School on Numerical Methods for Materials Science Related to Renewable Energy Applications
ICTP - Trieste
26 – 30 November 2012

Time-dependent density functional theory and how it is used

Ralph Gebauer

The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

DEMOCRITOS
DEmocritos MOdeling Center for
Research In aTOmistic Simulation
IOM

Thursday, November 29th, 2012

Overview

- Application of TDDFT to photovoltaics: large scale simulations

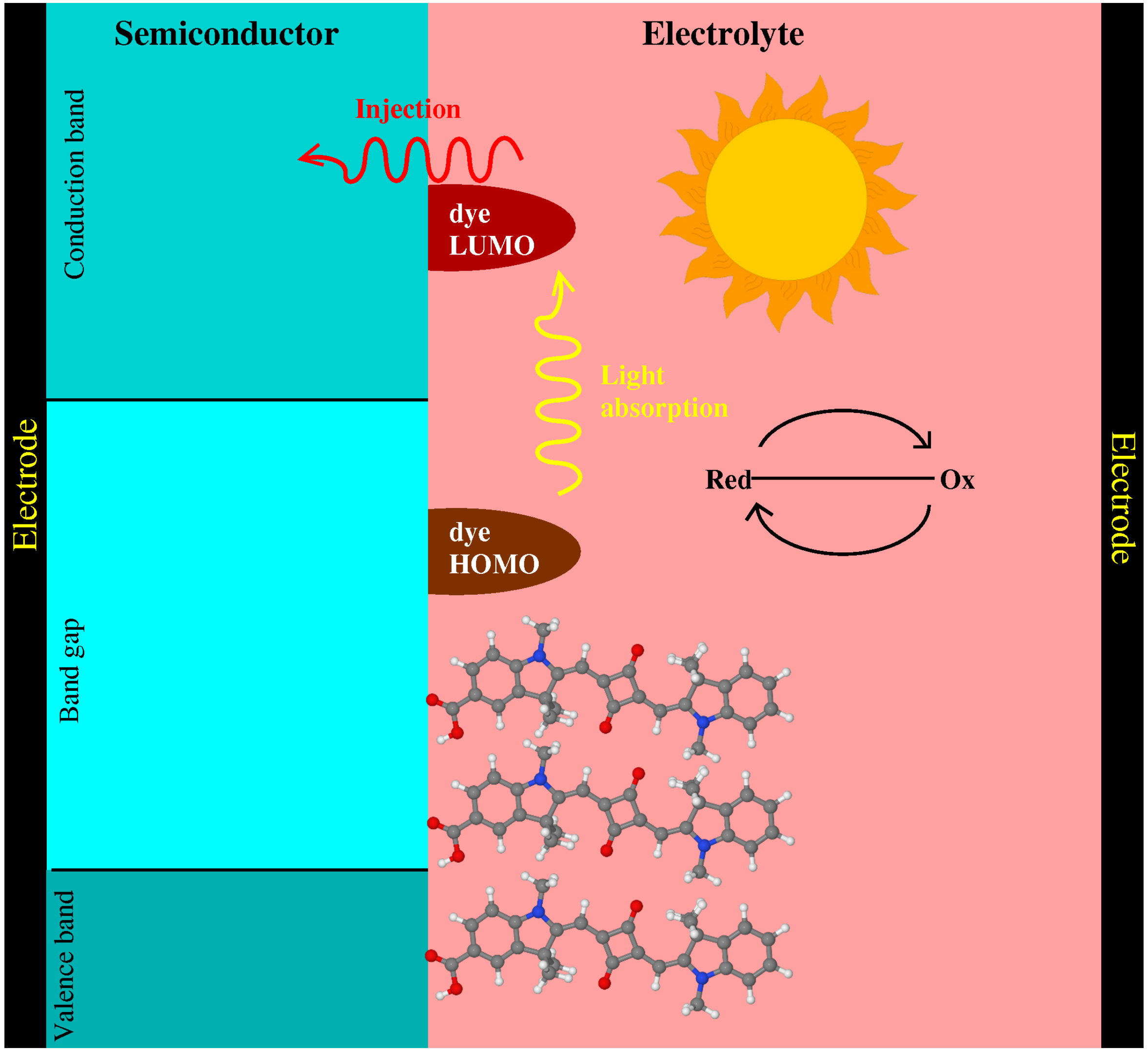
The basics

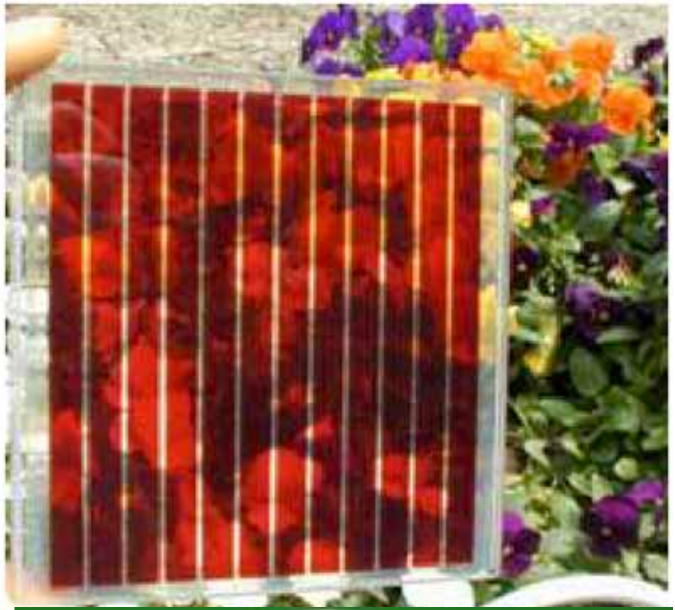
- From the ground-state to excited states: The Runge-Gross theorem

