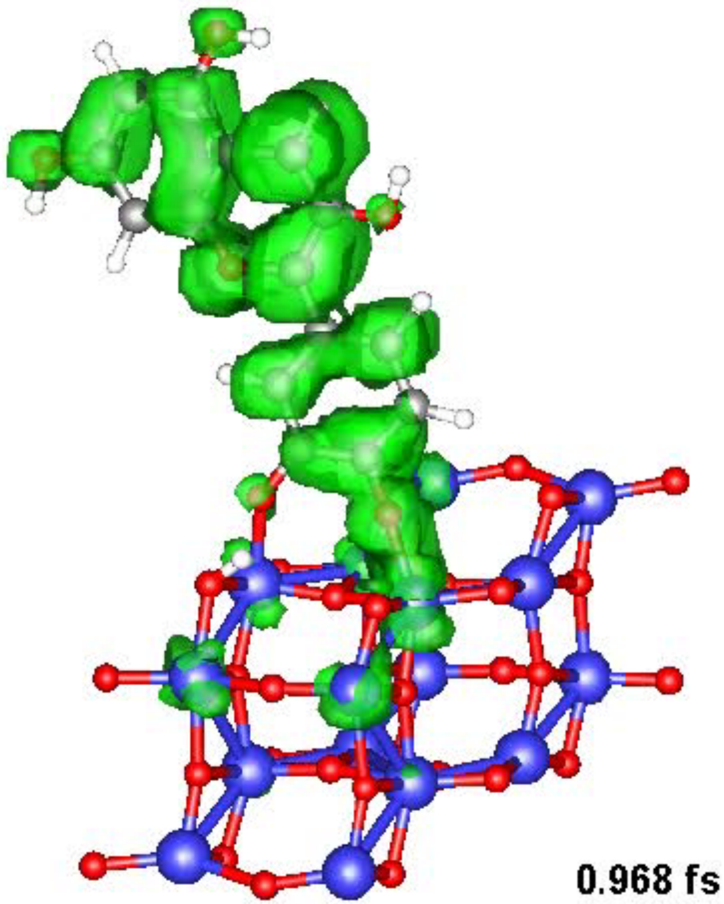
Fit: t_0 = 32 fs, t_1 = 40 fs

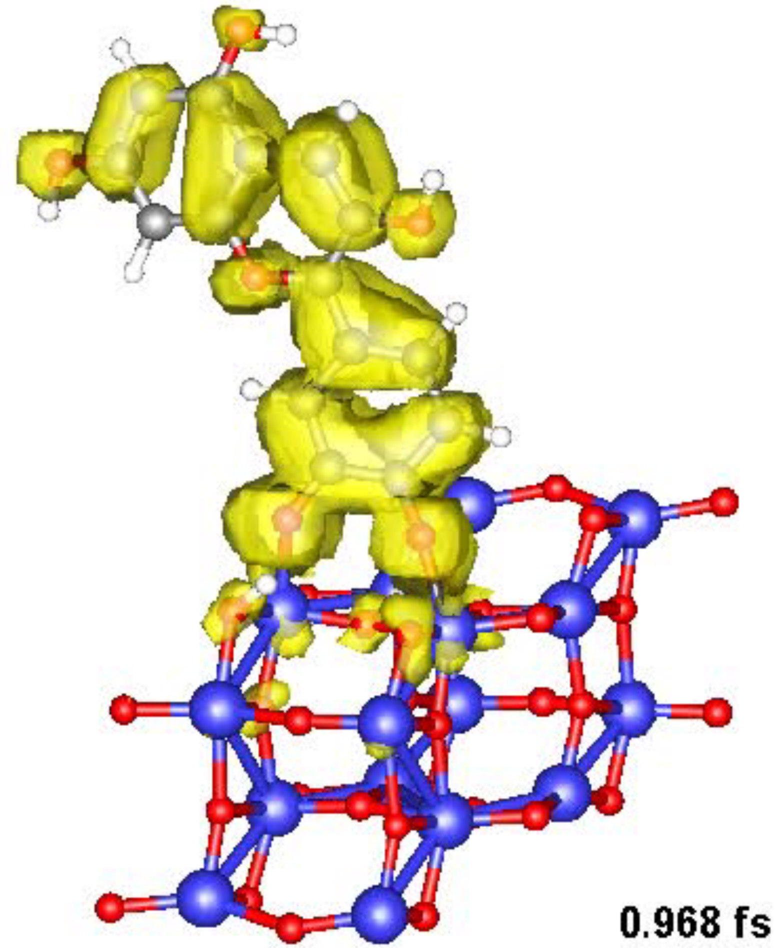
Expt.[a)] : <100 fs

