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Hands-on Tutorial on Electronic Structure Computations

14 - 18 January 2013

Time-dependent DFT

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Time-dependent density functional theory and how it is used

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International Centre for Theoretical Physics

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Tuesday, January 15th, 2013

Overview

- Application of TDDFT to photovoltaics: large scale simulations

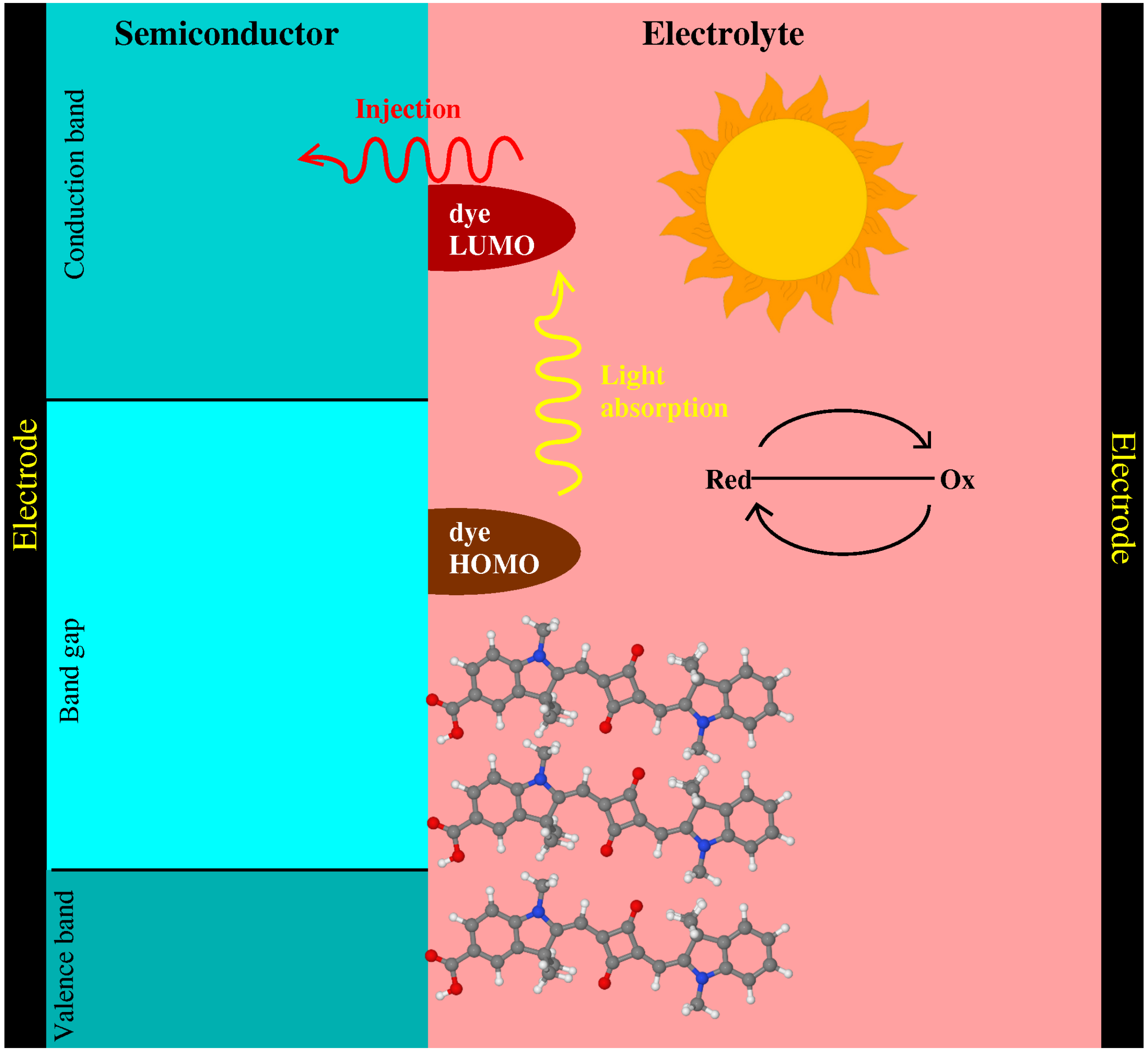
The basics

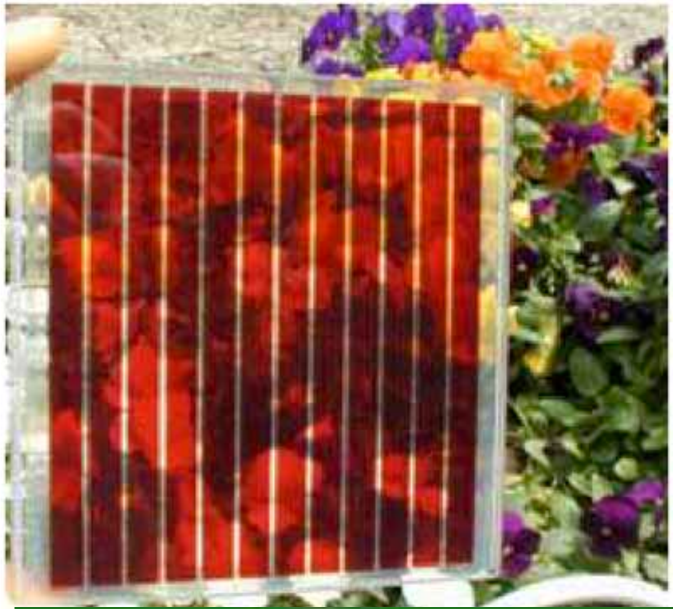
- From the ground-state to excited states: The Runge-Gross theorem

How TDDFT is used in practice

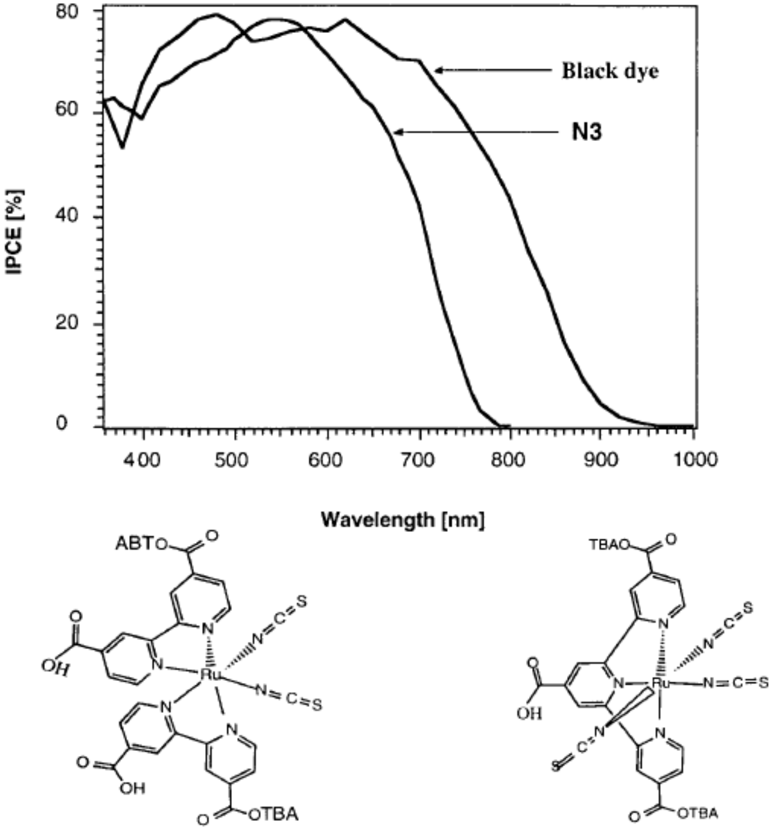
- A first look at TDDFT in practice: Real-time propagations & photochemistry
- TDDFT for optical spectra
  - real-time
  - Casida equation
  - TDDFPT-Lanczos scheme

Functioning of a Grätzel cell





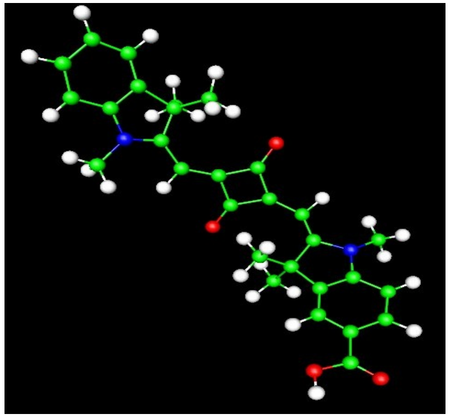
Various dyes



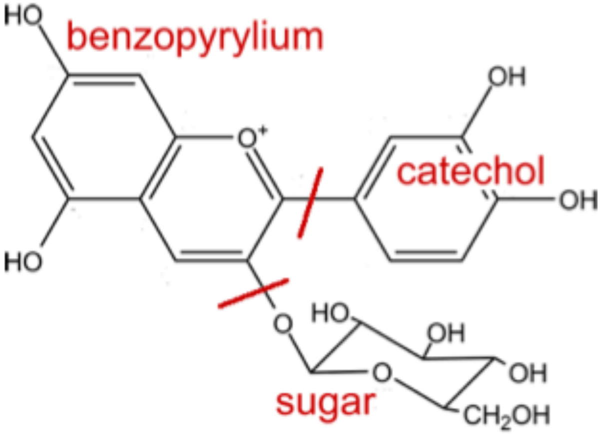
N3 **Black dye**

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

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

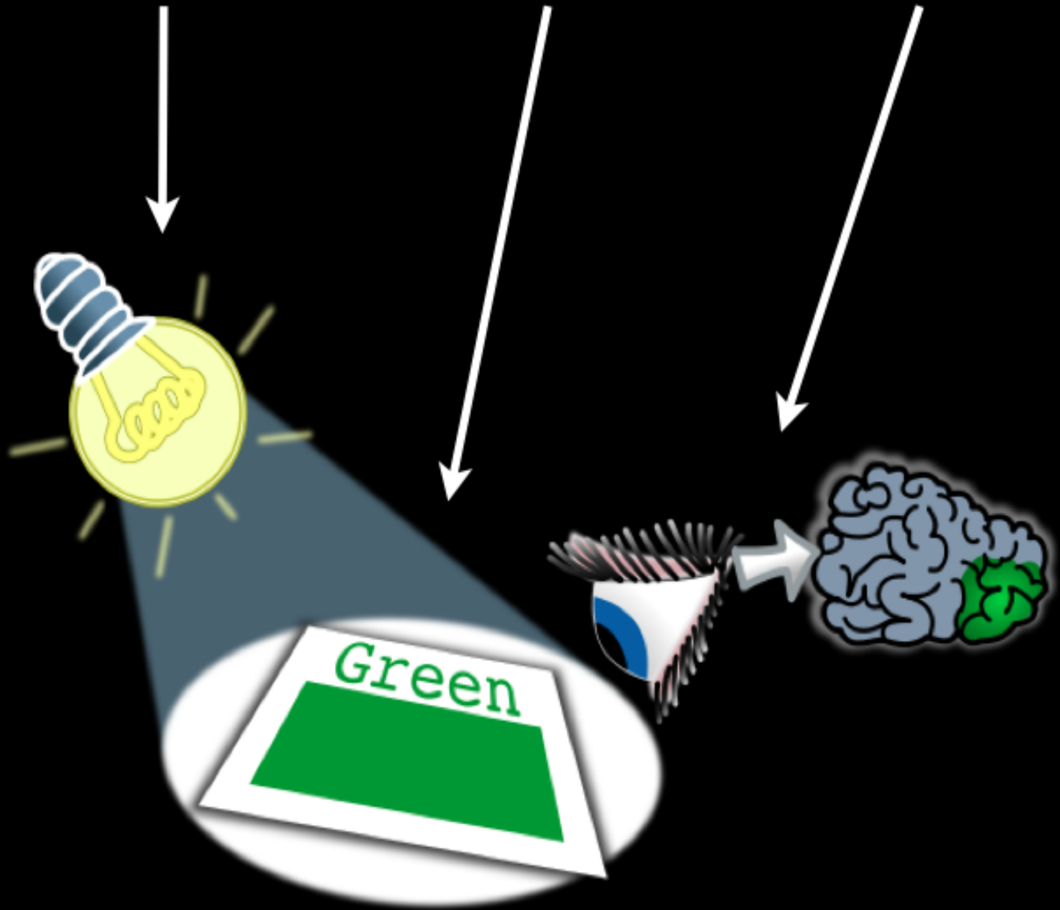


Squaraine dye



Cyanidin-3-glucoside ("Cyanin")

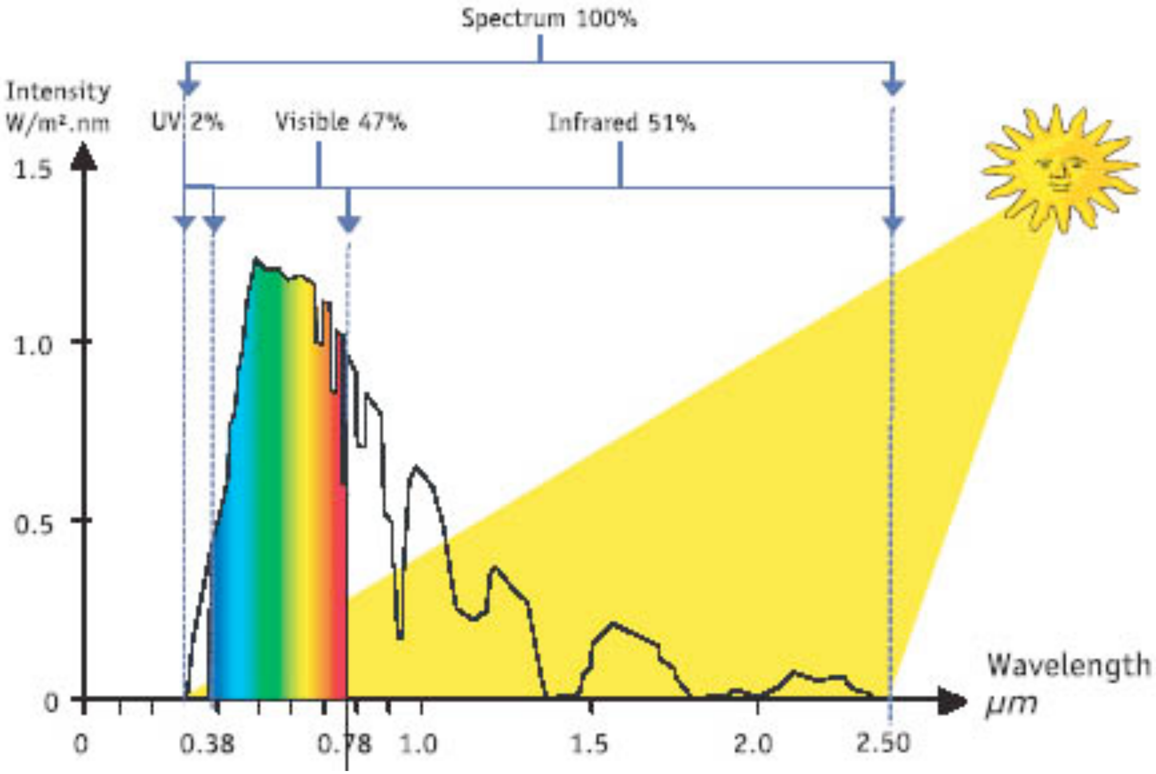
ab initio colors



stimulus =

illuminant × trasmission × sensitivity

SOLAR SPECTRUM



stimulus =

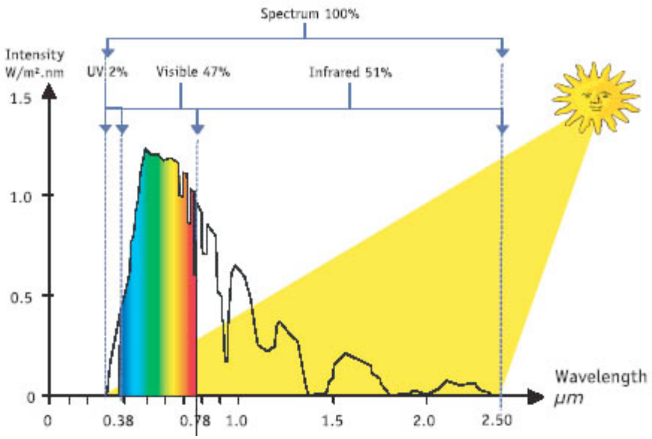
illuminant × trasmission × sensitivity

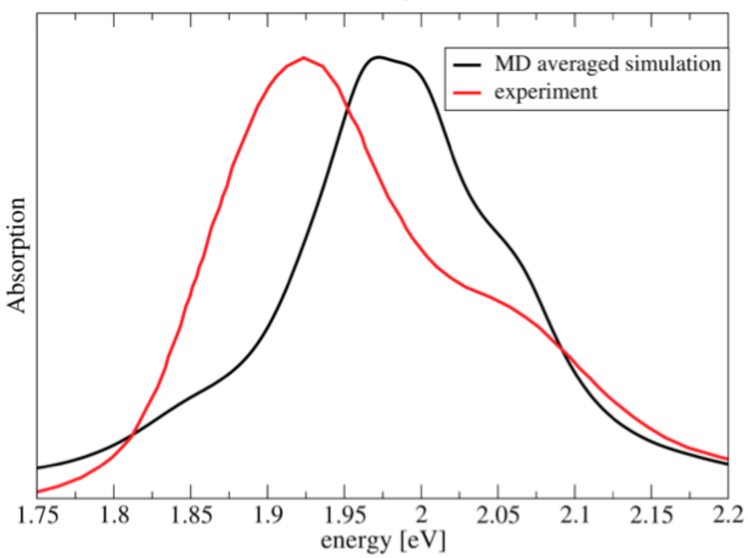
stimulus =

illuminant × trasmission × sensitivity

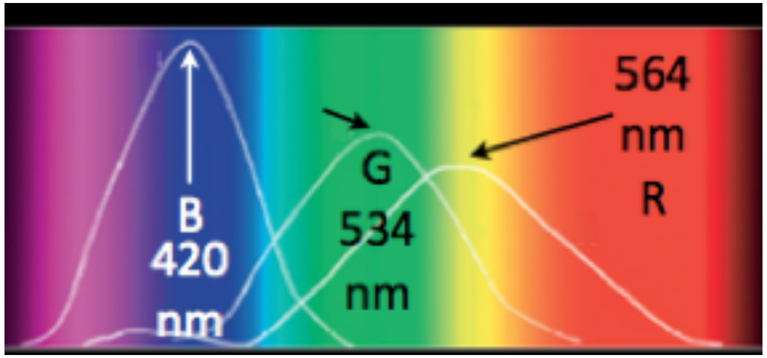
$$T(x, \lambda) = S(\lambda)e^{-\alpha(\lambda)x}$$