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

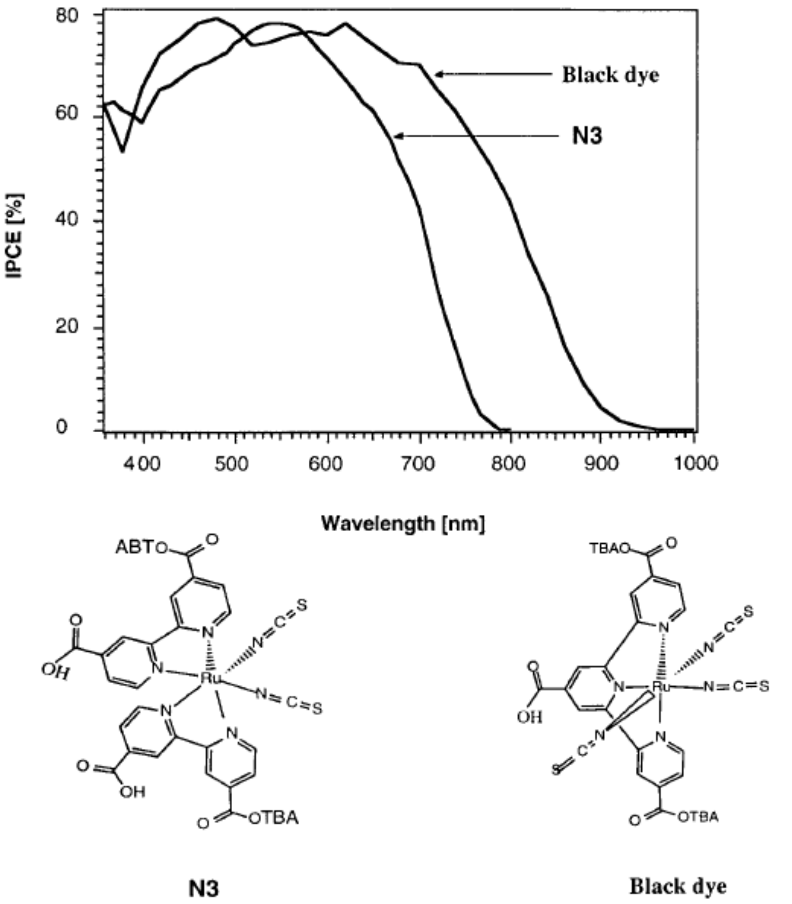
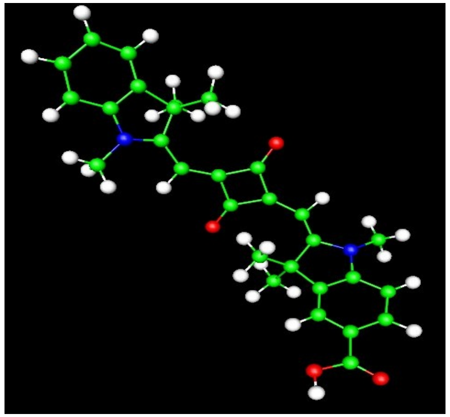
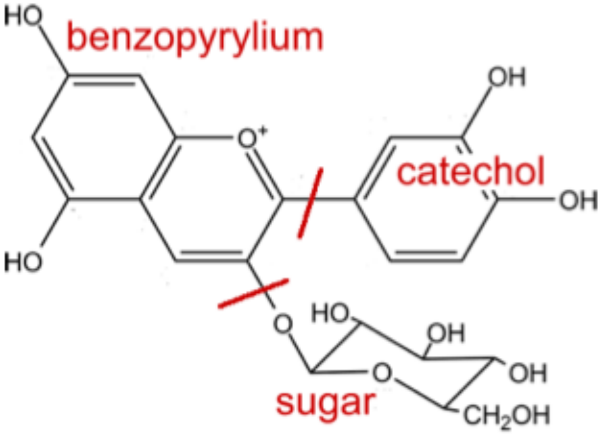


Figure 3. Spectral response curve of the photocurrent for the DYSC sensitized by N3 and the black dye. The incident photon to current conversion efficiency is plotted as a function of wavelength

