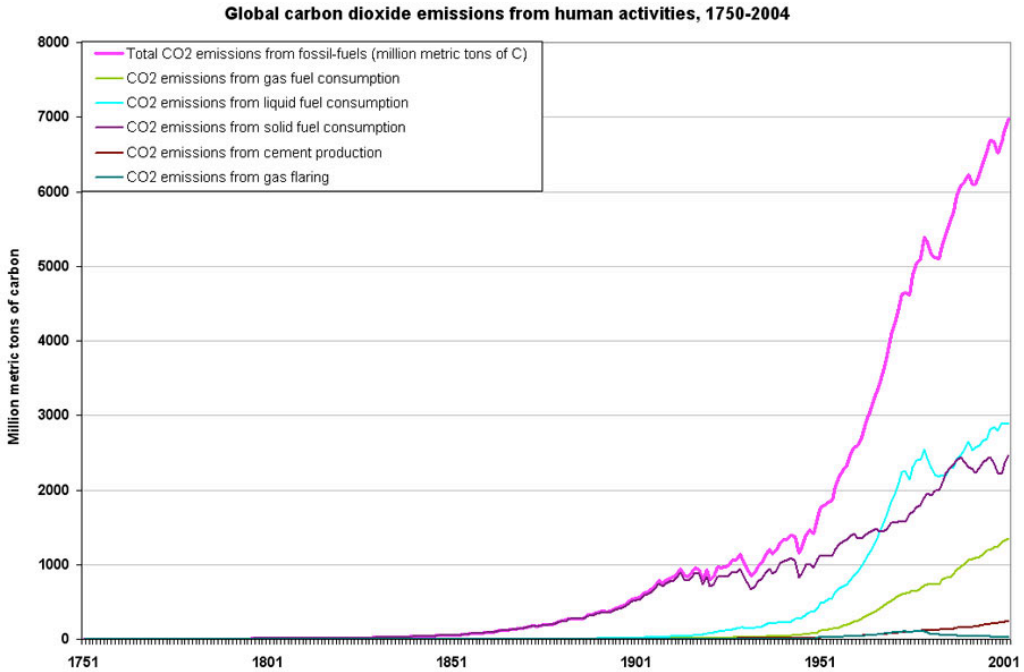
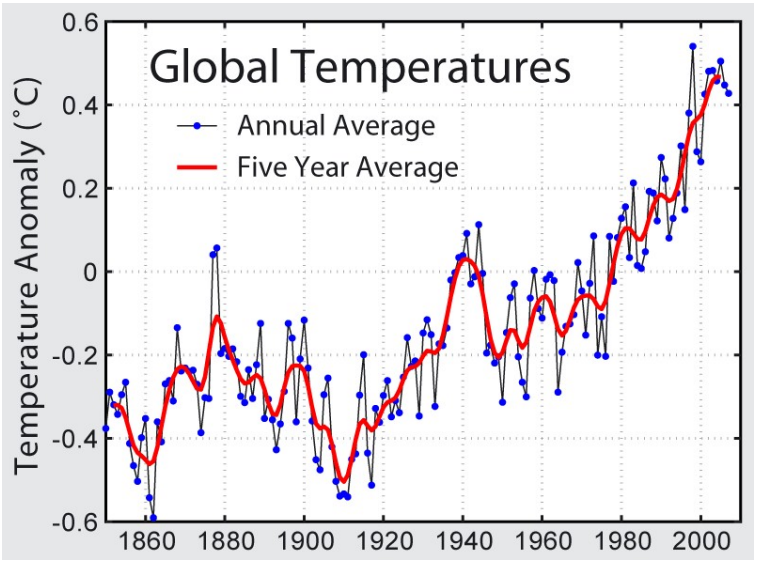
Ab-initio studies of optical excitations in solids and molecules

- Motivation
- Short review of experimental results
- Methodology
- Applications

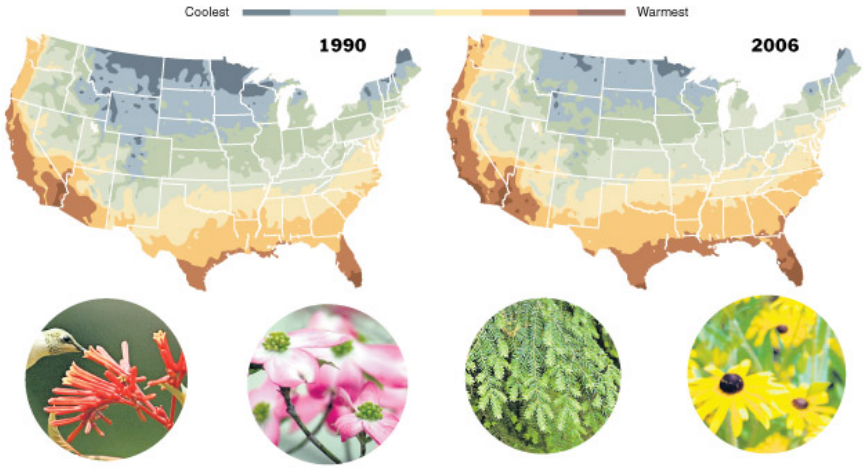
Thomas Young Center,
University College London
July 3, 2014

Motivation: The need for alternative energy sources





The zones in the maps correspond to low temperatures. As warmer zones cover more of the United States, different types of plants will grow in many areas.



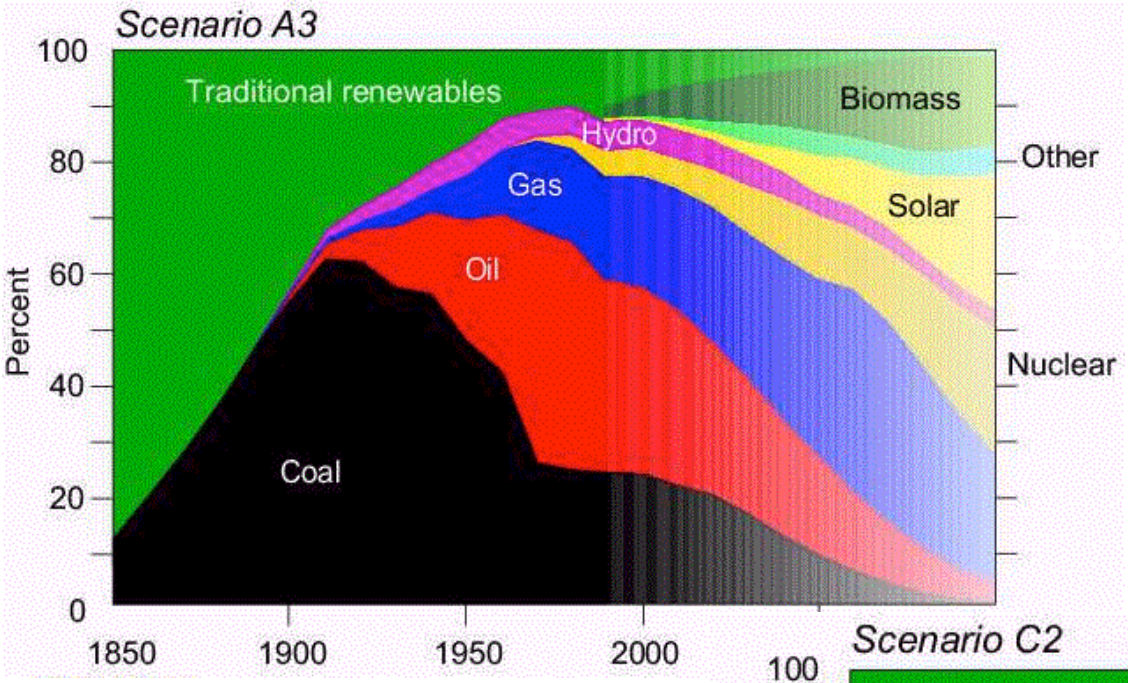
1990 zones are by the United States Department of Agriculture. 2006 zones are by the National Arbor Day Foundation.

Sources: National Arbor Day Foundation; National Wildlife Federation

The New York Times

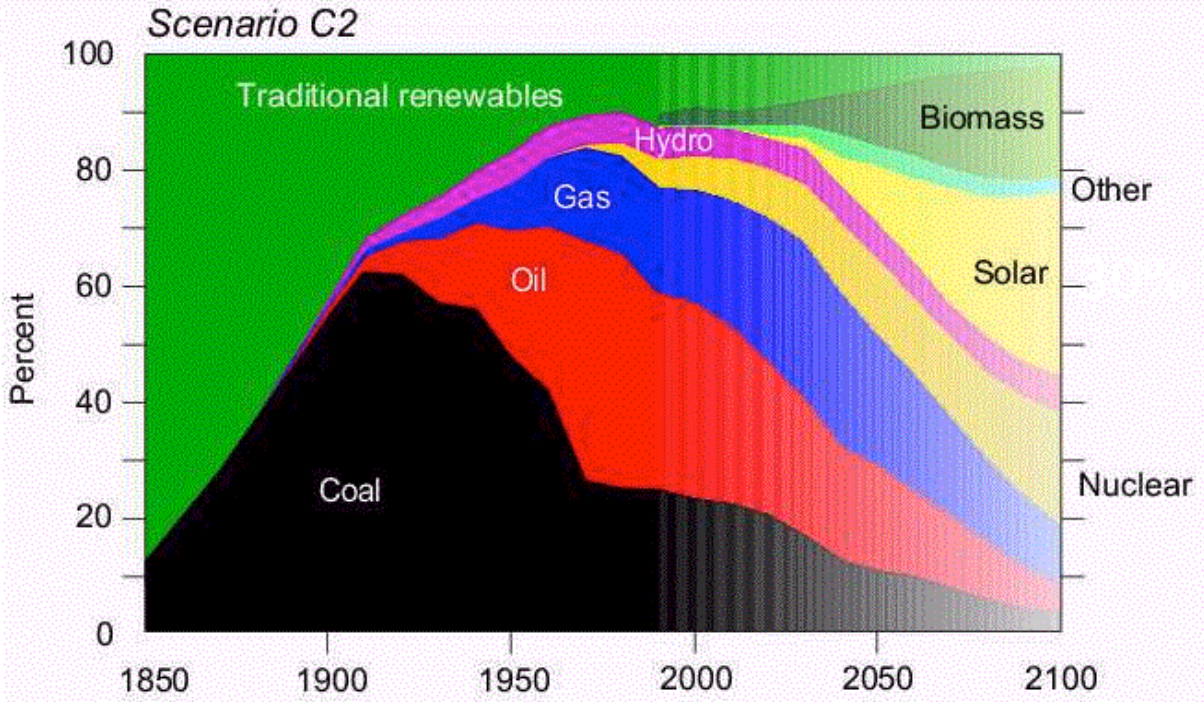
http://www.celsias.com/2007/03/20/channel-4-distances-itself-from-global-warming-documentary/