SOLAR SPECTRUM



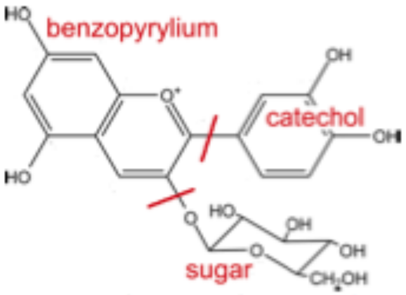


The colour we perceive

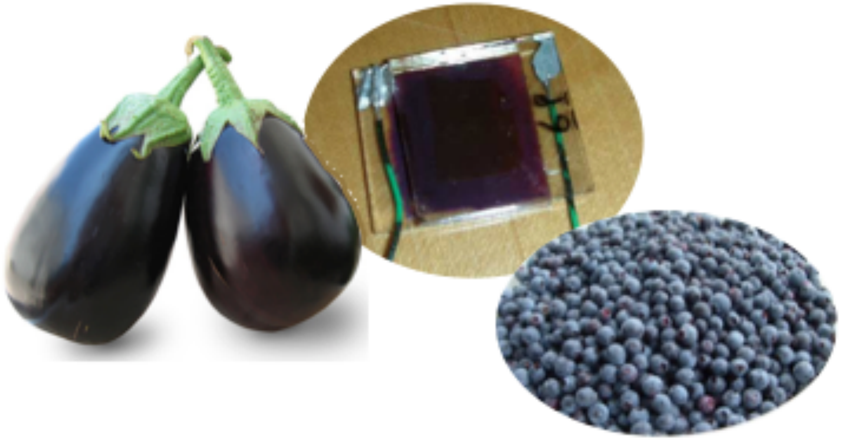


$$RGB(x) = \int S(\lambda) e^{-\alpha(\lambda)x} rgb(\lambda) d\lambda$$

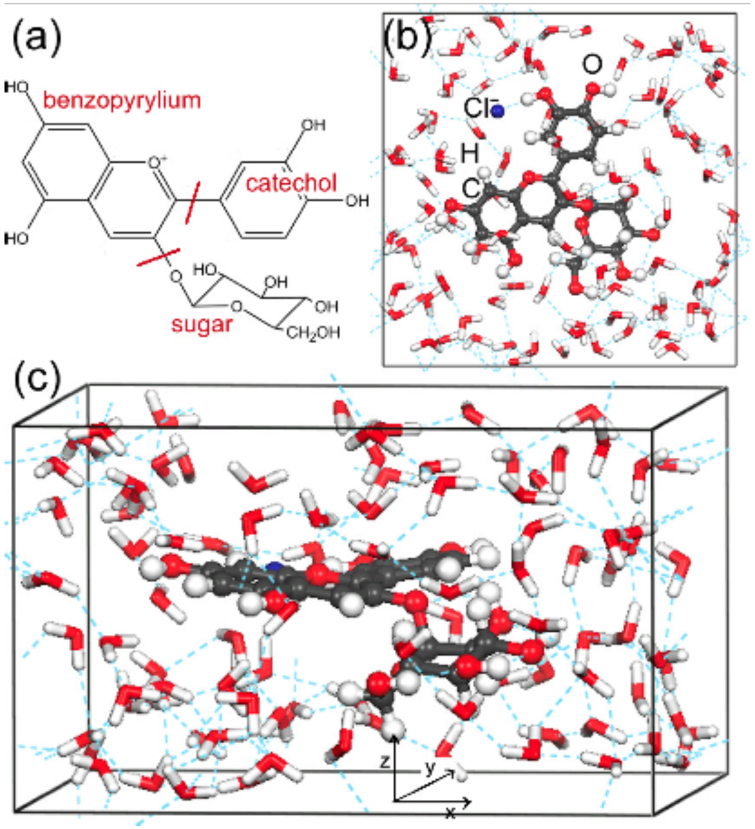
color and function of anthocyanins



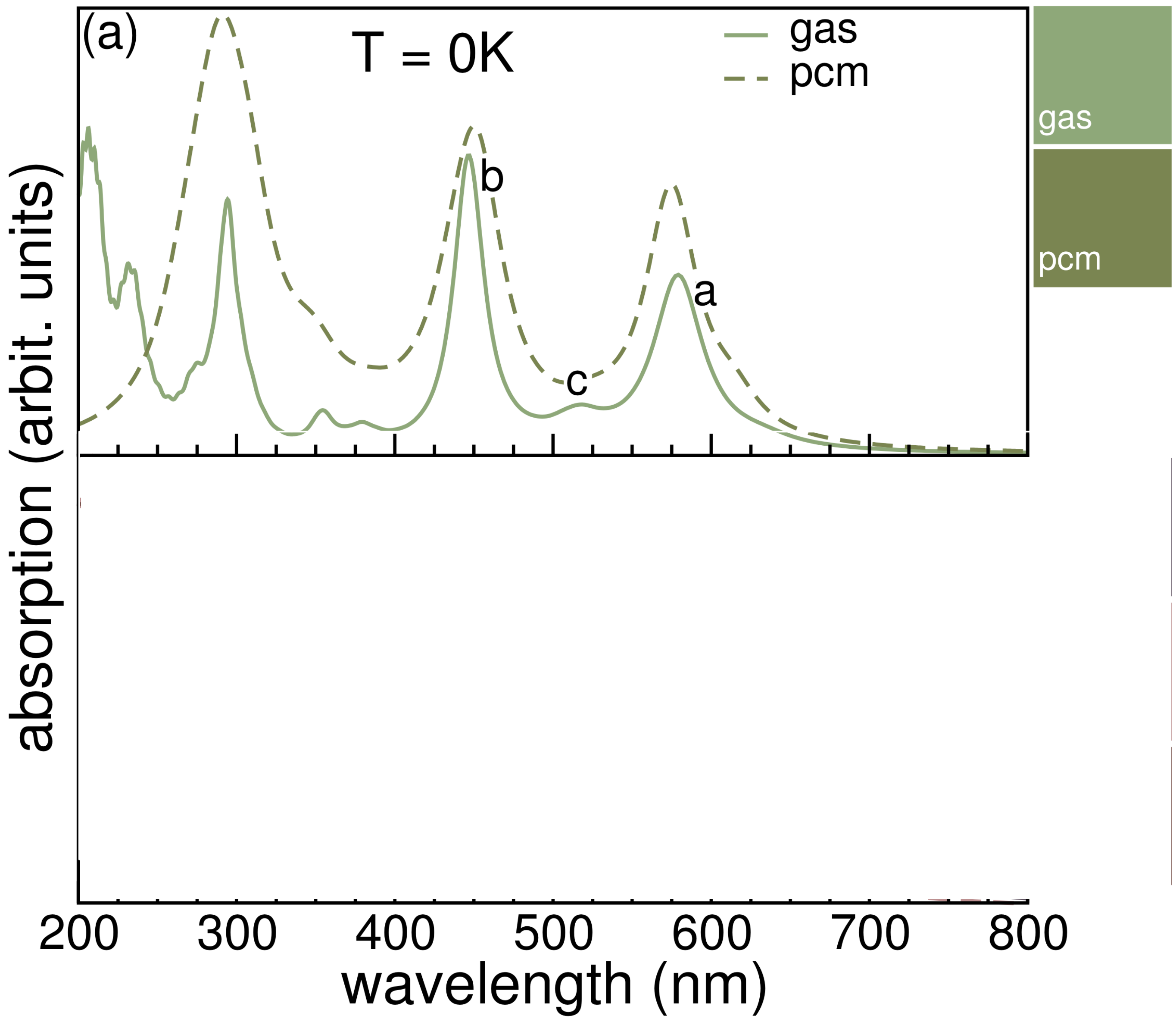
cyanidin-3-glucoside



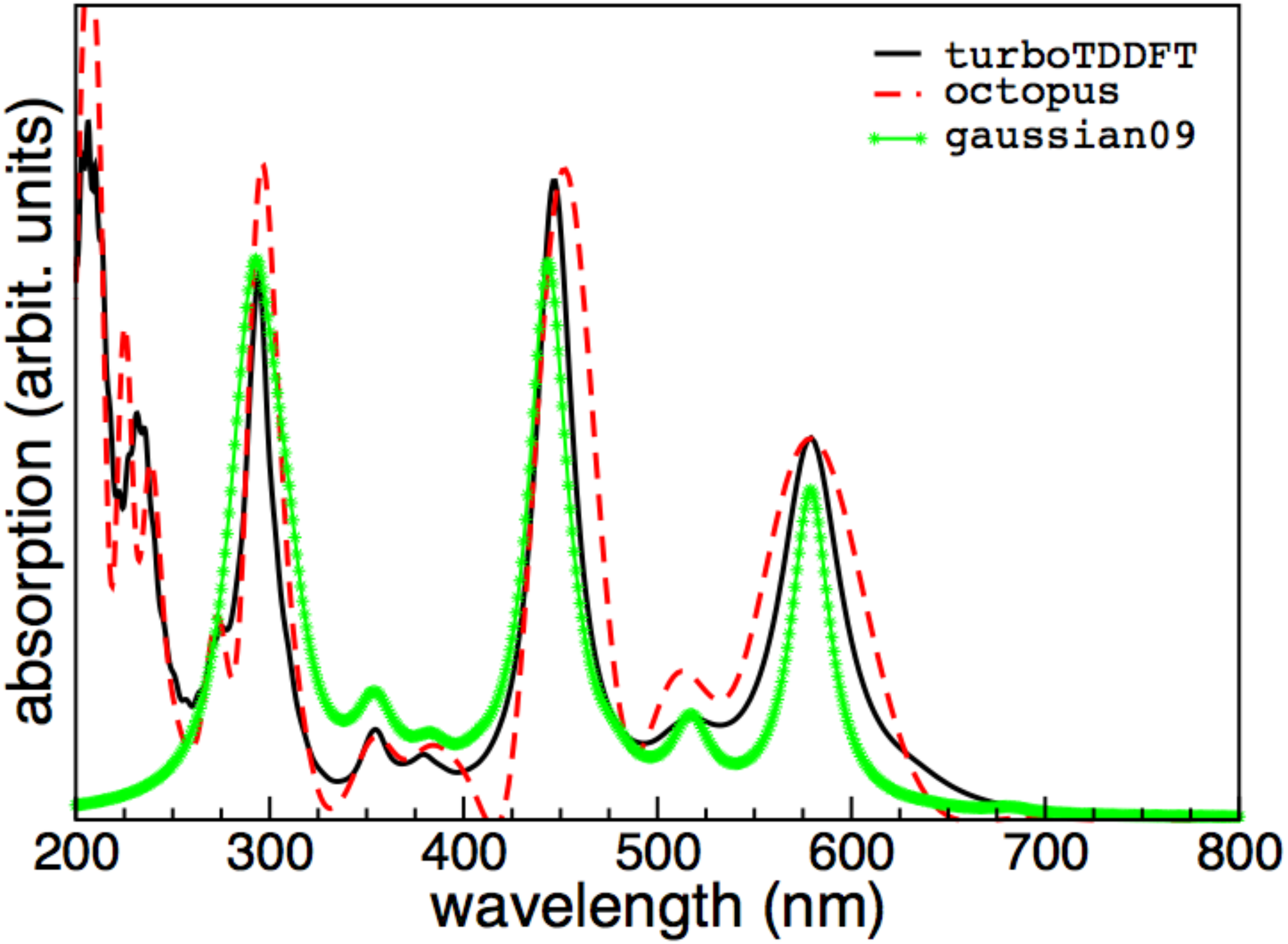
color and function of anthocyanins



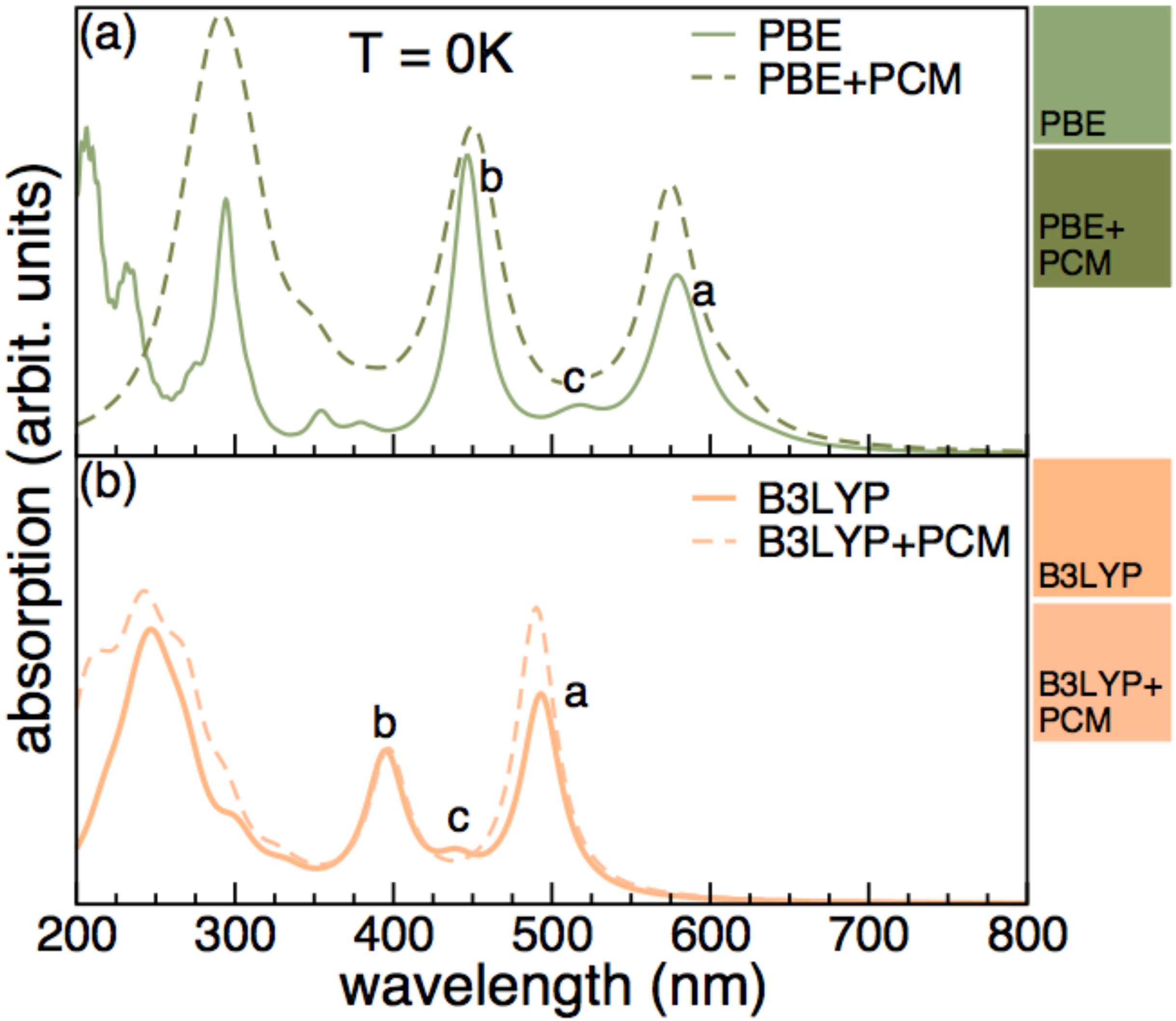
Optical spectra in the gas phase



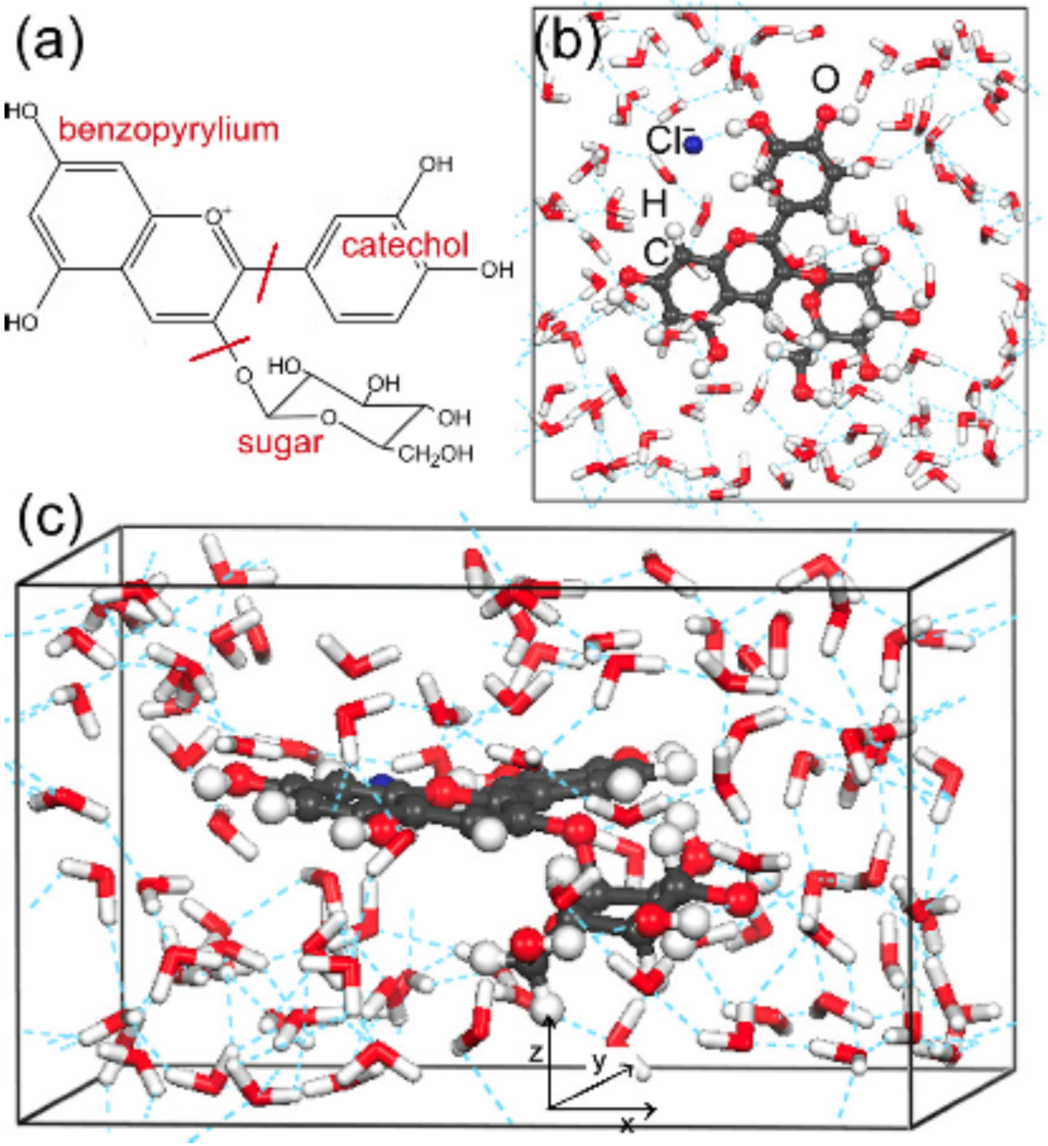
Spectra computed with various codes:



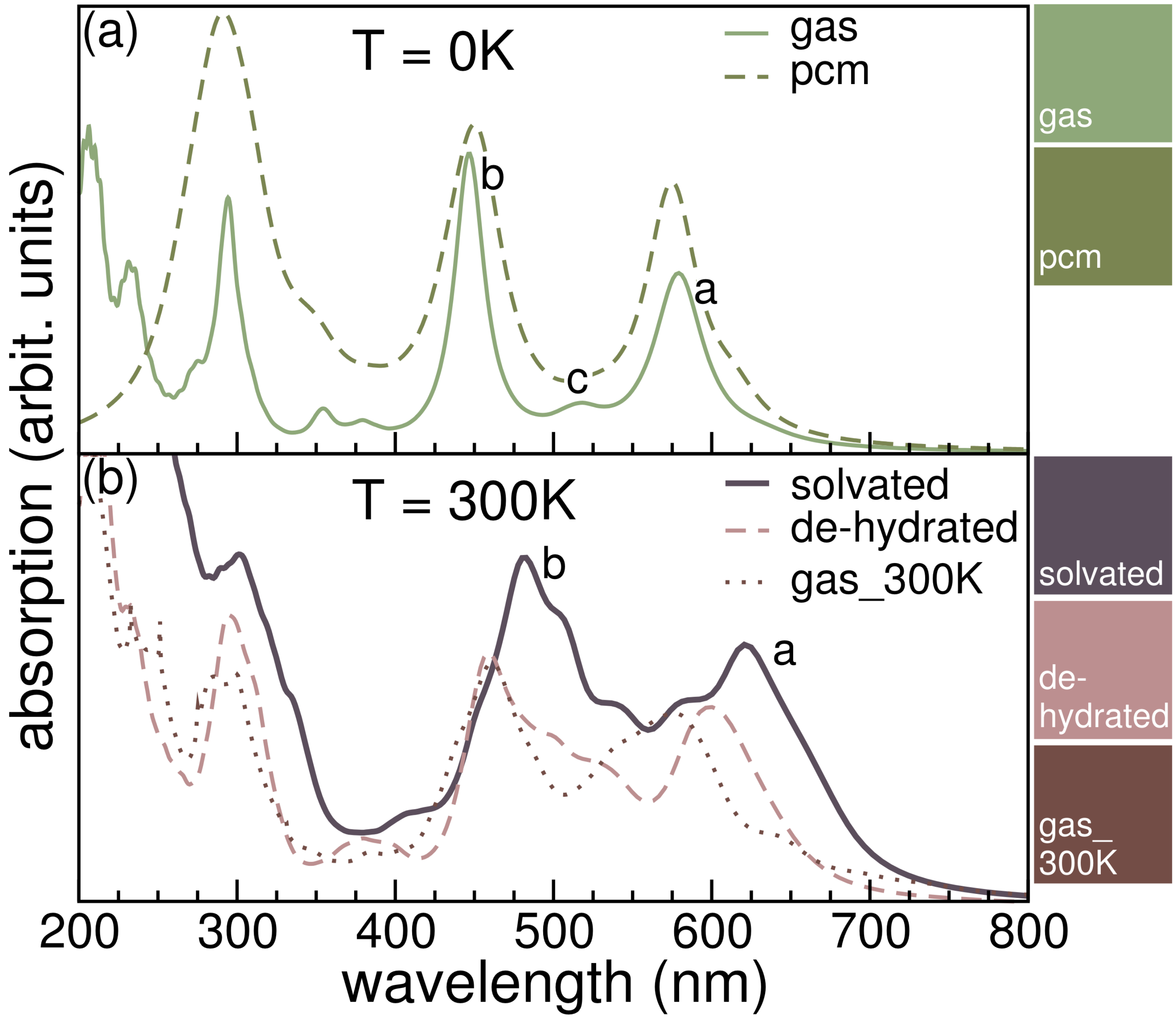
Spectra computed with various functionals:



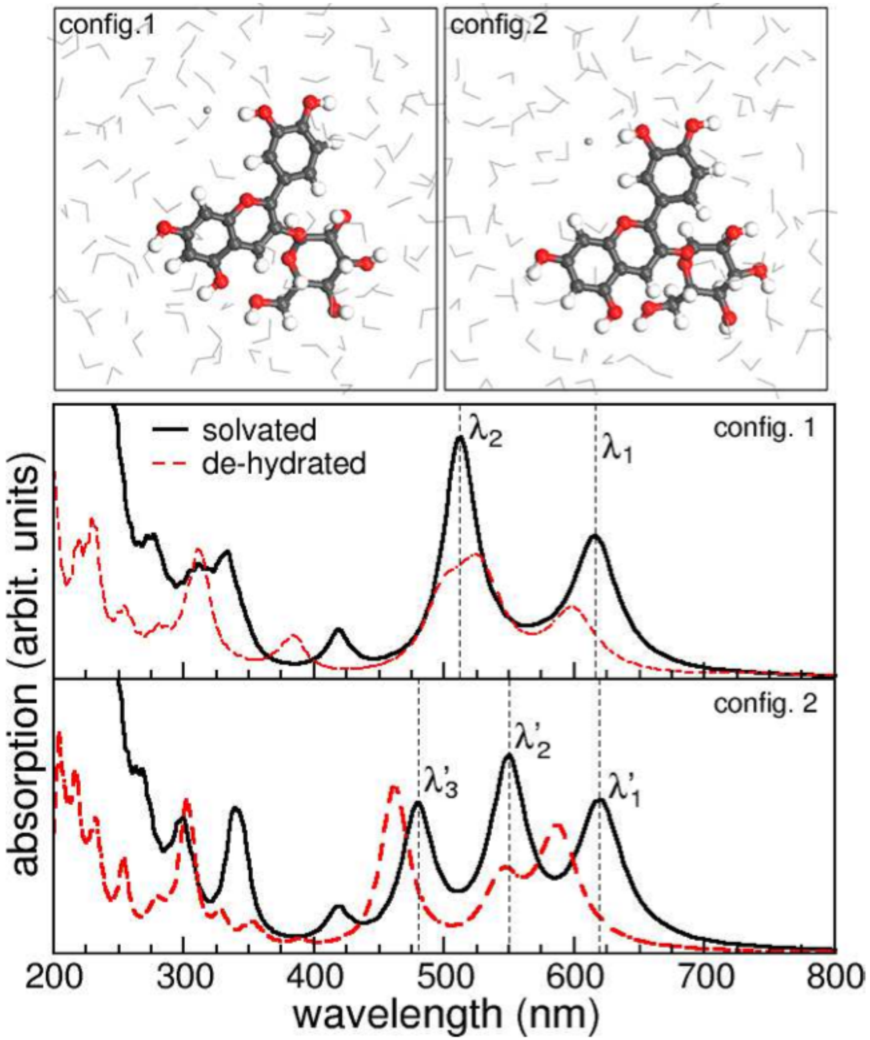
More realistic model of solvent

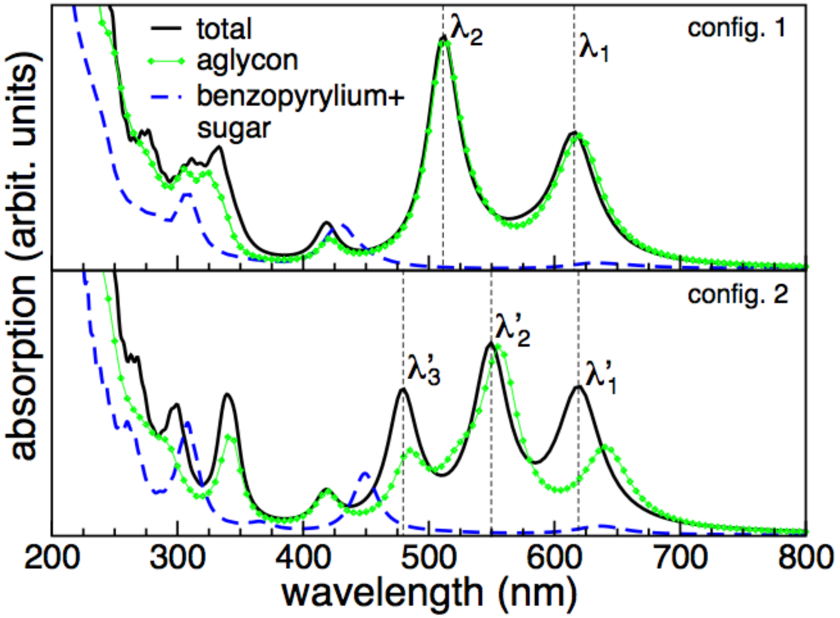


Including Molecular Dynamics

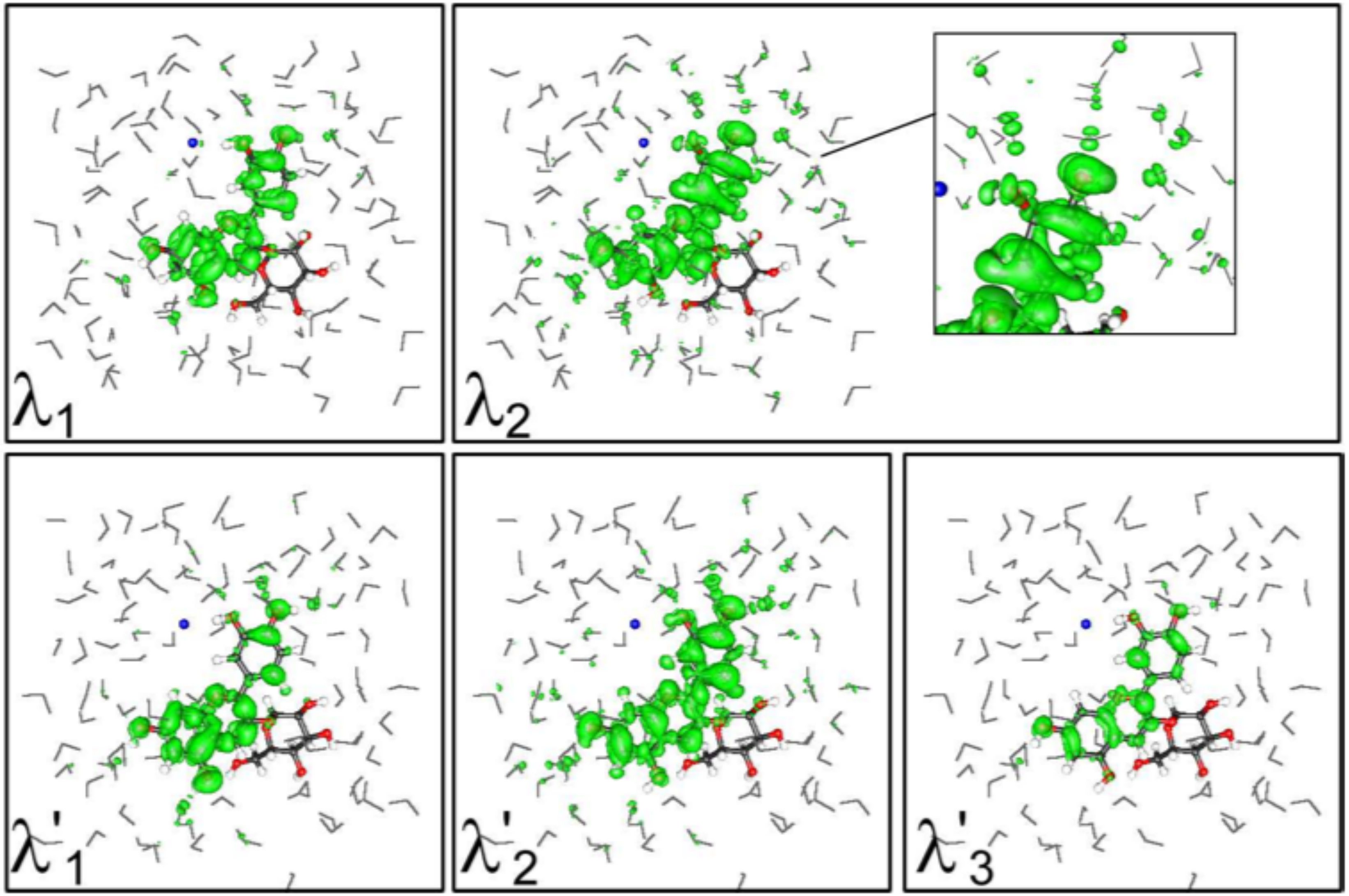


Analyzing configurational snapshots

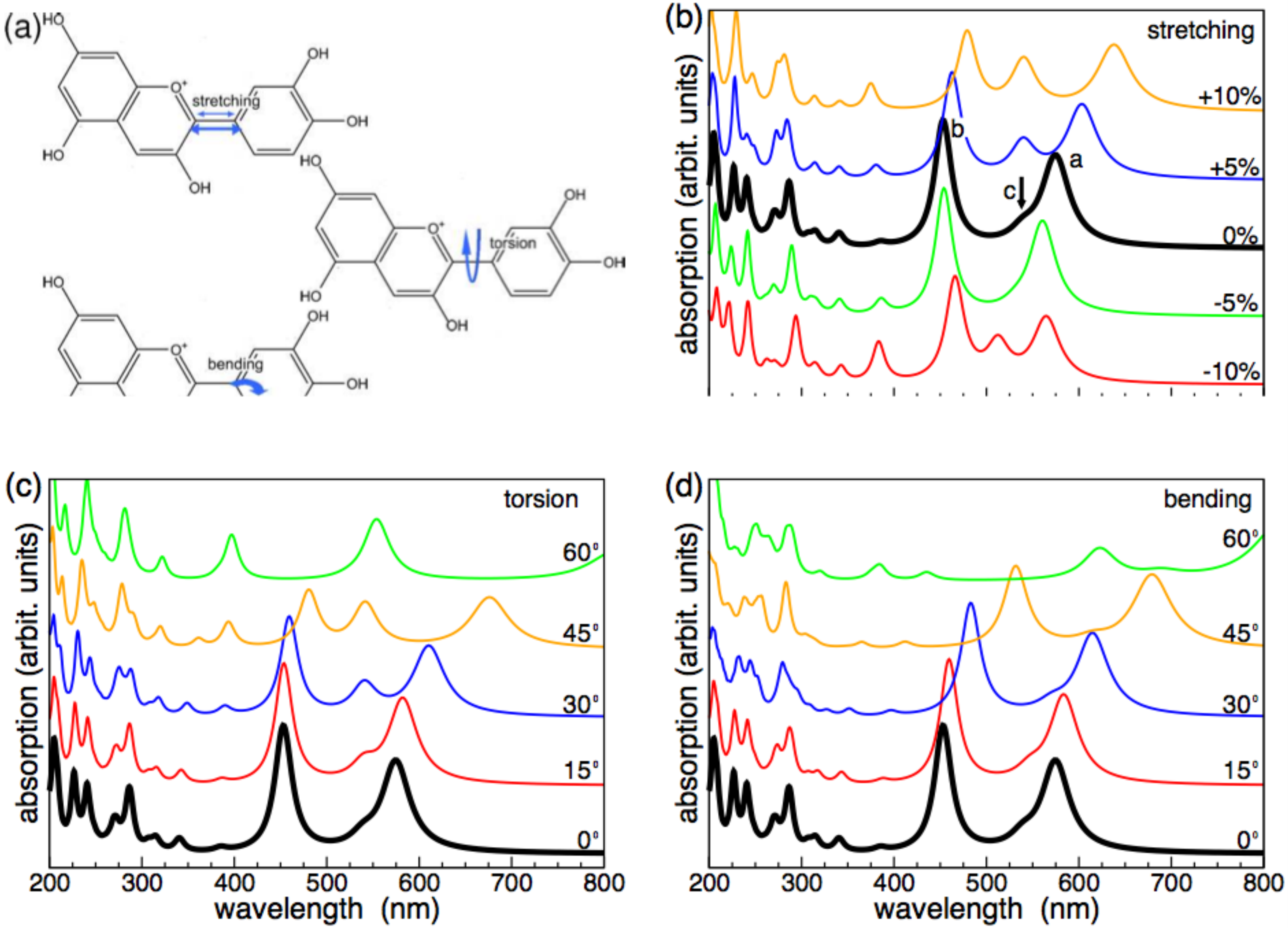




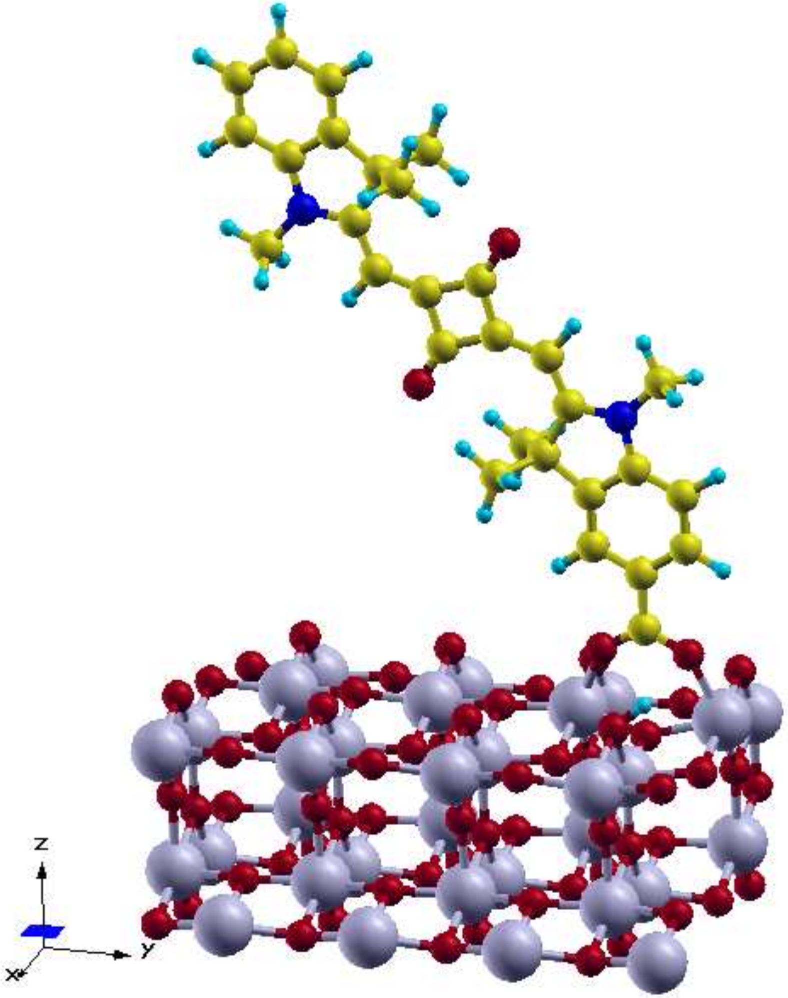
Response charge density at selected frequencies



Influence of various geometrical distortions



Model of a photovoltaic device: Squaraine on TiO_2 slab

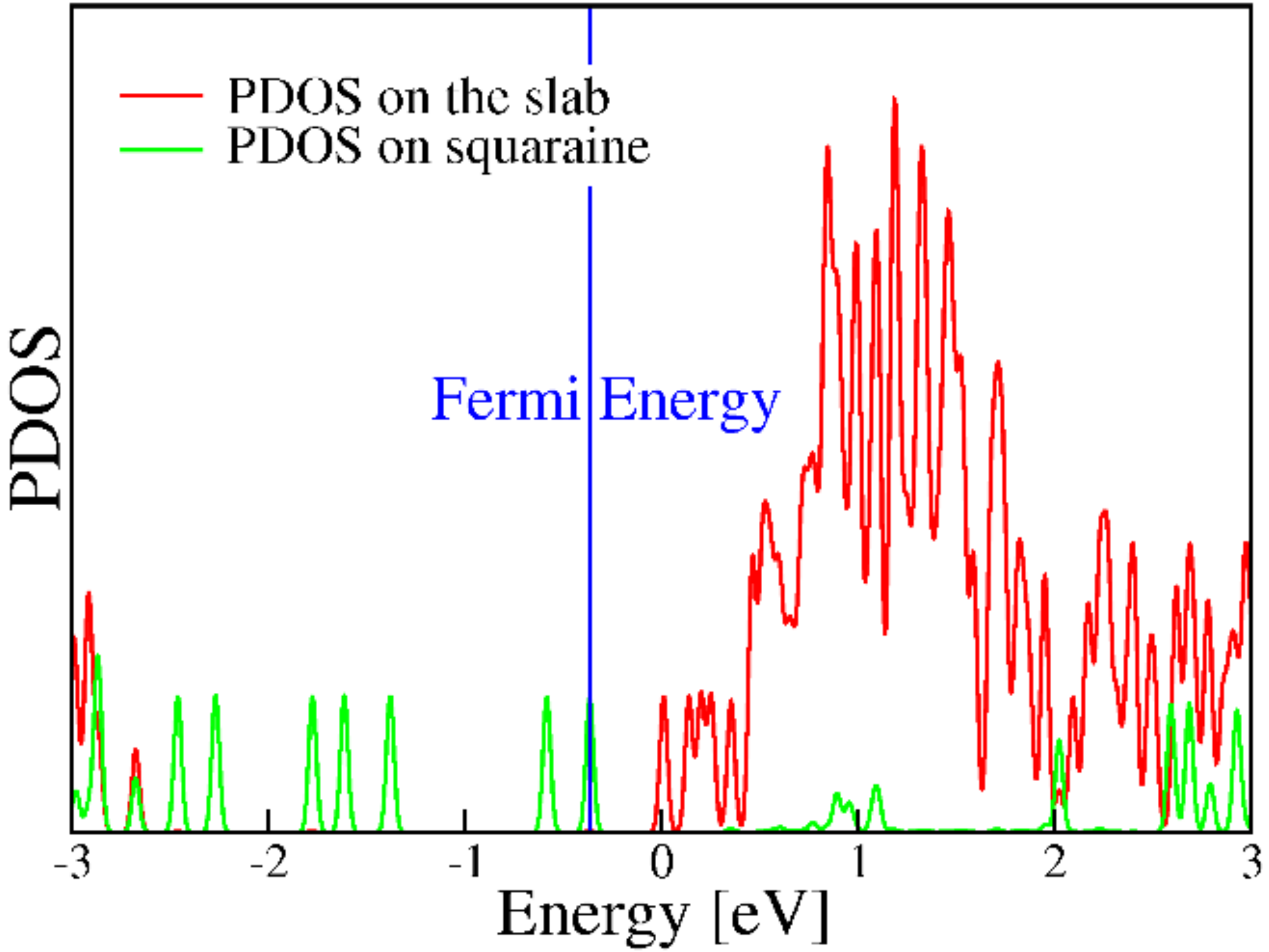


Slab geometry:
1x4 TiO2 anatase slab,
Exposing (101) surface

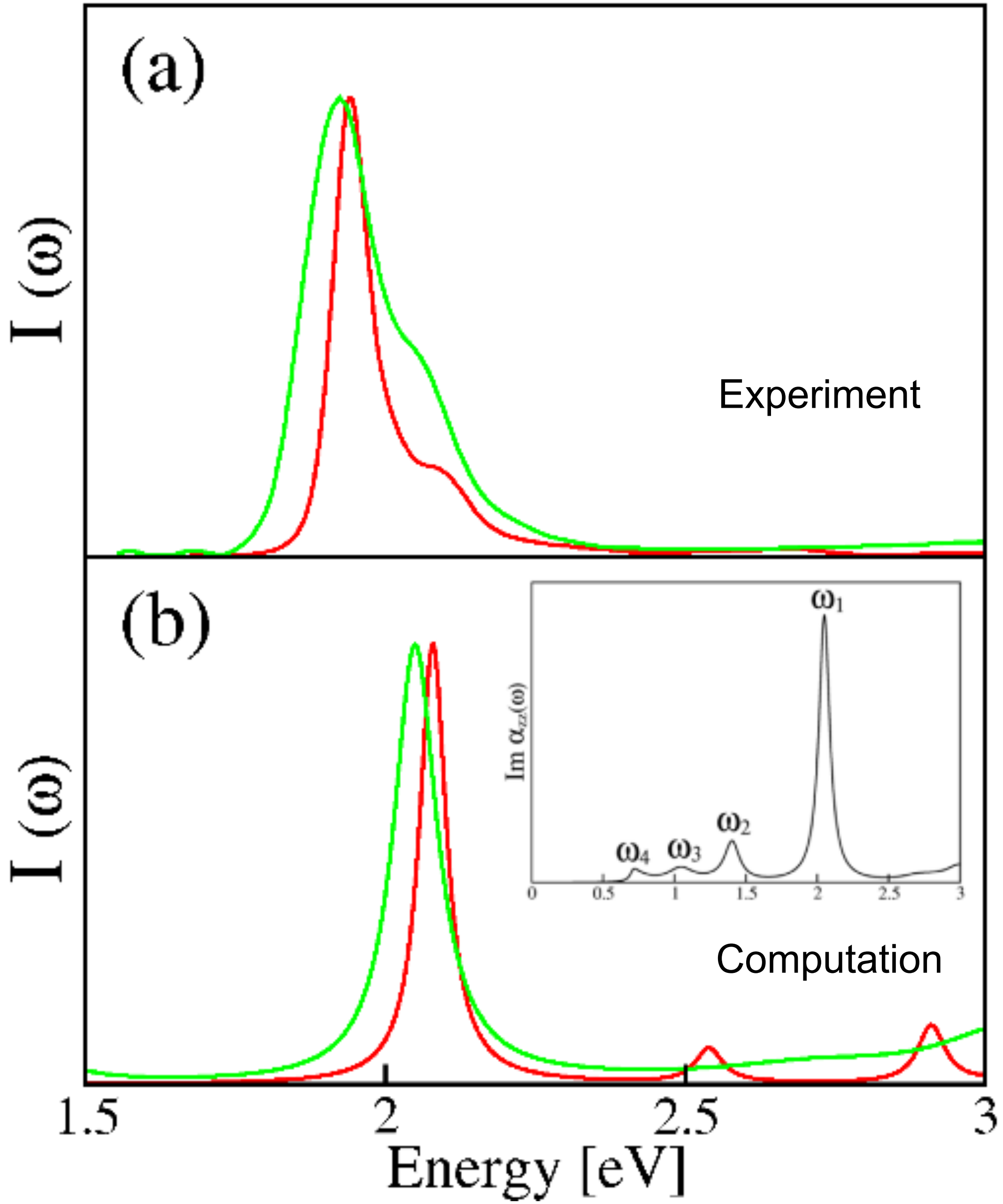
PBE functional, PW basis set
(Quantum-ESPRESSO code)

Shown here: minimum energy
configuration

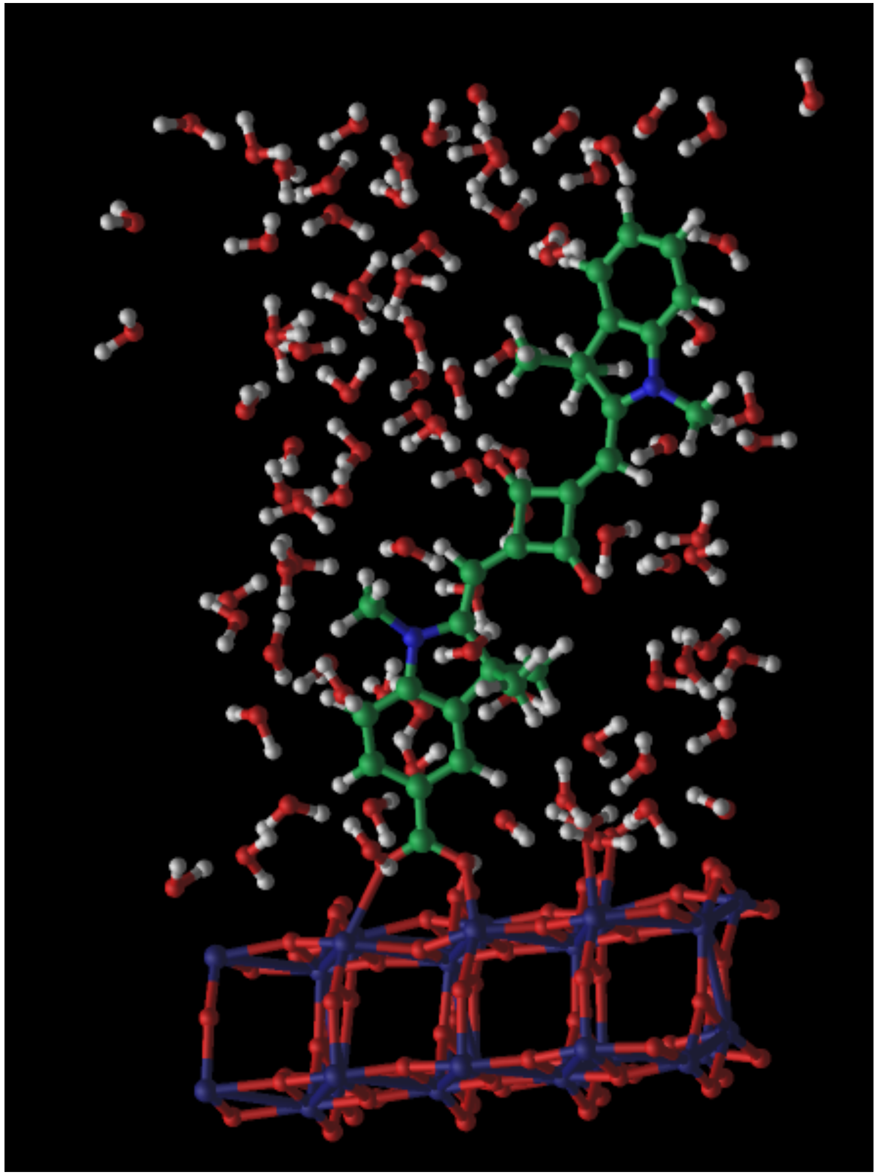
TiO2 slab with squaraine dye



Experimental and TDDFT absorption spectra



A more realistic system: Including the solvent



TDDFT calculation of optical spectra and related quantities

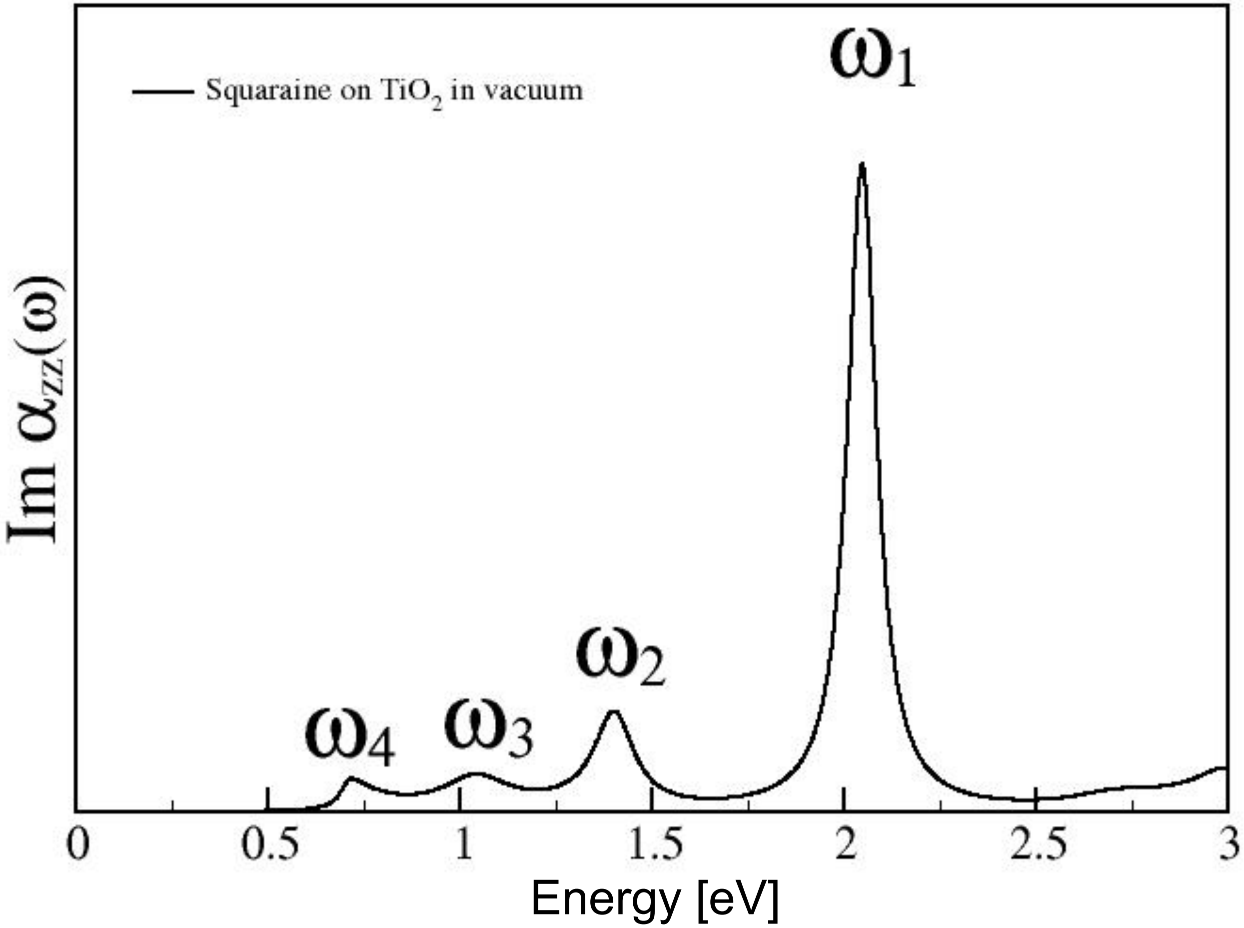
Various challenges:

- 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

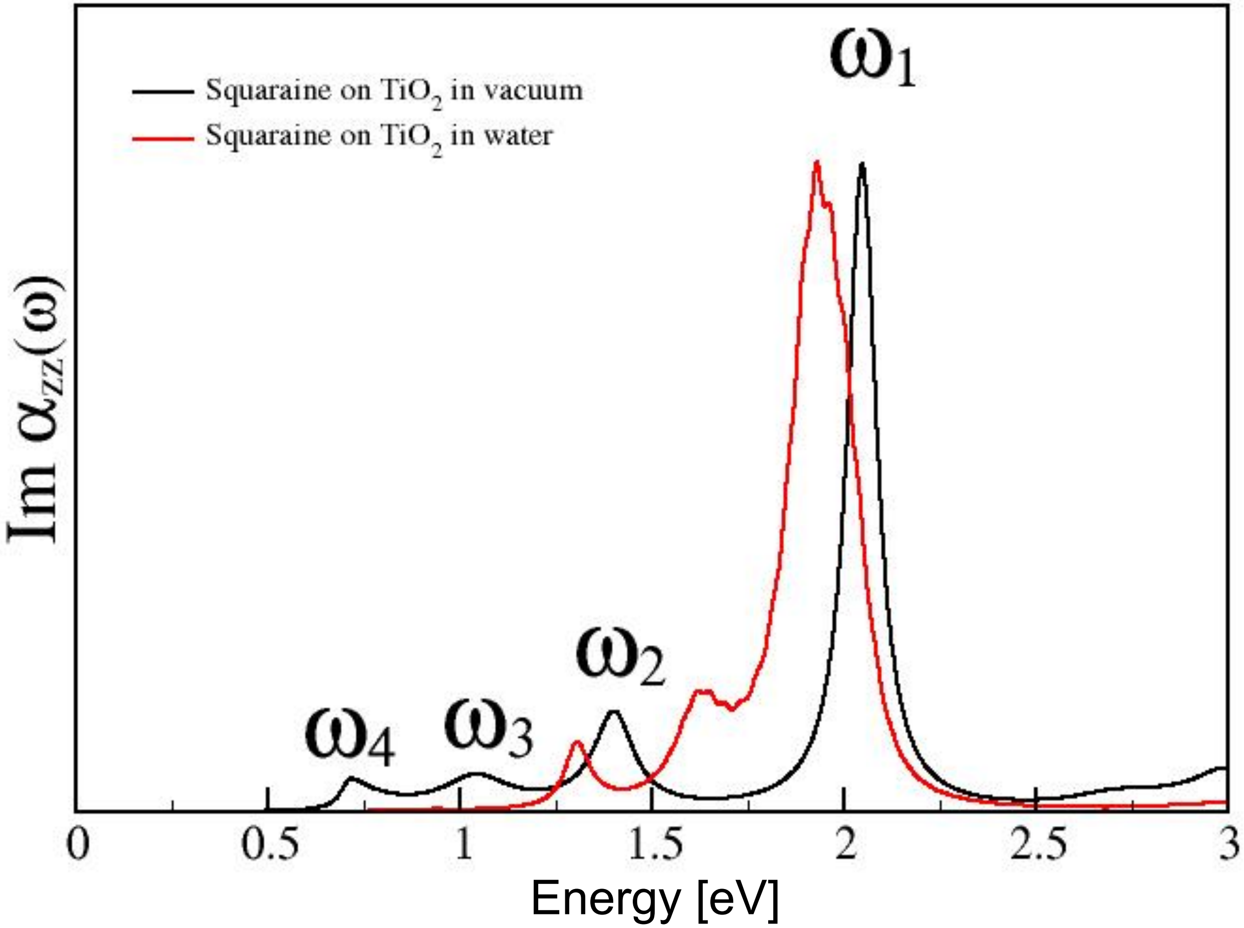
Computational tool:

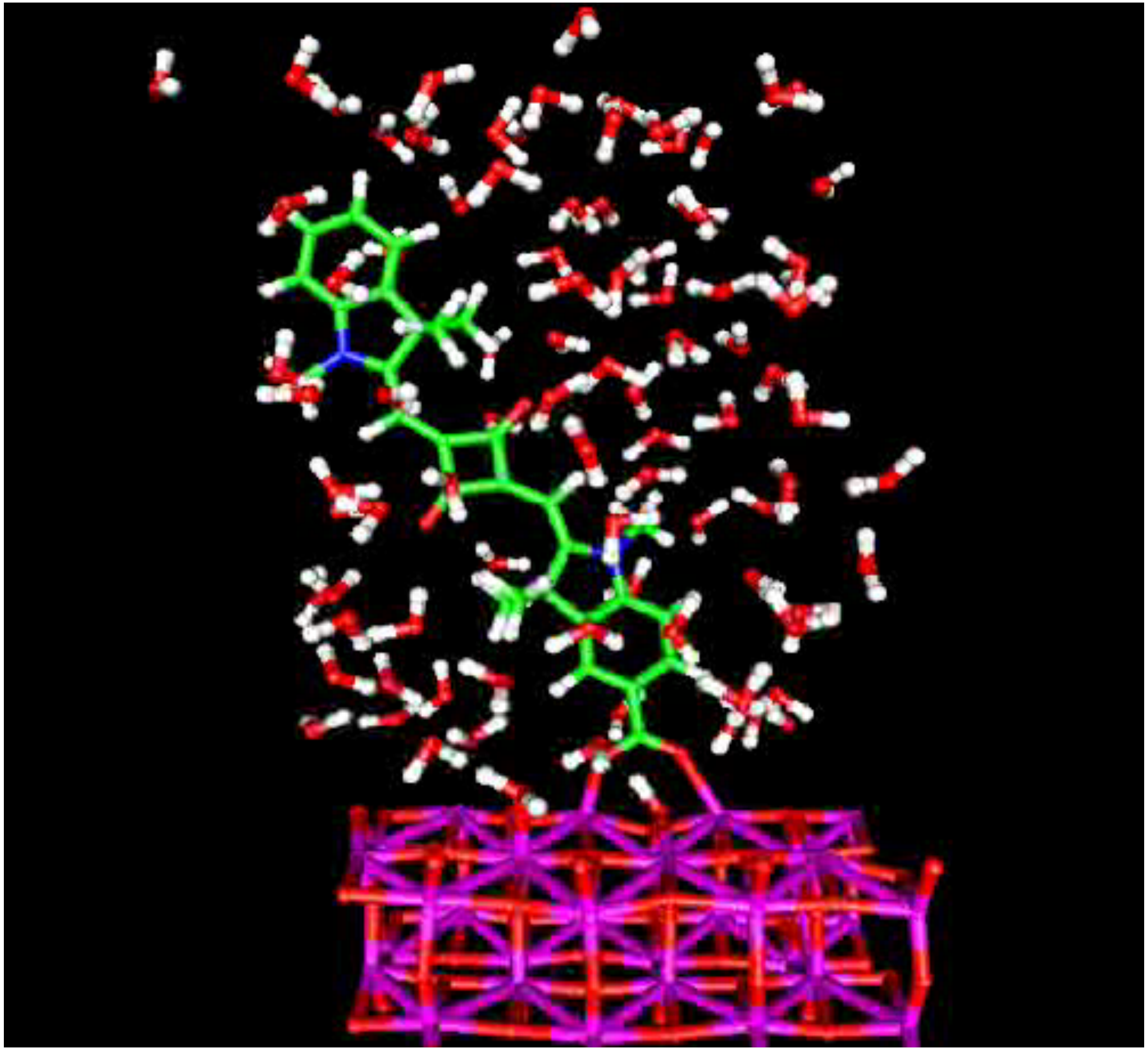
- Recursive Lanczos algorithm for TDDFT

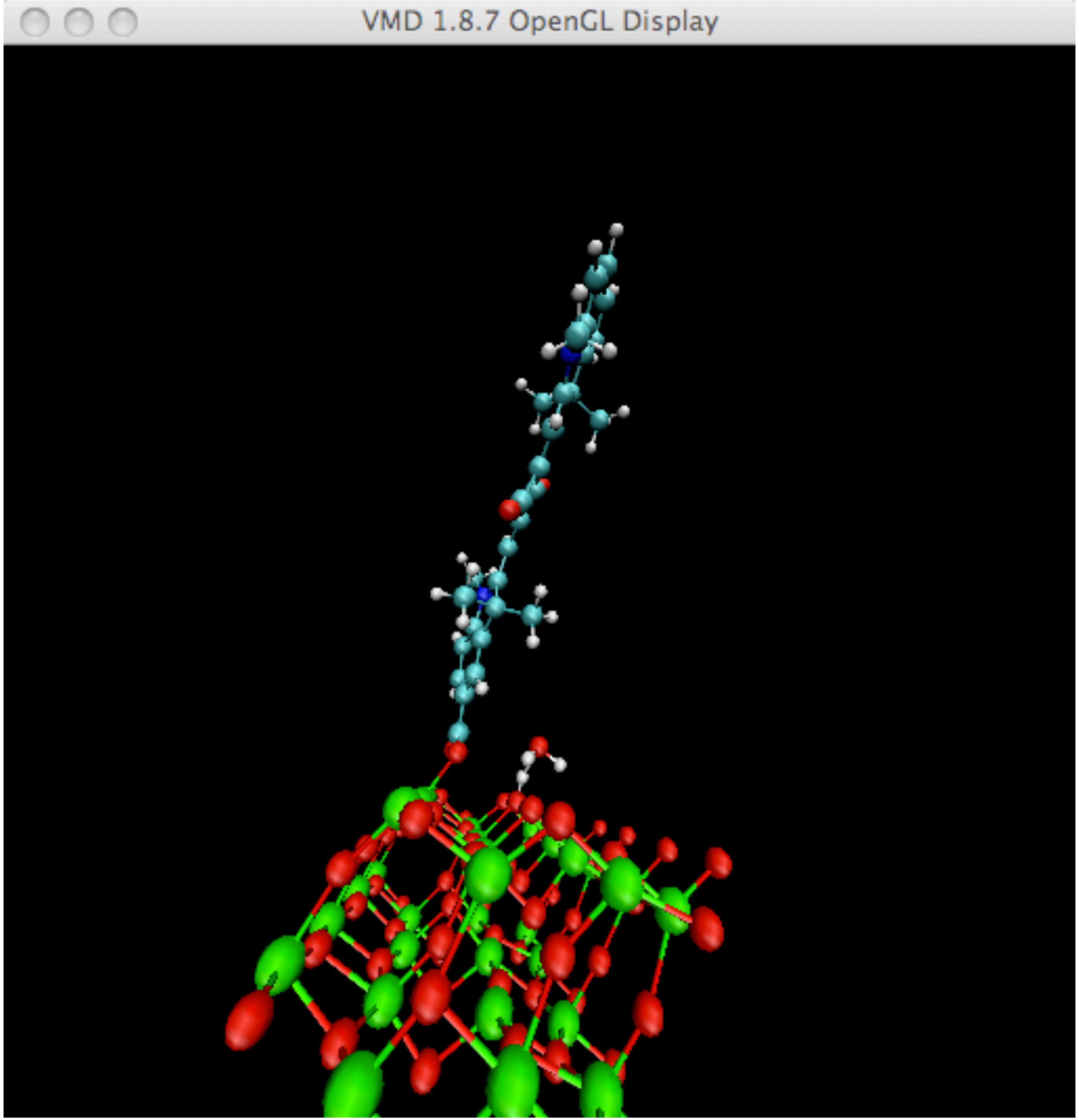
TDDFT optical spectrum: dry system

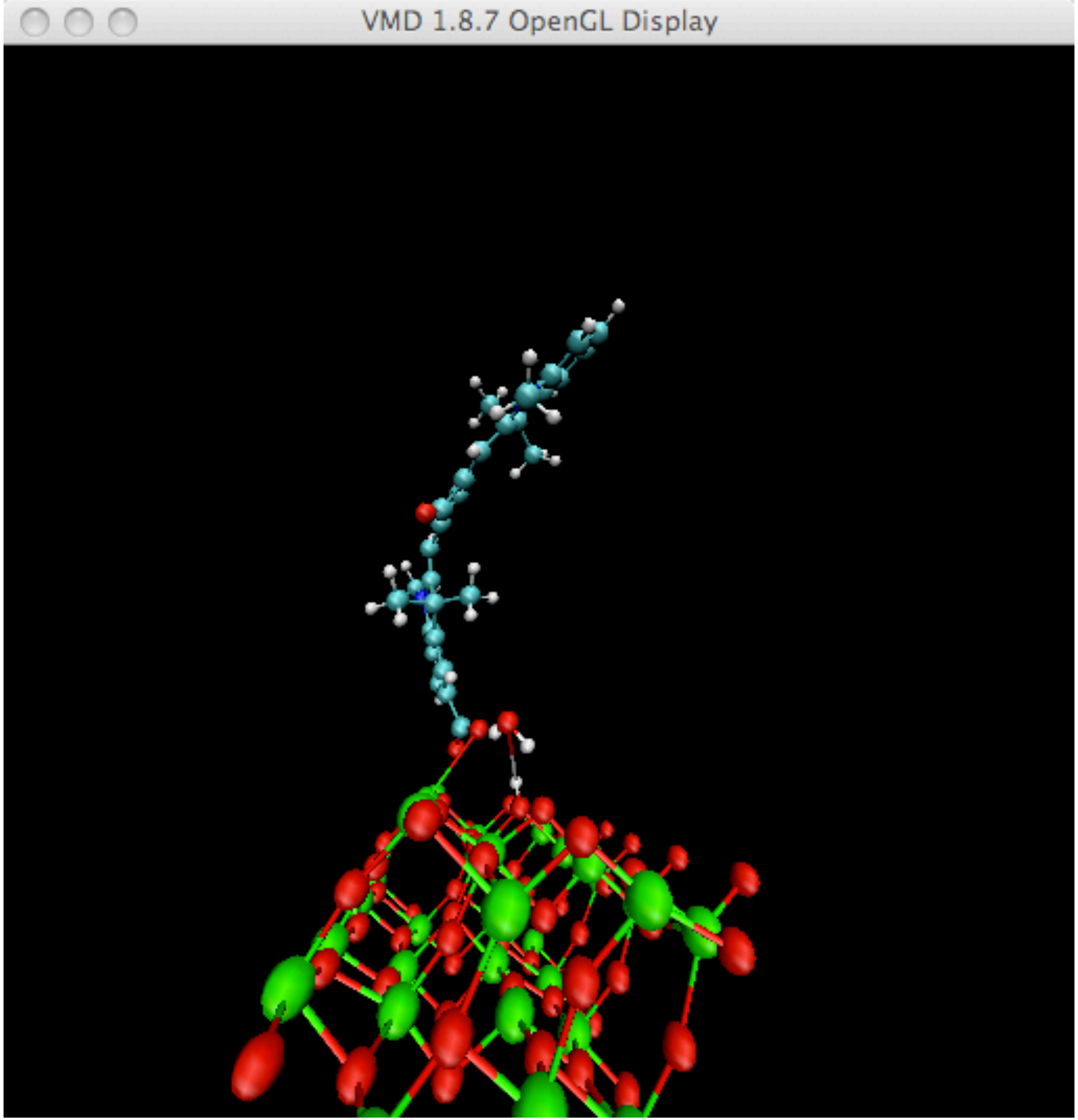


TDDFT optical spectrum including solvent



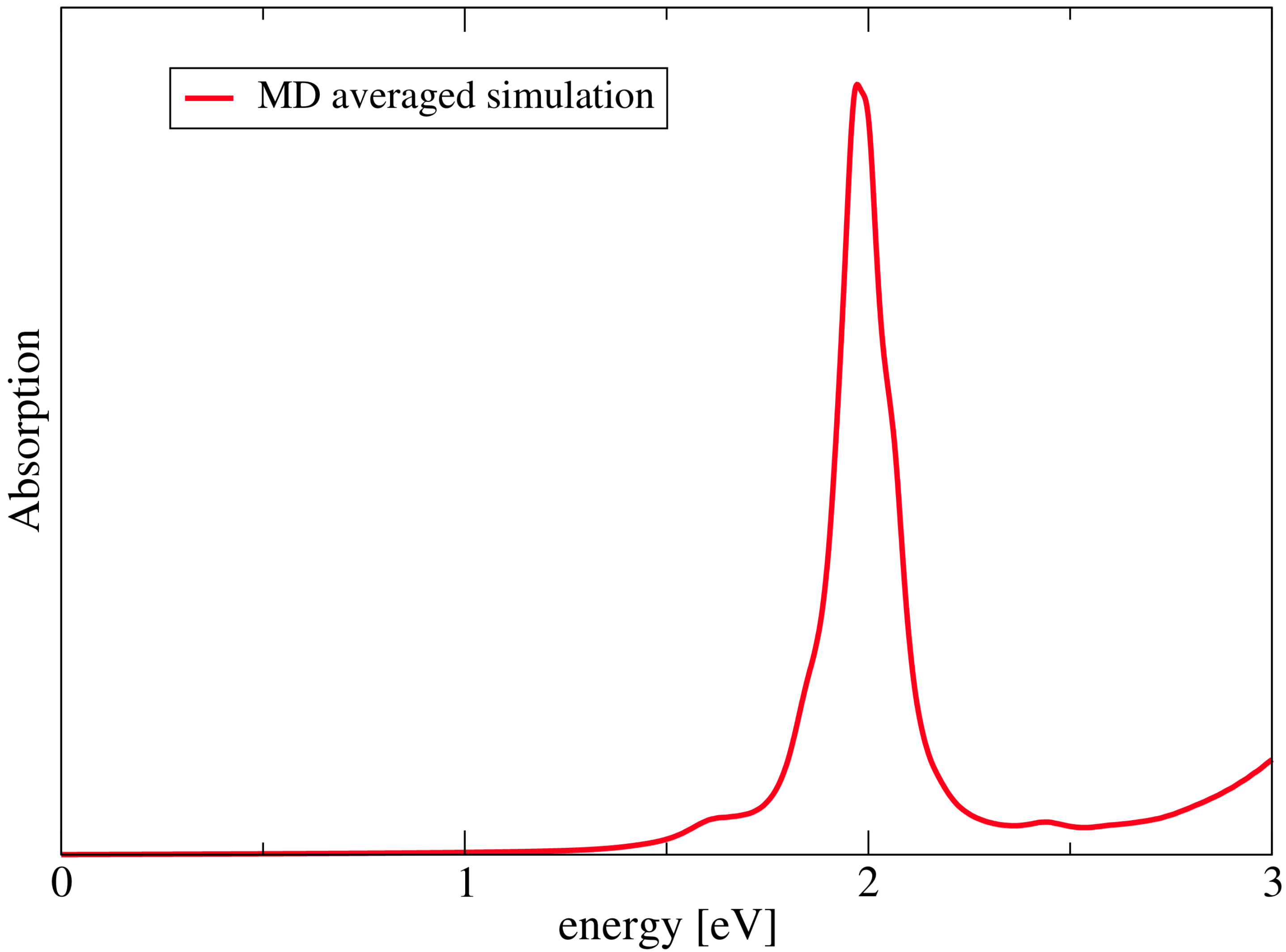



VMD 1.8.7 OpenGL Display


VMD 1.8.7 OpenGL Display

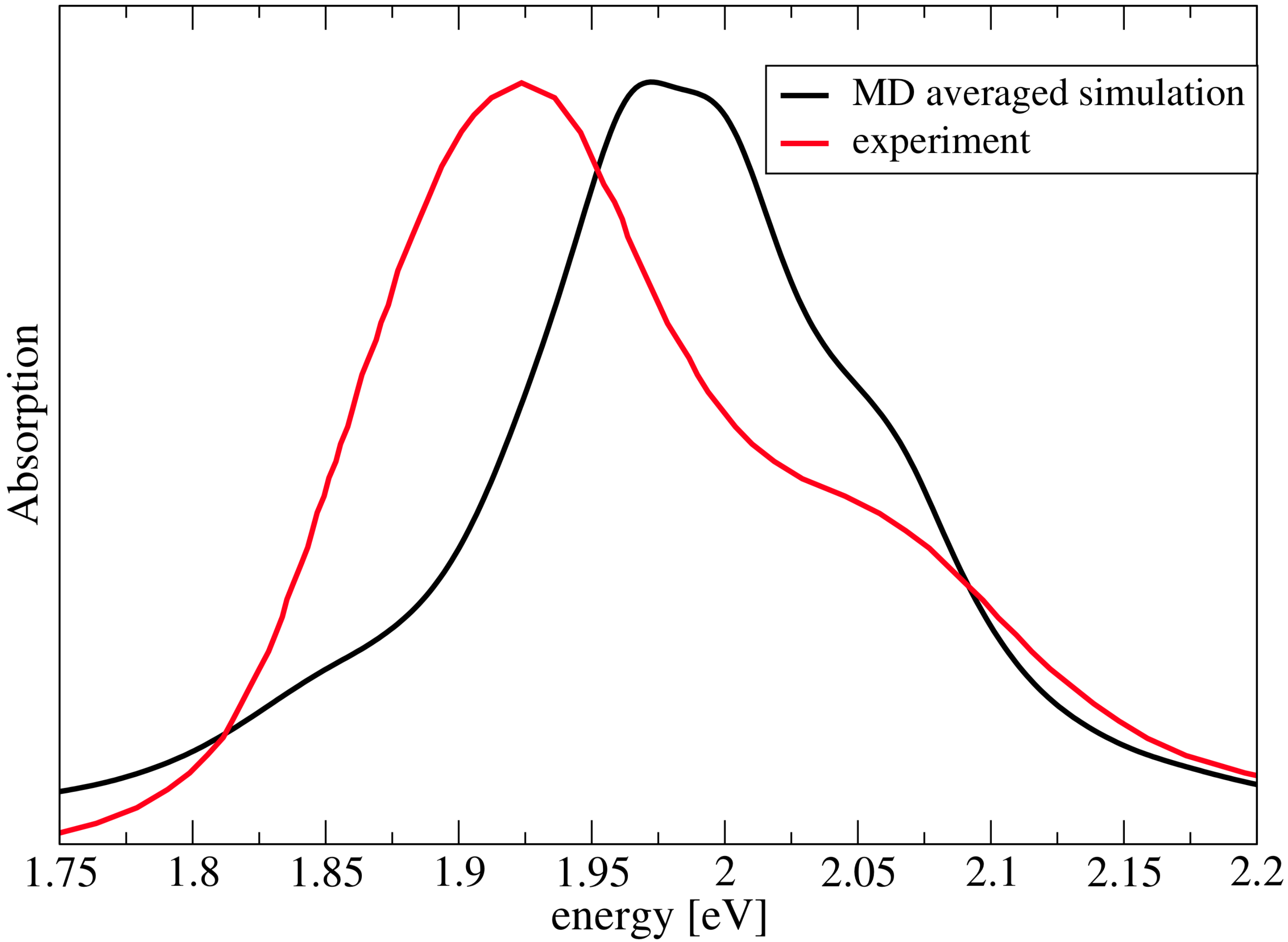
Squaraine on TiO_2

Simulation in explicit water



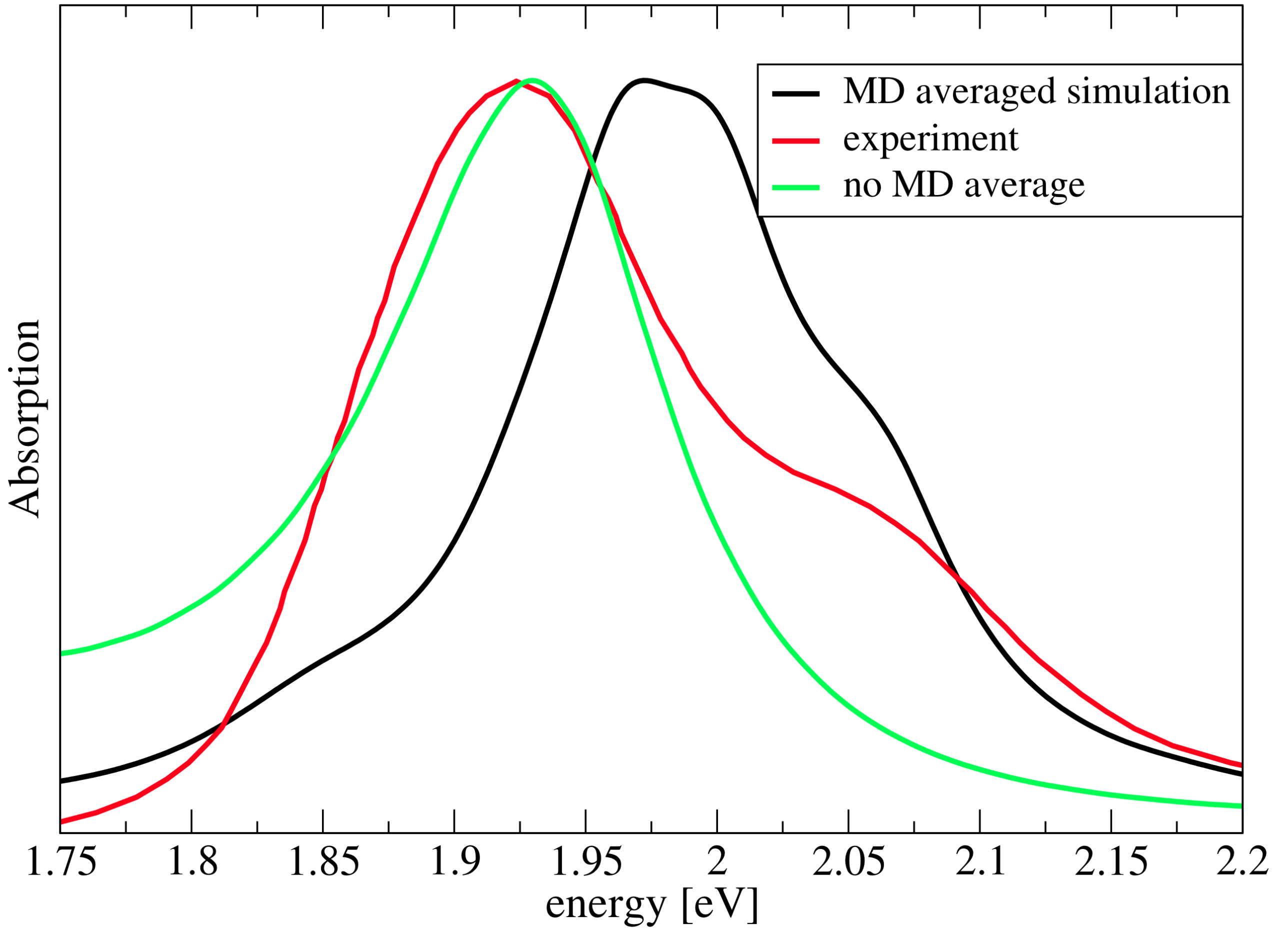
Squaraine on TiO_2

Simulation in explicit water

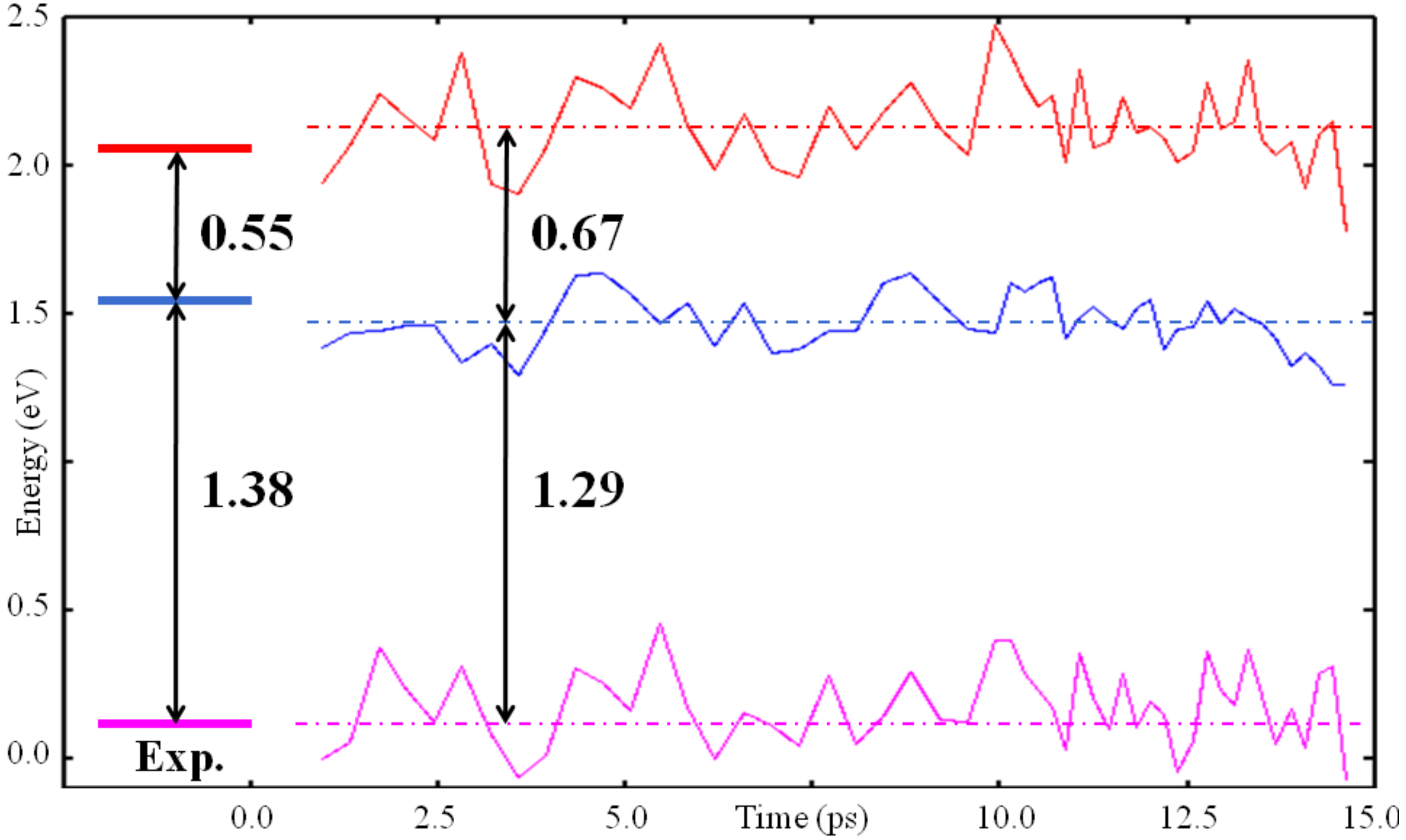


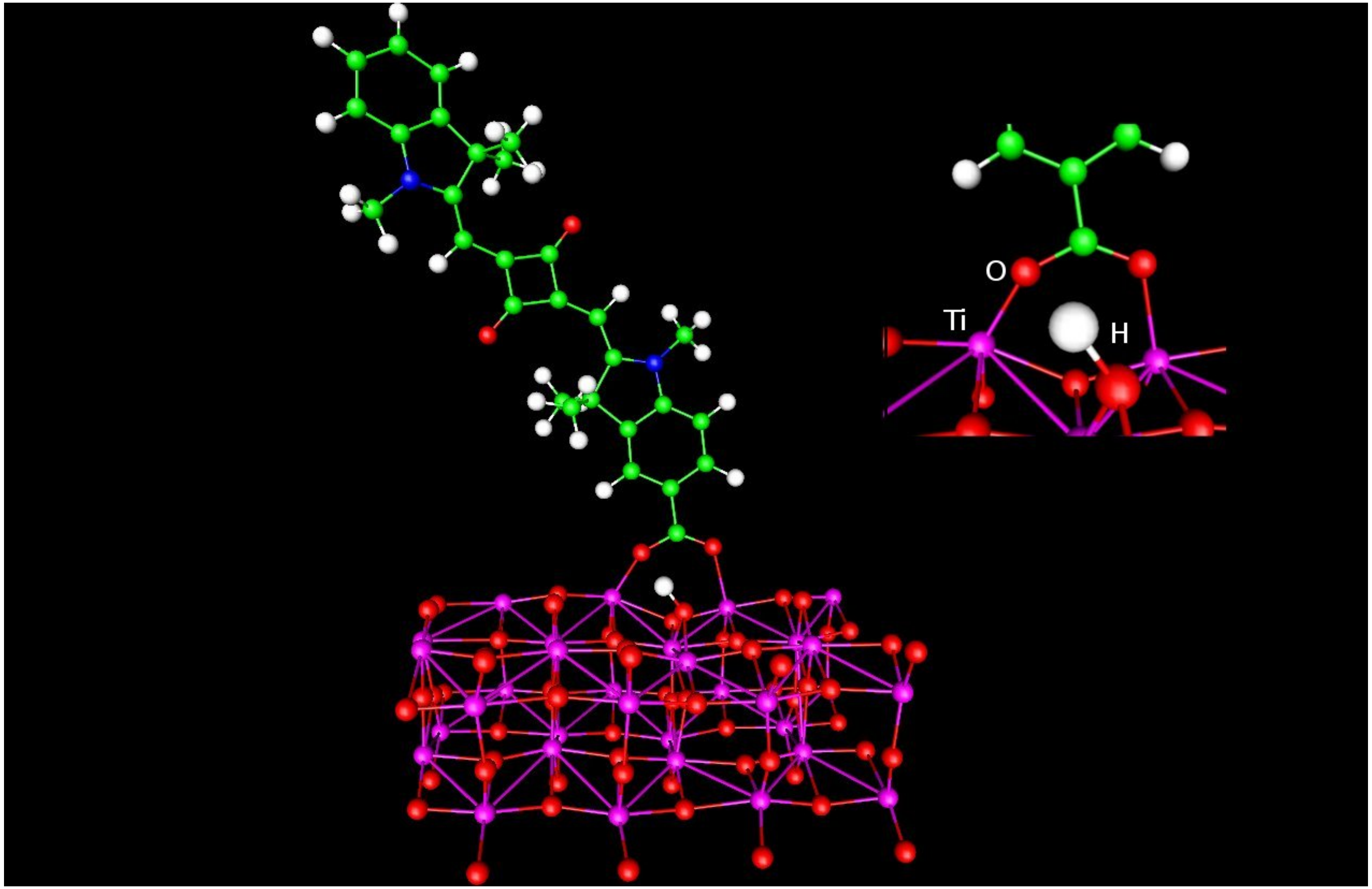
Squaraine on TiO_2

Simulation in explicit water

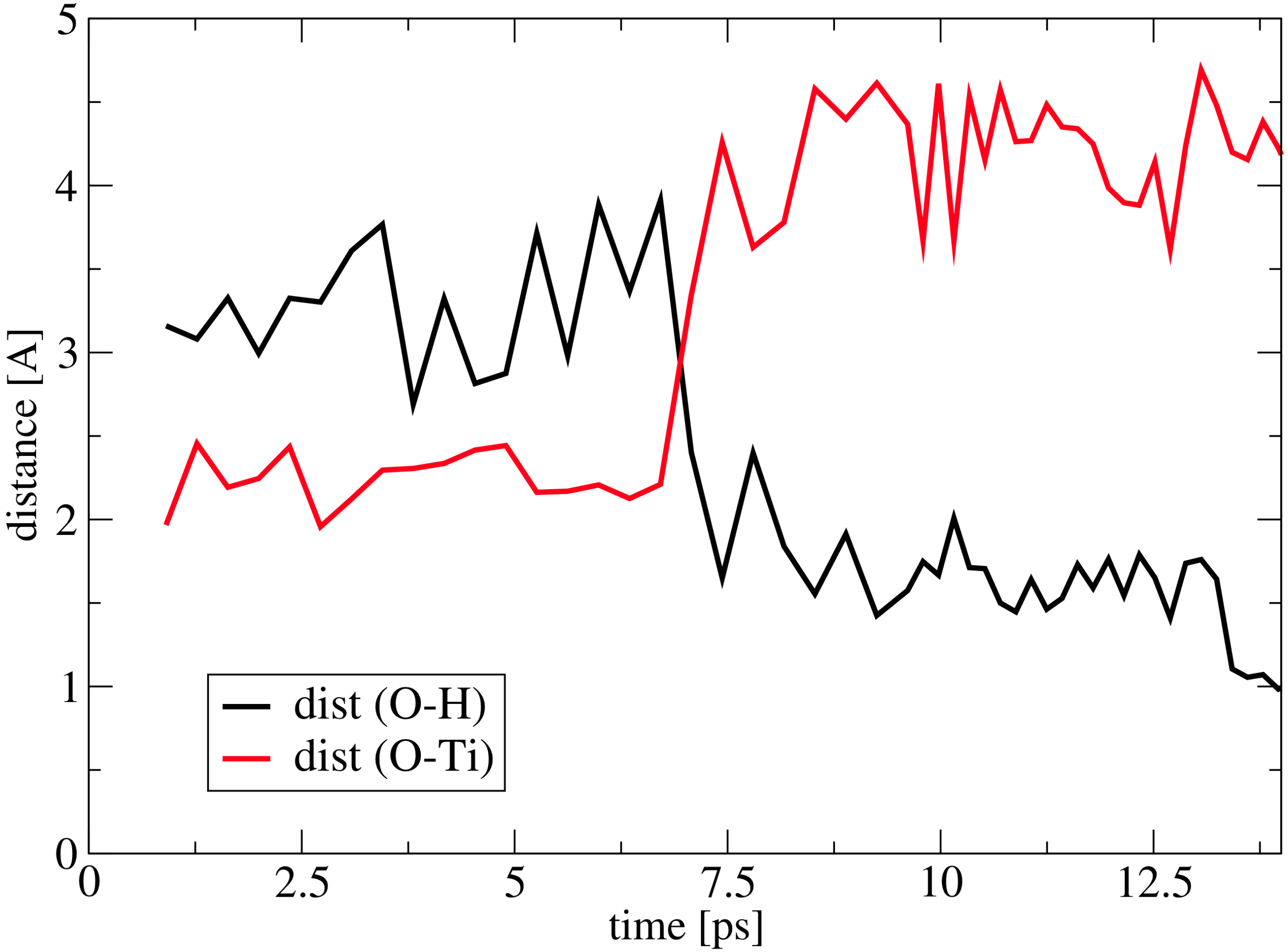


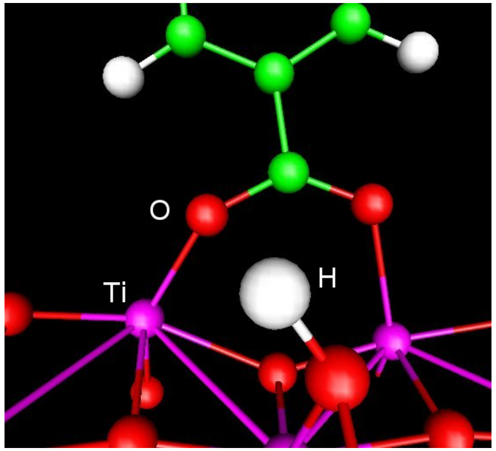
Energy level fluctuations and electron injection driving force



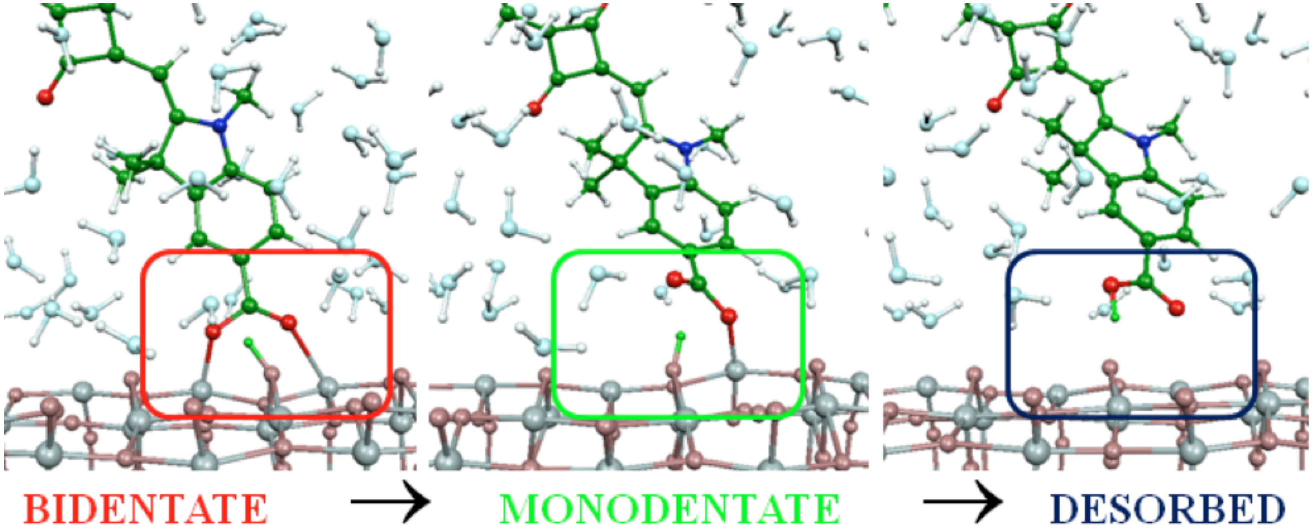

O
Ti
H

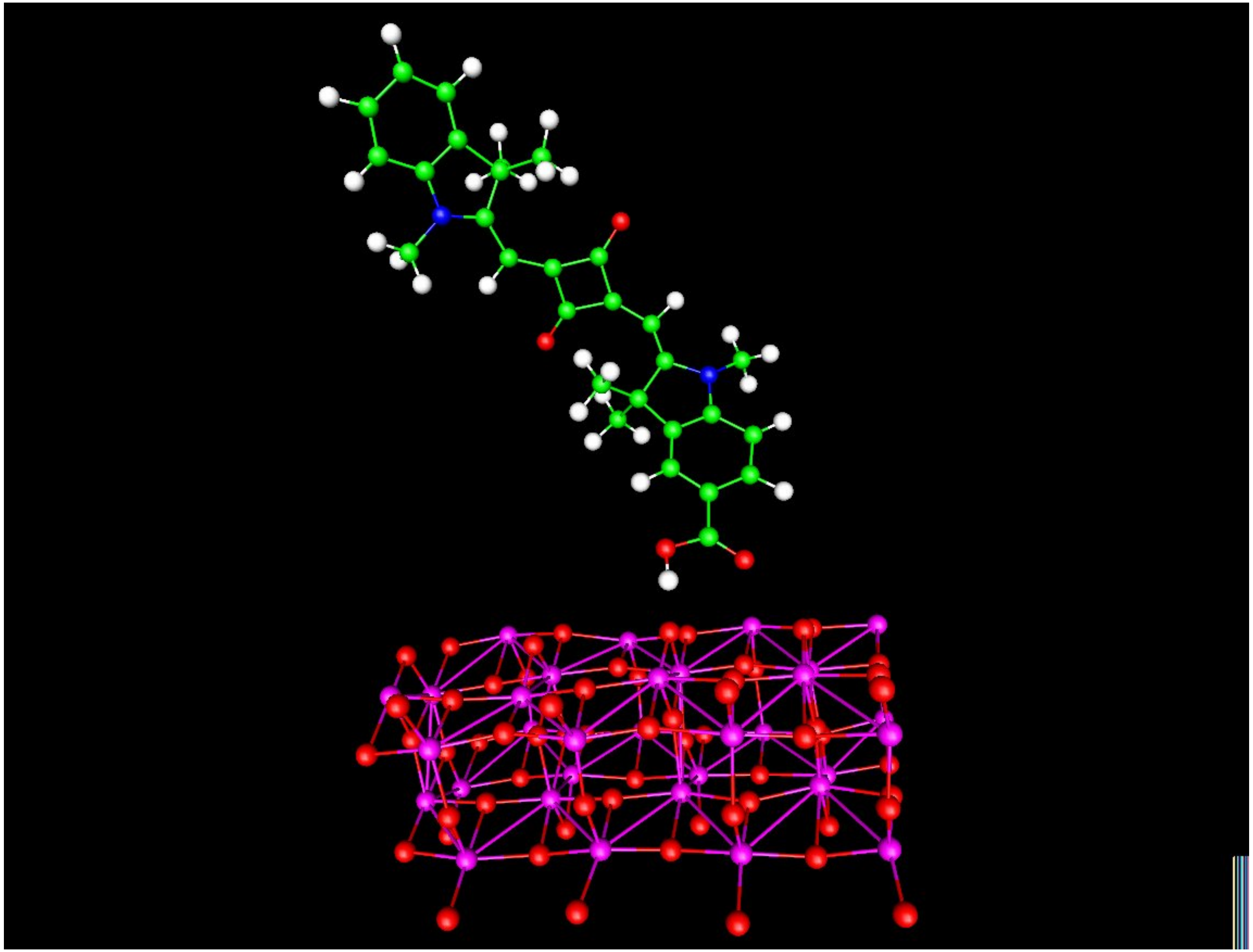
Squaraine adsorption on TiO_2





Dye desorption steps:





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

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

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.