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



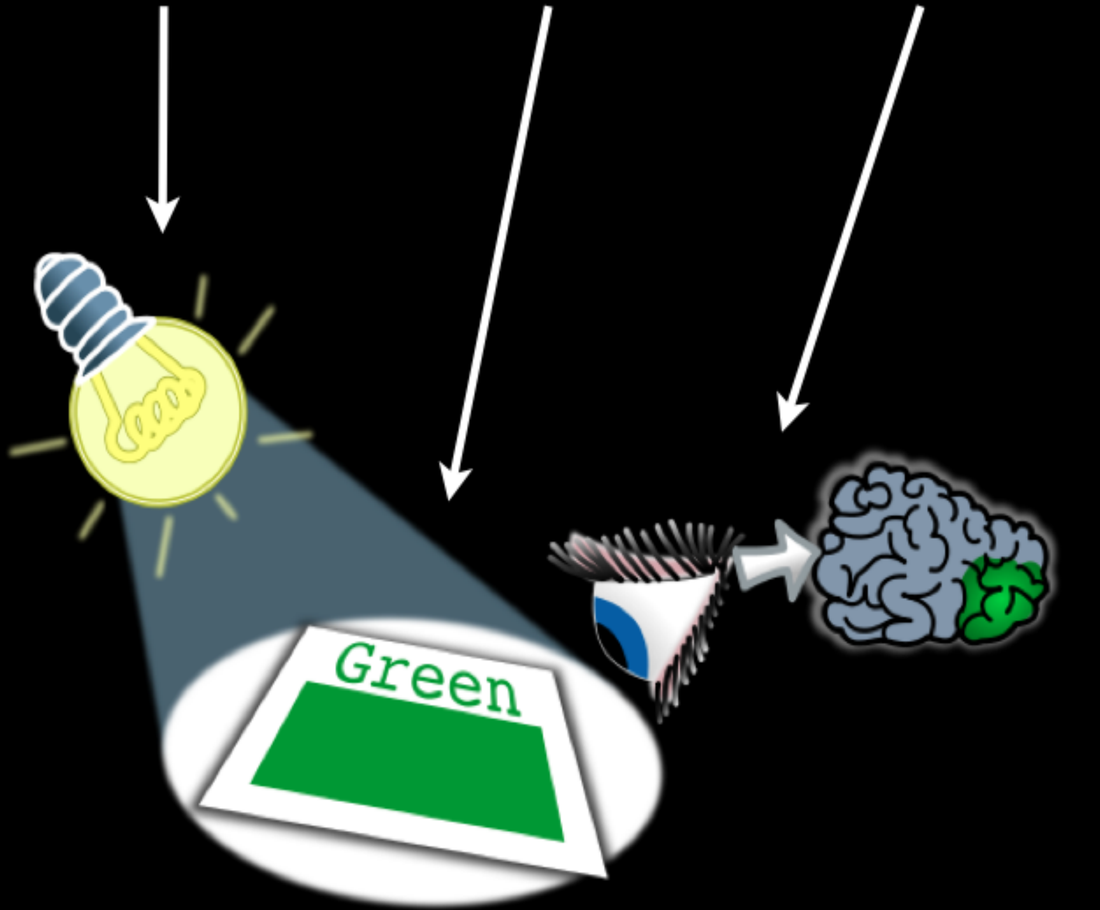
Squaraine dye

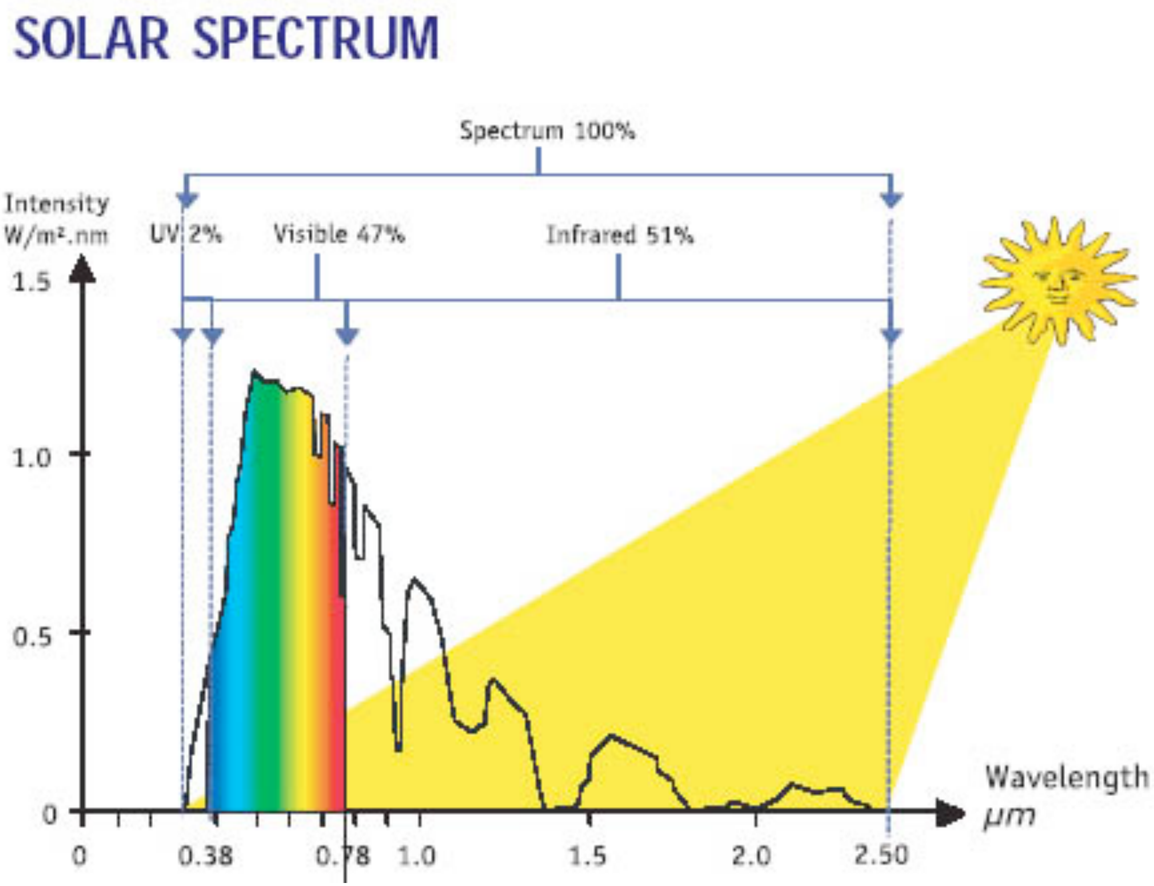


Cyanidin-3-glucoside
("Cyanin")

ab initio colors

stimulus =
illuminant × trasmission × sensitivity





stimulus =

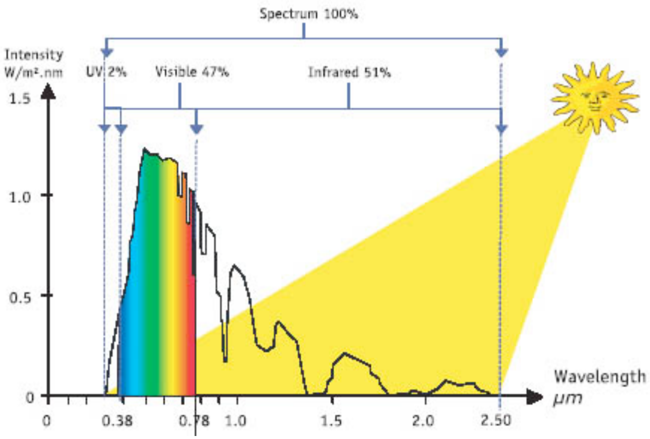
illuminant × trasmission × sensitivity

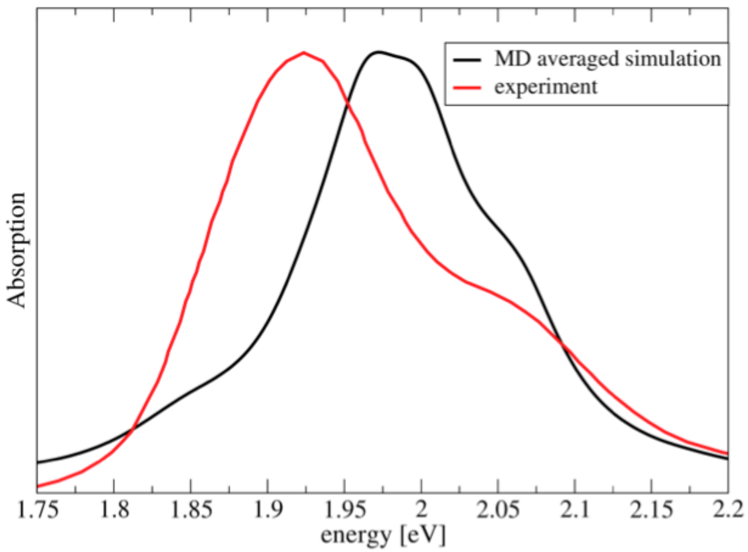
stimulus =

illuminant × trasmission × sensitivity

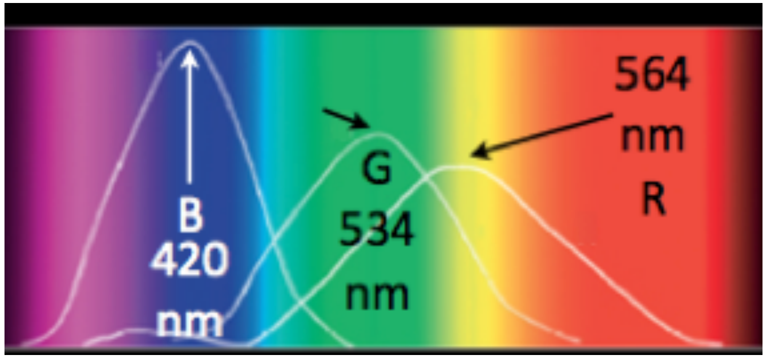
$$\mathrm{T}(x,\lambda) = \mathrm{S}(\lambda)\mathrm{e}^{-\alpha(\lambda)x}$$

