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Spring College on Computational Nanoscience

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Time-dependent Density Functional Theory and its Applications to Linear and Non-linear Optical Properties

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INFM

Monday, May 24th, 2010

Overview

The basics

- From the ground-state to excited states: The Runge-Gross theorem

How TDDFT is used in practice

- A first look at TDDFT in practice: Photochemistry
- TDDFT for optical spectra
- Some applications in next generation solar cells

Framework: What is TDDFT all about?

1964: Hohenberg and Kohn: Density Functional Theory (DFT)

work in terms of electron density (instead of many-particle wavefunctions)

DFT is a **ground state** theory

1984: Runge and Gross: **Time-Dependent** Density Functional Theory (TDDFT)

$$\text{Given } |\Psi(t=0)\rangle : V(\boldsymbol{r},t) \Leftrightarrow n(\boldsymbol{r},t)$$

like DFT, TDDFT is **formally exact**

Recall: Basic ground-state DFT

For practical calculations: Kohn-Sham framework

$$n_\sigma(\boldsymbol{r}) = \sum_i^{N_\sigma} \left|\phi_{i\sigma}(\boldsymbol{r})\right|^2$$

The density is written in terms of Kohn-Sham orbitals which satisfy

$$\left[-\frac{\nabla^2}{2} + v_\sigma^{KS}\left[n_\uparrow, n_\downarrow\right](\boldsymbol{r})\right]\phi_{i\sigma}(\boldsymbol{r}) = \epsilon_{i\sigma}\phi_{i\sigma}(\boldsymbol{r})$$

$$\boxed{\begin{aligned} F\left[n_\uparrow, n_\downarrow\right] &= T_s\left[n_\uparrow, n_\downarrow\right] + E_{Hartree} + E_{xc}\left[n_\uparrow, n_\downarrow\right] \\ E_{Hartree} &= \frac{1}{2}\int d^3r \int d^3r' \frac{n(\boldsymbol{r})\, n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \\ E_{xc}^{LDA} &= \int d^3r\, n(\boldsymbol{r})\epsilon_{xc}^{unif}\left(n_\uparrow(\boldsymbol{r}), n_\downarrow(\boldsymbol{r})\right) \end{aligned}}$$

The Runge-Gross Theorem

Generalizing the HK theorem to time-dependent systems

There exists a one-to-one correspondence between the external v(r,t) and the electron density n(r,t), for systems evolving from a fixed many-body state.

Proof:

$$\begin{aligned} |\Psi(t_0)\rangle &= |\Psi'(t_0)\rangle \equiv |\Psi_0\rangle \\ n(\boldsymbol{r},t_0) &= n'(\boldsymbol{r},t_0) \equiv n^0(\boldsymbol{r}) \\ \boldsymbol{j}(\boldsymbol{r},t_0) &= \boldsymbol{j}'(\boldsymbol{r},t_0) \equiv \boldsymbol{j}^0(\boldsymbol{r}) \end{aligned}$$

Step 1: Different potentials v and v’ yield different current densities j and j’

Step 2: Different current densities j and j’ yield different densities n and n’

$$v(\boldsymbol{r},t) \neq v'(\boldsymbol{r},t) + c(t) \qquad \Rightarrow \qquad n(\boldsymbol{r},t) \neq n'(\boldsymbol{r},t)$$

Using TDDFT in practice

Finding an equivalent of the Kohn-Sham formalism

$$\mathrm{i}\frac{\partial}{\partial t}\varphi_{i\sigma}(\boldsymbol{r},t) = \hat{H}_\sigma^{\mathrm{KS}}(\boldsymbol{r},t)\varphi_{i\sigma}(\boldsymbol{r},t)$$

With a time-dependent Hamiltonian:

$$\hat{H}_\sigma^{\mathrm{KS}}(\boldsymbol{r},t) = -\frac{\nabla^2}{2} + v_\sigma^{\mathrm{KS}}[n_\uparrow, n_\downarrow](\boldsymbol{r},t)$$

Density and potentials are now defined like:

$$n_\sigma(\boldsymbol{r},t) = \sum_i^{N_\sigma} |\varphi_{i\sigma}(\boldsymbol{r},t)|^2$$

$$v_\sigma^{\mathrm{KS}}[n_\uparrow, n_\downarrow](\boldsymbol{r},t) = v_\sigma(\boldsymbol{r},t) + \int \mathrm{d}^3r' \, \frac{n(\boldsymbol{r}',t)}{|\boldsymbol{r}-\boldsymbol{r}'|} + v_\sigma^{\mathrm{xc}}[n_\uparrow, n_\downarrow](\boldsymbol{r},t)$$

Which functional to use ?

The easiest and probably most widely used functional is the

Adiabatic Local Density Approximation (ALDA)

$$v_\sigma^{\mathrm{xc\ ALDA}}(\boldsymbol{r},t) = \frac{\partial}{\partial n_\sigma}\left[n\,\varepsilon_{\mathrm{xc}}^{\mathrm{unif}}(n_\uparrow,n_\downarrow)\right]\Big|_{n_\alpha=n_\alpha(\boldsymbol{r},t)}$$

TDDFT in real time:

(1996:Bertsch; 2001: Octopus code)

- Consider a general time-dependent perturbation:

$$V_{pert}(\boldsymbol{r}, t)$$

- Obtain orbitals, charge density, and potentials by solving the Schrödinger equation explicitly in real time:

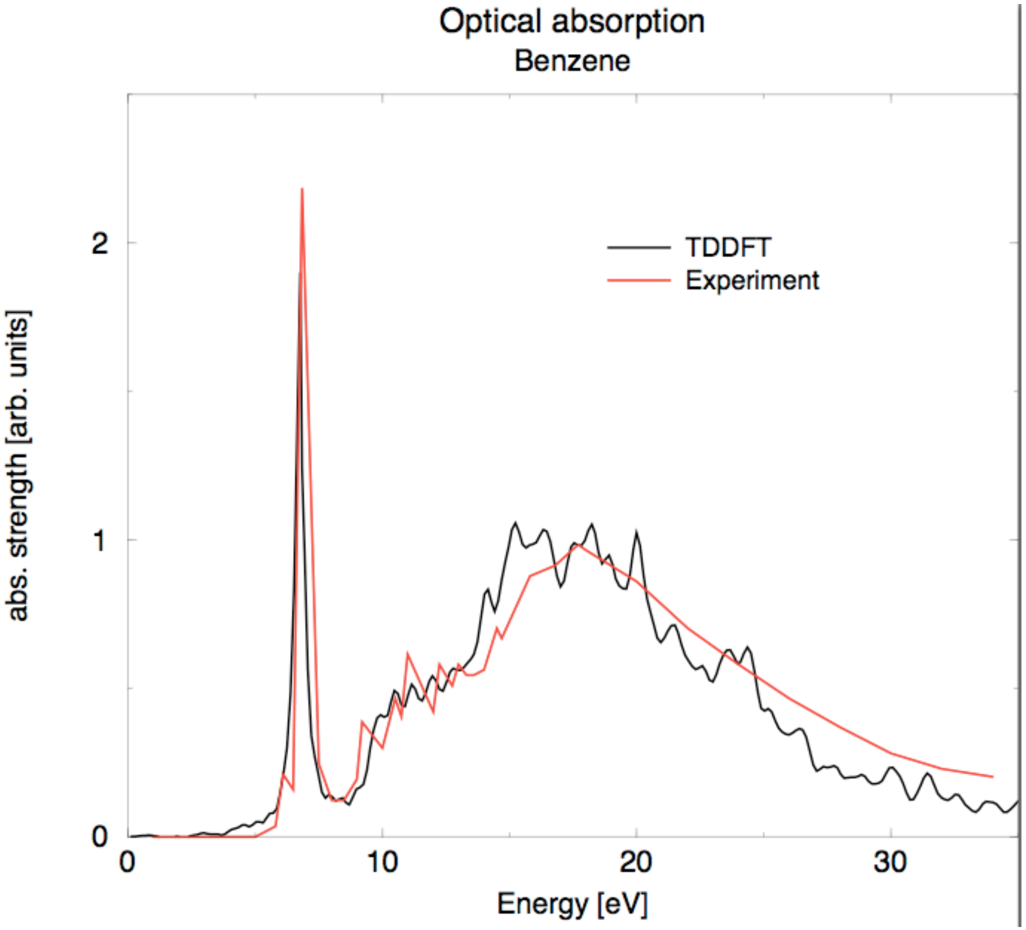
$$\psi_j(t+\Delta) = \exp\left(-iH(t+\frac{\Delta}{2})\Delta\right)\psi_j(t)$$

(*Nonlinear* TD Schrödinger equation)

- Can be used for *linear response* calculations, or for general TD *non-linear* problems.

How well does it work?

Example: Optical absorption of Benzene



Experimental data from:
Koch, E.E., Otto, A.
Chem. Phys. Lett. **12**, 476 (1972)

A first application: Photochemistry

- Recent experimental progress made it possible to produce ultra-short intense laser pulses (few fs)
- This allows one to probe bond breaking/formation, charge transfer, etc. on the relevant time scales

- Nonlinear real-time TDDFT calculations can be a valuable tool to understand the physics of this kind of probe.

- Visualizing chemical bonds: Electron localization function

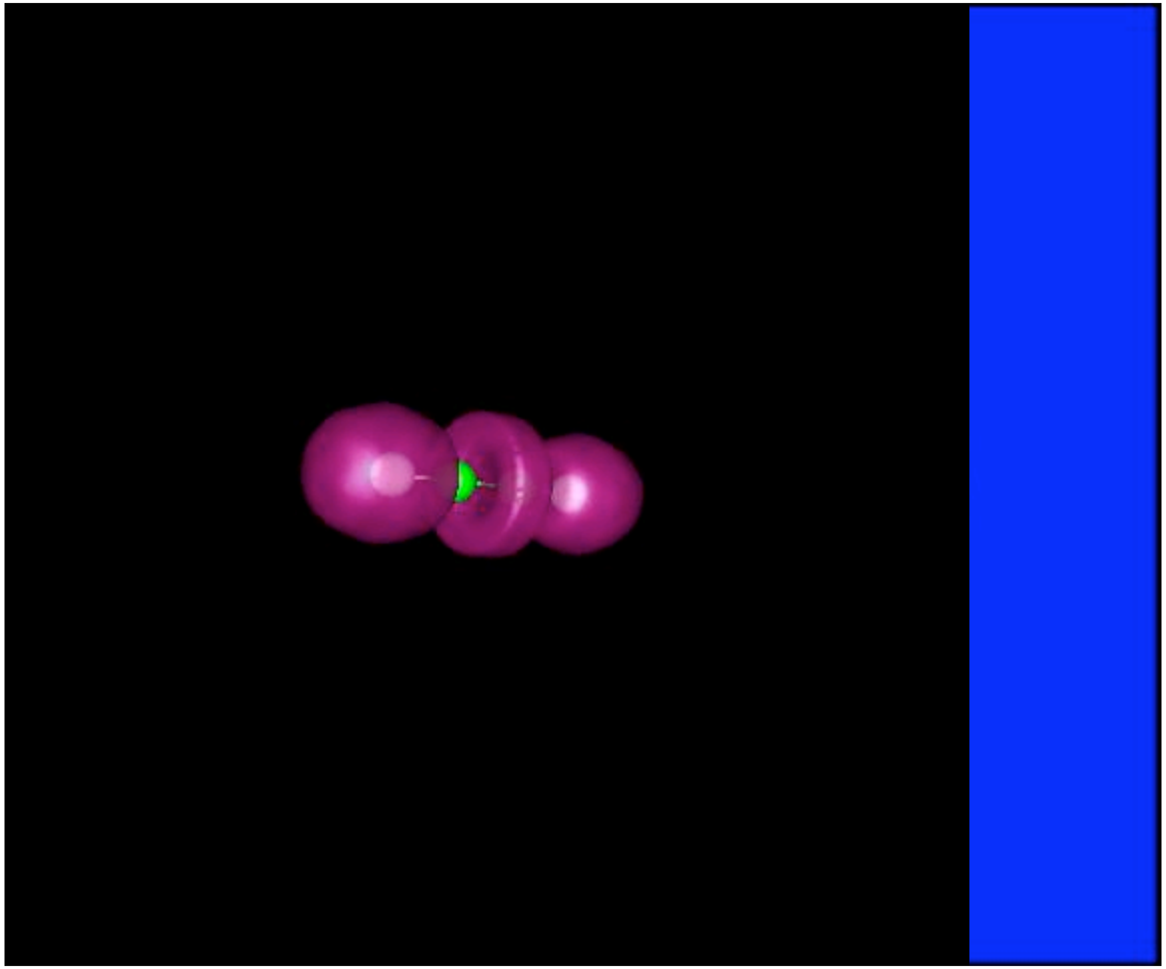
Nonlinear optical response

- Electron localization function:

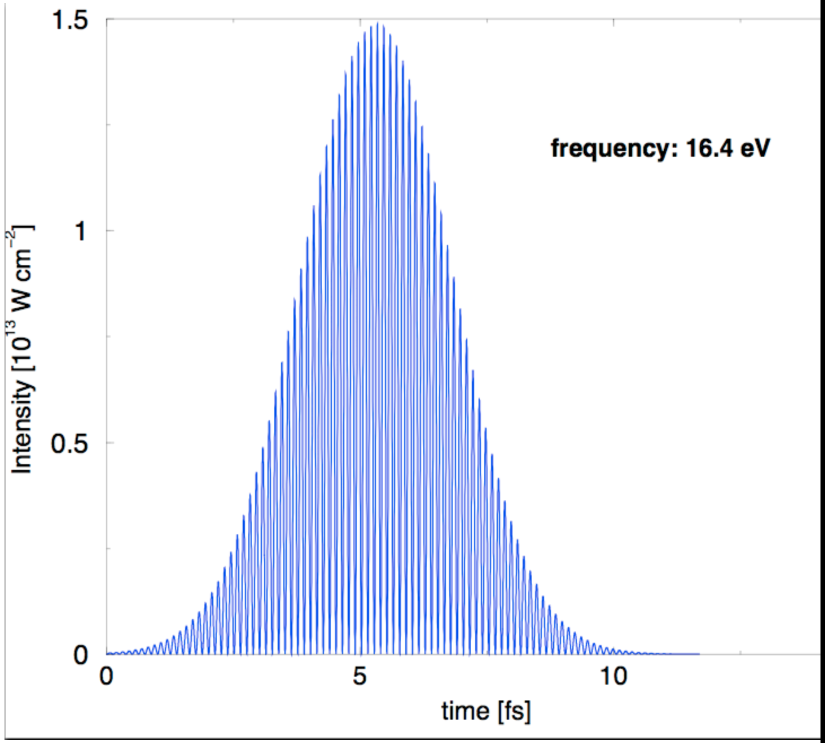
$$ELF(\boldsymbol{r},t) = \frac{1}{1+[D_\sigma(\boldsymbol{r},t)/D_\sigma^0(\boldsymbol{r},t)]^2}$$

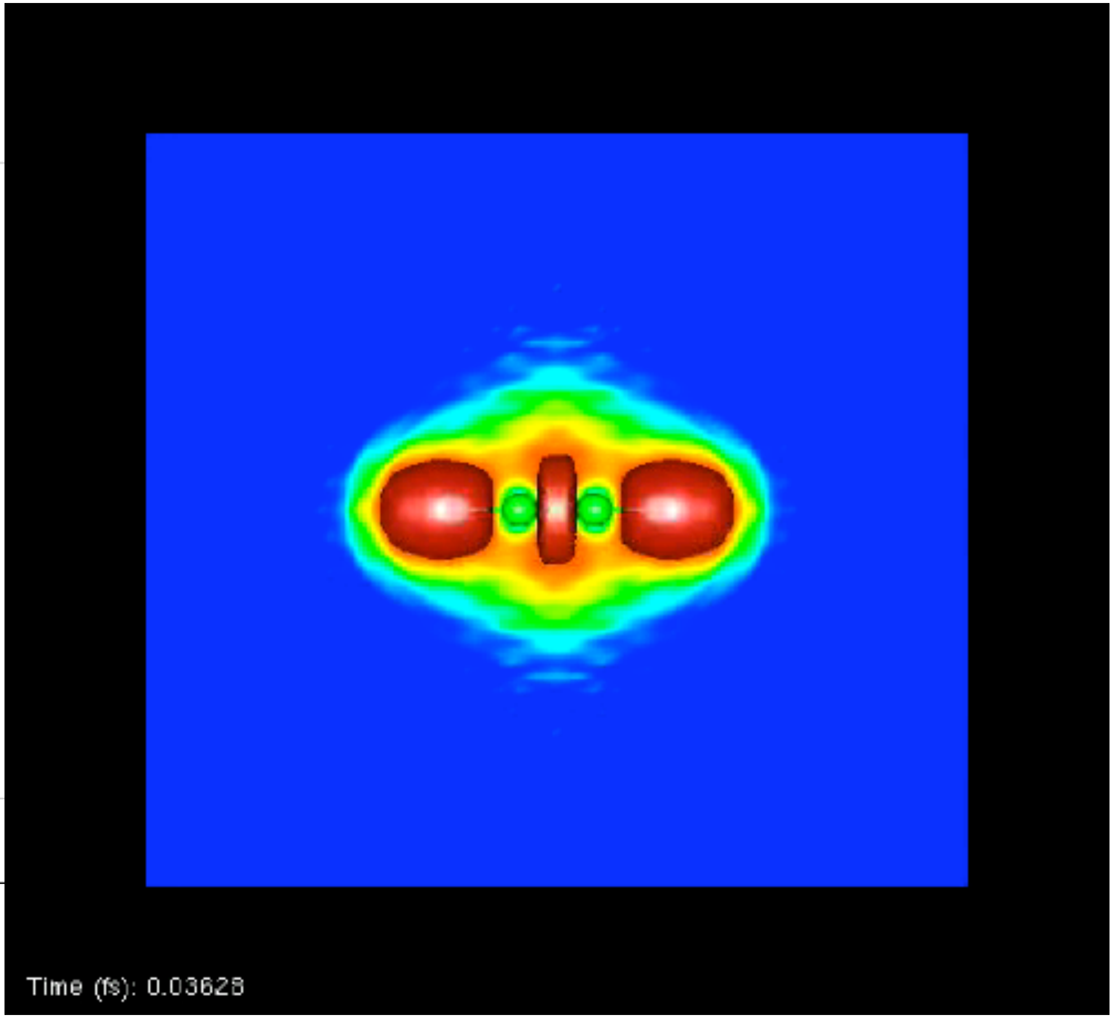
$$D_\sigma(\boldsymbol{r},t) = \tau_\sigma(\boldsymbol{r},t) - \frac{1}{4}\frac{[\nabla n_\sigma(\boldsymbol{r},t)]^2}{n_\sigma(\boldsymbol{r},t)} - \frac{j_\sigma^2(\boldsymbol{r},t)}{n_\sigma(\boldsymbol{r},t)}$$

Example: Ethyne C_2H_2



Example: Ethyne C_2H_2





How can we calculate optical spectra?

Consider a perturbation δV applied to the ground-state system:

$$\delta n(r,t) = \int d^3r' dt' \chi(r,r';t-t')\,\delta V(r',t')$$

The induced dipole is given by the induced charge density:

$$d(t) = \int d^3r\, \delta n(r,t)\hat{r}$$

Consider the perturbation due to an electric field:

$$\delta V(r,t) = -eE_{ext}(t)\cdot\hat{r}$$

How can we calculate optical spectra?

The dipole susceptibility is then given by:

$$d(t) = \int dt' \, \alpha(t - t') \, E_{ext}(t')$$

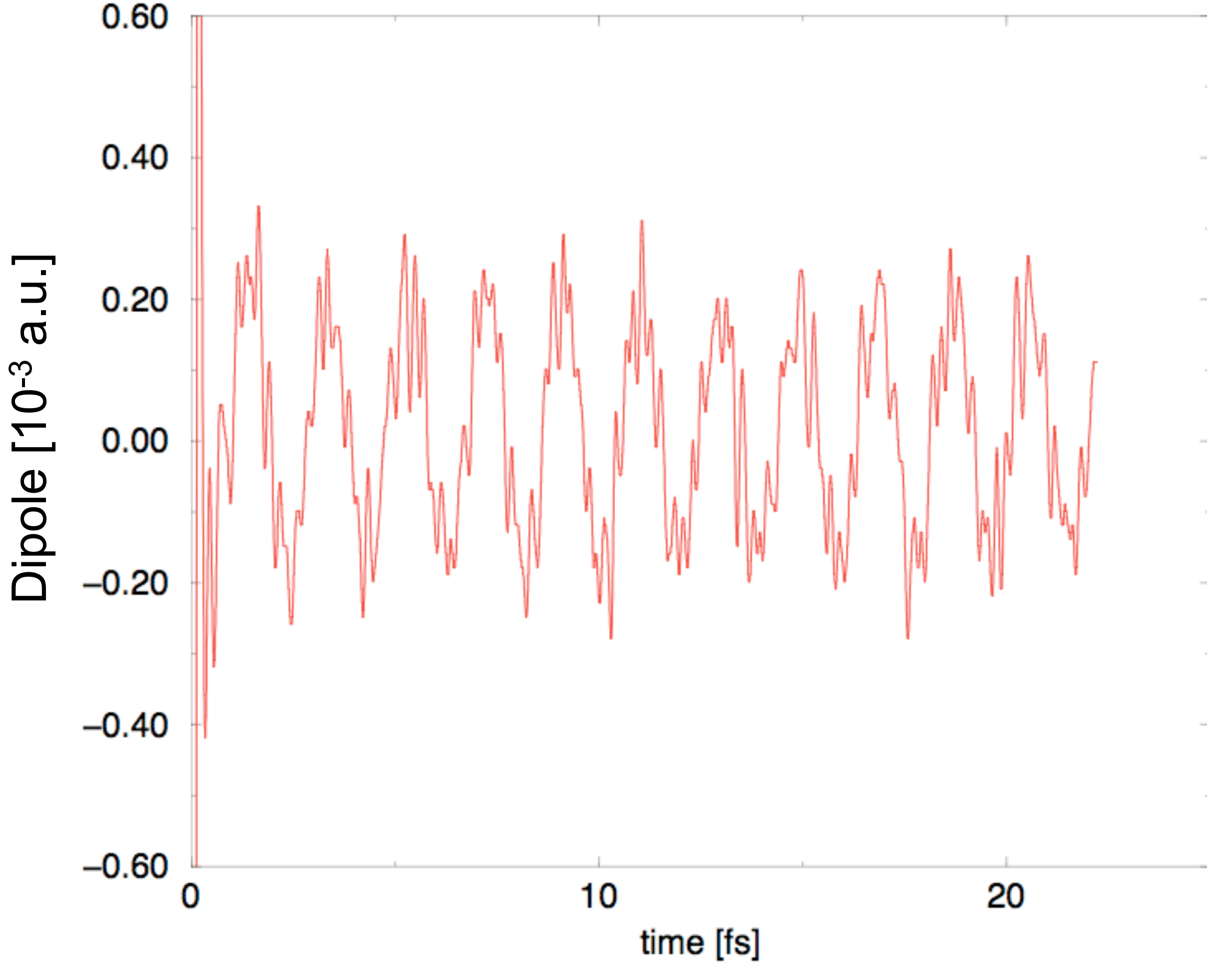
The experimentally measured strength function S is related to the Fourier transform of α:

$$S(\omega) = \frac{2m}{\pi e^2 \hbar} \omega \, \mathrm{Im} \, \alpha(\omega)$$

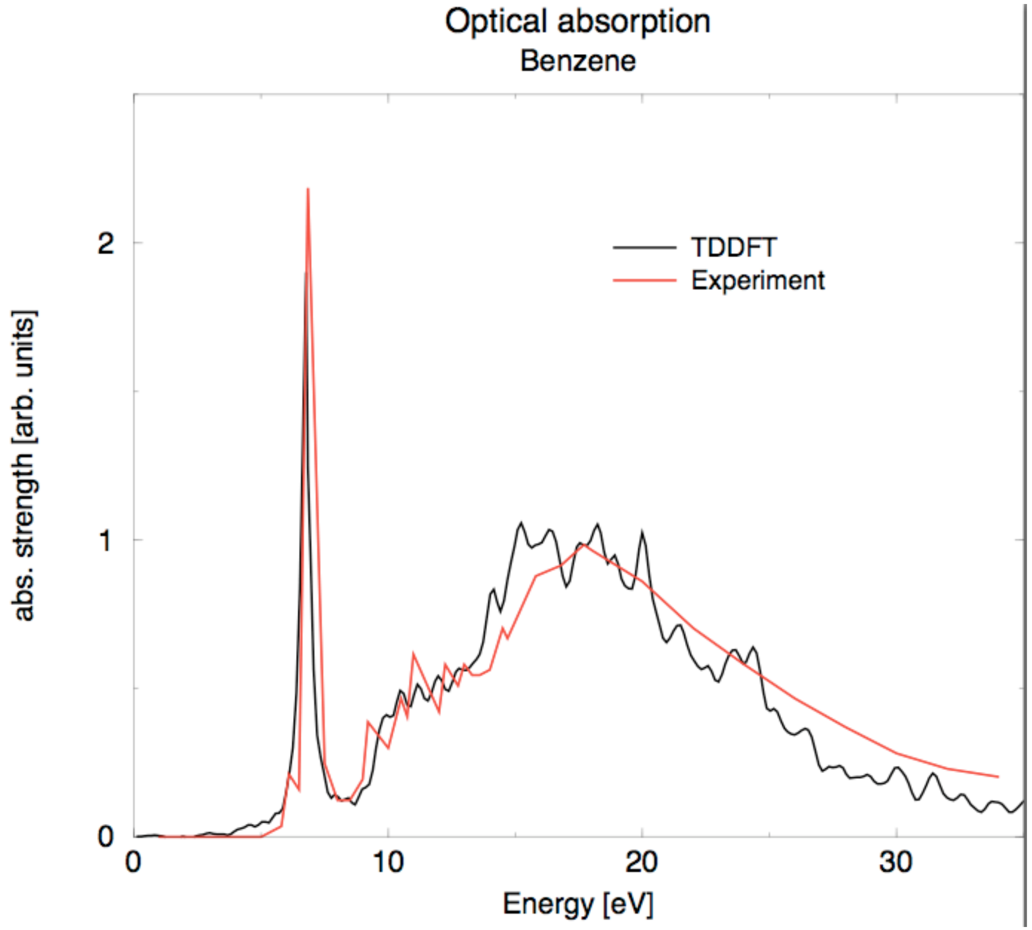
In practice: We take an E-field pulse $E_{ext} = E_0 \, \delta(t)$, calculate d(t), and obtain the spectrum $S(\omega)$ by calculating

$$d(\omega) = \int_0^\infty dt \, e^{i\omega t - \delta t} \, d(t)$$

A typical dipole-function d(t) …

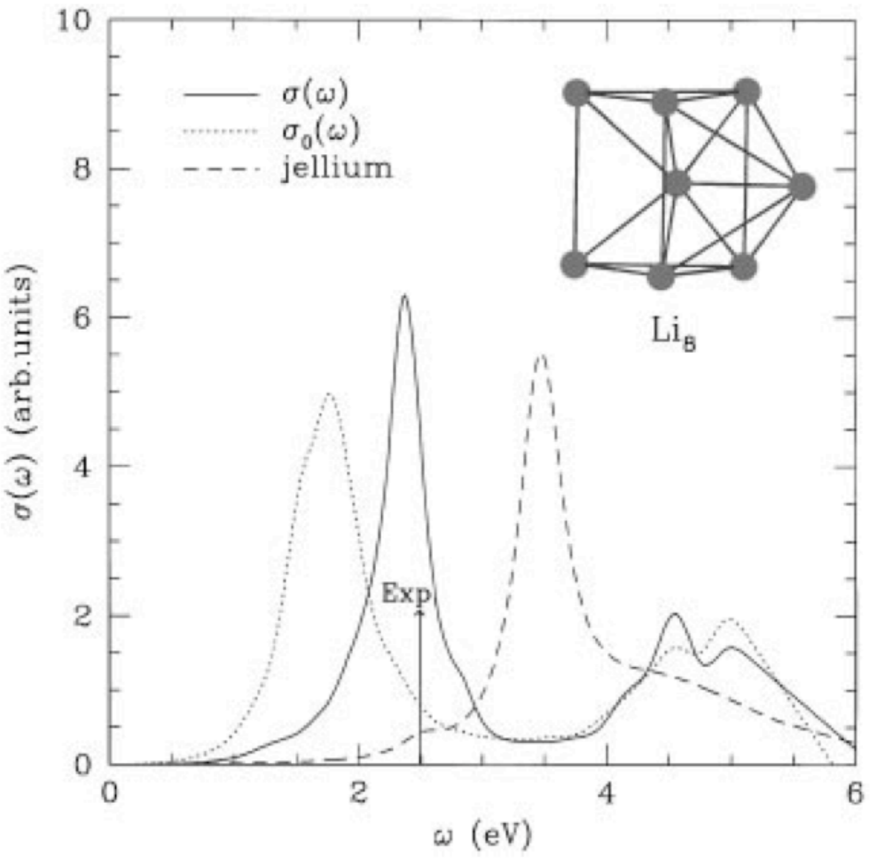


… and the resulting spectrum



How good are ALDA-TDDFT spectra in nanosystems?

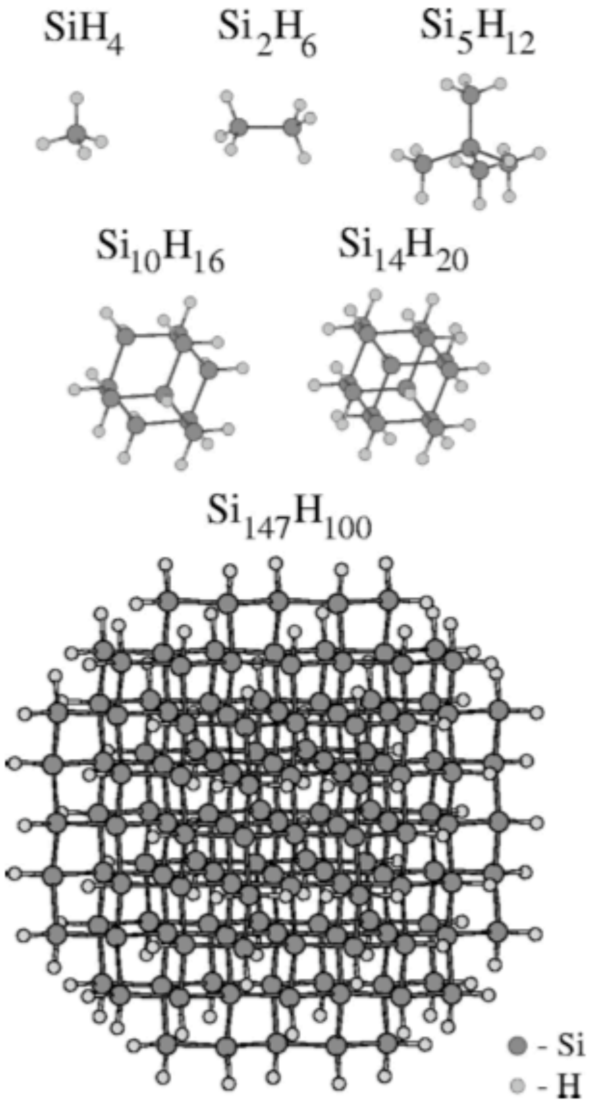
Metallic nanoclusters:



From: A. Rubio et al.
Phys. Rev. Lett. **77**, 247 (1996)

How good are ALDA-TDDFT spectra in nanosystems?

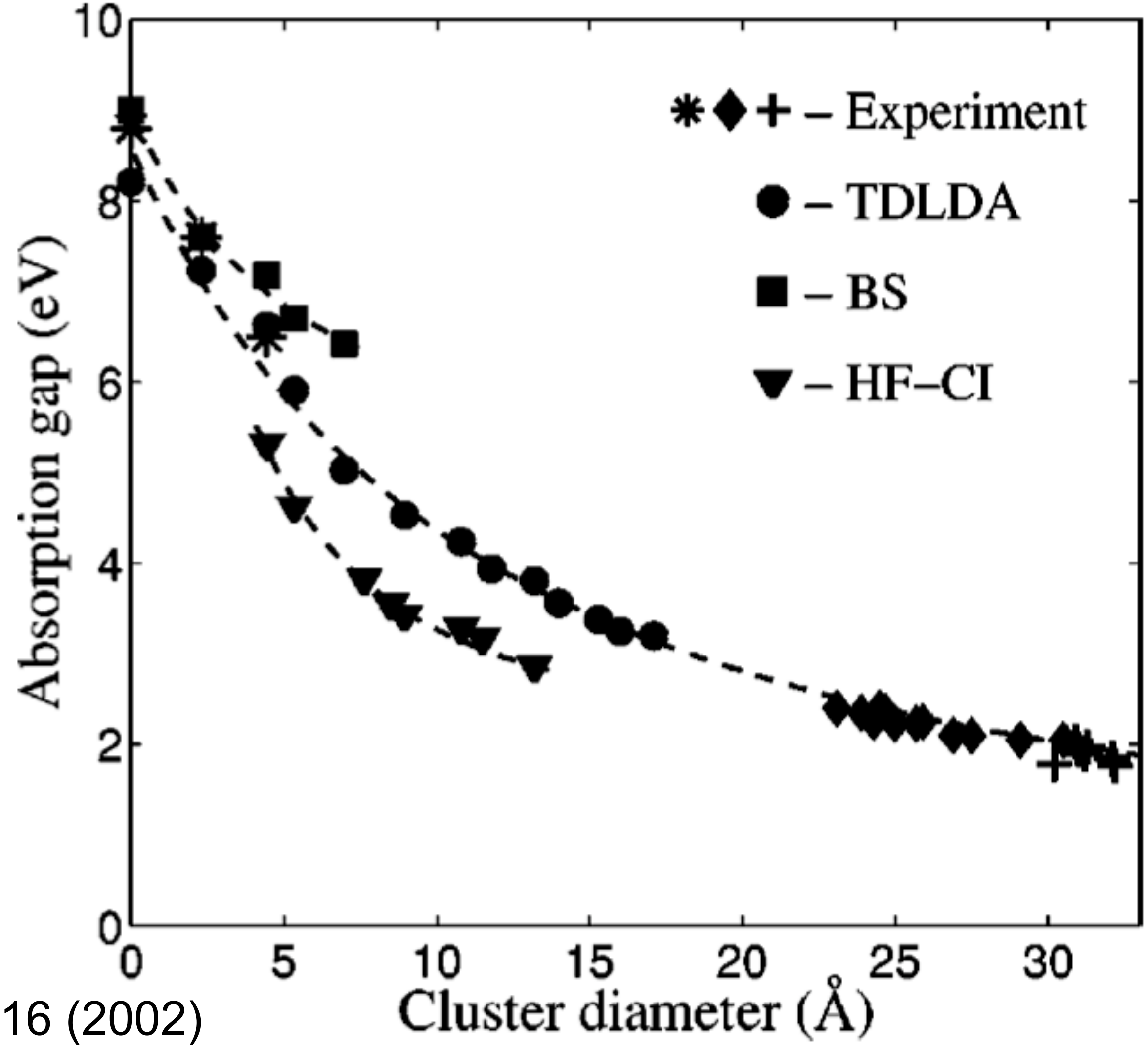
Si_nH_m nanoclusters:



From: I. Vasiliev et al.
Phys. Rev. B **65**, 115416 (2002)

How good are ALDA-TDDFT spectra in nanosystems?