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

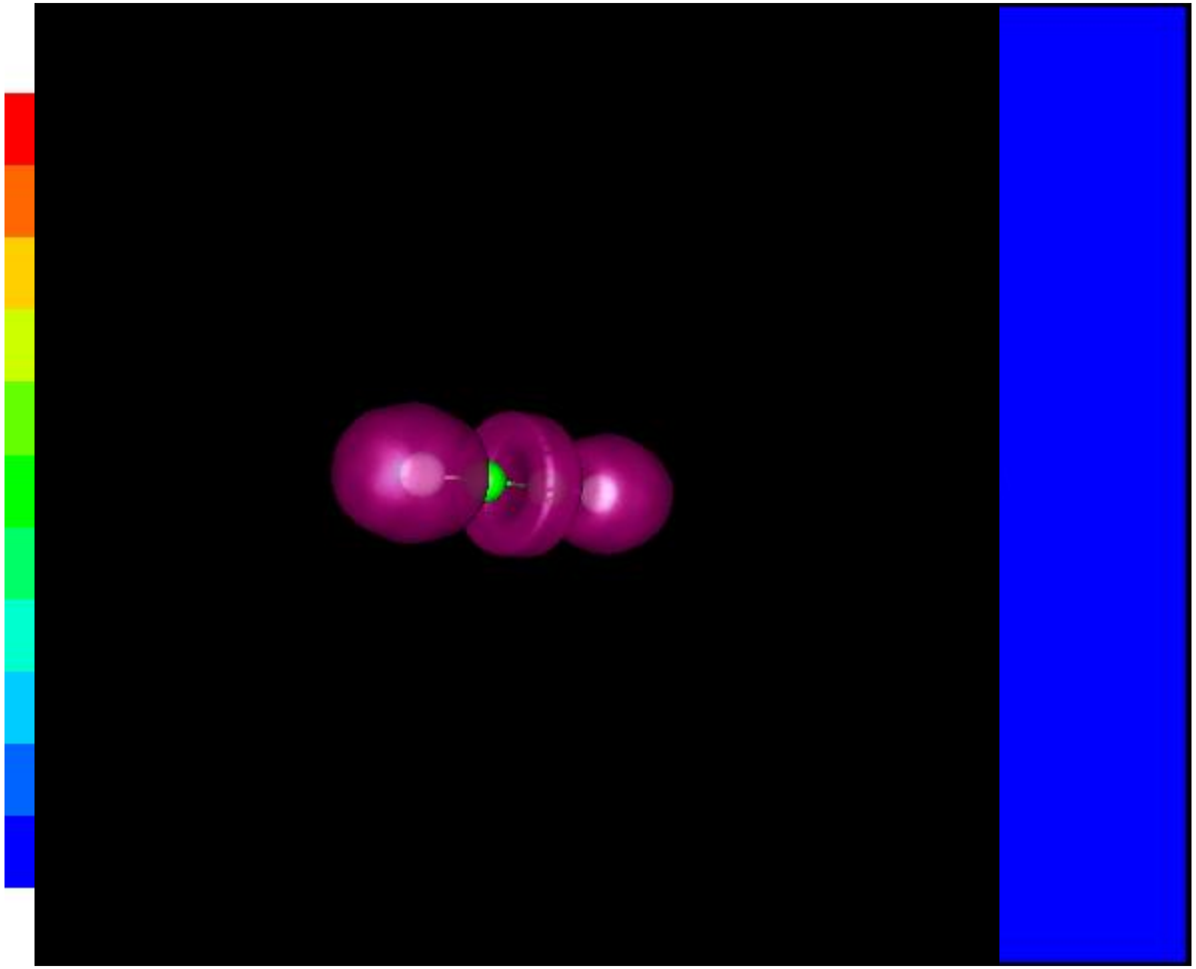
Nonlinear optical response

- Electron localization function:

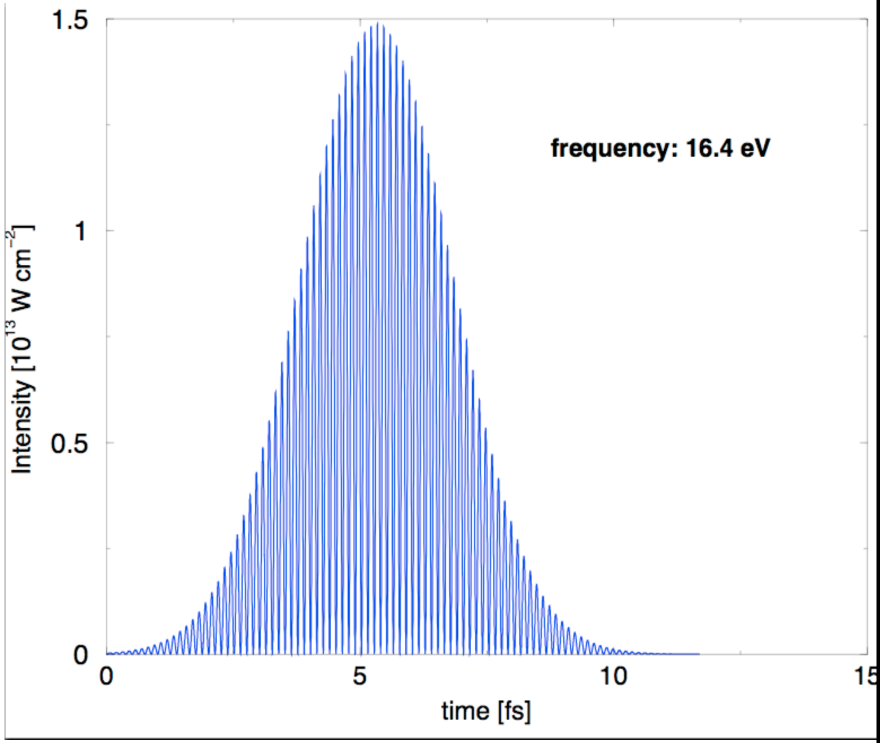
$$ELF(\boldsymbol{r},t) = \frac{1}{1 + [D_\sigma(\boldsymbol{r},t)/D_\sigma^0(\boldsymbol{r},t)]^2}$$

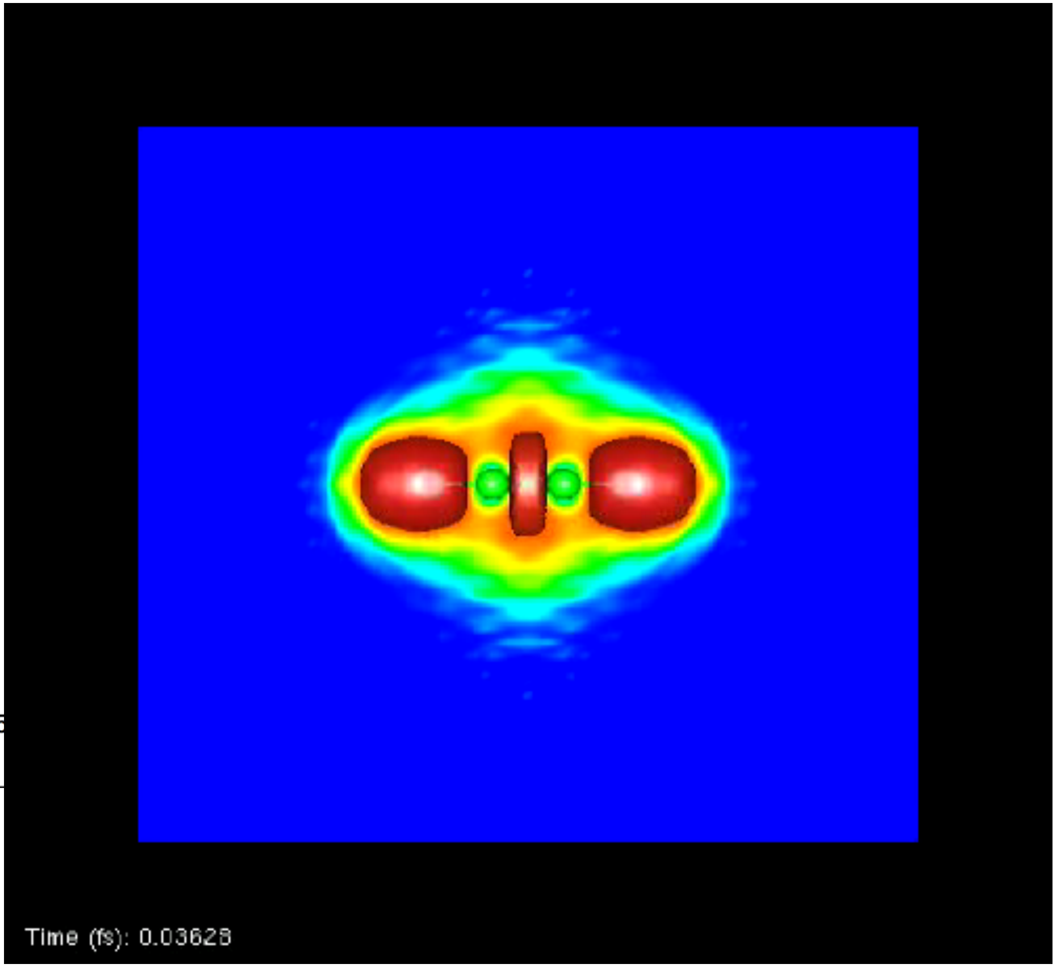
$$D_\sigma(\boldsymbol{r},t) = \tau_\sigma(\boldsymbol{r},t) - \frac{1}{4}\frac{[\nabla n_\sigma(\boldsymbol{r},t)]^2}{n_\sigma(\boldsymbol{r},t)} - \frac{j_\sigma^2(\boldsymbol{r},t)}{n_\sigma(\boldsymbol{r},t)}$$

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:

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

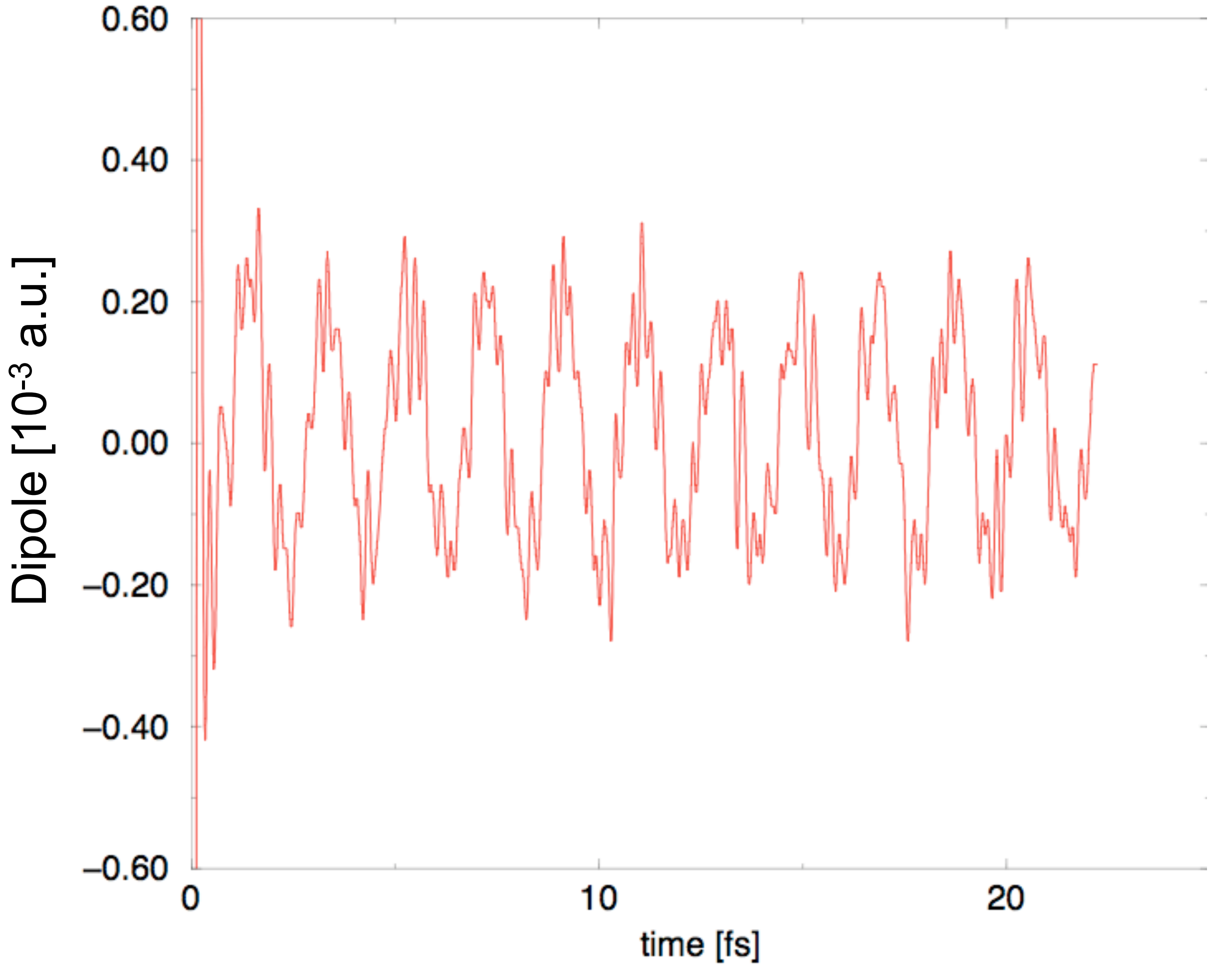
The experimentally measured strength function S is related to the Fourier transform of α:

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

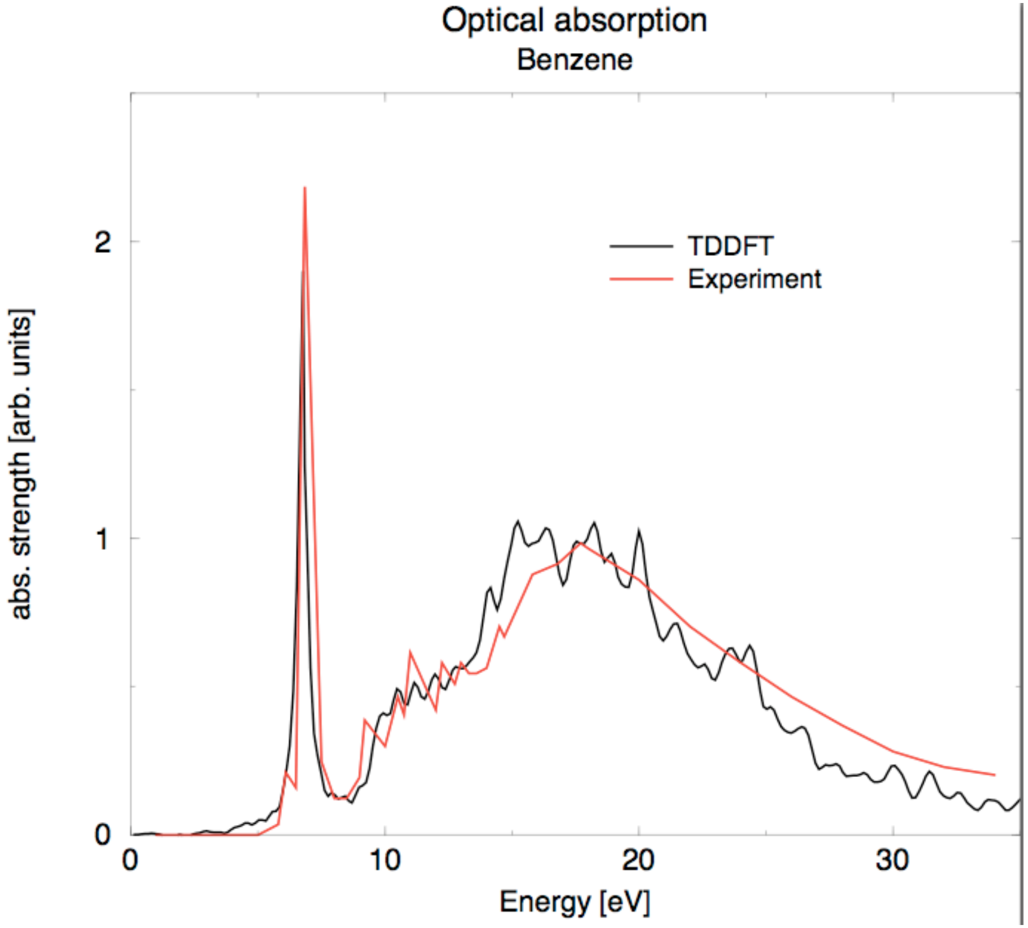
In practice: We take an E-field pulse $E_{ext} = E_0 \, \delta(t)$, calculate d(t), and obtain the spectrum $S(\omega)$ by calculating

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

A typical dipole-function d(t) …



… and the resulting spectrum



Linear response formalism in TDDFT:

- Calculate the system's ground state using DFT
- Consider a monochromatic perturbation:

$$V_{pert}(\boldsymbol{r},t) = V_0(\boldsymbol{r})\left(\exp(i\omega t) + \exp(-i\omega t)\right)$$

- Linear response: assume the time-dependent response:

$$\psi_j(t) = e^{-i\epsilon_j t}\left(\psi_j^0 + \delta\psi_j^+ e^{i\omega t} + \delta\psi_j^- e^{-i\omega t}\right)$$

$$\delta n(\boldsymbol{r},t) = \delta n^+(\boldsymbol{r})e^{i\omega t} + \delta n^-(\boldsymbol{r})e^{-i\omega t}$$

$$\delta V(\boldsymbol{r},t) = V_{pert}(\boldsymbol{r},t) + \delta V_{SCF}^+(\boldsymbol{r})e^{i\omega t} + \delta V_{SCF}^-(\boldsymbol{r})e^{-i\omega t}$$

- Put these expressions into the TD Schrödinger equation

Linear response formalism in TDDFT:

$$
\begin{aligned}
\omega\delta\psi_v^+(\boldsymbol{r}) &= \left(H_{KS}^0 - \epsilon_v^0\right)\delta\psi_v^+ + \hat{P}_{\mathbf{c}}\left(\delta V_{SCF}^+(\boldsymbol{r}) + V_{pert}(\boldsymbol{r})\right)\psi_v^0(\boldsymbol{r}) \\
-\omega\delta\psi_v^-(\boldsymbol{r}) &= \left(H_{KS}^0 - \epsilon_v^0\right)\delta\psi_v^- + \hat{P}_{\mathbf{c}}\left(\delta V_{SCF}^-(\boldsymbol{r}) + V_{pert}(\boldsymbol{r})\right)\psi_v^0(\boldsymbol{r})
\end{aligned}
$$

Now define the following linear combinations:

$$
\begin{aligned}
x_v(\boldsymbol{r}) &= \frac{1}{2}\left(\delta\psi_v^+(\boldsymbol{r}) + \delta\psi_v^-(\boldsymbol{r})\right) \\
y_v(\boldsymbol{r}) &= \frac{1}{2}\left(\delta\psi_v^+(\boldsymbol{r}) - \delta\psi_v^-(\boldsymbol{r})\right)
\end{aligned}
$$

$$(\omega - \mathcal{L})\,|\boldsymbol{x}, \boldsymbol{y}\rangle = |\boldsymbol{0}, \boldsymbol{v}\rangle \qquad \mathcal{L} = \begin{pmatrix} 0 & D \\ K & 0 \end{pmatrix}$$

With the following definitions:

$$\begin{aligned} D\,|\boldsymbol{x}\rangle &= \left\{\left(H^0_{KS} - \epsilon_i\right) x_i(\boldsymbol{r})\right\} \\ K\,|\boldsymbol{x}\rangle &= \left\{\left(H^0_{KS} - \epsilon_i\right) x_i(\boldsymbol{r}) + \psi^0_i(\boldsymbol{r}) \sum_j \int d\boldsymbol{r}' \; f_{Hxc}(\boldsymbol{r}, \boldsymbol{r}')\psi^0_{i'}(\boldsymbol{r}') x_{i'}(\boldsymbol{r}')\right\} \end{aligned}$$

$$\begin{pmatrix} 0 & D \\ K & 0 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \omega \begin{pmatrix} x \\ y \end{pmatrix}$$

Linear response TD-DFT essentially means solving a non-hermitean eigenvalue equation of dimension $2\ N_v \times N_c$.

Standard way to proceed (Casida's equations):

- Solve the time-independent problem to completely diagonalize the ground-state Hamiltonian.

  [Some computer time can be saved by limiting the diagonalization to the lower part of the spectrum]

- Obtain as many eigenstates/frequencies of the TD-DFT problem as needed (or as possible).

  [Some computer time can be saved by transforming the non-hermitean problem to a hermitean one (e.g. Tamm-Dancoff approx.)]

Advantages:

One obtains not only the frequency (and oscillator strength), but the fulll eigenvector of each elementary excitation.

[Info can be used for spectroscopic assignments, to calculate forces, etc]

Disadvantages:

One obtains not only the frequency (and oscillator strength), but the fulll eigenvector of each elementary excitation.

[Info is often not needed, all the information is immediately destroyed after computation]

Computationally extremely demanding (large matrices to be diagonalized)

Time-dependent density functional perturbation theory (TDDFPT)

Remember: The photoabsorption is linked to the dipole polarizability $\alpha(\omega)$

$$d(t) = \int dt' \alpha(t - t') \mathcal{E}(t')$$

If we choose $\mathcal{E}(t') = \mathcal{E}_0 \delta(t')$, then knowing d(t) gives us α(t) and thus $\alpha(\omega)$.