The challenge of sustainable energy sources



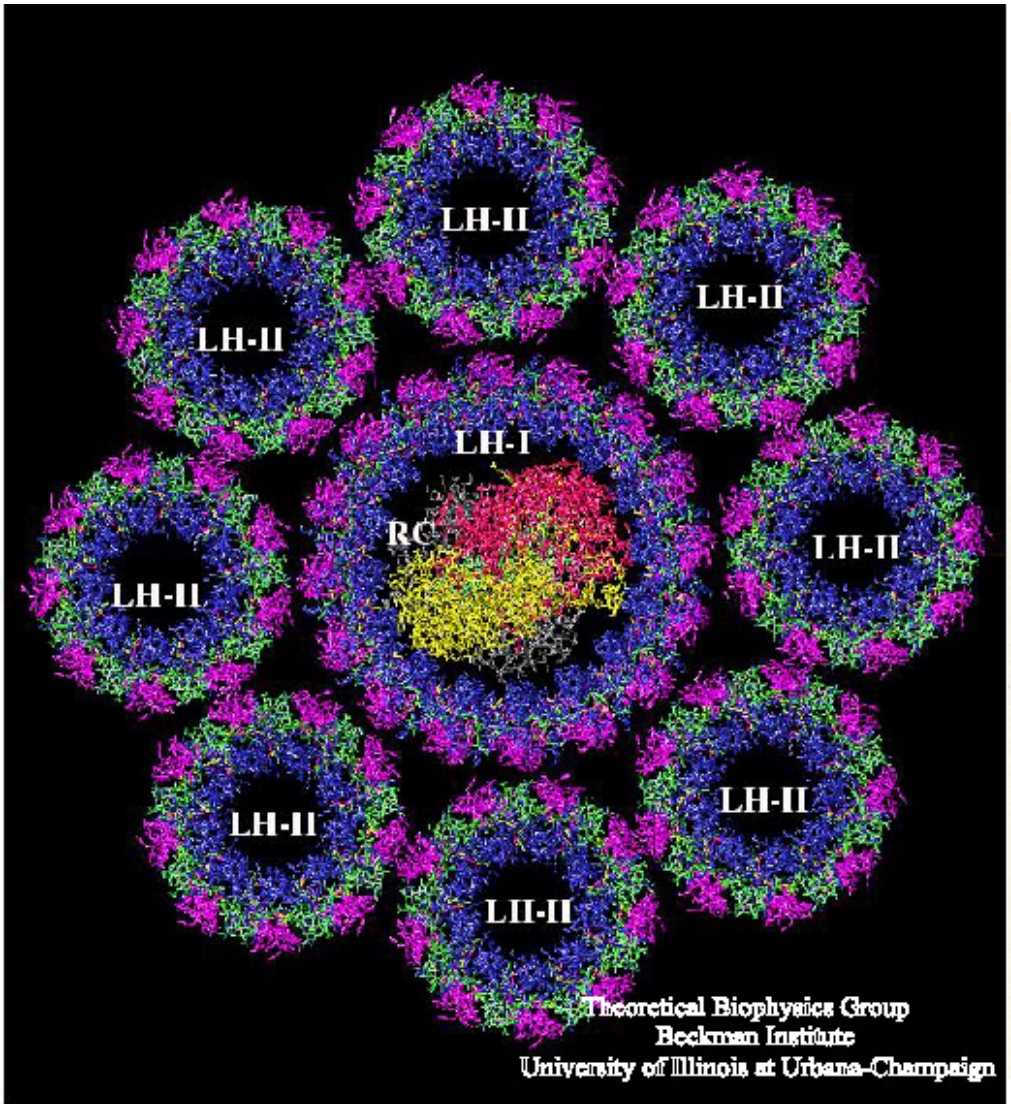
Time and resources running out – fundamental science can play key role in enabling technology

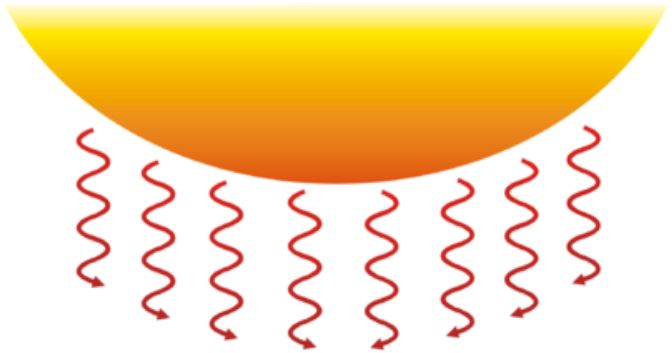
Report of Intergovernmental Panel on Climate Change

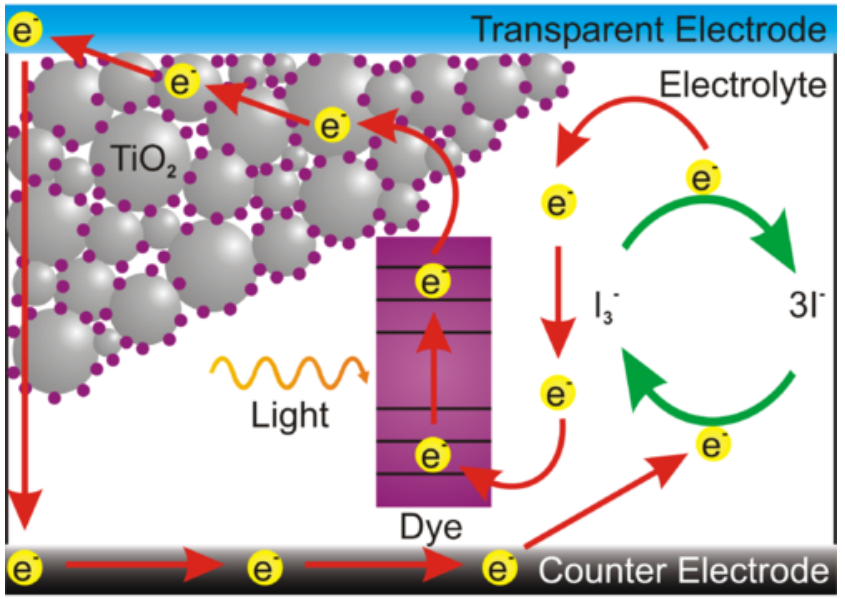


The dye-sensitized solar cell (M. Graetzel, 1991)

The Principle: separate light-absorption and charge collection processes



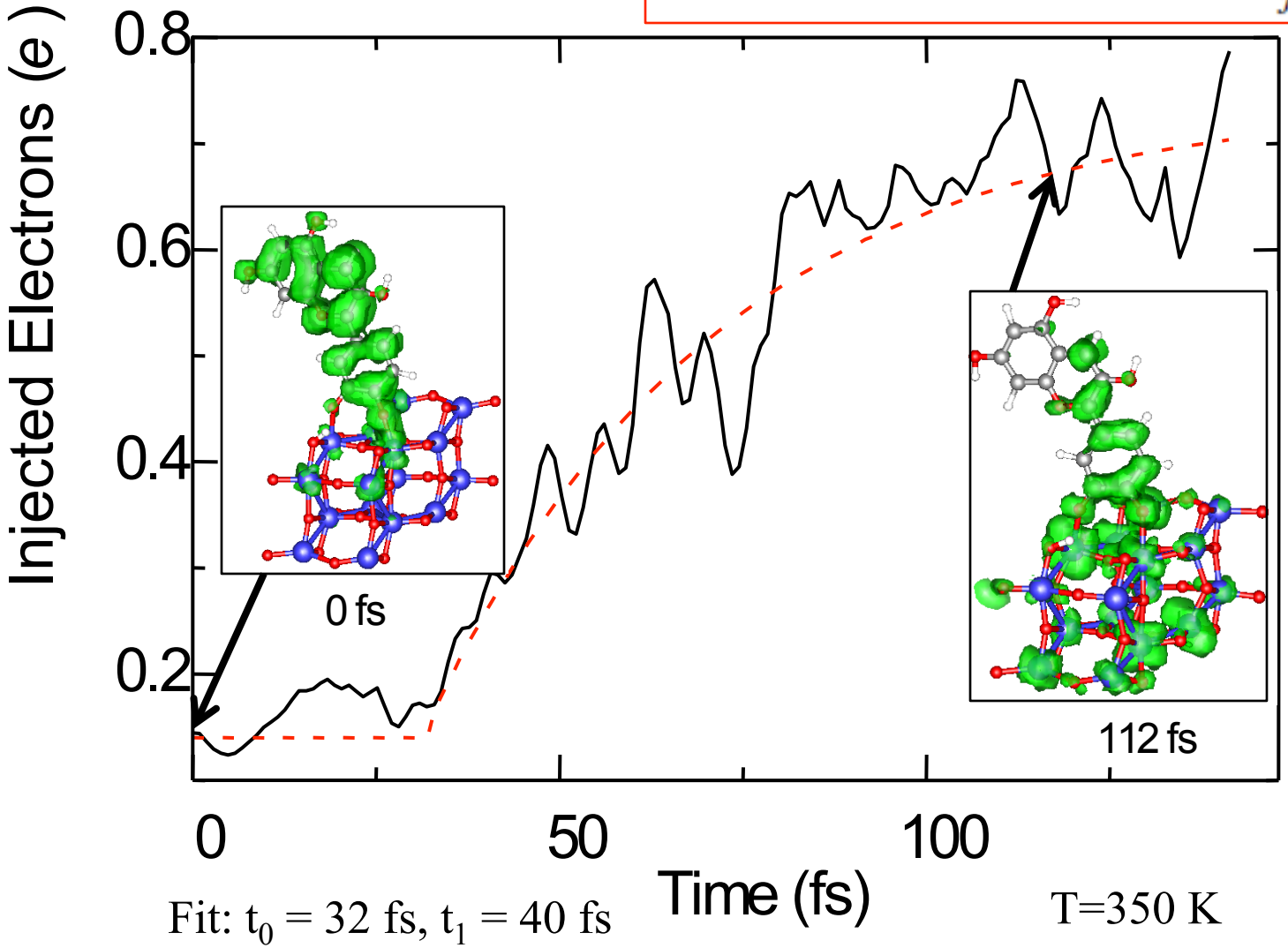




Major issues:
- stability
- efficiency (Inc.Ph.Cur.Eff.)