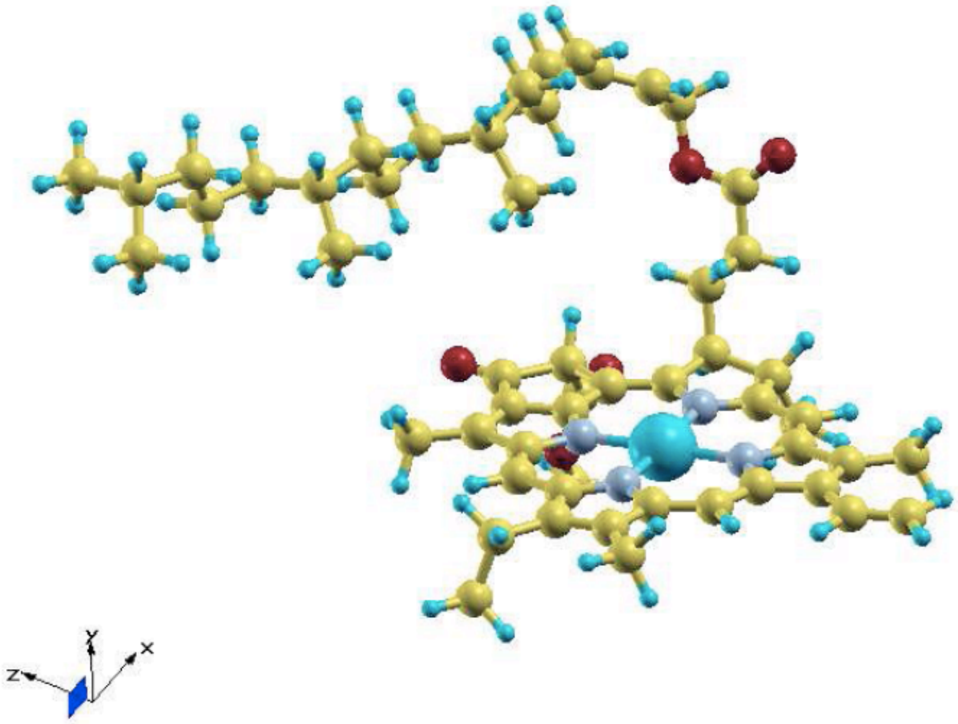
Si_nH_m nanoclusters:



From: I. Vasiliev et al.
Phys. Rev. B **65**, 115416 (2002)

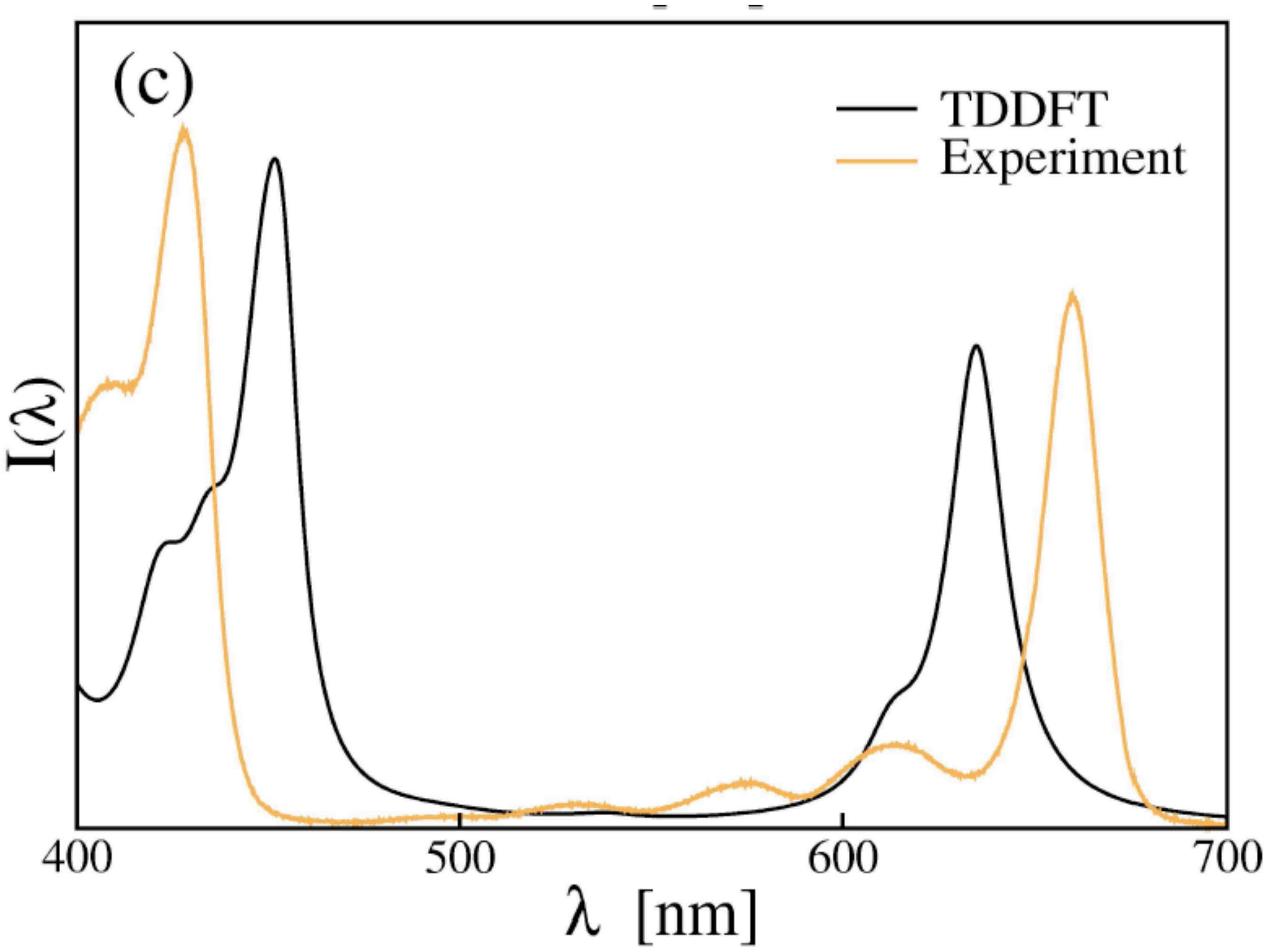
Application to a biomolecule:

Chlorophyll a:



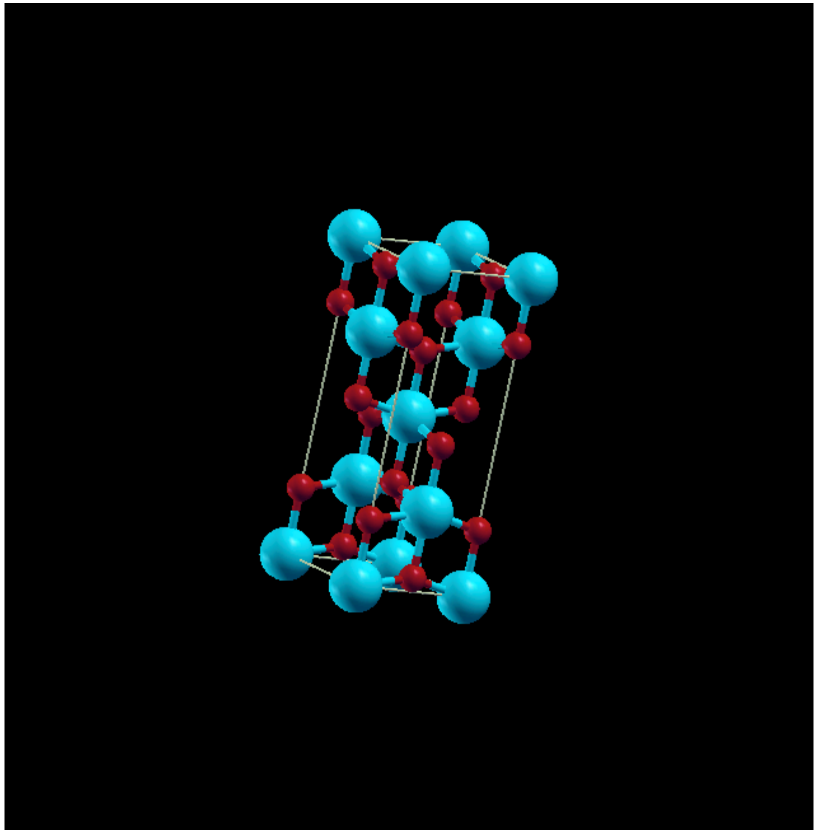
Application to a biomolecule:

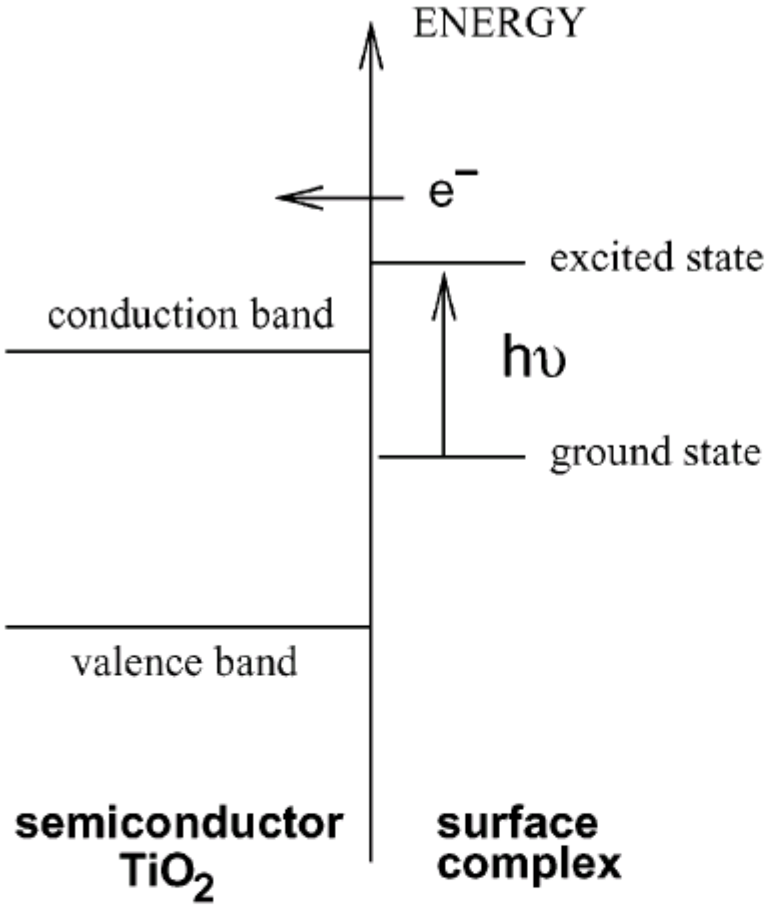
Chlorophyll a:



Electron transfer in sensitized semiconductor surfaces

Idea (Graetzel solar cells):





Nanostructured TiO_2 surface

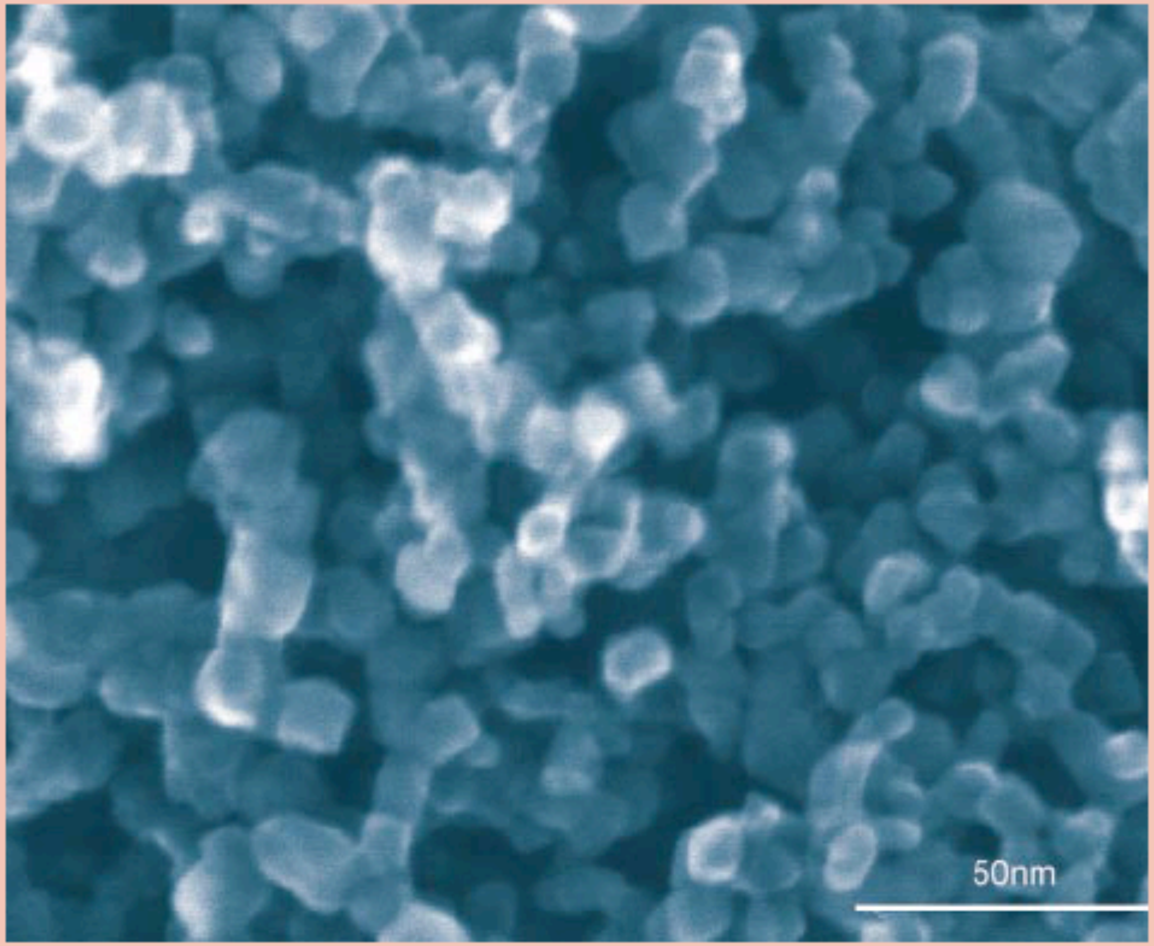


Figure 4 Scanning electron micrograph of the surface of a mesoporous anatase film prepared from a hydrothermally processed TiO_2 colloid. The exposed surface planes have mainly {101} orientation.

Source:
M. Grätzel, Nature **414**, 338 (2001)

Functioning of a Grätzel cell

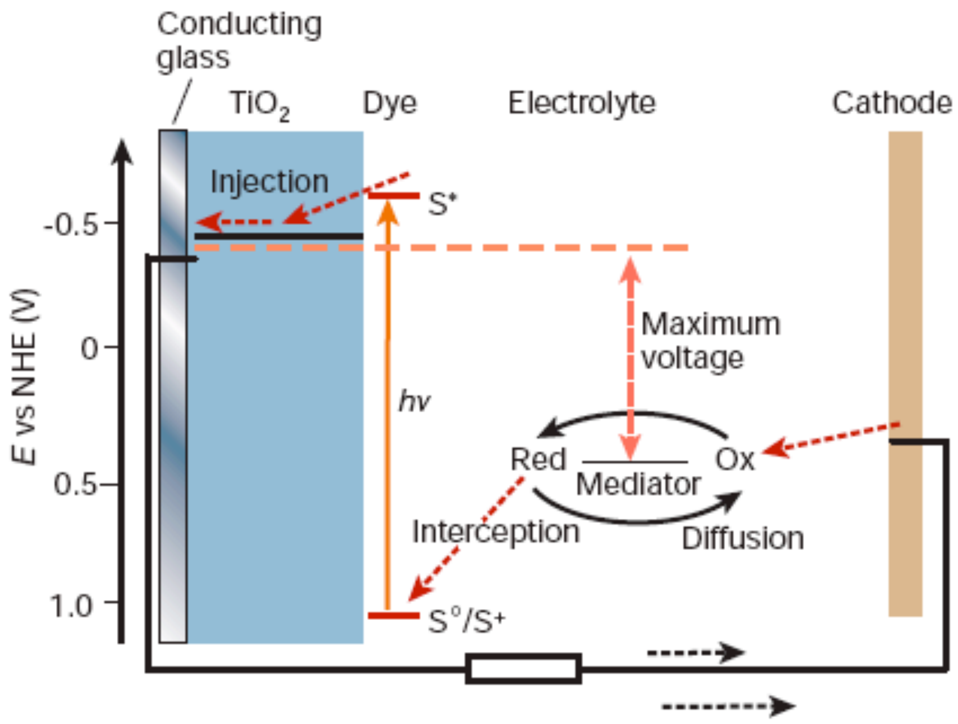


Figure 3 Schematic of operation of the dye-sensitized electrochemical photovoltaic cell. The photoanode, made of a mesoporous dye-sensitized semiconductor, receives electrons from the photo-excited dye which is thereby oxidized, and which in turn oxidizes the mediator, a redox species dissolved in the electrolyte. The mediator is regenerated by reduction at the cathode by the electrons circulated through the external circuit. Figure courtesy of P. Bonhôte/EPFL-LPI.

Source:
M. Grätzel, Nature **414**, 338 (2001)

Various dyes are extensively studied

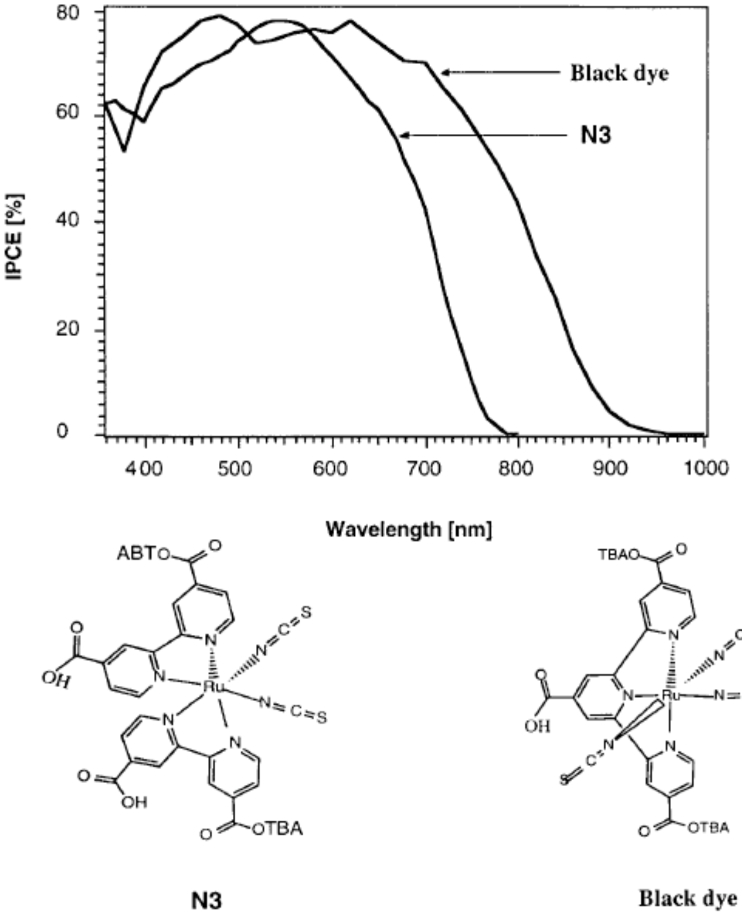
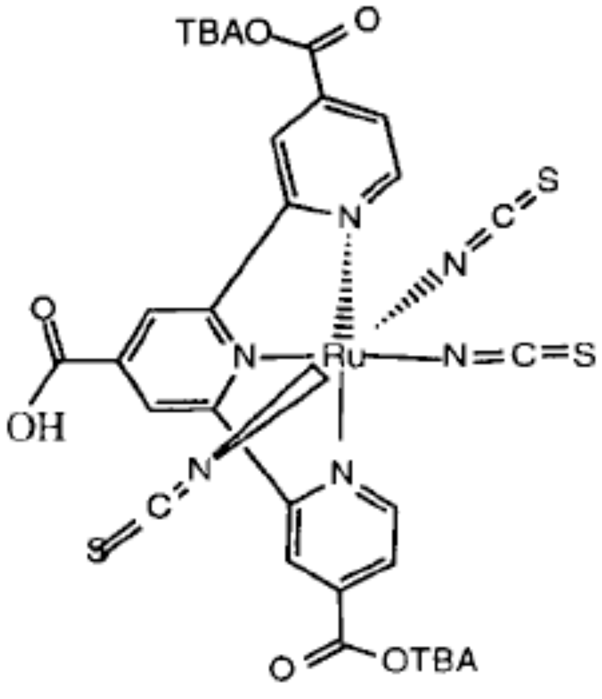


Figure 3. Spectral response curve of the photocurrent for the DYSC sensitized by N3 and the black dye. The incident photon to current conversion efficiency is plotted as a function of wavelength