Therefore, we need a way to calculate the observable d(t), given the electric field perturbation $\mathcal{E}_0 \delta(t)$.

Consider an observable A:

$$A(t) = \sum_i \left(\left\langle \delta\psi_i(t) \middle| \hat{A} \middle| \psi_i^0 \right\rangle + \left\langle \psi_i^0 \middle| \hat{A} \middle| \delta\psi_i(t) \right\rangle \right)$$

Its Fourier transform is:

$$\begin{aligned}
\tilde{A}(\omega) &= \sum_i \left(\left\langle \psi_i^0 \middle| \hat{A} \middle| \delta\psi_i^-(\omega) \right\rangle + \left\langle \psi_i^0 \middle| \hat{A} \middle| \delta\psi_i^+(\omega) \right\rangle \right) \\
&= 2 \sum_i \left\langle \psi_i^0 \middle| \hat{A} \middle| x_i(\omega) \right\rangle \\
&= 2 \left\langle \boldsymbol{a}, \boldsymbol{0} \middle| \boldsymbol{x}, \boldsymbol{y} \right\rangle
\end{aligned}$$

$$\begin{aligned}\tilde{A}(\omega) &= \sum_i \left(\left\langle \psi_i^0 \middle| \hat{A} \middle| \delta\psi_i^-(\omega)\right\rangle + \left\langle \psi_i^0 \middle| \hat{A} \middle| \delta\psi_i^+(\omega)\right\rangle\right) \\ &= 2\sum_i \left\langle \psi_i^0 \middle| \hat{A} \middle| x_i(\omega)\right\rangle \\ &= 2\left\langle \boldsymbol{a}, 0 \middle| \boldsymbol{x}, \boldsymbol{y}\right\rangle\end{aligned}$$

Recall: $(\omega - \mathcal{L})\left|\boldsymbol{x}, \boldsymbol{y}\right\rangle = \left|\mathbf{0}, \boldsymbol{v}\right\rangle$

Therefore:

$$\tilde{A}(\omega) = 2\left\langle \boldsymbol{a}, \mathbf{0} \middle| (\omega - \mathcal{L})^{-1} \middle| \mathbf{0}, \boldsymbol{v}\right\rangle$$

Thus in order to calculate the spectrum, we need to calculate one given matrix element of $(\omega - \mathcal{L})^{-1}$.

In order to understand the method, look at the hermitian problem:

$$\langle v|\,(\omega - H)^{-1}\,|v\rangle$$

Build a Lanczos recursion chain:

$$\begin{aligned}
\phi_{-1} &= 0 \\
\phi_0 &= |v\rangle \\
\boxed{b_{n+1}}\phi_{n+1} &= (H - \boxed{a_n})\phi_n - \boxed{b_n}\phi_{n-1} \\
\langle\phi_{n+1}|\phi_{n+1}\rangle &= 1 \\
a_n &= \langle\phi_n|H|\phi_n\rangle
\end{aligned}$$

$$H = \begin{pmatrix}
\boxed{a_0} & \boxed{b_1} & 0 & \cdots & 0 \\
\boxed{b_1} & \boxed{a_1} & \boxed{b_2} & 0 & \vdots \\
0 & \boxed{b_2} & \boxed{a_2} & \ddots & 0 \\
\vdots & 0 & \ddots & \ddots & \boxed{b_n} \\
0 & \cdots & 0 & \boxed{b_n} & \boxed{a_n}
\end{pmatrix}$$

$$H = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & a_n \end{pmatrix}$$

$$(\omega - H) = \begin{pmatrix} \omega - a_0 & -b_1 & 0 & \cdots & 0 \\ -b_1 & \omega - a_1 & -b_2 & 0 & \vdots \\ 0 & -b_2 & \omega - a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & -b_n \\ 0 & \cdots & 0 & -b_n & \omega - a_n \end{pmatrix}$$

$$(\omega - H) = \begin{pmatrix} \omega - a_0 & -b_1 & 0 & \cdots & 0 \\ -b_1 & \omega - a_1 & -b_2 & 0 & \vdots \\ 0 & -b_2 & \omega - a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & -b_n \\ 0 & \cdots & 0 & -b_n & \omega - a_n \end{pmatrix}$$

$$(\omega - H)^{-1} = \cfrac{1}{\omega - a_0 + \cfrac{b_1^2}{\omega - a_1 + \cfrac{b_2^2}{\omega - a_2 + \cdots}}}$$

Back to the calculation of spectra:

Recall: $(\omega - \mathcal{L})\,|\boldsymbol{x}, \boldsymbol{y}\rangle = |\boldsymbol{0}, \boldsymbol{v}\rangle$

Therefore:

$$\tilde{A}(\omega) = 2\left\langle \boldsymbol{a}, \boldsymbol{0} \middle| (\omega - \mathcal{L})^{-1} \middle| \boldsymbol{0}, \boldsymbol{v} \right\rangle$$

Use a recursion to represent L as a tridiagonal matrix:

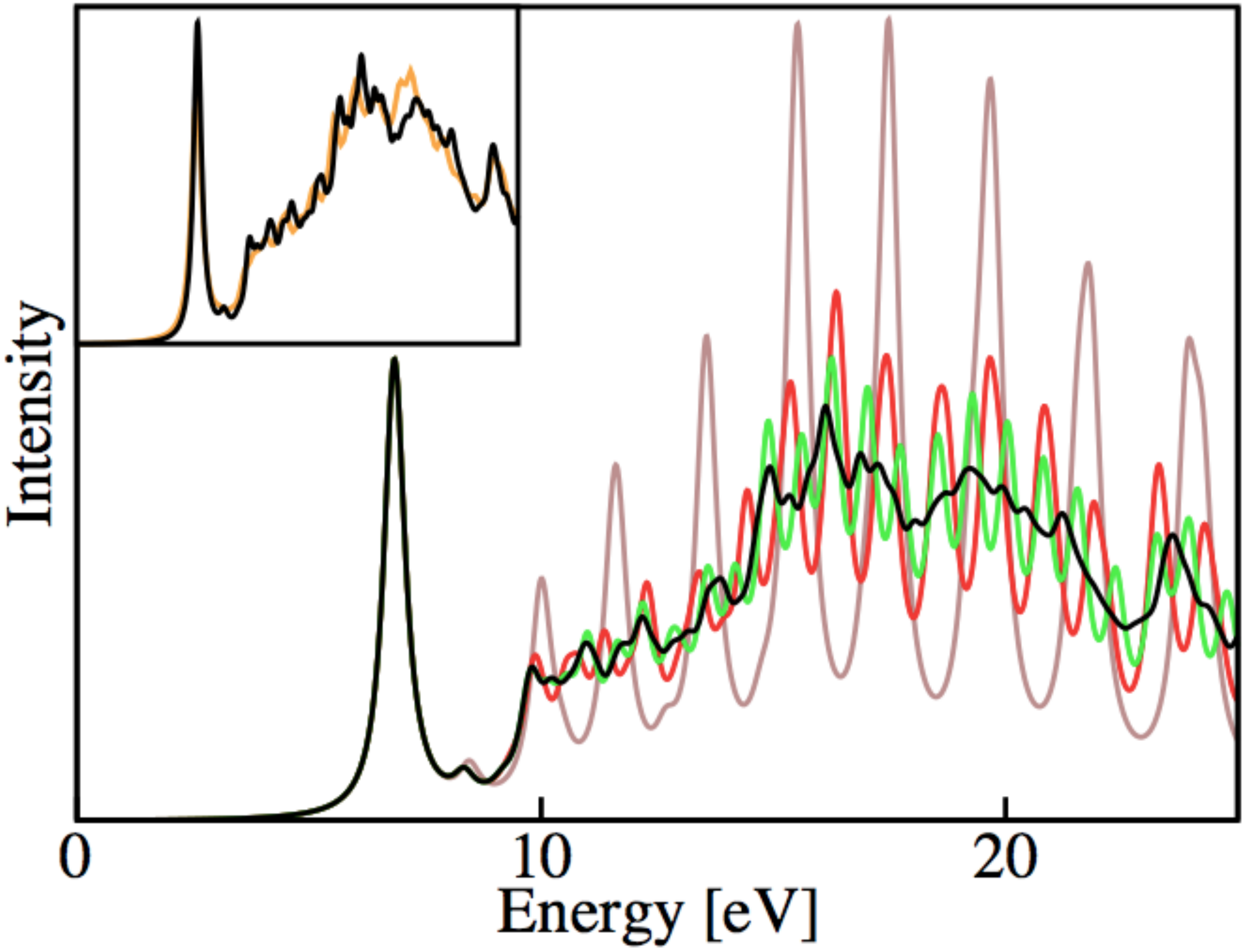
$$\mathcal{L} = \begin{pmatrix} a_1 & b_1 & 0 & & & & \\ c_1 & a_2 & b_2 & & & & \\ 0 & c_2 & a_3 & b_3 & & & \\ & & & \ddots & \ddots & \ddots & b_{N-1} \\ & & & & & c_{N-1} & a_N \end{pmatrix}$$

And the response can be written as a continued fraction!

$$
\begin{aligned}
\tilde{A}(\omega) &= 2\left\langle \boldsymbol{a}, \mathbf{0} \middle| (\omega - \mathcal{L})^{-1} \middle| \mathbf{0}, \boldsymbol{v} \right\rangle \\
&= \frac{1}{\omega - a_1 + b_2 \frac{1}{\omega - a_2 + \cdots} c_2}
\end{aligned}
$$

How does it work?

Benzene spectrum



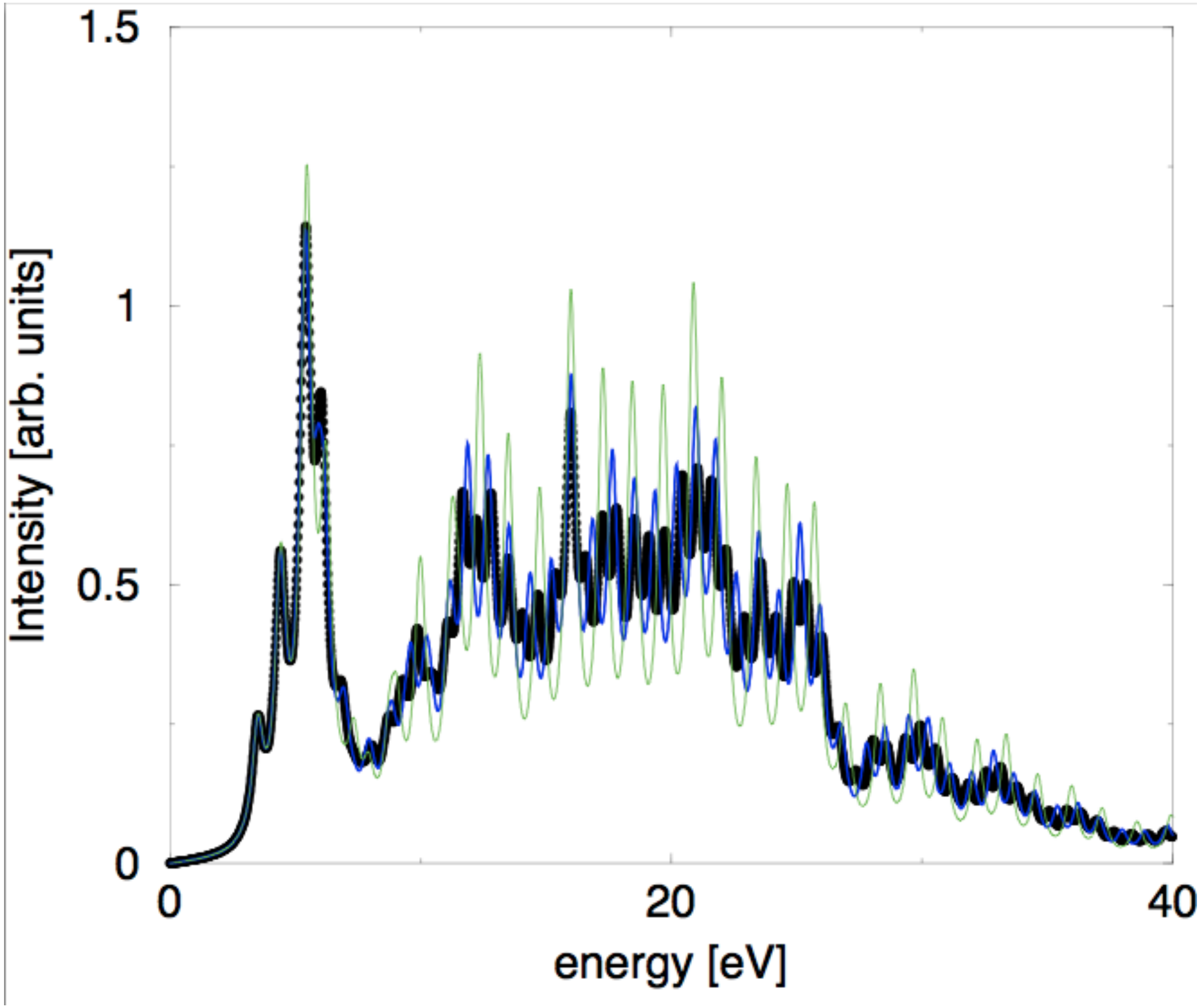
Plum: 1000

Red: 2000

Green: 3000

Black: 6000

Spectrum of C_{60}

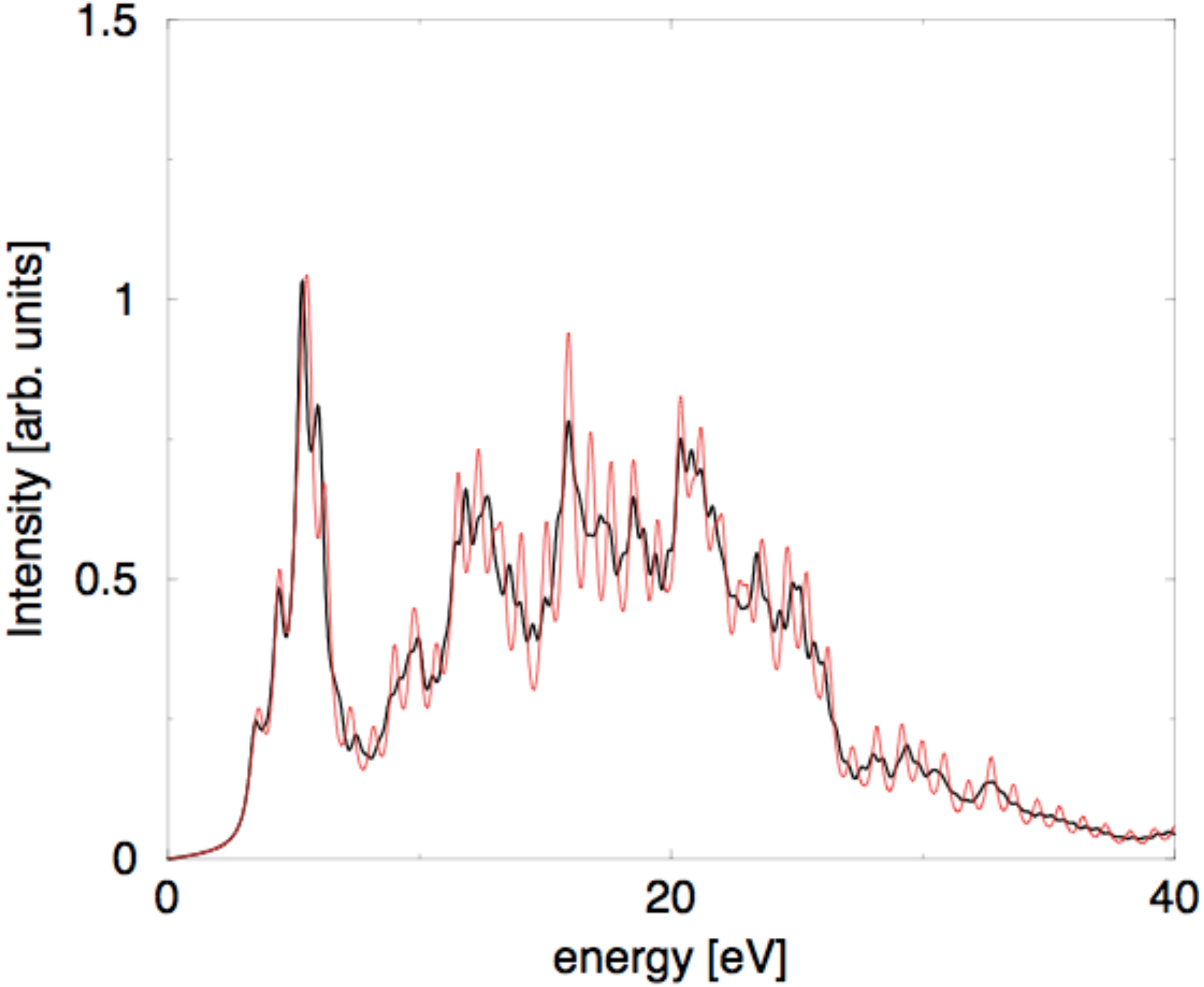


Black: 4000

Blue: 3000

Green: 2000

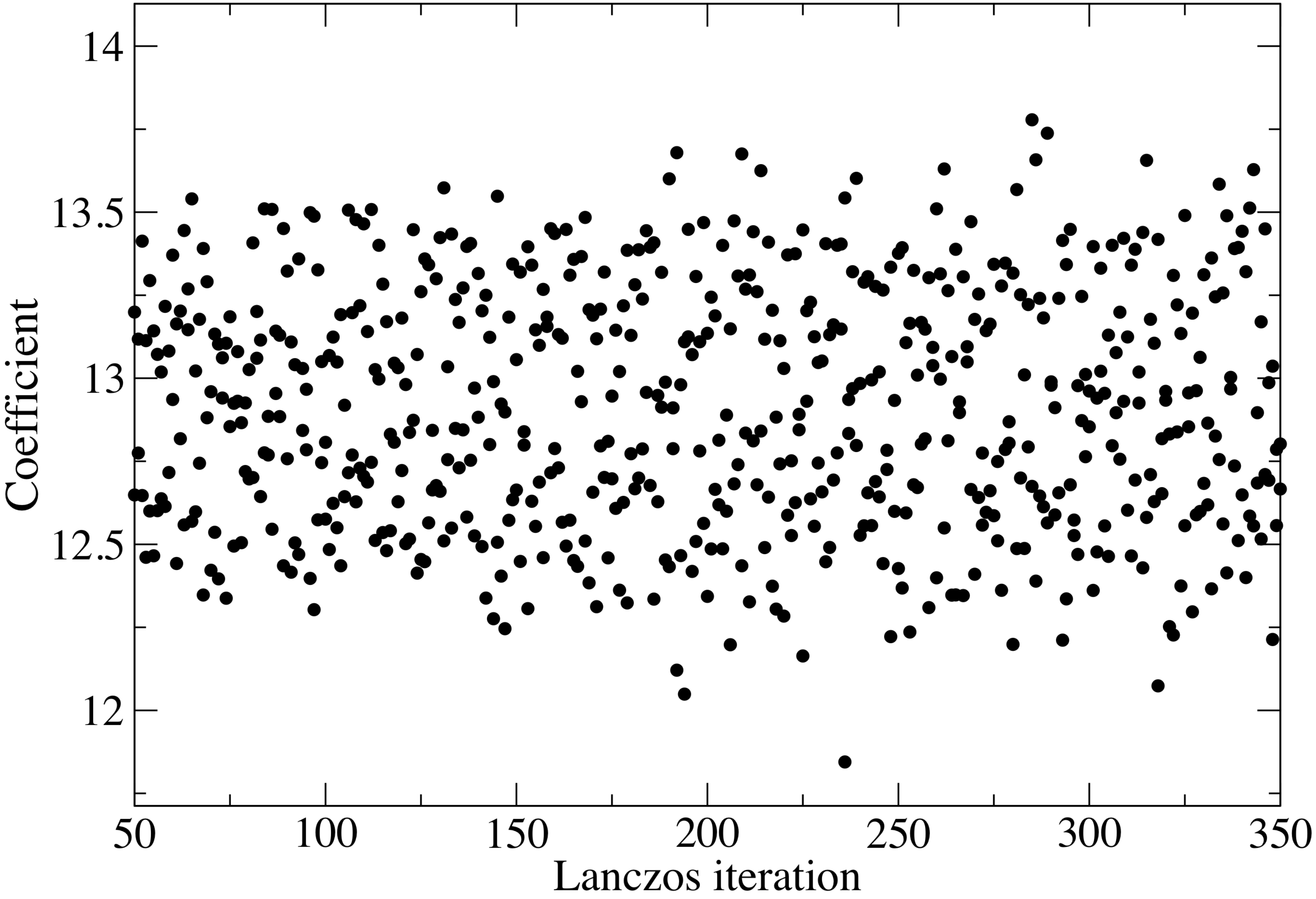
Spectrum of C_{60}: Ultrasoft pseudopotenitals