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

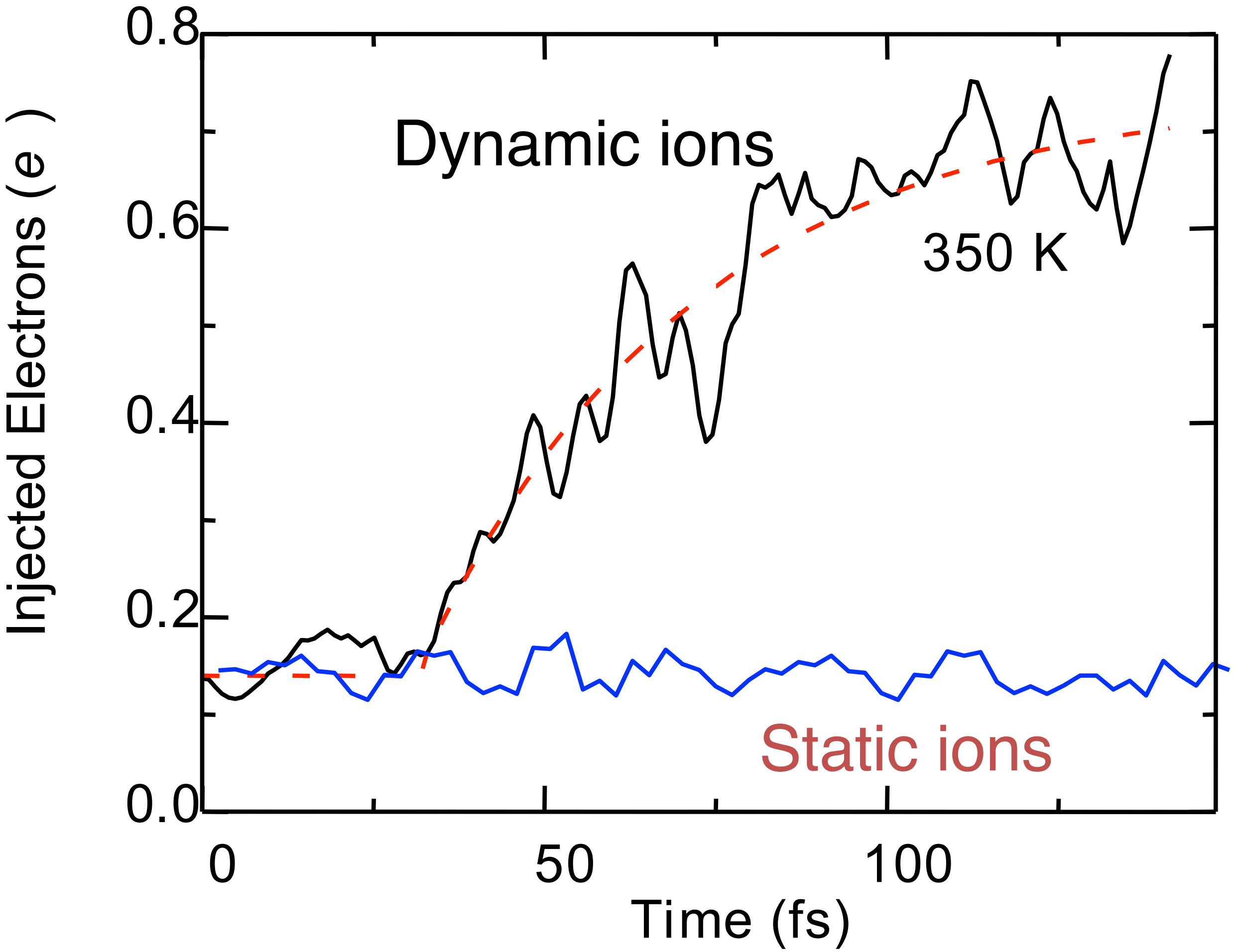
T=350 K

δt=0.02419 fs

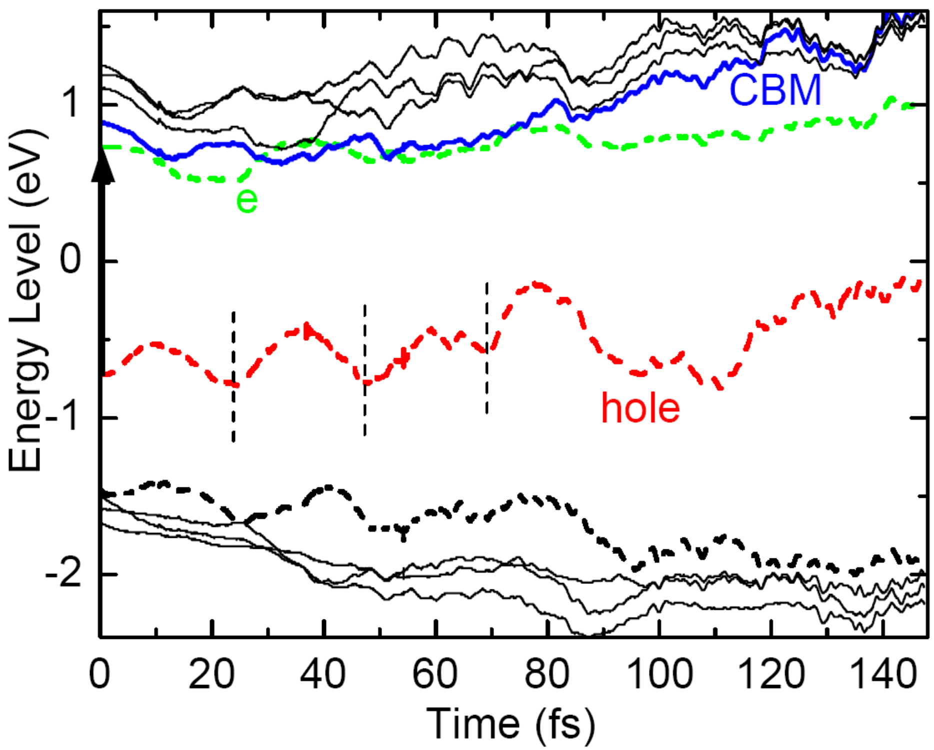