SOLAR SPECTRUM



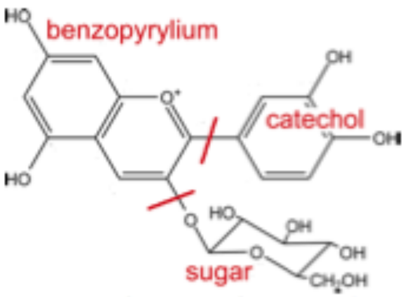


The colour we perceive

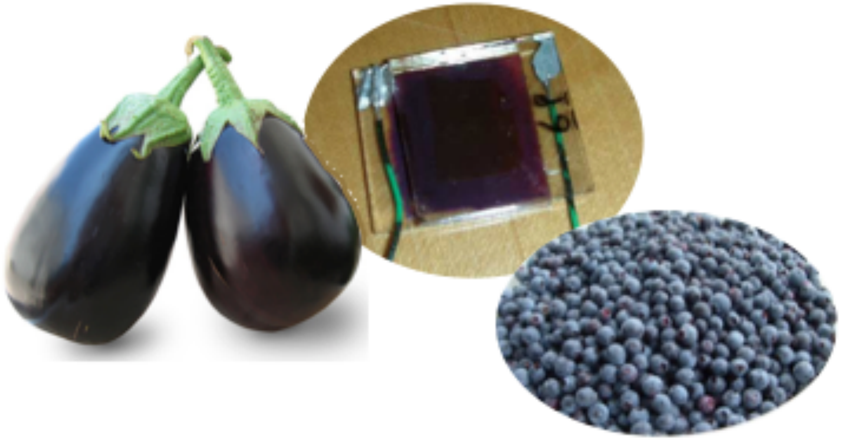


$$\mathrm{RGB}(x) = \int \mathrm{S}(\lambda)\mathrm{e}^{-\alpha(\lambda)x}\,\mathrm{rgb}(\lambda)\,d\lambda$$