Charge injection dynamics:

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



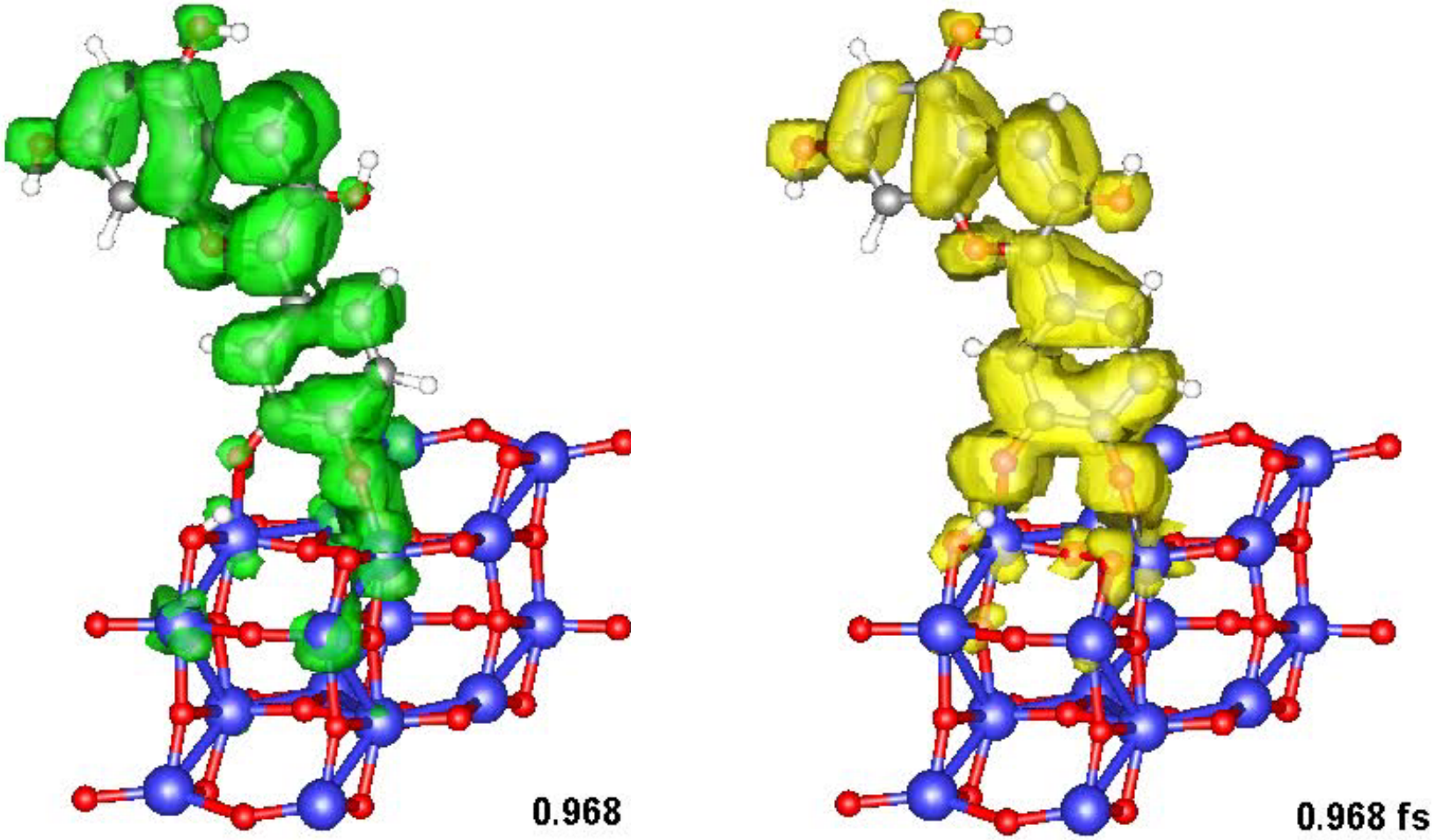
Fit: t_0 = 32 fs, t_1 = 40 fs

Expt.[a] : <100 fs

T=350 K

δt=0.02419 fs

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

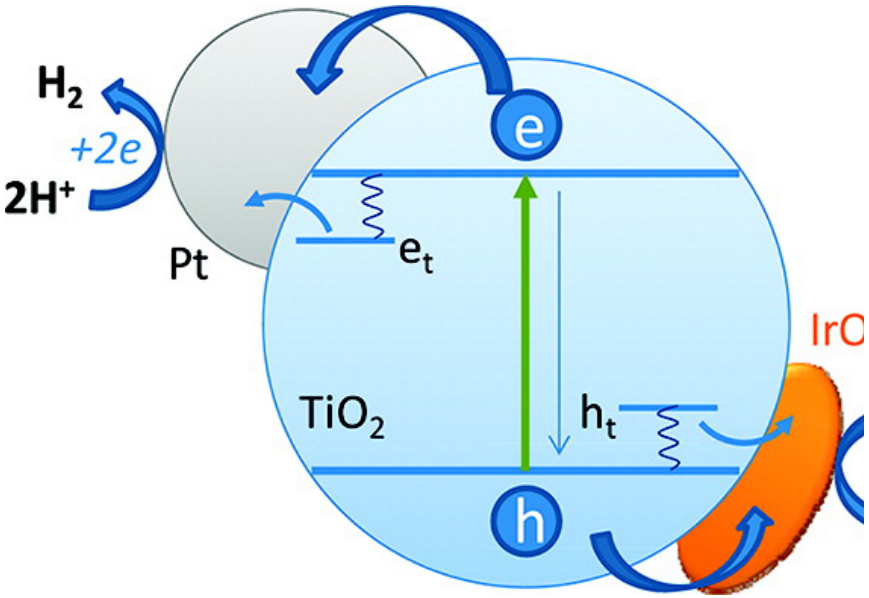


Design of Dye Acceptors for Photovoltaics from First-Principles Calculations

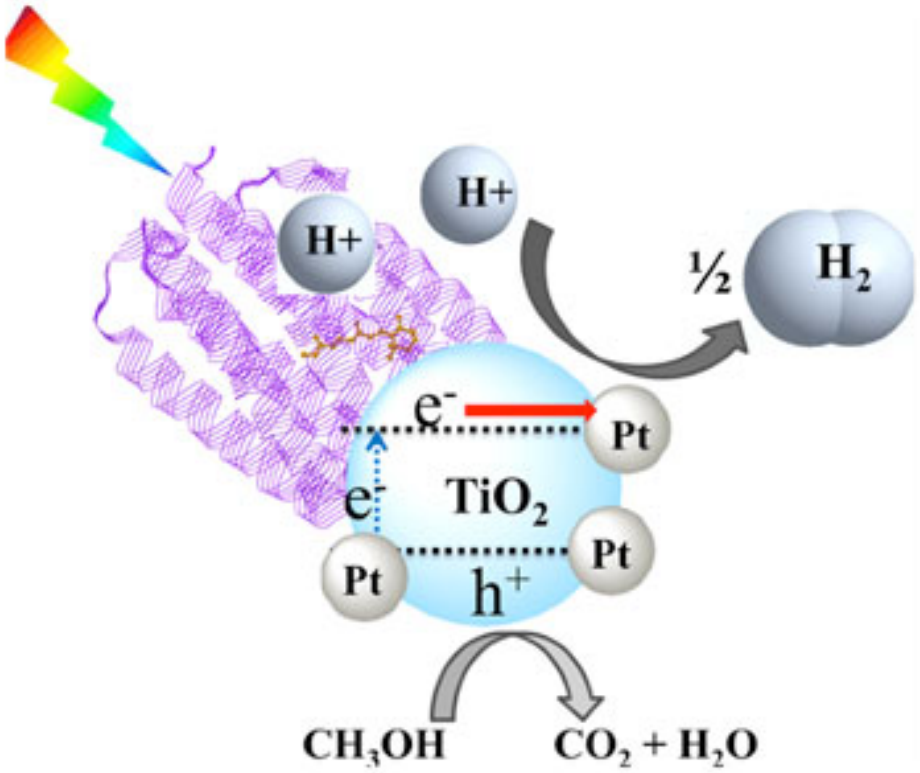
Sheng Meng, Efthimios Kaxiras, Md. K. Nazeeruddin, and Michael Gratzel

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

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)

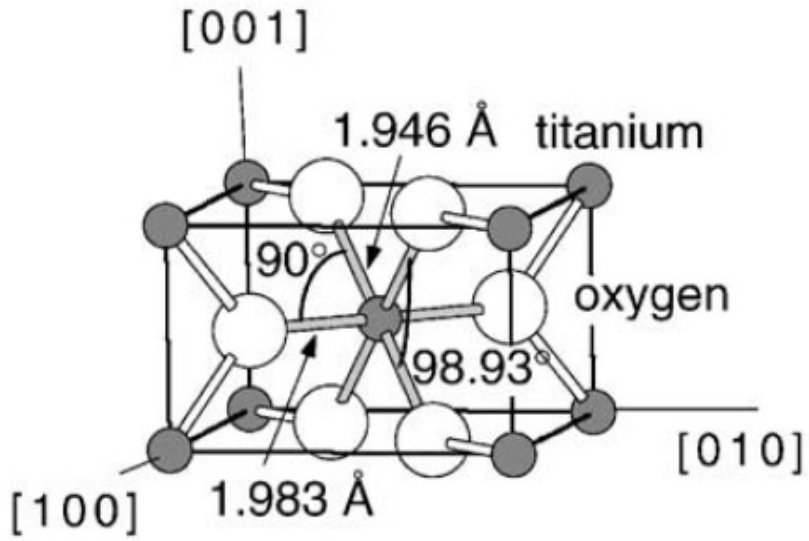
Simulation of photo-oxidation of water and methanol on TiO_2 (110)

Dmitry Vinichenko,
Grigory Kolesov,
Georgios Tritsaris
(SEAS, Harvard)

in collaboration with the group of
Prof. C. M. Friend
(Dept. CCB, Harvard)

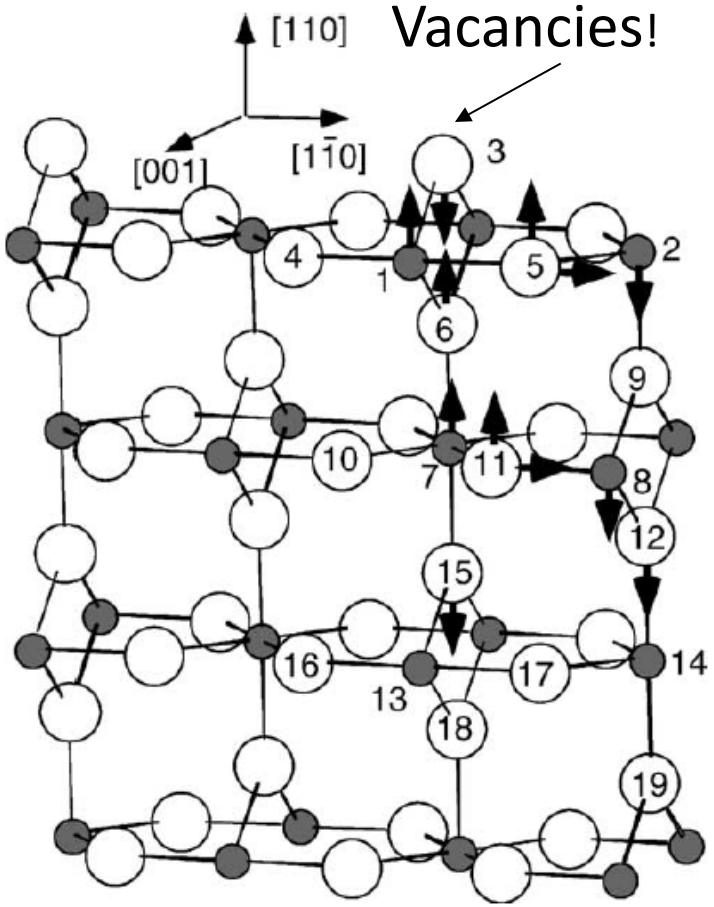
Rutile TiO_2 (110) – a model photocatalyst