0.968 fs

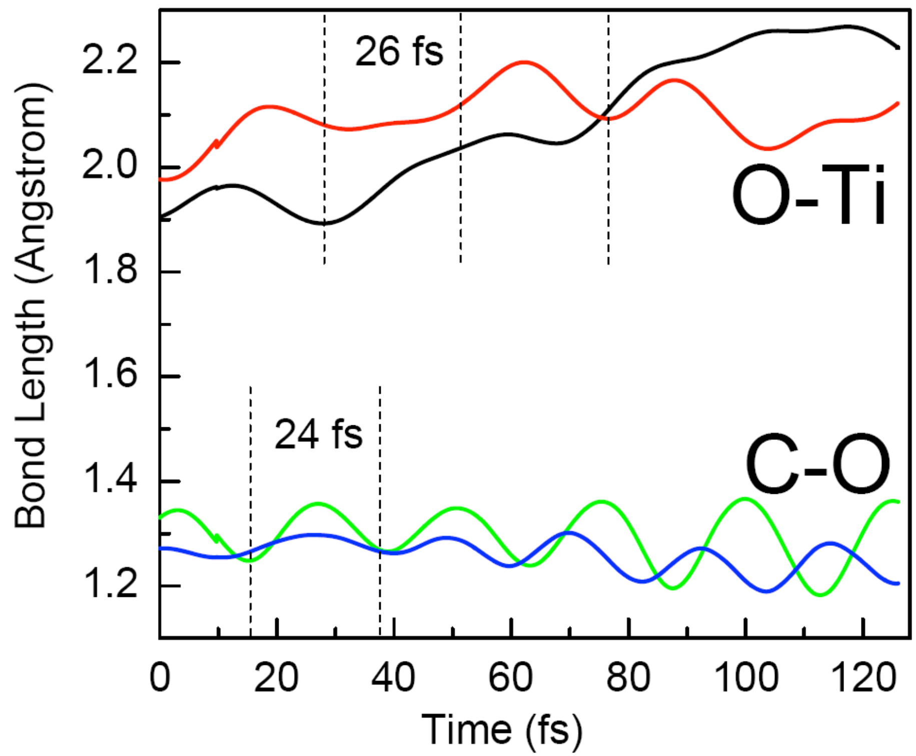

0.968 fs

Importance of coupled e-ion dynamics

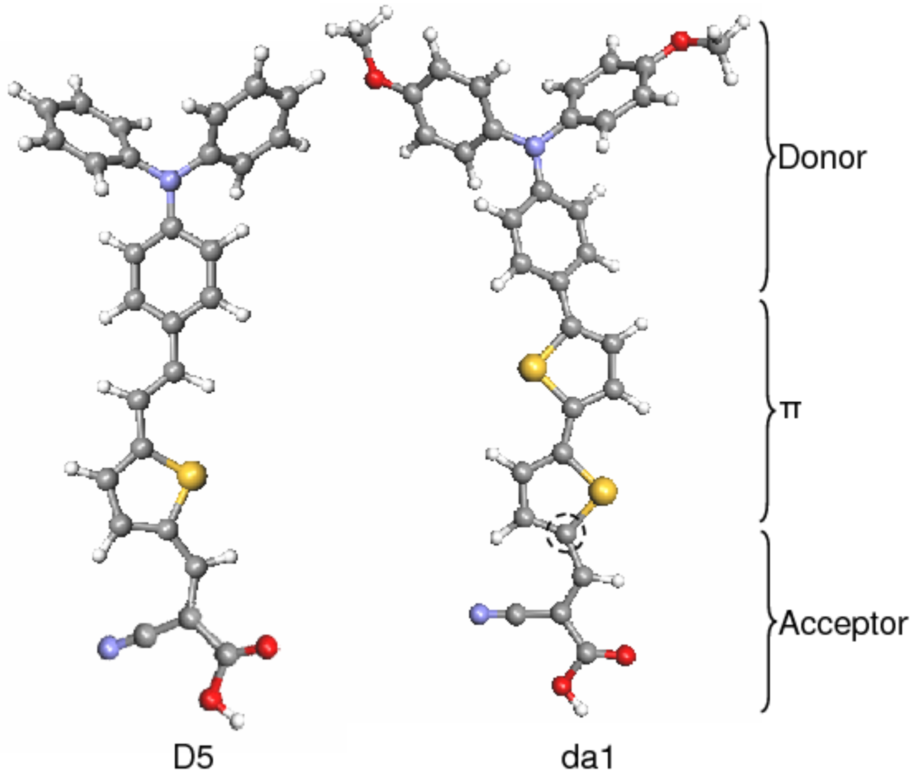