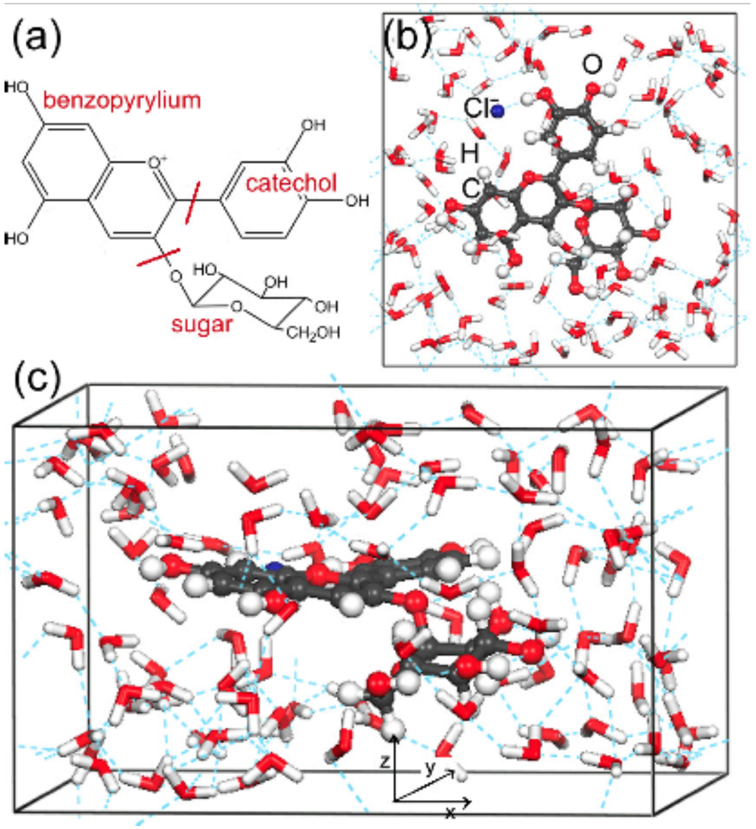
color and function of anthocyanins



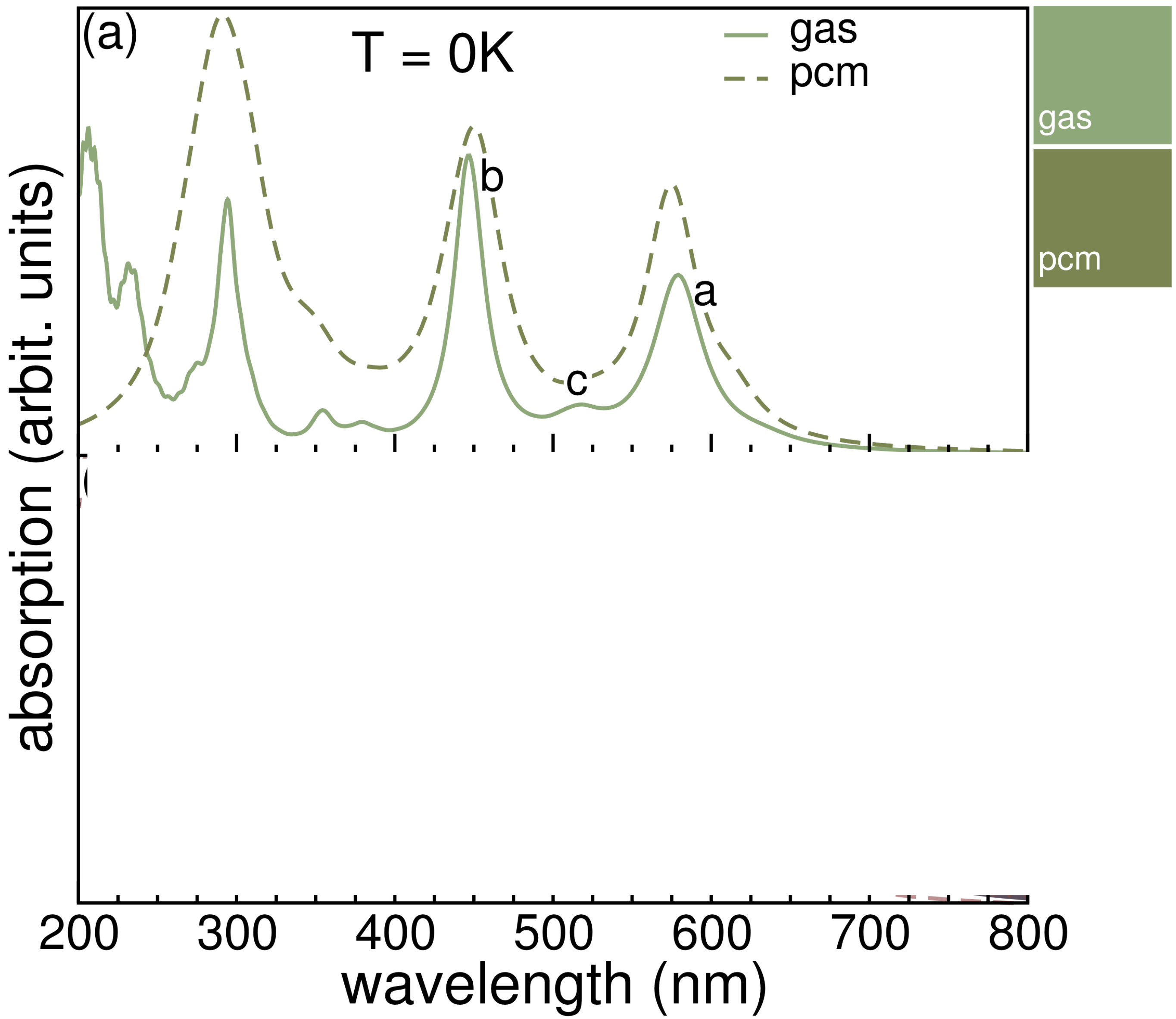
cyanidin-3-glucoside



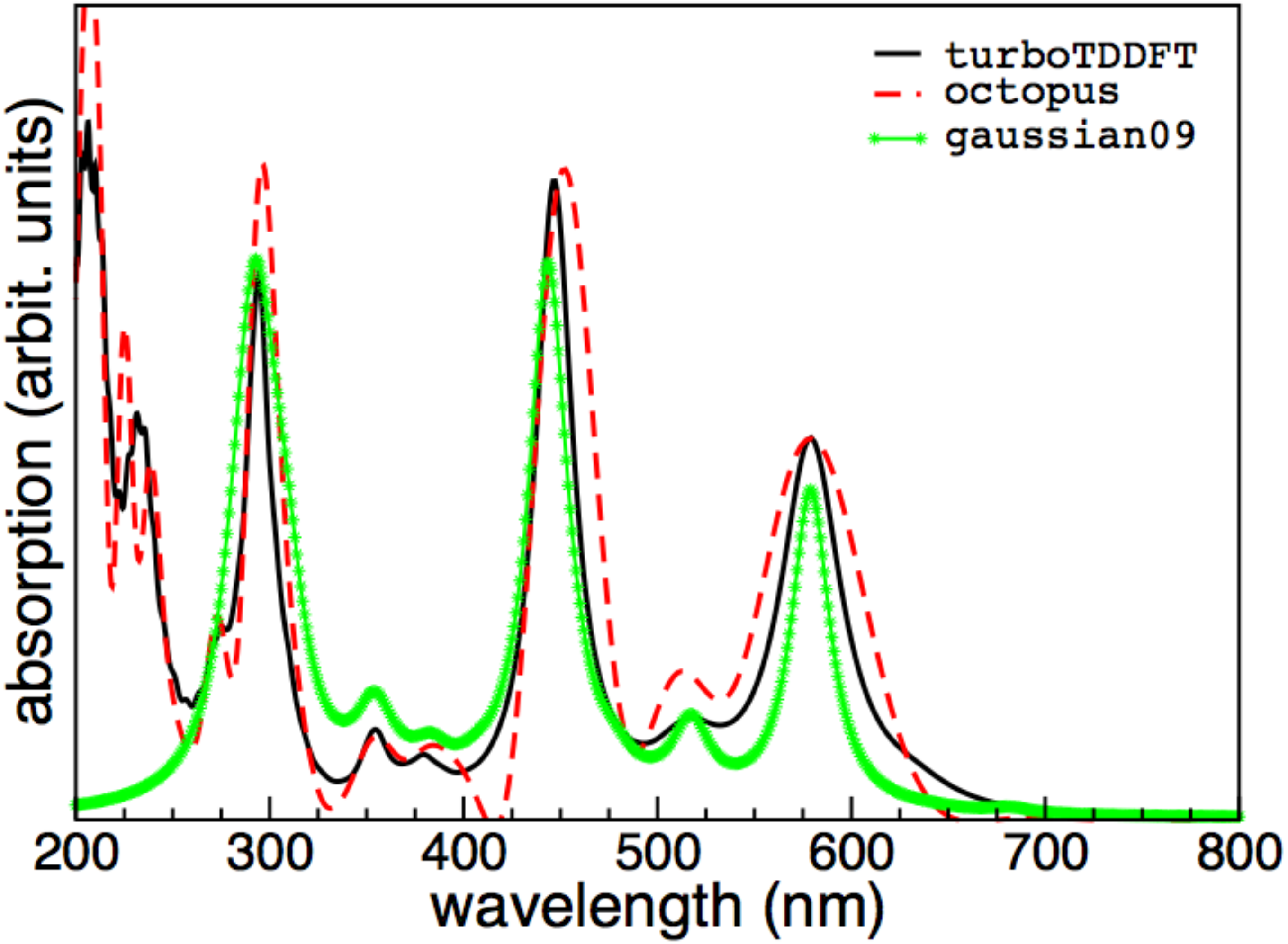