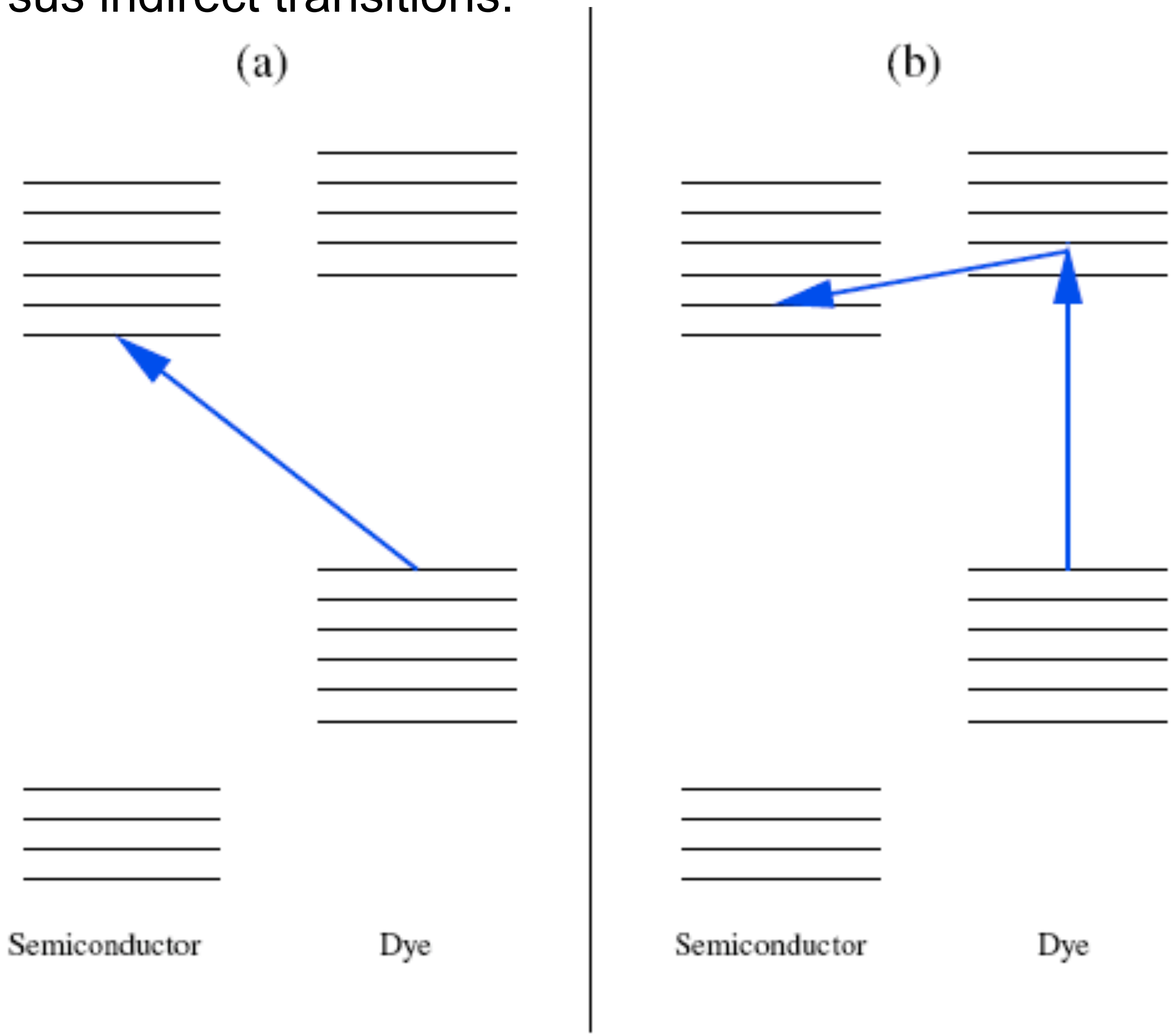


Black dye

Source: M. Grätzel, Prog. Photovolt. Res. Appl. 8, 171-185 (2000)

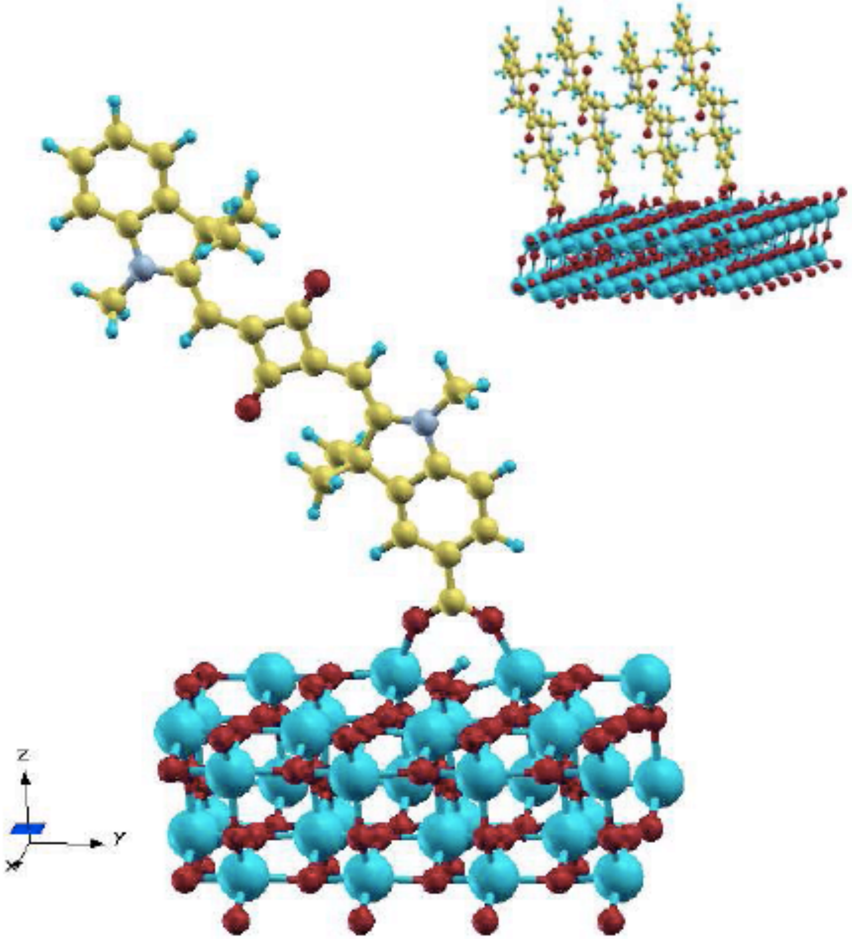
Electron transfer in sensitized semiconductor surfaces

Direct versus indirect transitions:



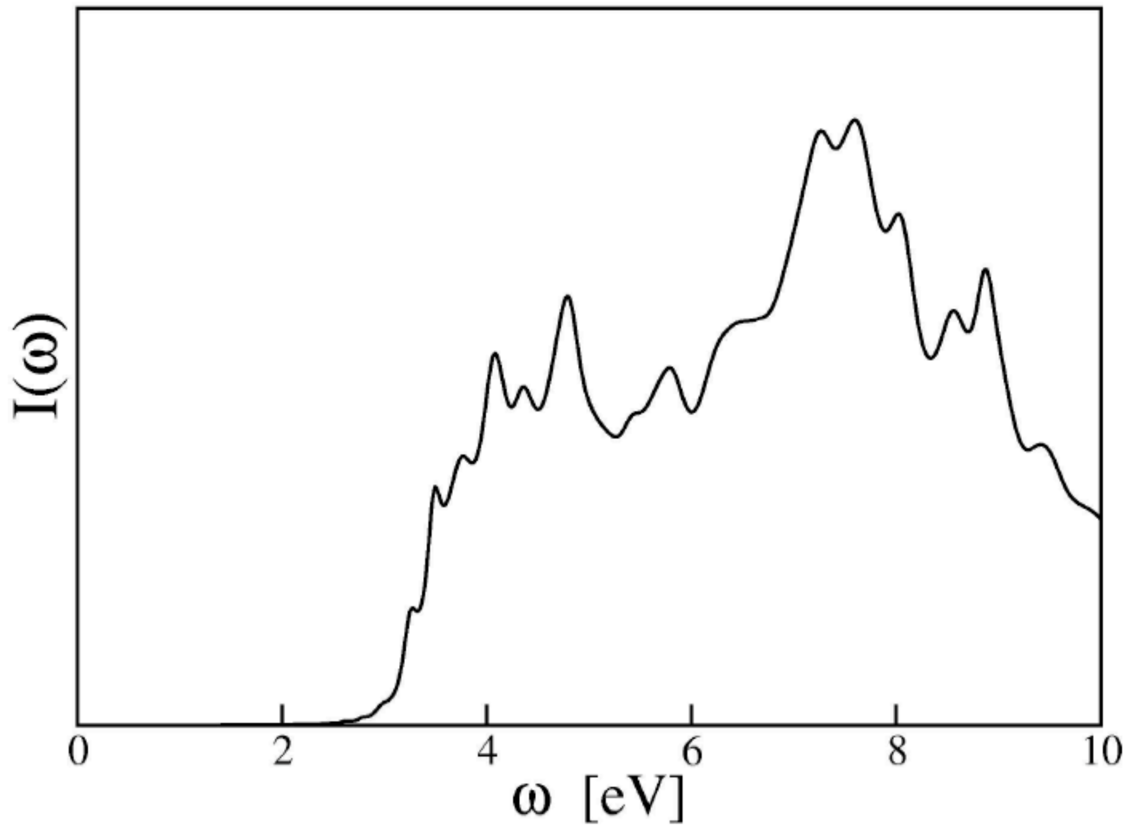
Electron transfer in sensitized semiconductor surfaces