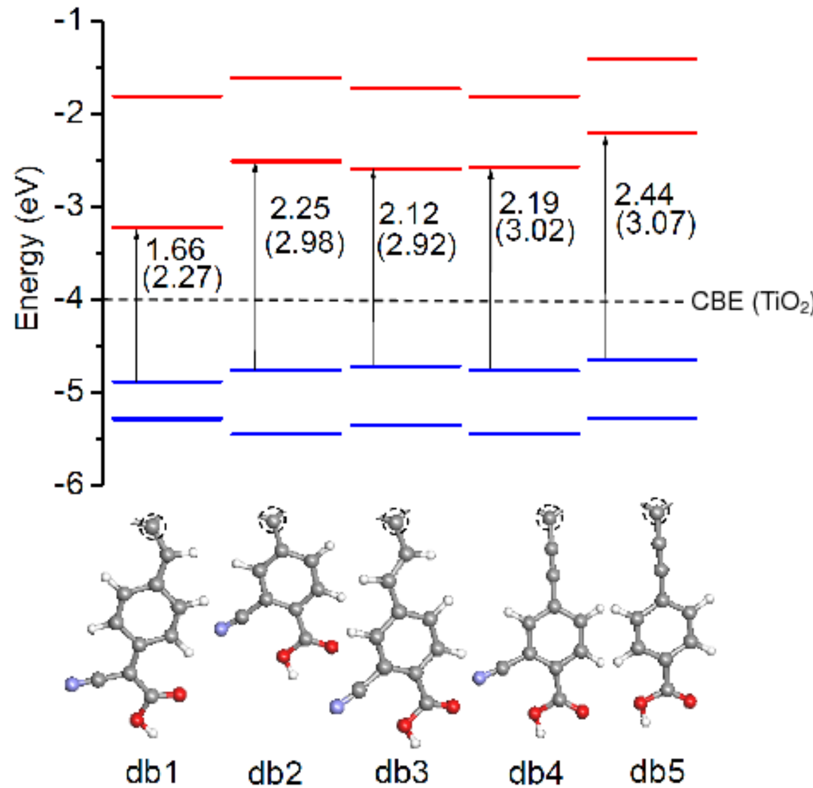
Coupling of electron-phonon motion





Design of new dyes (not yet tried in experiments)