Titania (TiO_2) – one of the most widely studied materials in transition metal oxide photocatalysis since the seminal publication of Fujishima [1] in 1972



Rutile bulk crystal structure

Ti → 6-fold coordinated
O → 3-fold coordinated

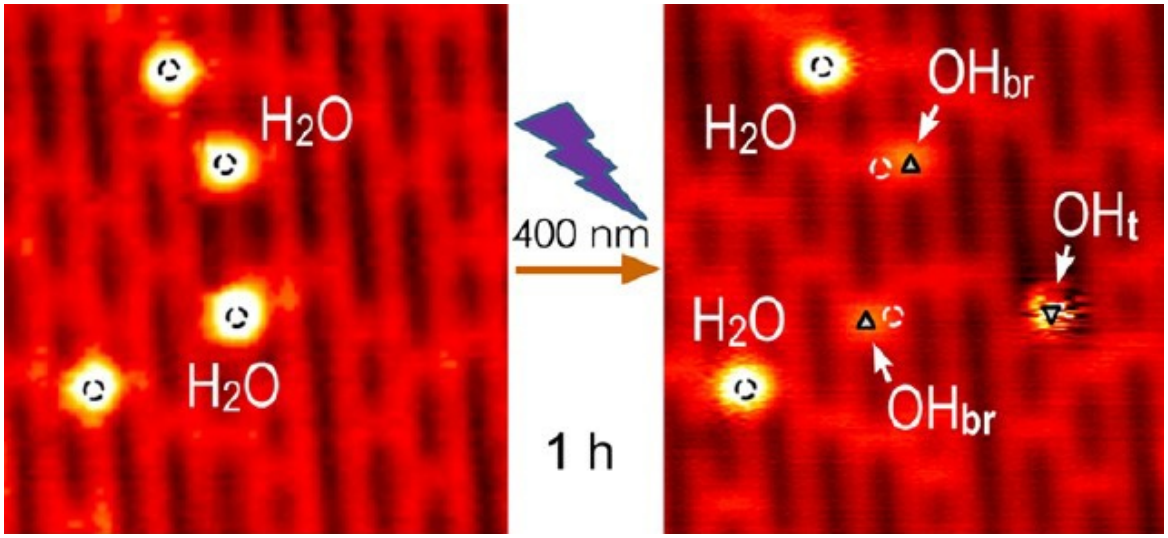


Model of the (110) surface

1- A. Fujishima, K. Honda. Nature, 238:37-38 (1972)
2- U. Diebold, Surf. Sci. Rep., 48:53-229 (2003)

Water photooxidation – experimental data

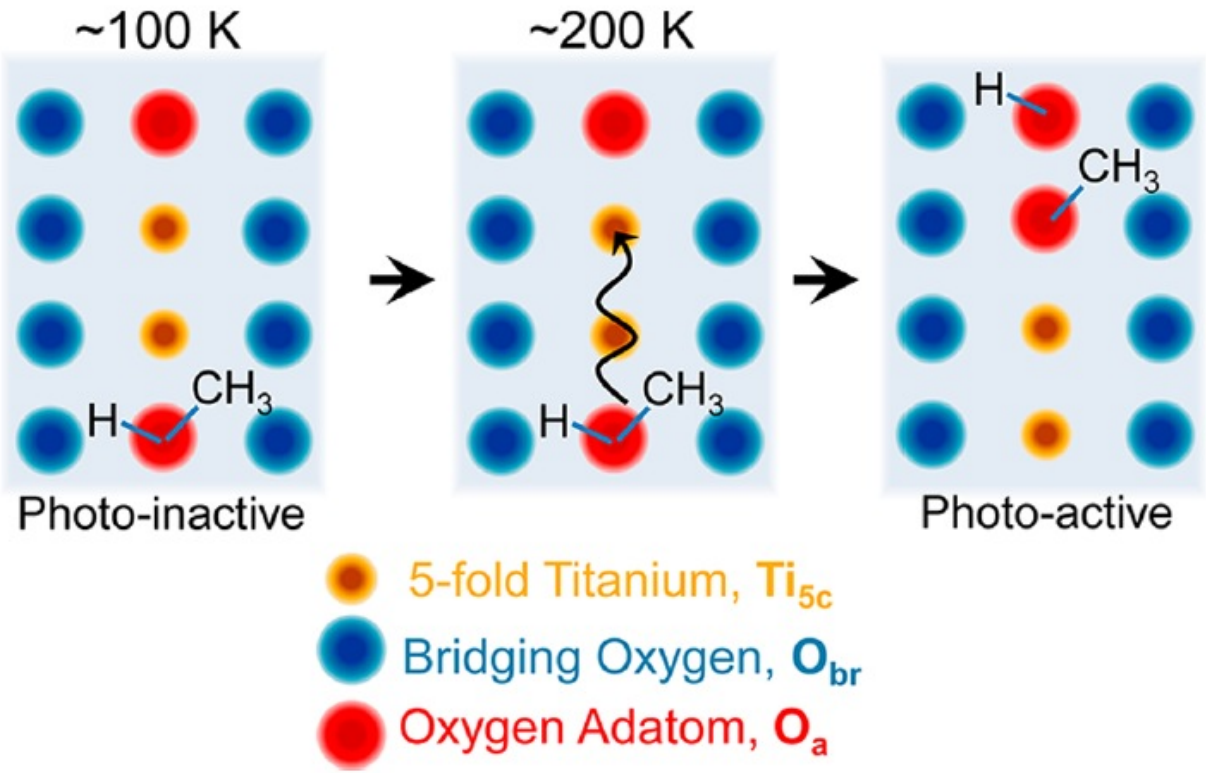
Water can undergo photodissociation under UV illumination, as shown in an STM study [1]



However, it is contradictory to the earlier experimental data: No hydrogen is formed upon illumination of rutile TiO2 in presence of water vapor at RT [2]

1 – S. Tan et al., JACS. 134:9978-9985 (2012)
2 – S. Sato, J. White, Chem Phys Lett, 72:83 (1980)

Methanol photochemistry – experimental data



Next step: methoxy dissociation:

$$CH_3O_{(a)} + O_{(a/br)} + h^+ \rightarrow H_2CO_{(a)} + OH_{(a/br)}$$

M. Shen, M. Henderson, JPCC, 116:25465 (2012)

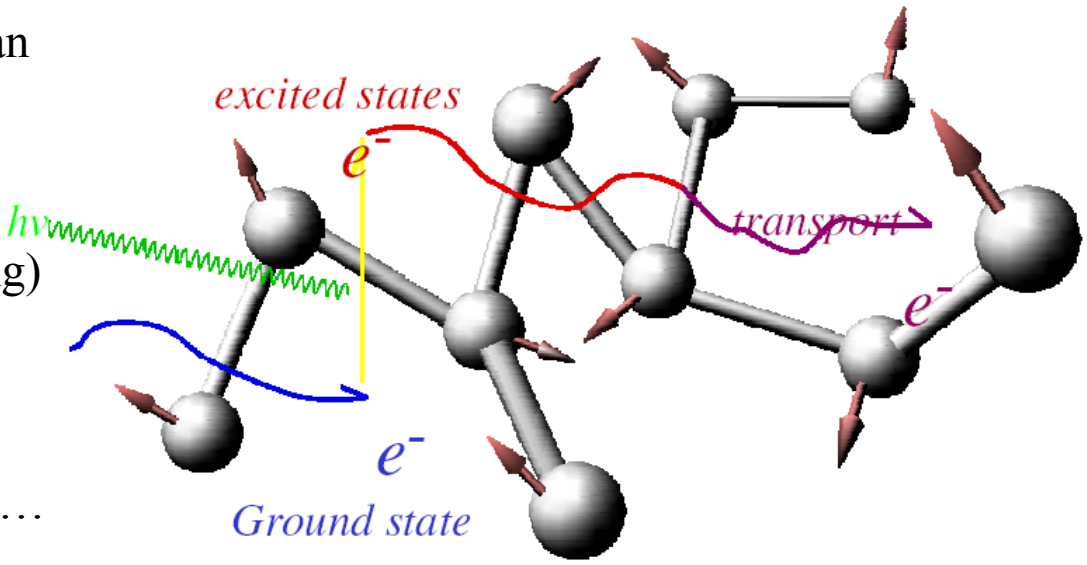
Main issue: coupled electron-ion dynamics

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).

Kohn-Sham Hamiltonian

Nuclei are assumed to be classical

$$\hat{H}_{KS}(t) = -\frac{\nabla_{\mathbf{r}}{}^2}{2} + v_{ext}(\mathbf{r},t) + v_{el-nuc}(\mathbf{r},\mathbf{R}(t)) + v_{Hartree}[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r},t)$$

This term contains all complex *e-e* interactions

$$v_{xc}[\rho](\mathbf{r},t) = v_{xc}[\rho(\mathbf{r}',t' \leq t)](\mathbf{r},t)$$

In principle, it depends on history

(In this work we will assume locality in time.)

TDDFT Ehrenfest dynamics

Nuclei are propagated classically:

$$M_J \frac{\partial^2 \mathbf{R}_J}{\partial t^2} = \langle \mathbf{F}_J \rangle = -\nabla_{\mathbf{R}_J} V_{KS}^J[\rho(\mathbf{r}, t)](\mathbf{R})$$

Forces are calculated according to:

Kunert, T. & Schmidt, R. Non-adiabatic quantum molecular dynamics: General formalism and case study h2+ in strong laser fields. *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics* **25**, 15–24 (2003).

Ojanperä, A., Havu, V., Lehtovaara, L. & Puska, M. Nonadiabatic ehrenfest molecular dynamics within the projector augmented-wave method. *The Journal of chemical physics* **136**, 144103 (2012).