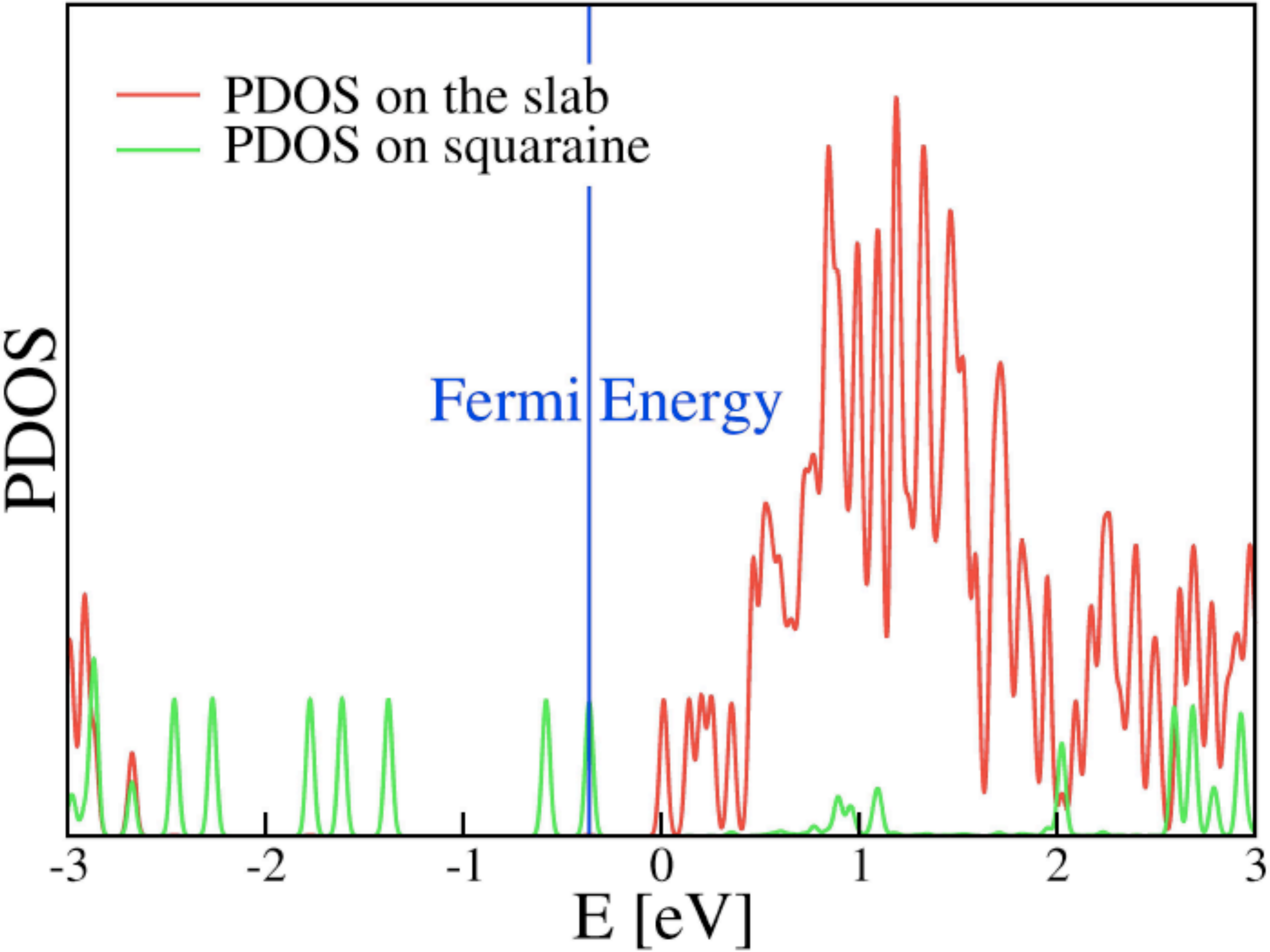
Our model: Squaraine DSSC



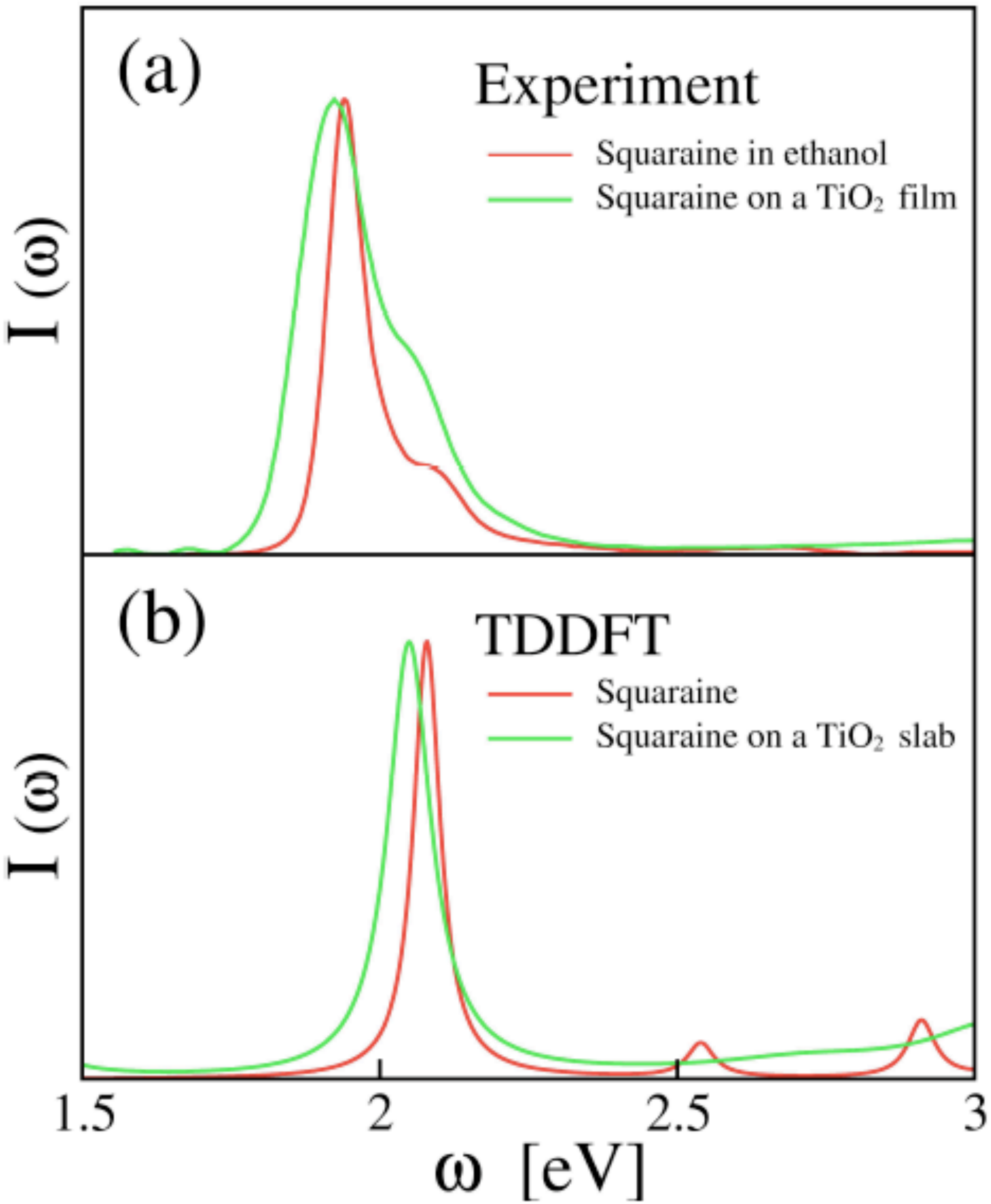
Electron transfer in sensitized semiconductor surfaces

Optical absorption of TiO_2 slab only:

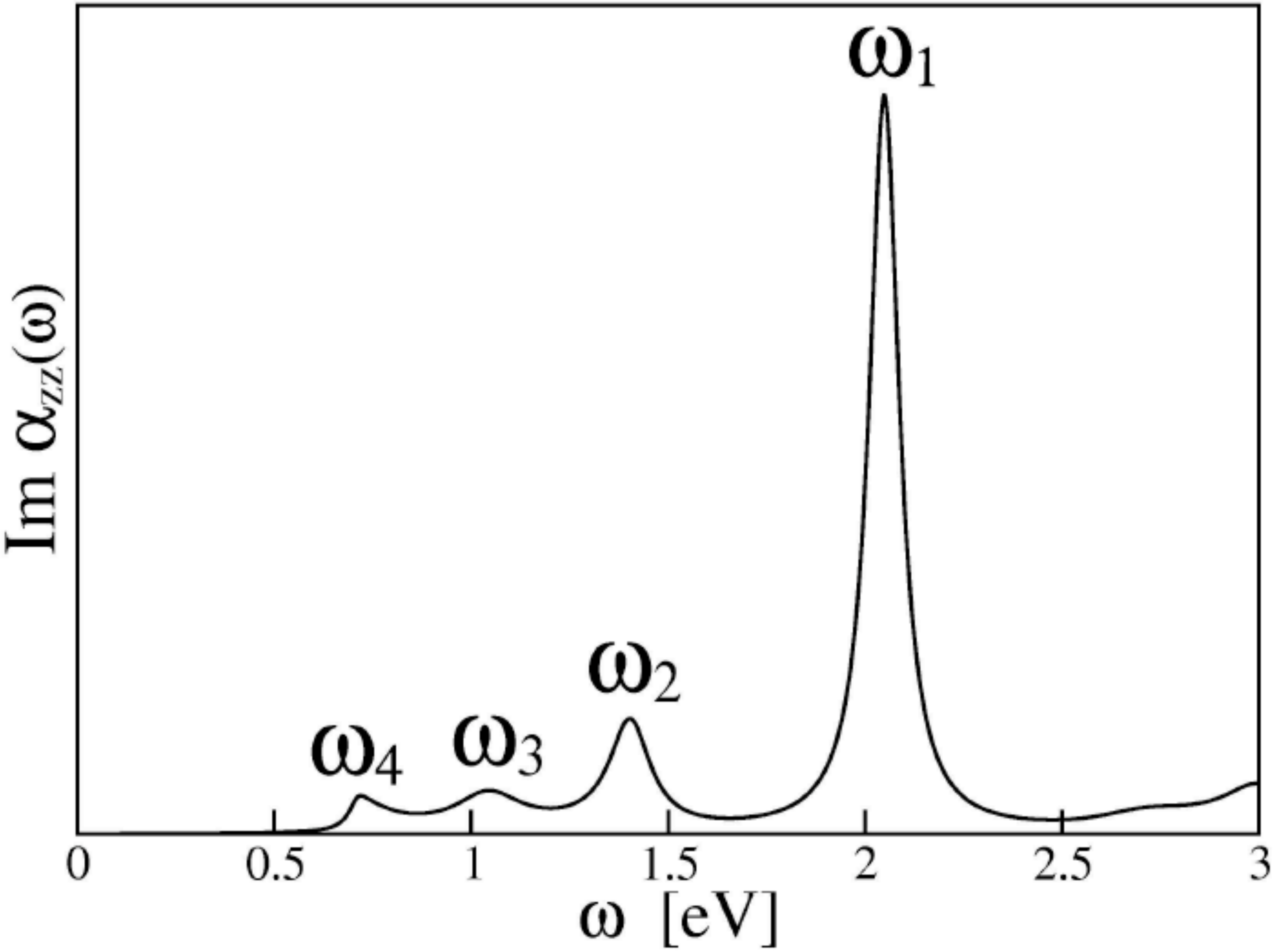


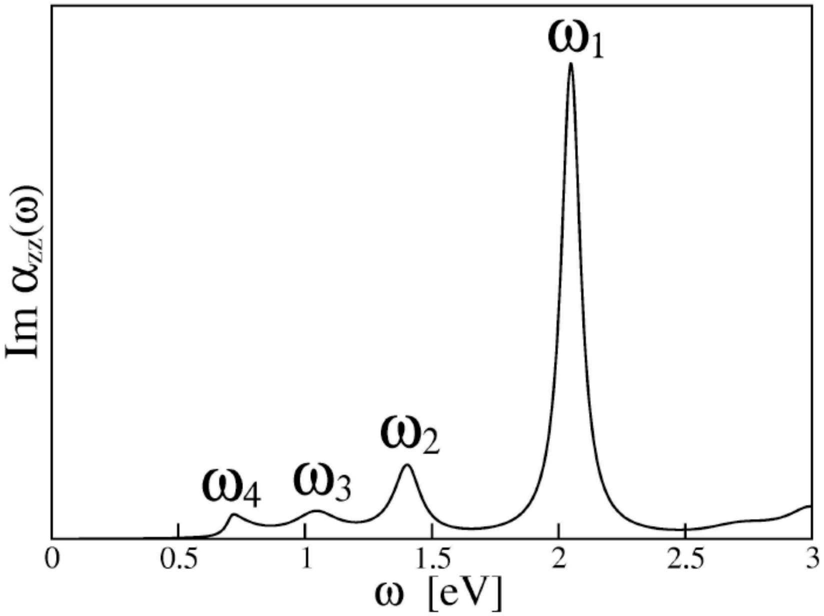

PDOS on the slab
PDOS on squaraine
Fermi Energy
PDOS
-3
-2
-1
0
1
2
3
E [eV]