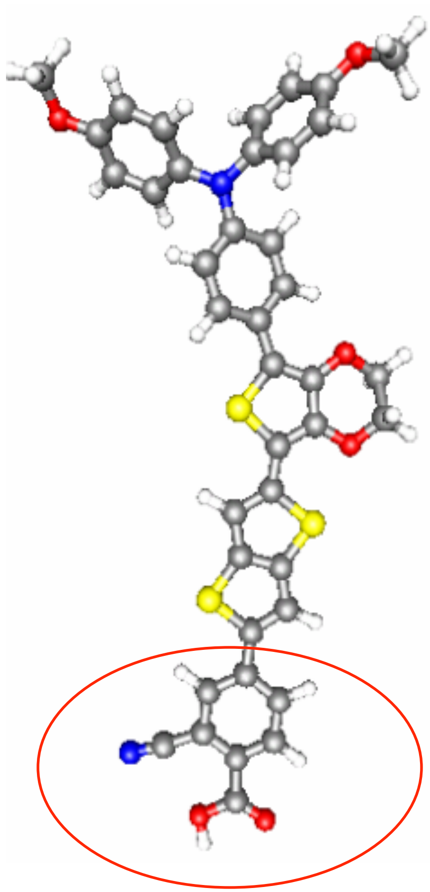


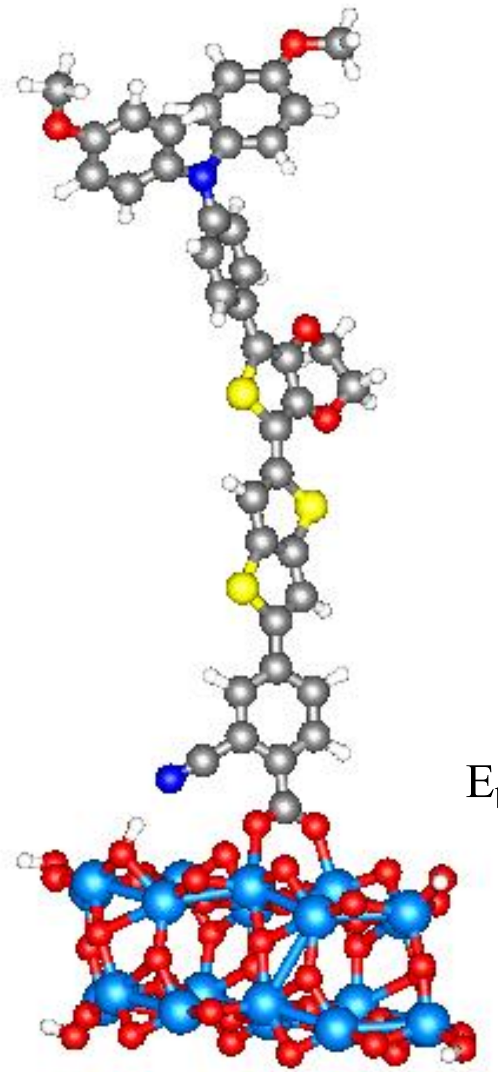
Design of Dye Acceptors for Photovoltaics from First-Principles Calculations