Finite, localized, atom-centered basis

$$\phi_n(\mathbf{r}, \mathbf{R}, t) = \sum_k c_{nk}(t)\chi_k(\mathbf{r}, \mathbf{R}(t))$$

$$i\frac{\partial \phi_n}{\partial t} = \hat{H}_{KS}\phi_n$$

Overlap matrix: $S_{ij} = \langle \chi_i | \chi_j \rangle$

Forces

Hellmann-Feinman (HF) forces

(correct when φ_n are eigenstates!):

$$\mathbf{F}^{HF}_{el\,on\,atom\,J} = -\sum_n \langle \phi_n | \nabla_{\mathbf{R}_J} \hat{H}_{el} | \phi_n \rangle = -\nabla_{\mathbf{R}_J} E_{el}[\rho] + \sum_n f_n \epsilon_n \mathbf{c}_n^* \nabla_{\mathbf{R}_J} \mathbf{S} c_n$$

Energy-conserving (EC) forces:

$$\mathbf{F}^{EC}_{el\,on\,atom\,J} = -\nabla_{\mathbf{R}} E_{el}[\rho] + \sum_n f_n \mathbf{c}_n^* \left(\mathbf{H}\mathbf{S}^{-1} \langle \chi_i | \frac{\partial \chi_j}{\partial \mathbf{R}_J} \rangle + c.c. \right) \mathbf{c}_n$$

Propagation of electronic KS wavefunctions

$$i\frac{\partial \phi_n(t)}{\partial t} = \hat{H}_{KS}[\rho](t)\phi_n(t)$$

Solution:

$$\phi_n(t) = \mathcal{U}(t, t_0)\phi_n(t_0)$$

$$\mathcal{U}(t, t_0) = \mathcal{T}exp\left(-i\int_{t_0}^{t} \hat{H}_{KS}(t')dt'\right)$$

Propagation : finite time steps

$$\phi_n(t+\Delta t) = \mathcal{U}(t+\Delta t, t)\phi_n(t)$$

$$\mathcal{U}(t+\Delta t, t) \approx exp\left\{-i\Delta t \hat{H}_{KS}\left(t+\frac{\Delta t}{2}\right)\right\}$$

$\hat{H}_{KS}\left(t+\frac{\Delta t}{2}\right)$: obtained self-consistently, by calculating hamiltonian at the end of each time-step

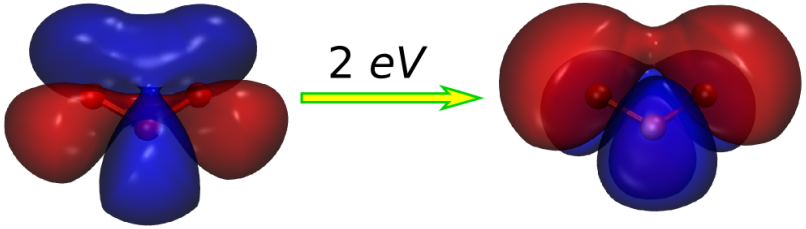
Ehrenfest dynamics scheme

1. System is heated to desired temperature
2. Electronic excitation (using ΔSCF method)
3. Electron propagation with TDDFT (to self-consistency)
4. Calculation of forces on nuclei
5. Nuclei propagation with Verlet MD
6. Go to 3.

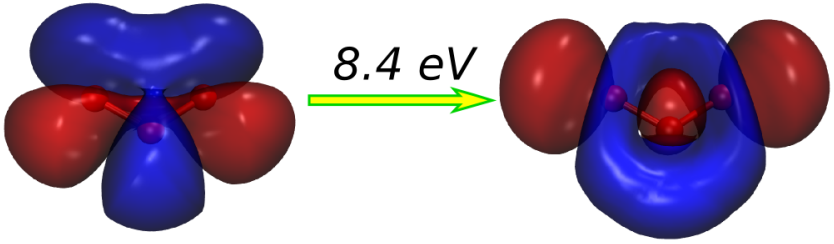
Meng, S. & Kaxiras, E. Real-time, local basis-set implementation of time-dependent density functional theory for excited state dynamics simulations. *The Journal of chemical physics* **129**, 054110 (2008).

Example: ozone photolysis

- Excitation HOMO to LUMO: slow dissociation

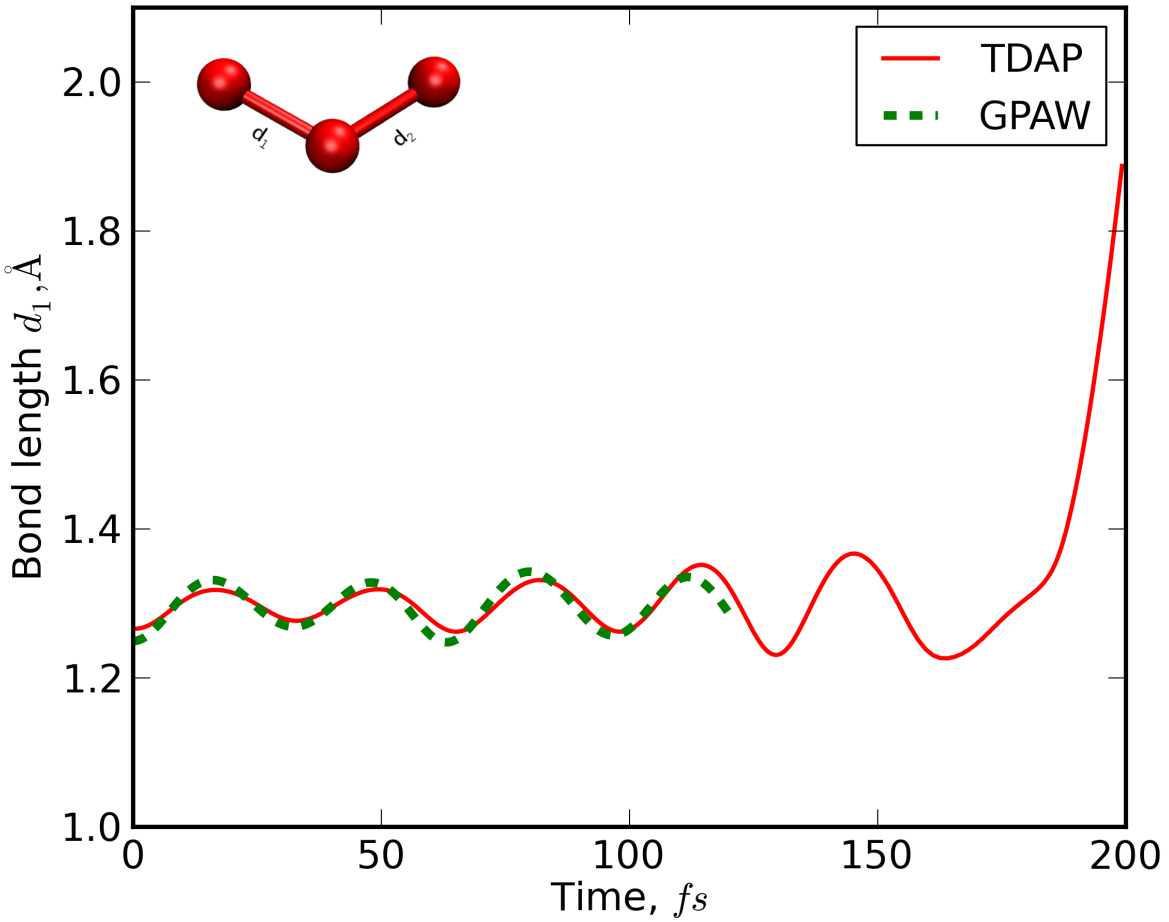


- Excitation HOMO to LUMO+1: quick dissociation



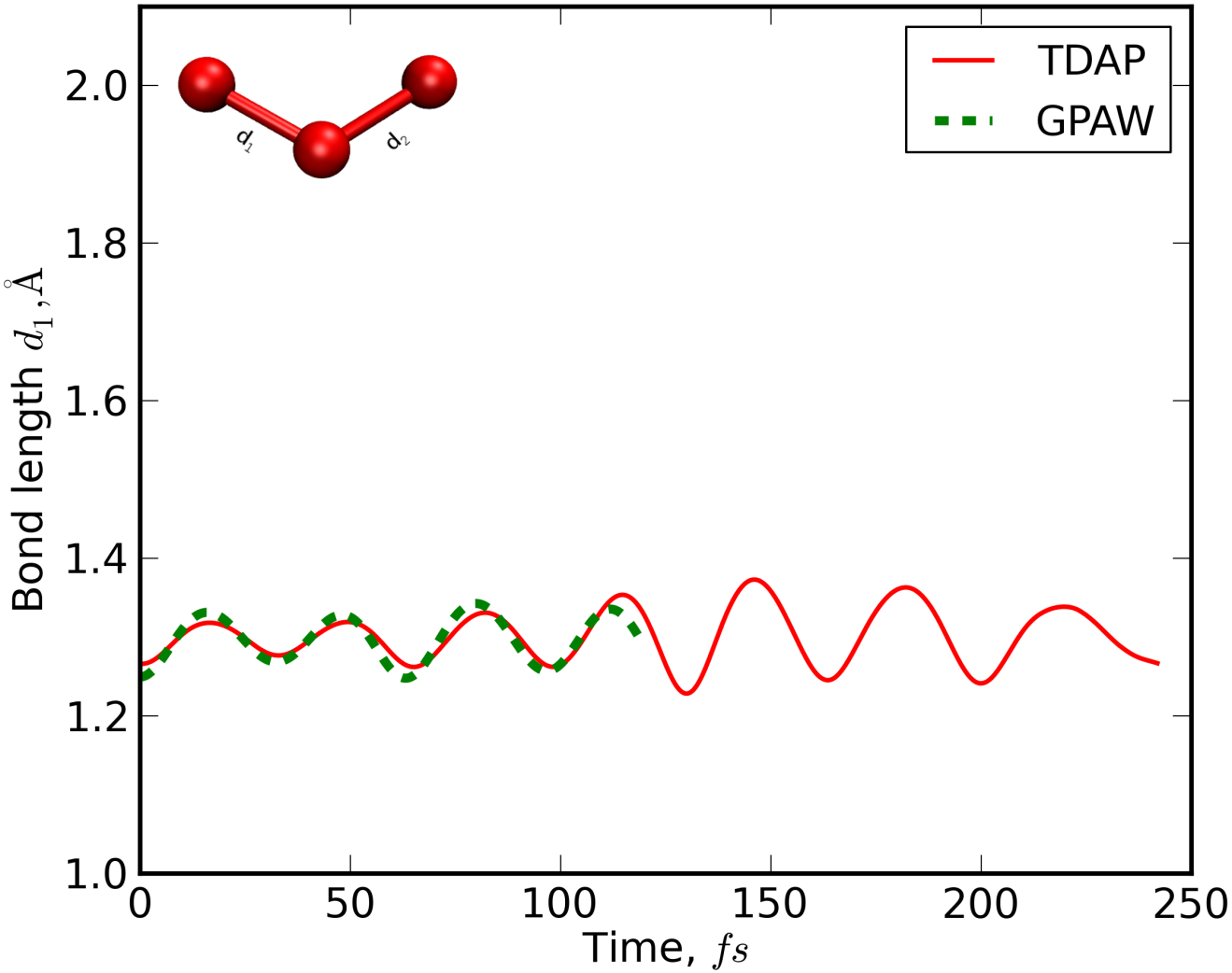
Matsumi, Y. & Kawasaki, M. Photolysis of atmospheric ozone in the ultraviolet region. *Chemical reviews* **103**, 4767–4782 (2003).