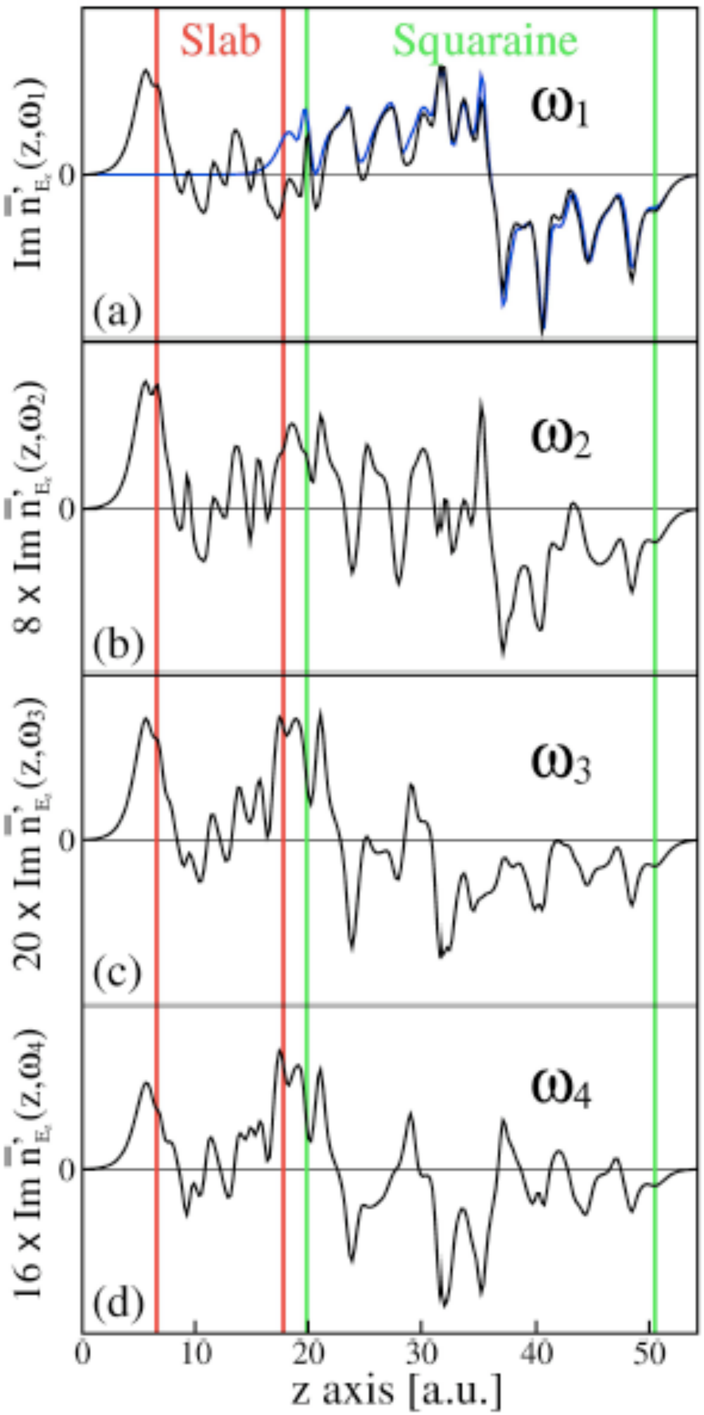
Optical
Absorption:



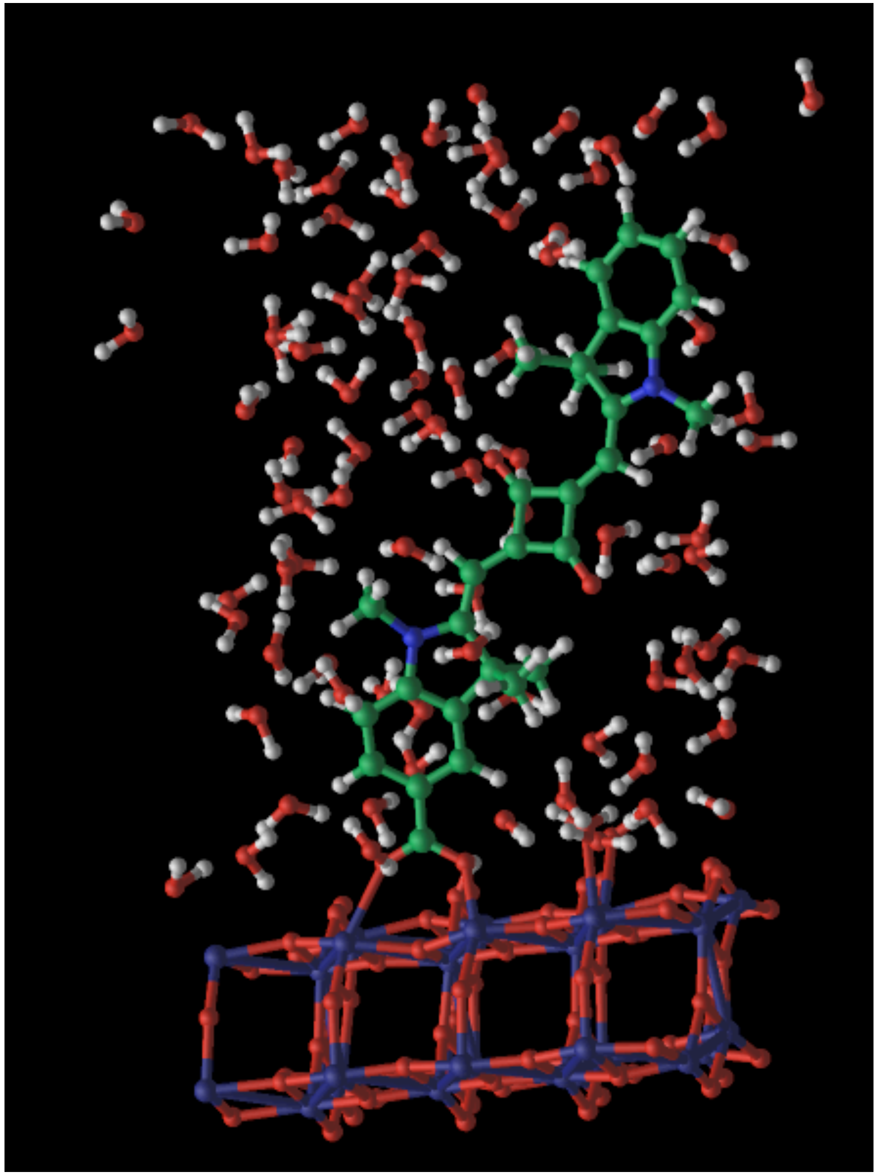
Look at the lower lying excitations:

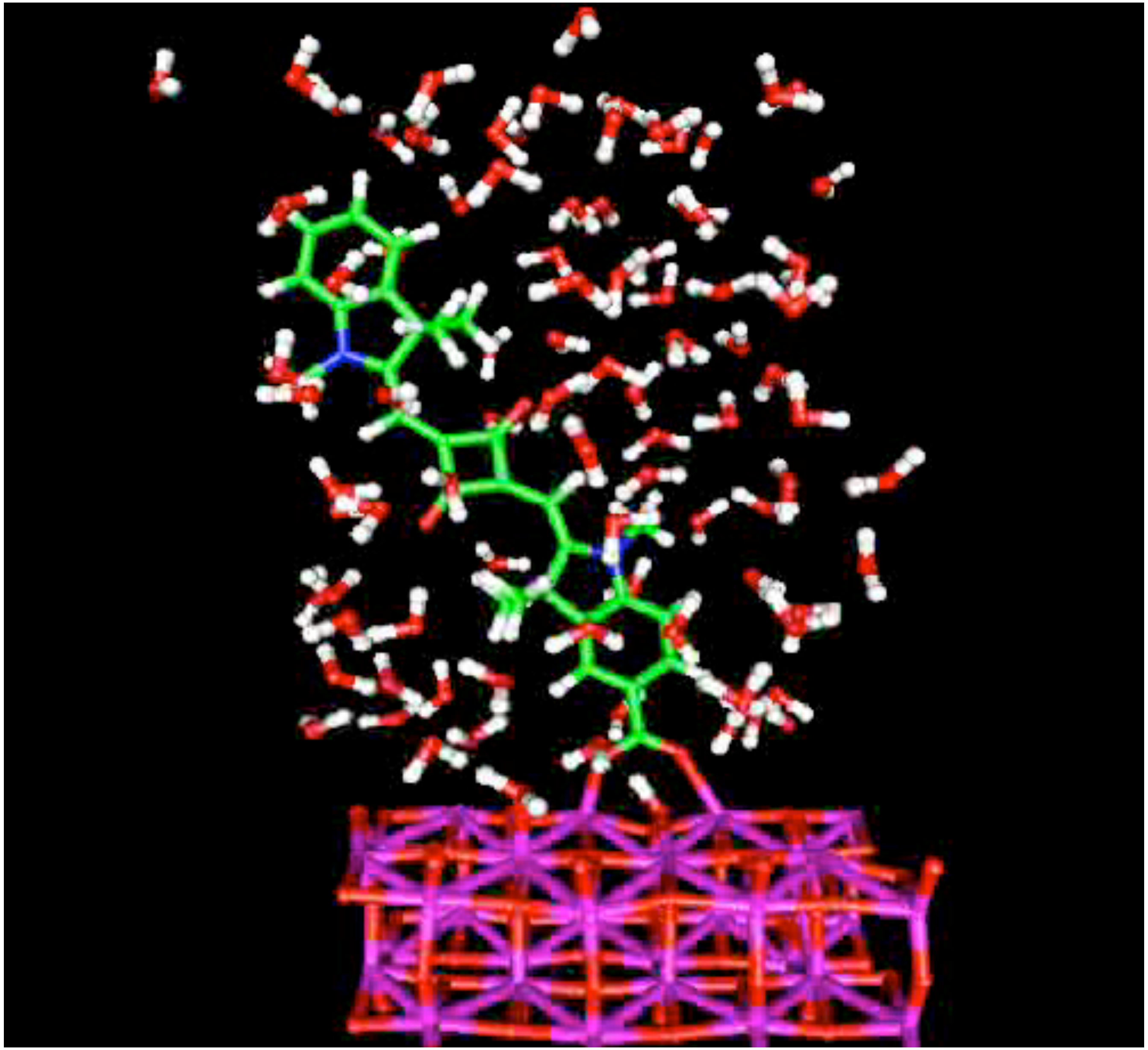



Im α_zz(ω)
ω1
ω2
ω3
ω4
0
0.5
1
1.5
2
2.5
3
ω [eV]


Slab
Squaraine
Im n̄'_Ez(z,ω1)
ω1
0
(a)
8 x Im n̄'_Ez(z,ω2)
ω2
0
(b)
20 x Im n̄'_Ez(z,ω3)
ω3
0
(c)
16 x Im n̄'_Ez(z,ω4)
ω4
0
(d)
0
10
20
30
40
50
z axis [a.u.]

A more realistic system: Including the solvent





Including the solvent in MD and TDDFT computations

- Solvent is treated at the same level of theory as molecule and surface slab.

- Solvent changes electrostatic conditions (dielectric constant …)

- Solvent participates actively:
  - in formation surface dipoles, etc.
  - dissociates
  - is essential for geometry of solute

TDDFT calculation of optical spectra and related quantities

Various challenges:

- System is large (429 atoms, 1.666 electrons, 181.581 PWs, resp. 717.690 PWs)
- Broad spectral region of interest
- Many excited states in spectral region

Computational tool:

- Recursive Lanczos algorithm for TDDFT
- Ideally suited for large systems, broad spectral region with large basis set
- Here: Adiabatic GGA functional

Conclusions

- TDDFT as a formally exact extension of ground-state DFT for electronic excitations

- Allows to follow the electronic dynamics in real time

- Using TDDFT in linear response allows one to calculate spectra

- Open issues: Which functional to use?

- How to link the electron dynamics with nuclear dynamics?

- How can one apply TDDFT to (very) large systems?

Thanks to:

- Stefano Baroni (SISSA & DEMOCRITOS, Trieste)
- Brent Walker (University College, London)
- Dario Rocca (UC Davis)
- Filippo De Angelis (Perugia)
- O. Baris Malcioglu (Trieste)

To know more:

- Phys. Rev. Lett. **96**, 113001 (2006)
- J. Chem. Phys. **127**, 164106 (2007)
- J. Chem. Phys. **128**, 154105 (2008)
- Chem. Phys. Lett. **475**, 49 (2009)