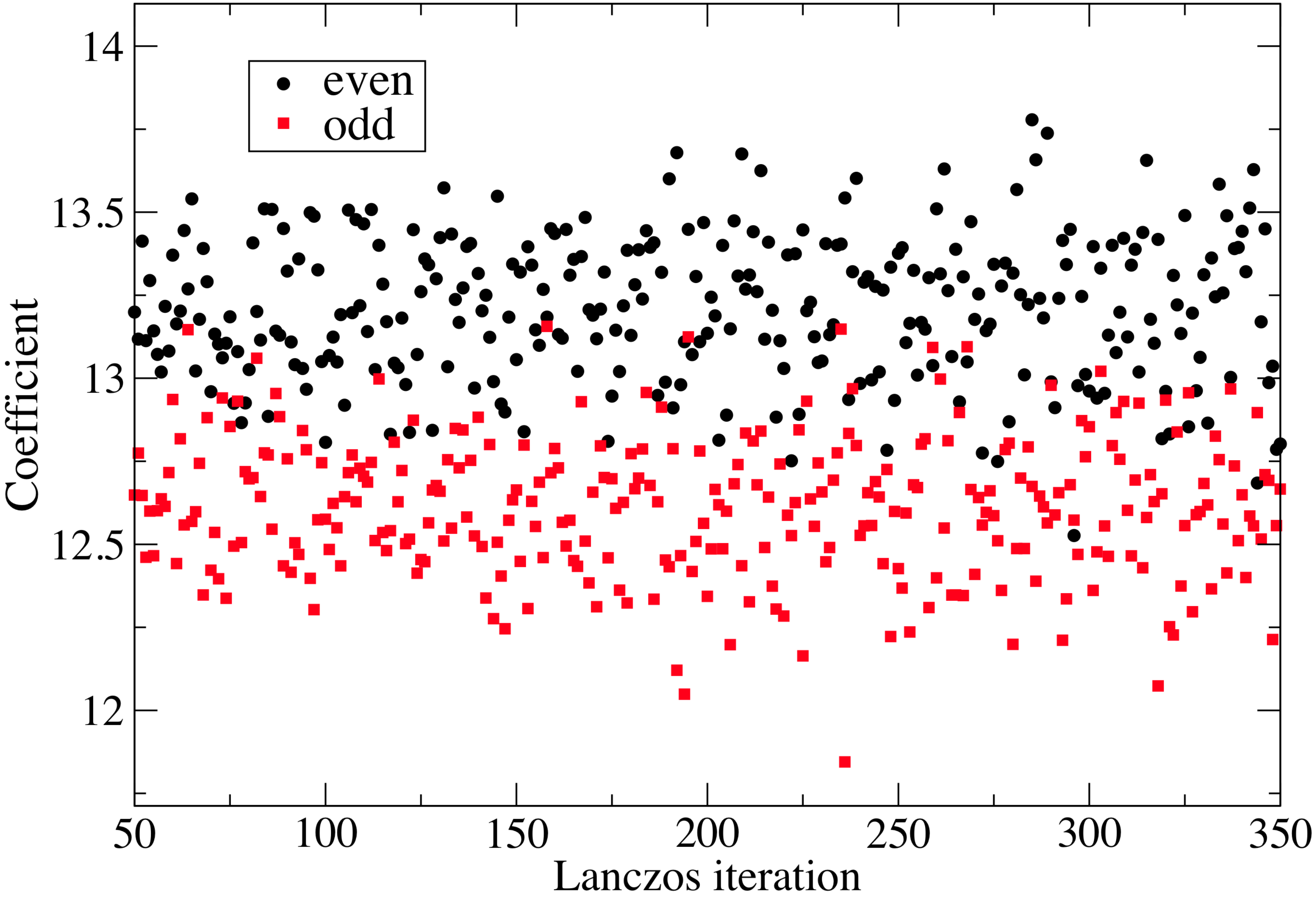
Black: 2000

Red: 1000

Speeding up convergence:
Looking at the Lanczos coefficients

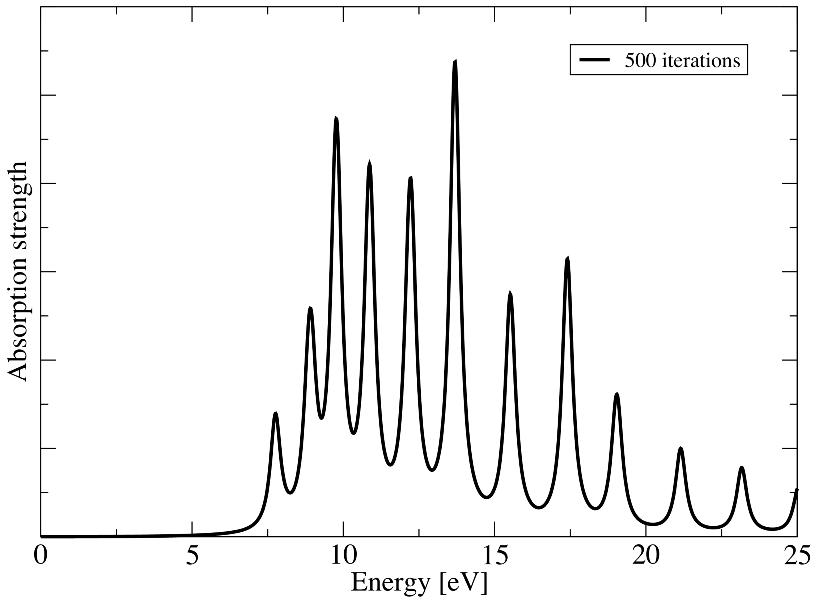


Speeding up convergence:
Looking at the Lanczos coefficients



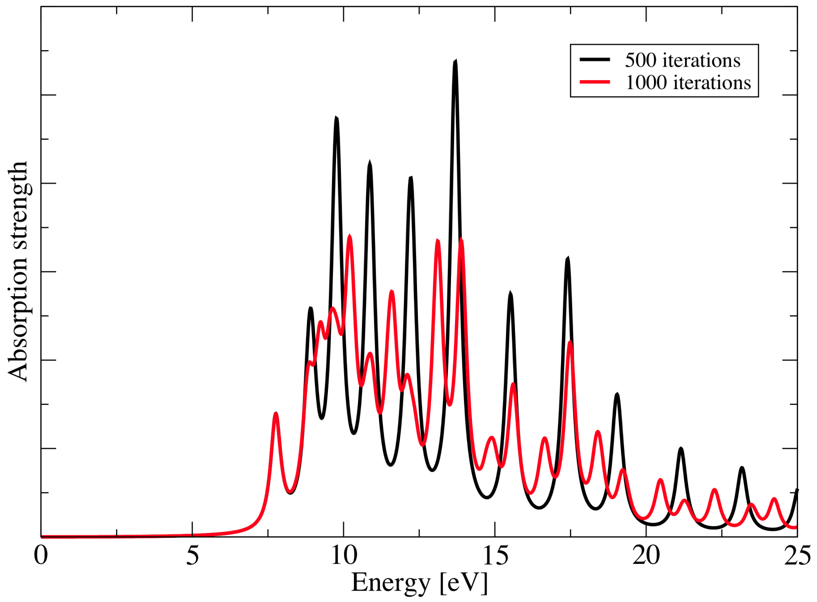
Effect of the terminator:

No terminator:



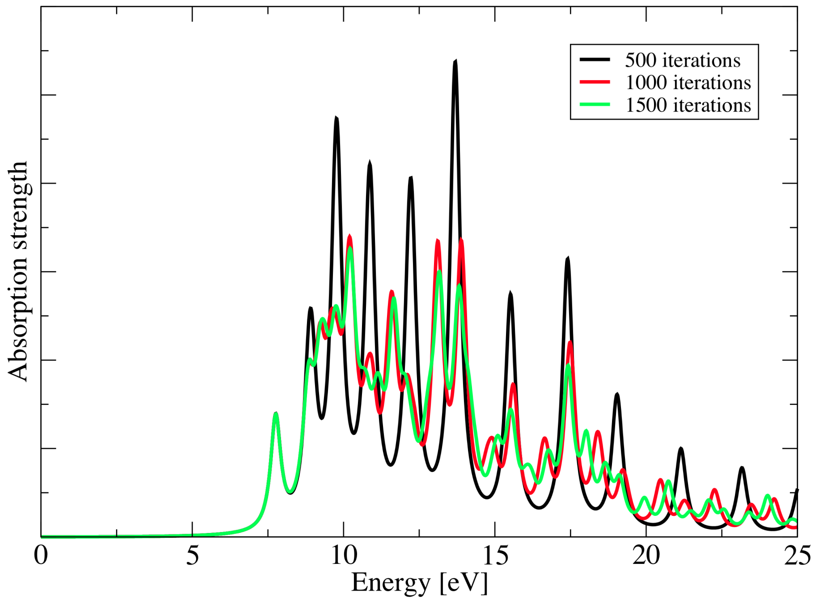
Effect of the terminator:

No terminator:



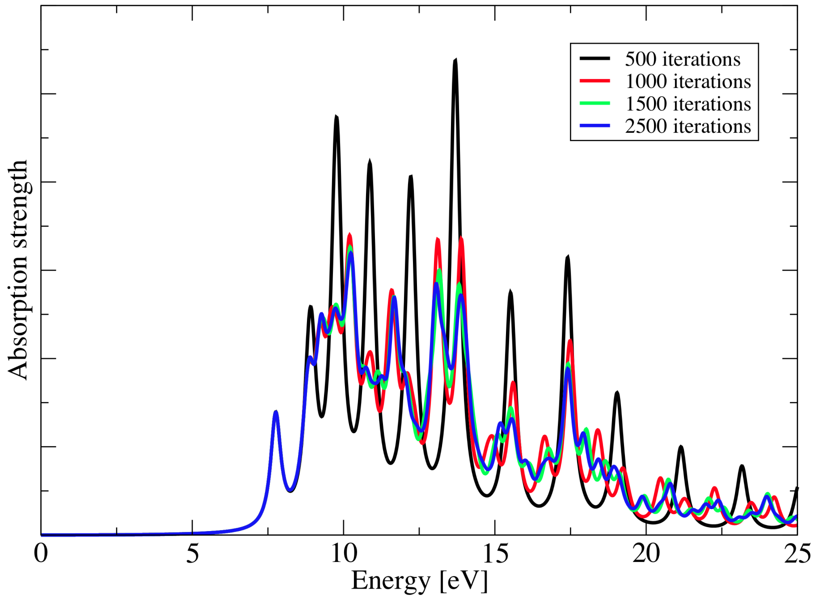
Effect of the terminator:

No terminator:

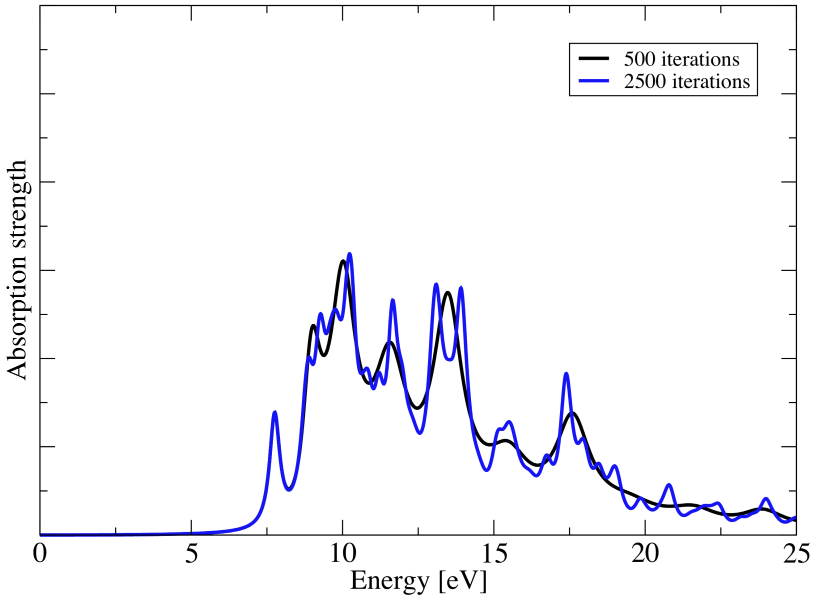


Effect of the terminator:

No terminator:

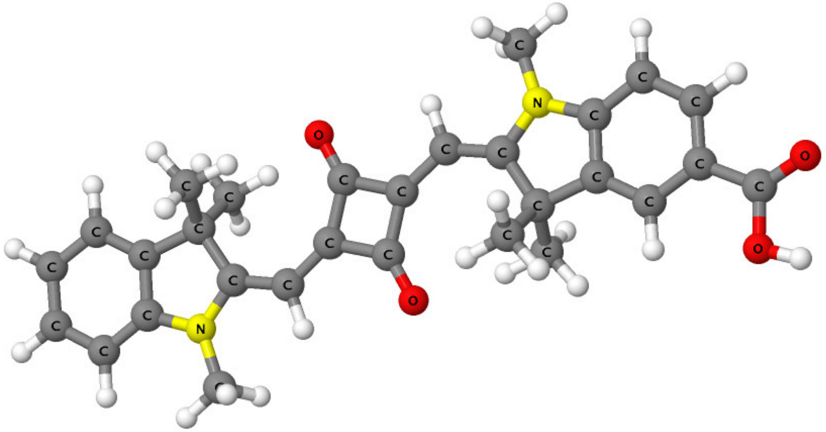


Terminator:



Analyzing the spectrum

Example of a squaraine dye:



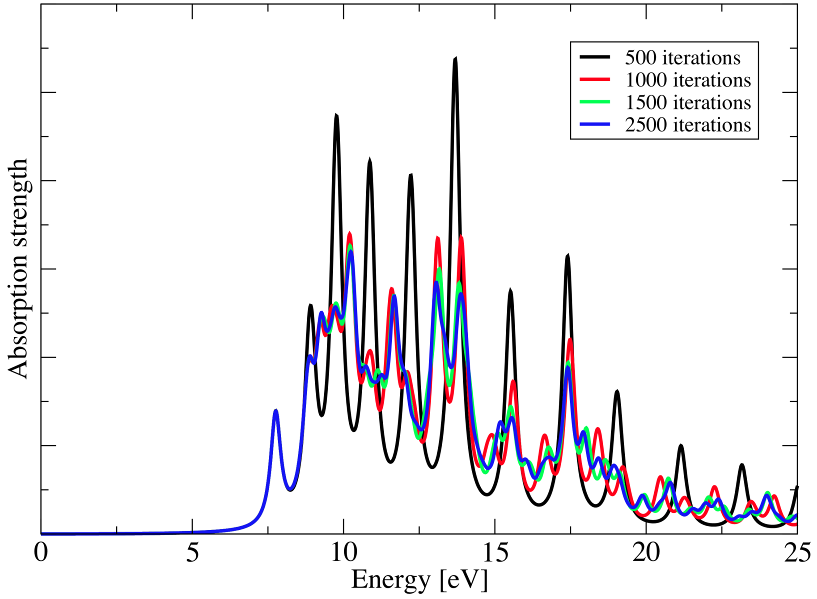
Can we analyze given features of the spectrum in terms of the electronic structure?

YES!

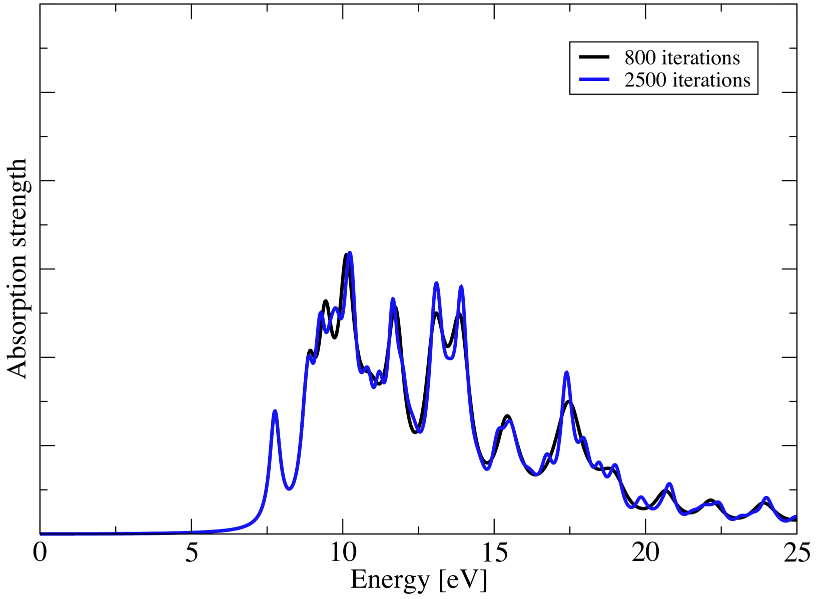
It is possible to compute the response charge density for any given frequency using a second recursion chain.

Effect of the terminator:

No terminator:

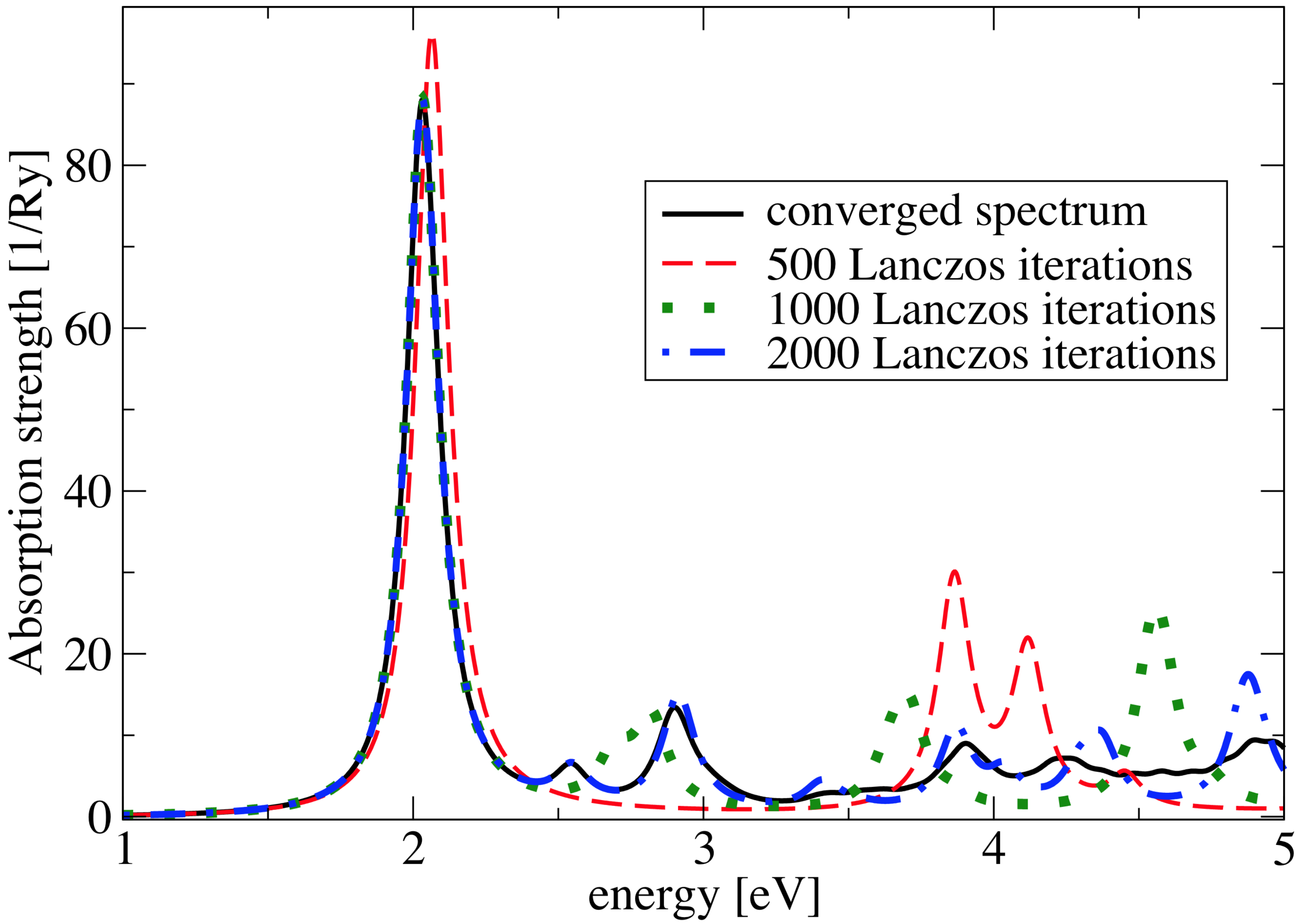


Terminator:

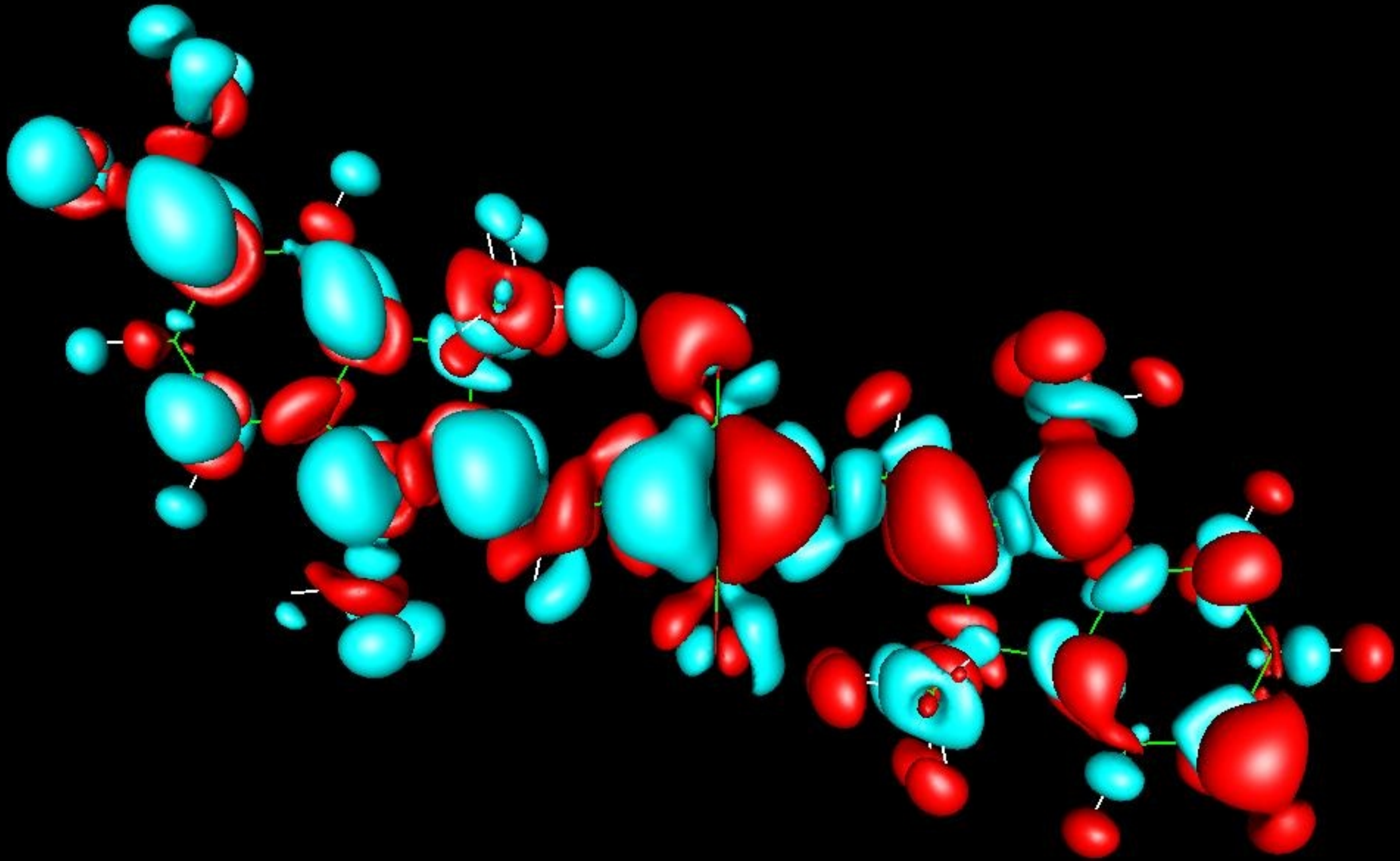


Convergence of the TDDFPT spectrum

Isolated squaraine molecule



Charge response at main absorption peak:



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

Thanks to:

- Filippo De Angelis (Perugia)

- Stefano Baroni (SISSA & DEMOCRITOS, Trieste)

- Brent Walker (University College, London)

- Dario Rocca (UC Davis)

- O. Baris Malcioglu (Univ. Liège)

- Arrigo Calzolari (Modena)

- Quantum ESPRESSO and its community

To know more:

Theory & Method:

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

Applications to DSSCs:

- New J. Phys. 13, 085013 (2011)
- Phys. Status Solidi RRL 5, 259 (2011)
- J. Phys. Chem. Lett. 2, 813 (2011)