Ozone 1st excited state trajectory: HF forces

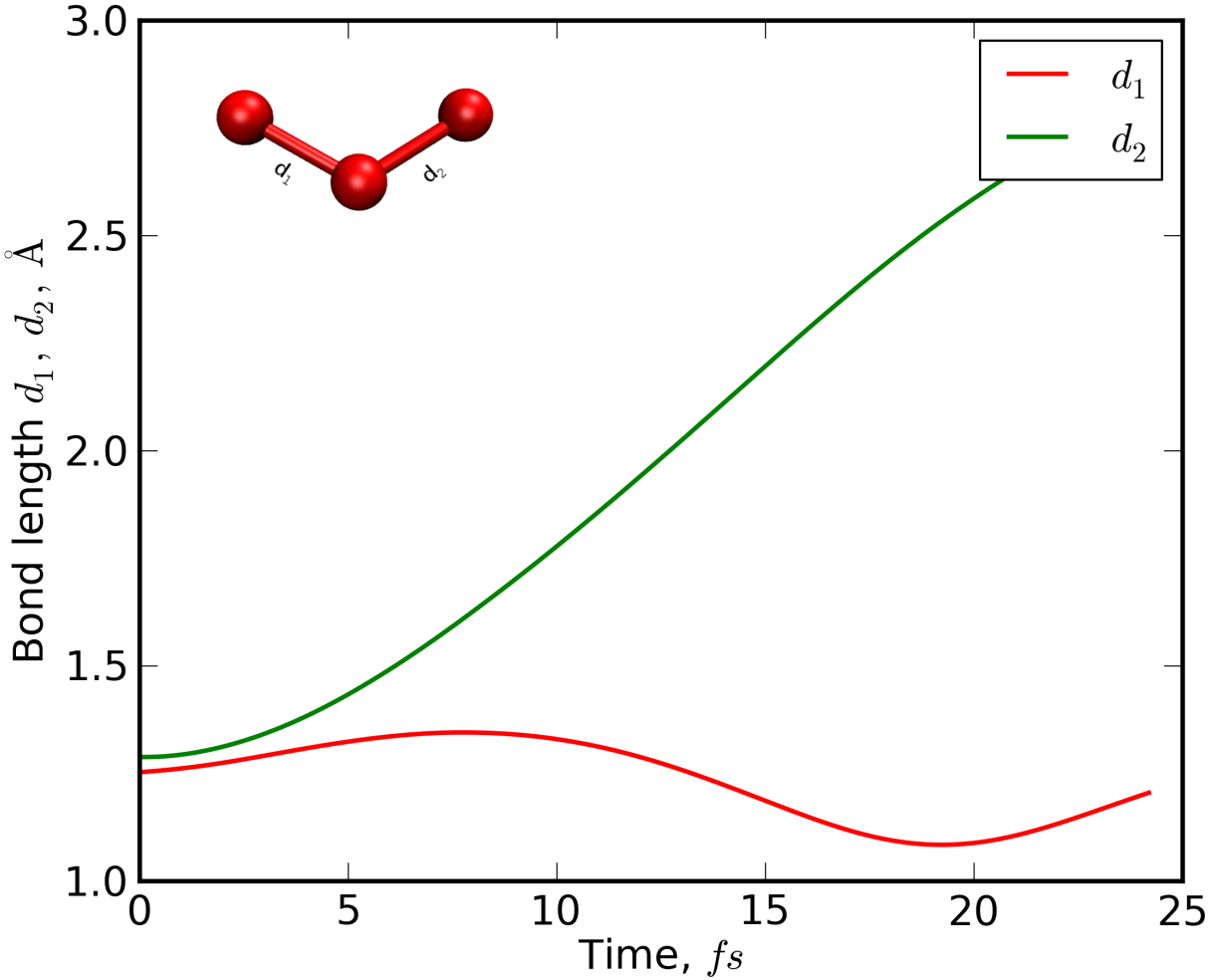


- GPAW computation time 37 days (4 cores)
- TDAP: 1 hour
- Time step: 5 attoseconds both
- T=0K

Ozone benchmark: importance of accurate forces – EC vs. HF



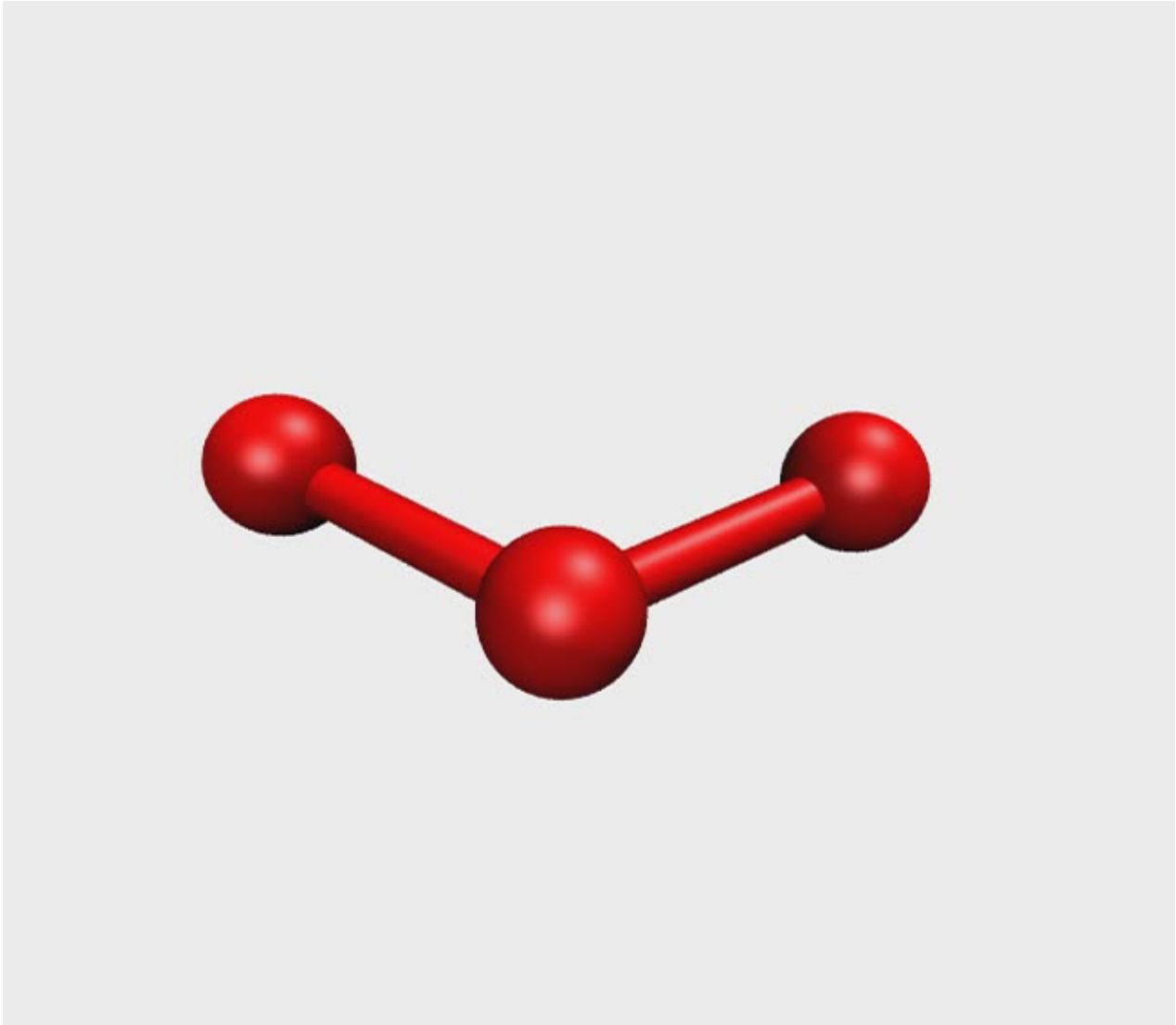
2nd excited state trajectory: ozone dissociates with either type of forces



2^{nd} excited state trajectory

- Movie:

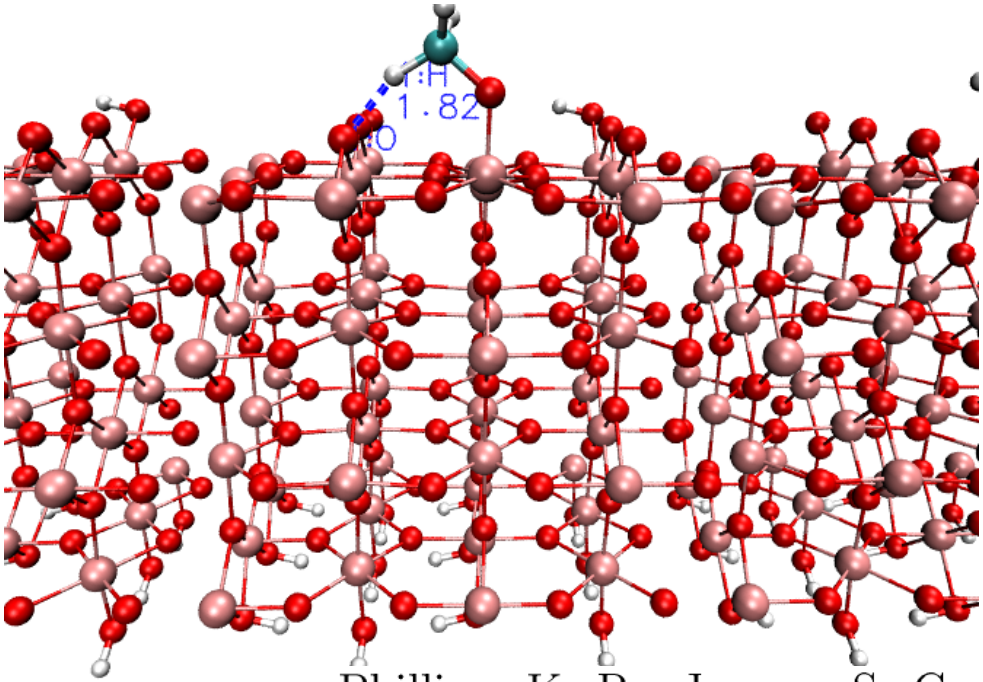
o3split.mov



Methoxy splitting on TiO_2 surface

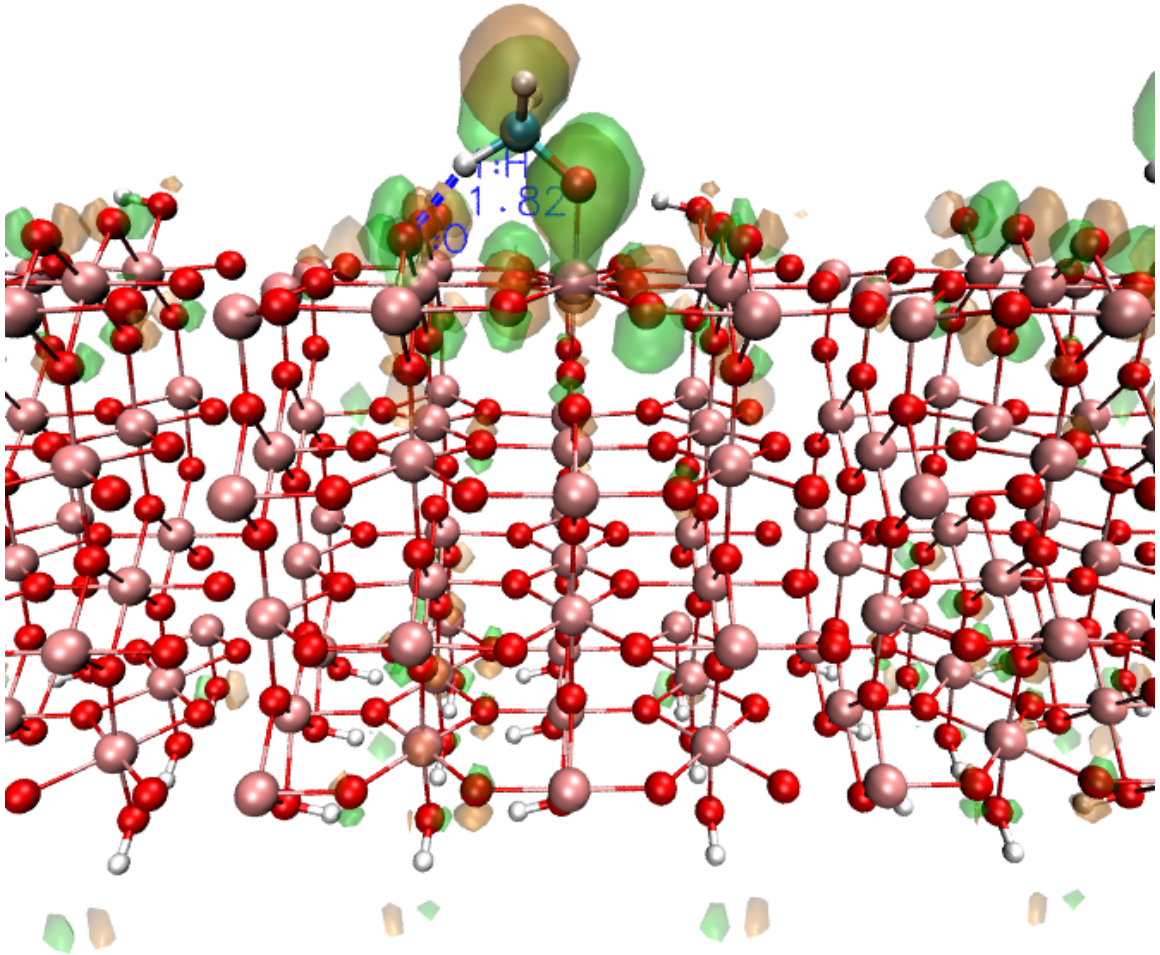
- Formaldehyde was photochemically produced from methoxy on TiO_2 (110) surface

$$CH_3O_{(a)} + O_{(a/br)} + h^+ \rightarrow H_2CO_{(a)} + OH_{(a/br)}$$

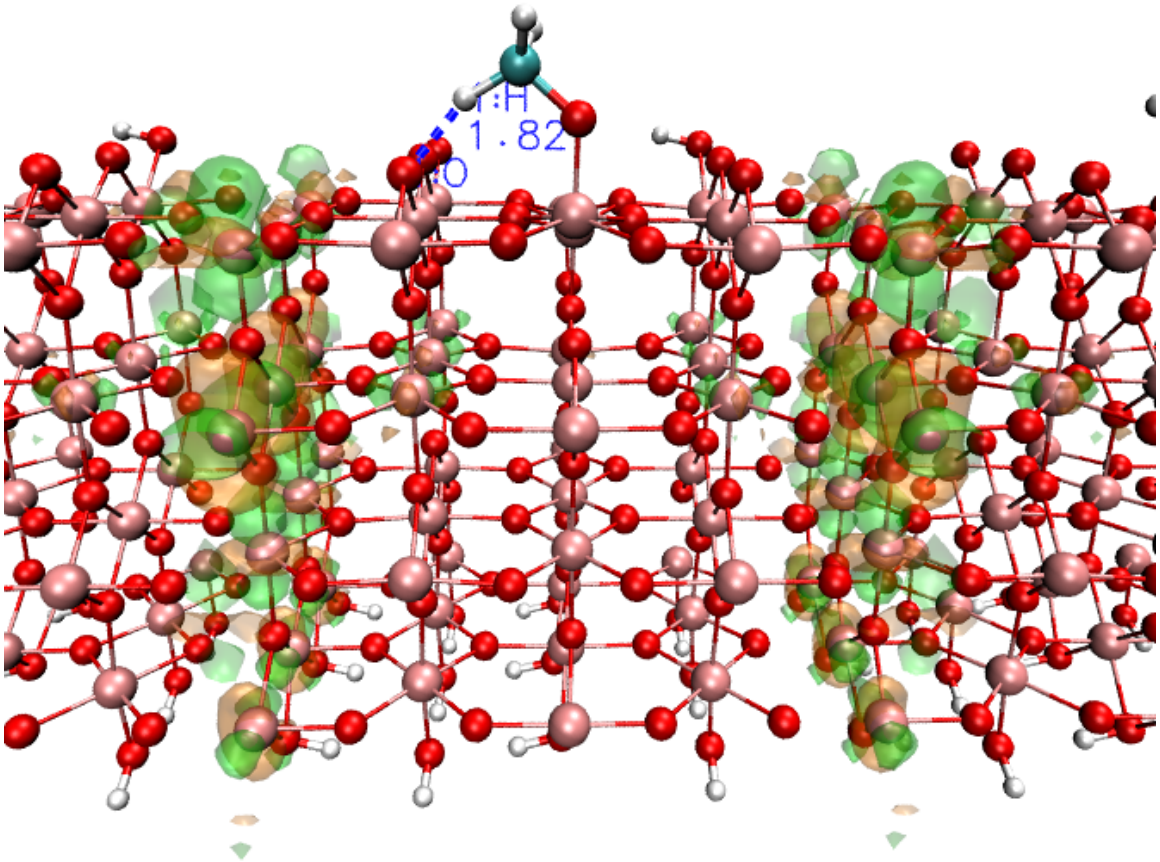


Phillips, K. R., Jensen, S. C., Baron, M., Li, S.-C. & Friend, C. M. Sequential photo-oxidation of methanol to methyl formate on TiO2 (110). *Journal of the American Chemical Society* **135**, 574–577 (2013).