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

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

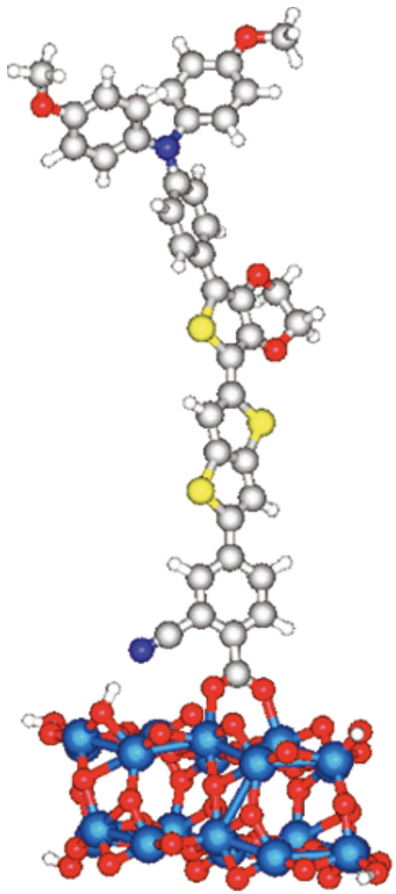
Enhanced dye binding to TiO_2

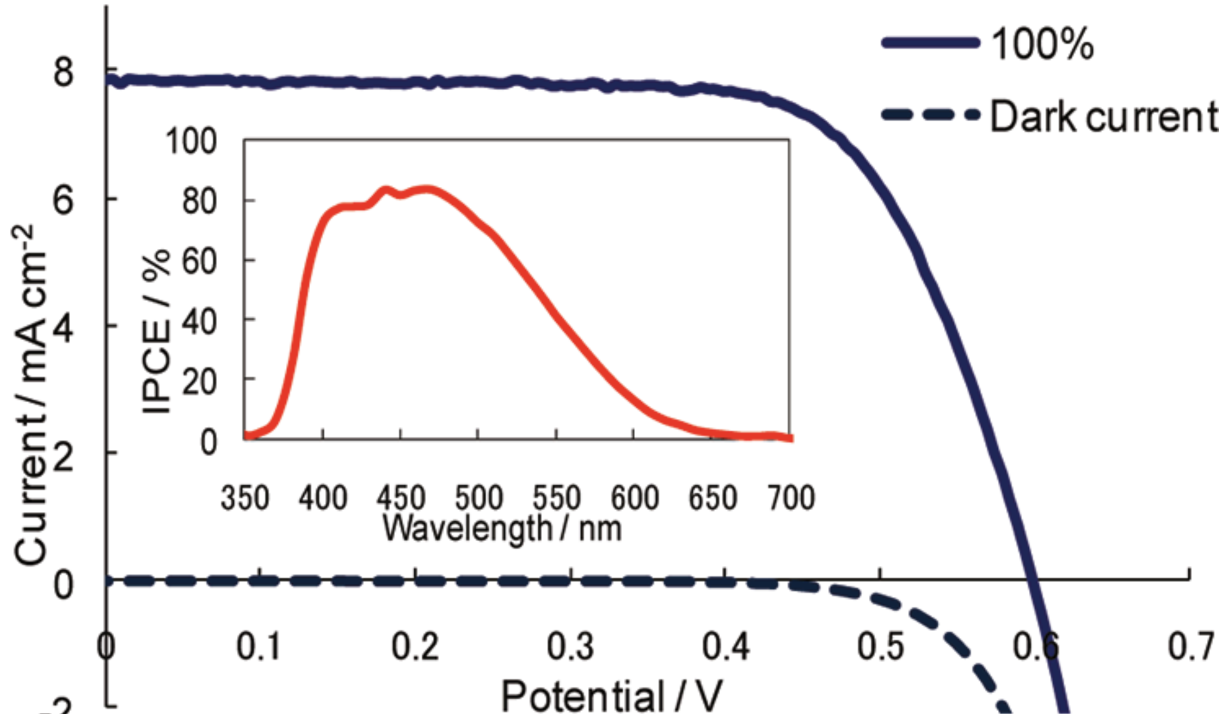




E_b=1.52 eV

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

HAPPY RETIREMENT SHI-YU!