Hole: HOMO-5 State



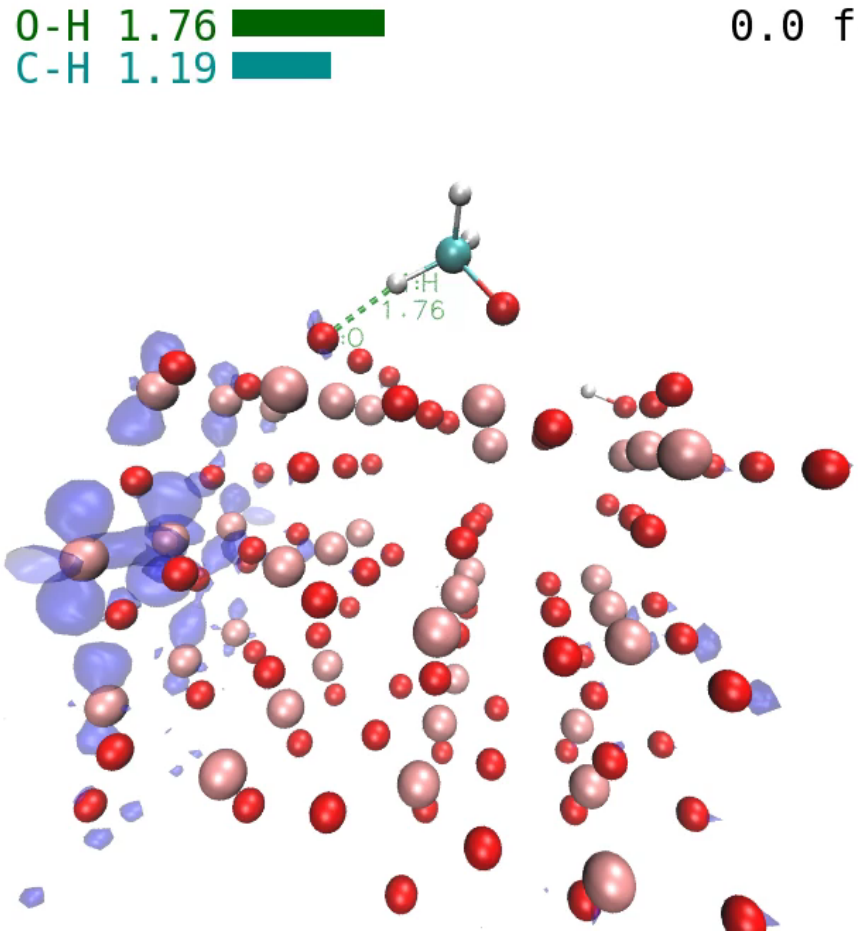
Electron: LUMO state

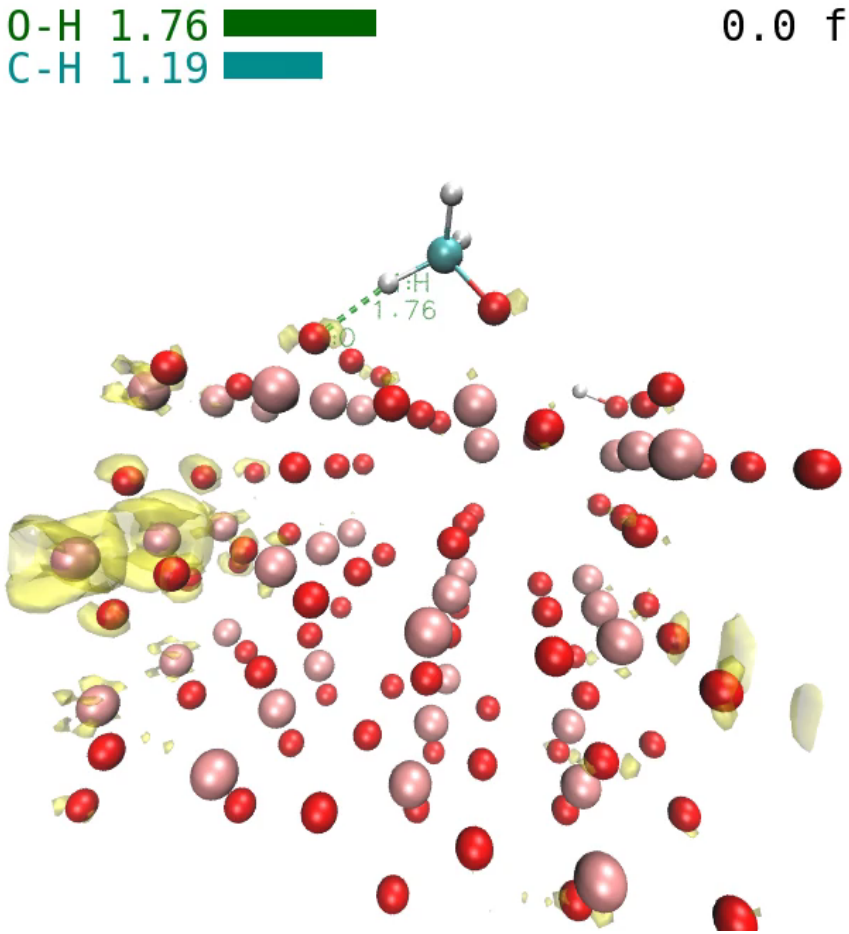


Computational setup

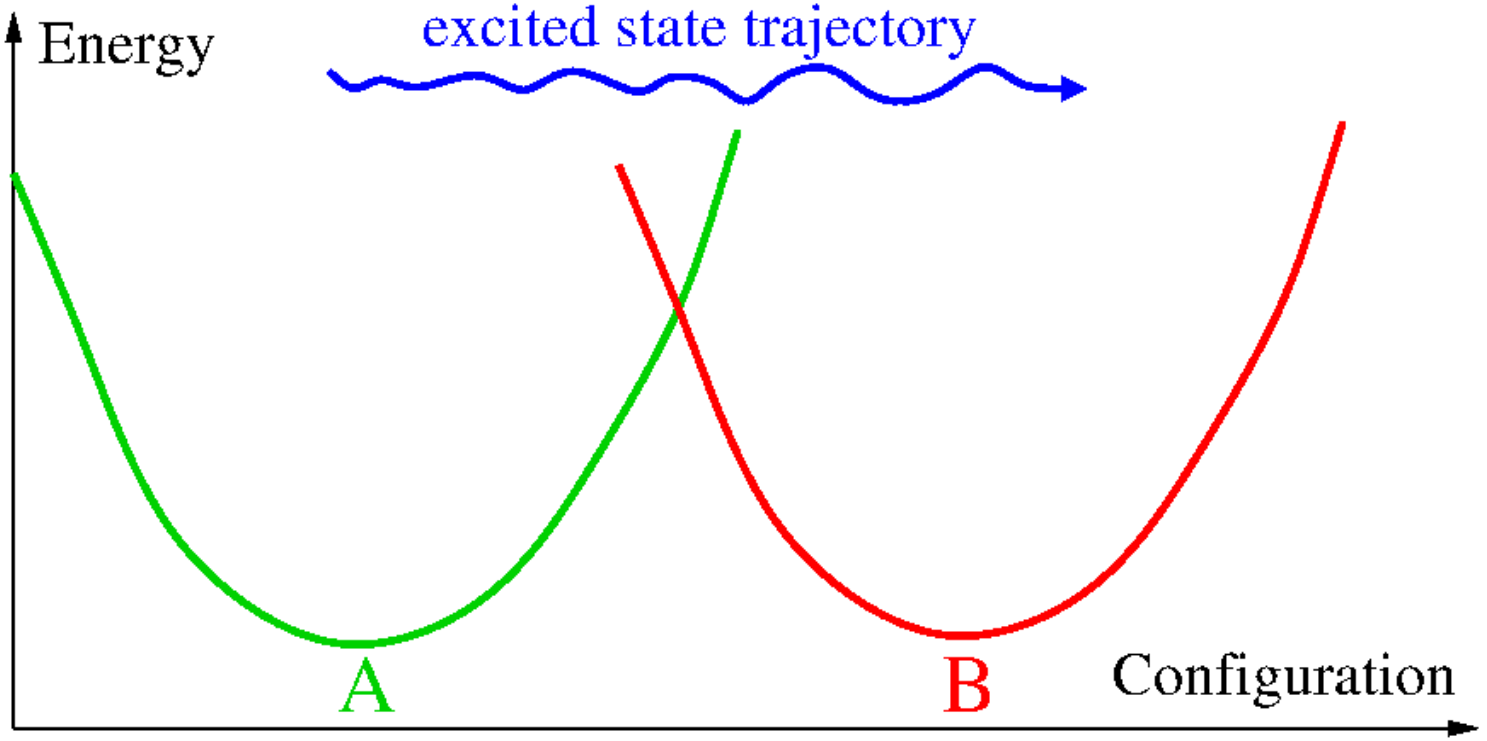
- System was heated to 200K
- Excitation modeled by promoting electron from
  - HOMO-5 to LUMO: **no splitting** after ~200 fs
  - HOMO to LUMO : **splitting** after ~70 fs
- In experiment 3-6 eV UV band was used
- The excitation was about 2.9 eV

TDDFT trajectory: charge density **difference** from **electronic** ground state (identical ionic)



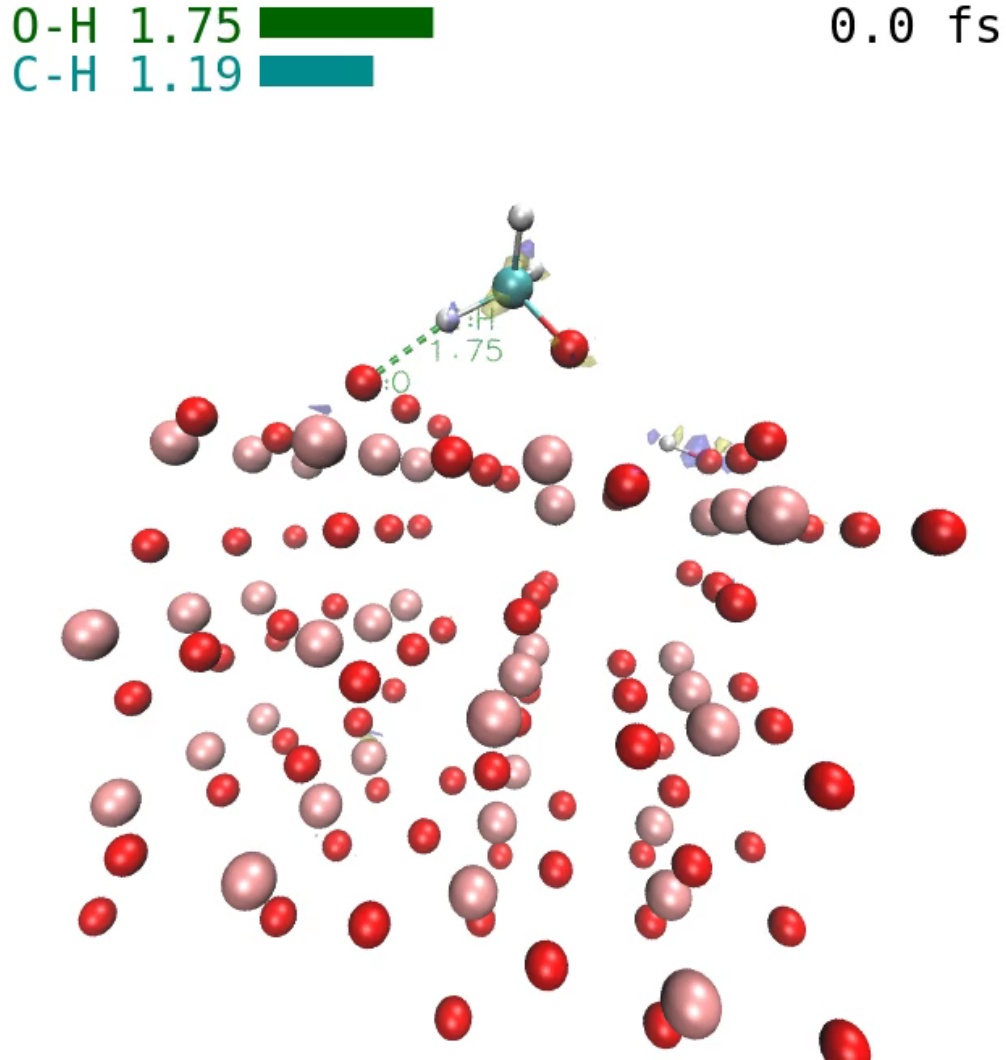


A simple physical picture for excited state dynamics:

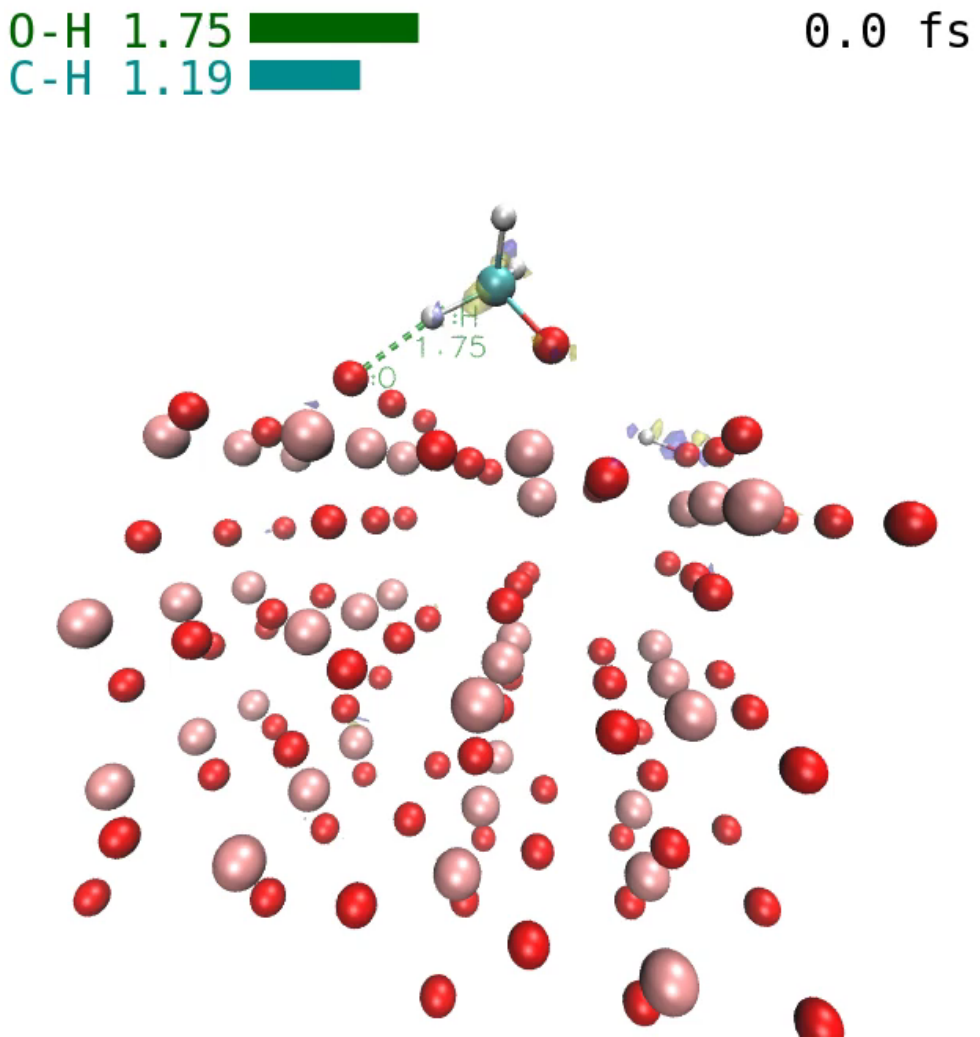


the “Birthday effect”

TDDFT trajectory:
dρ/dt of **excited** state electronic density (excluding changes from atomic motion)



TDDFT trajectory: dρ/dt of **ground** state electronic density (excluding changes from atomic motion)



Thanks for your attention!

Thanks for the hospitality to the Thomas Young Center, UCL, Prof.s Xiao Guo, Chris Pickard