color and function of anthocyanins



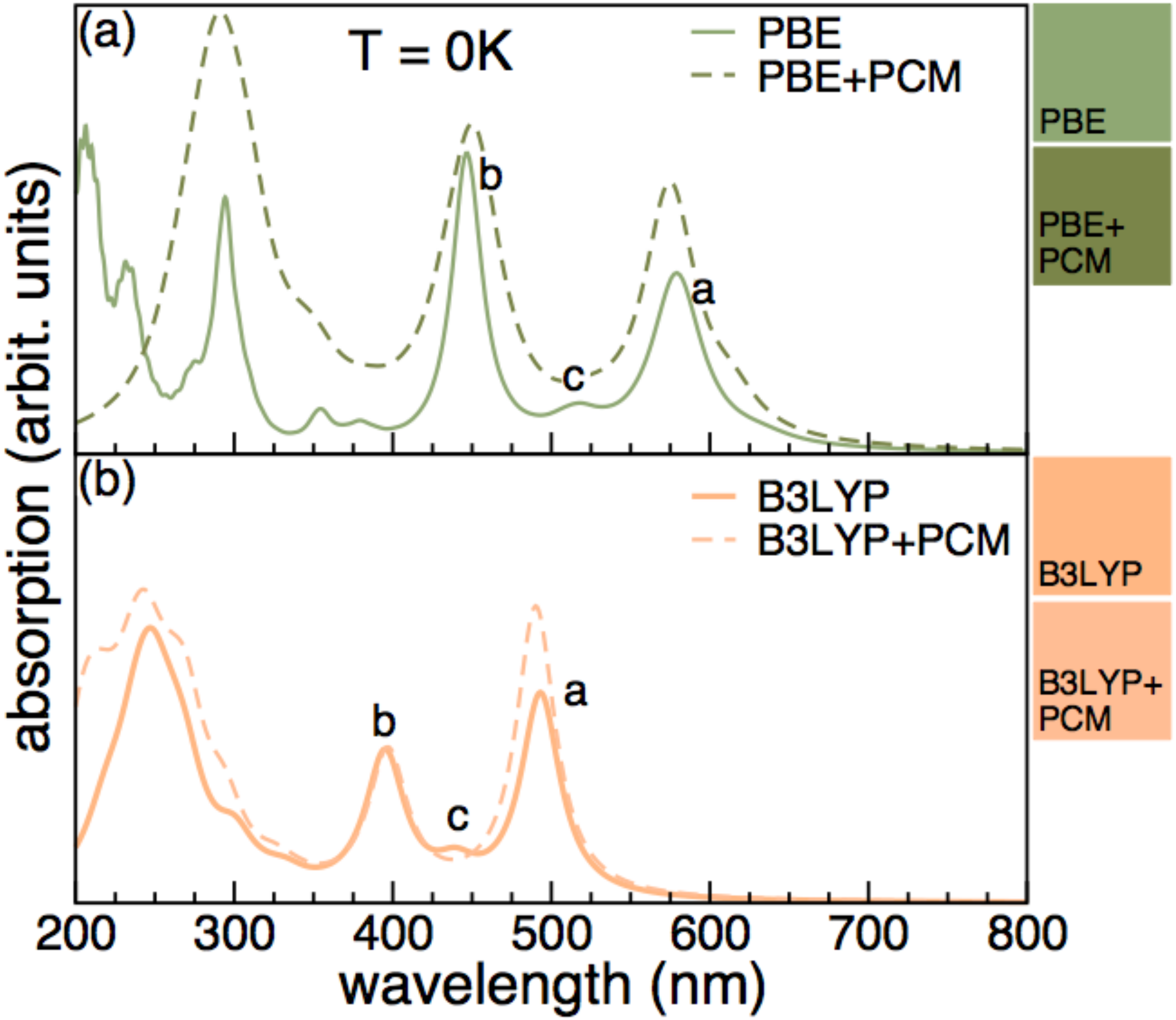
Optical spectra in the gas phase



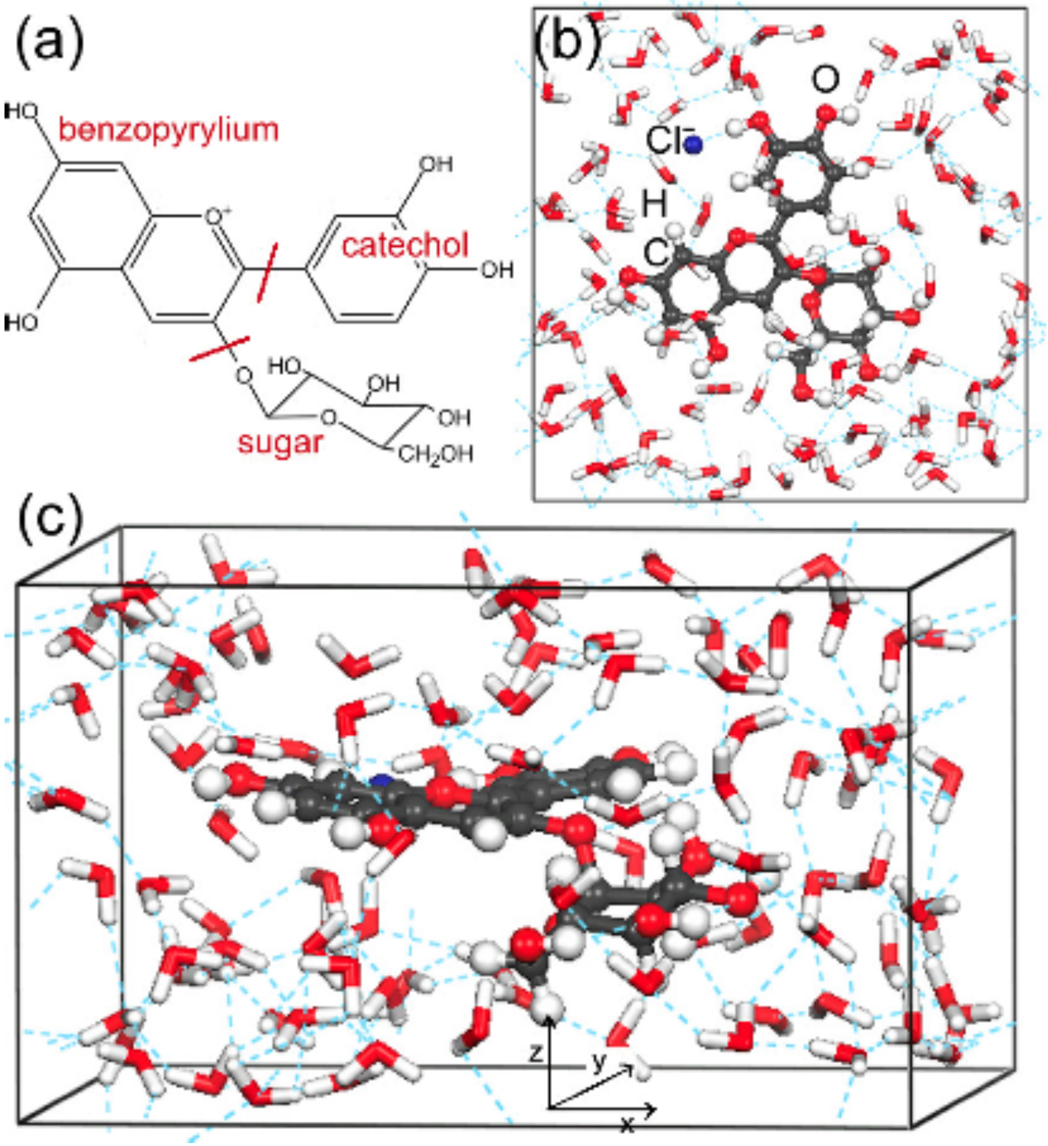
Spectra computed with various codes:



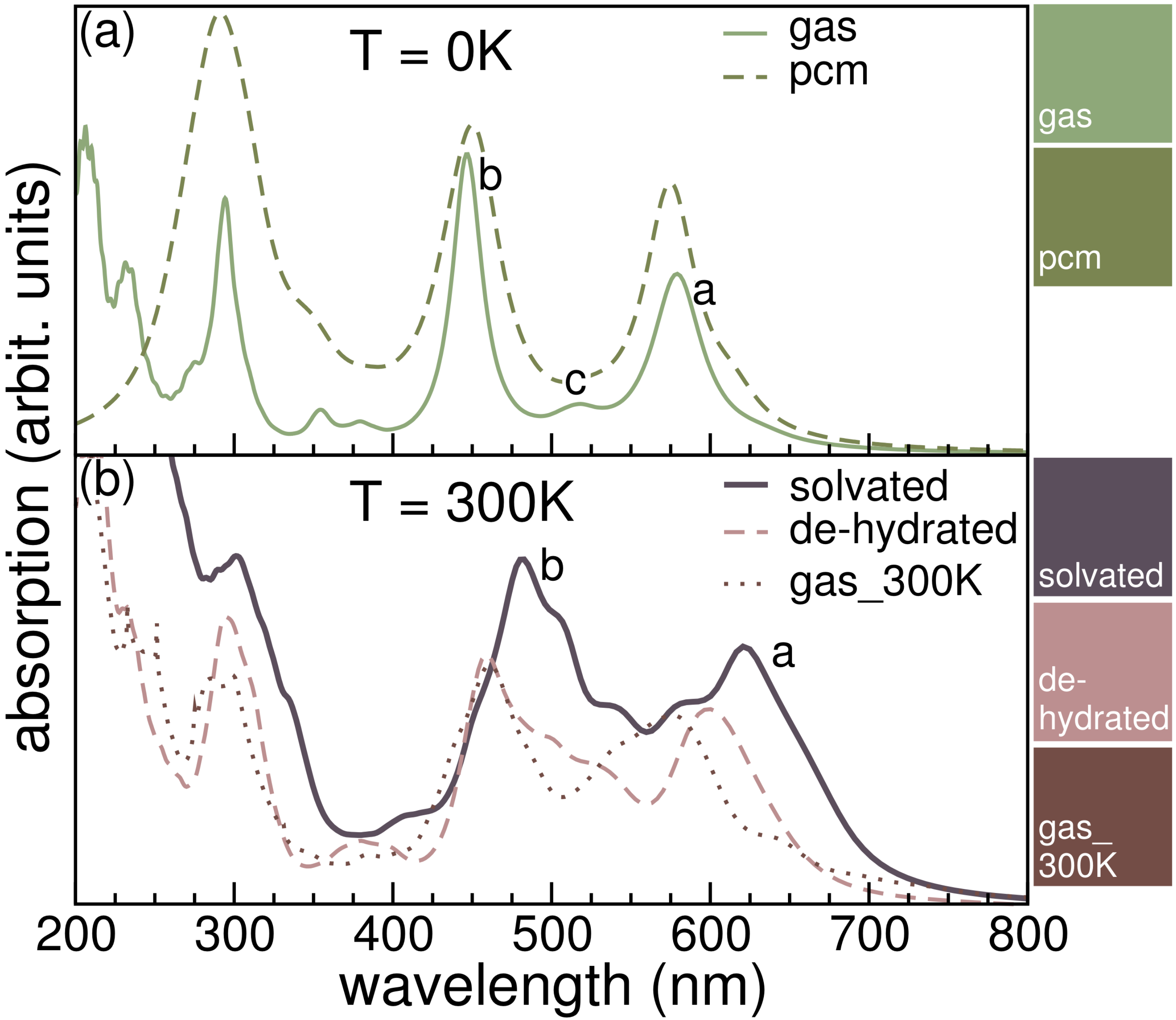
Spectra computed with various functionals:



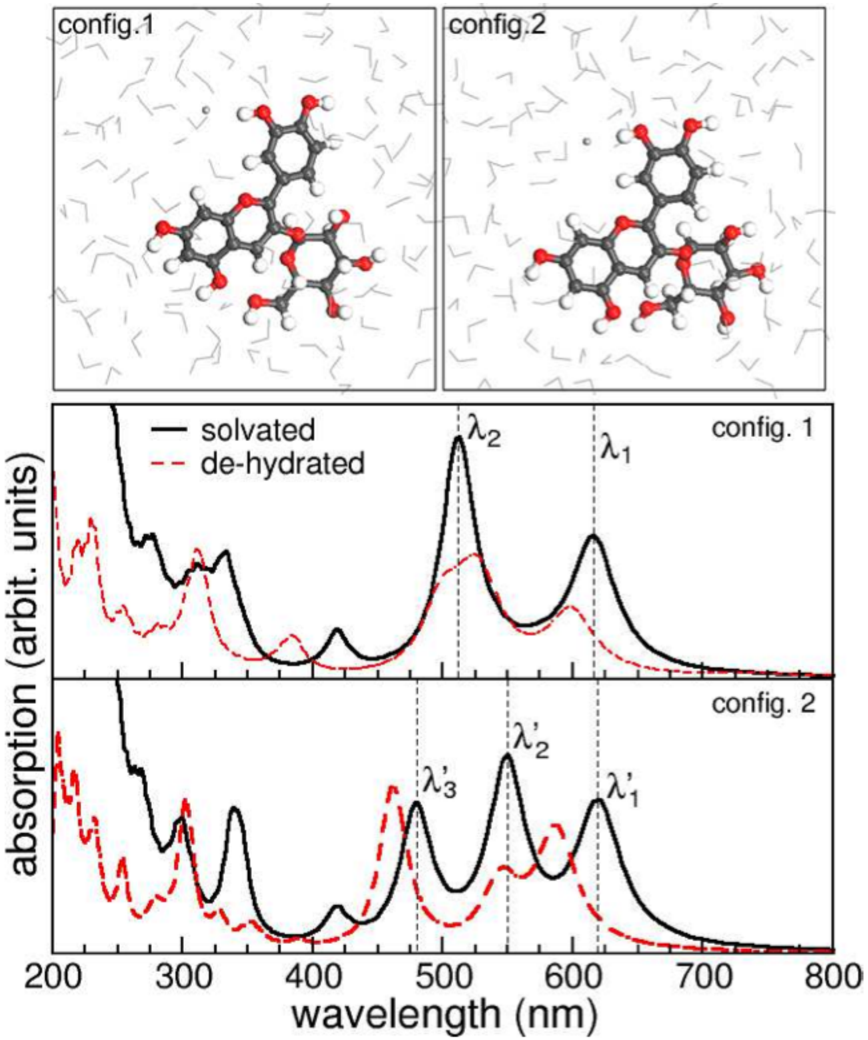
More realistic model of solvent



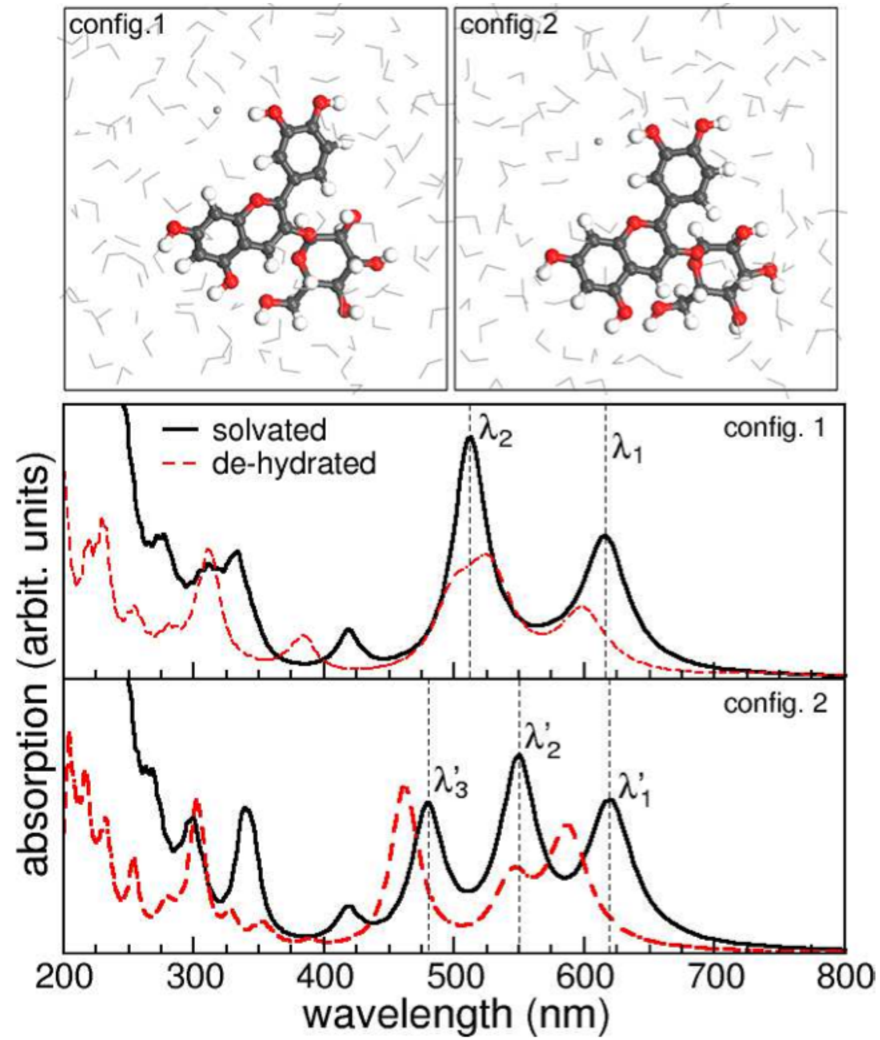
Including Molecular Dynamics

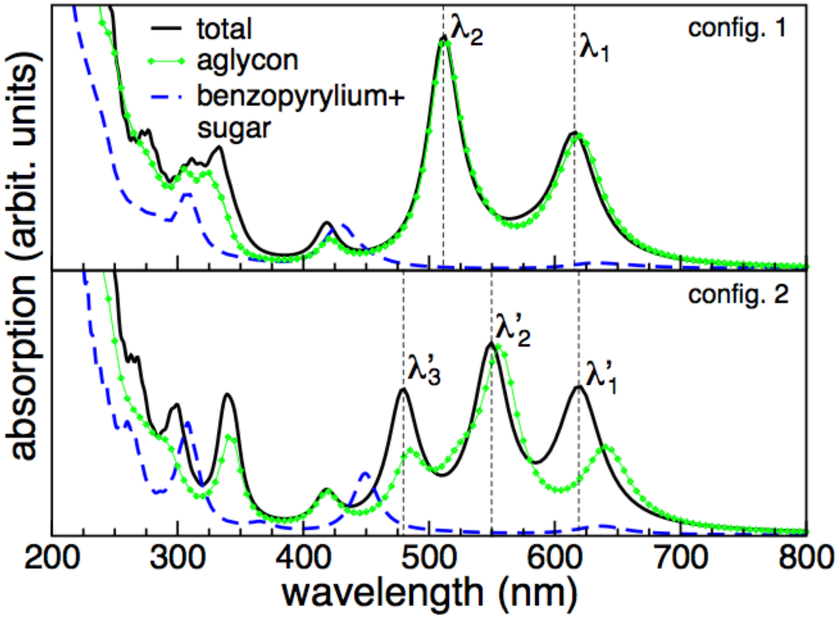


Analyzing configurational snapshots

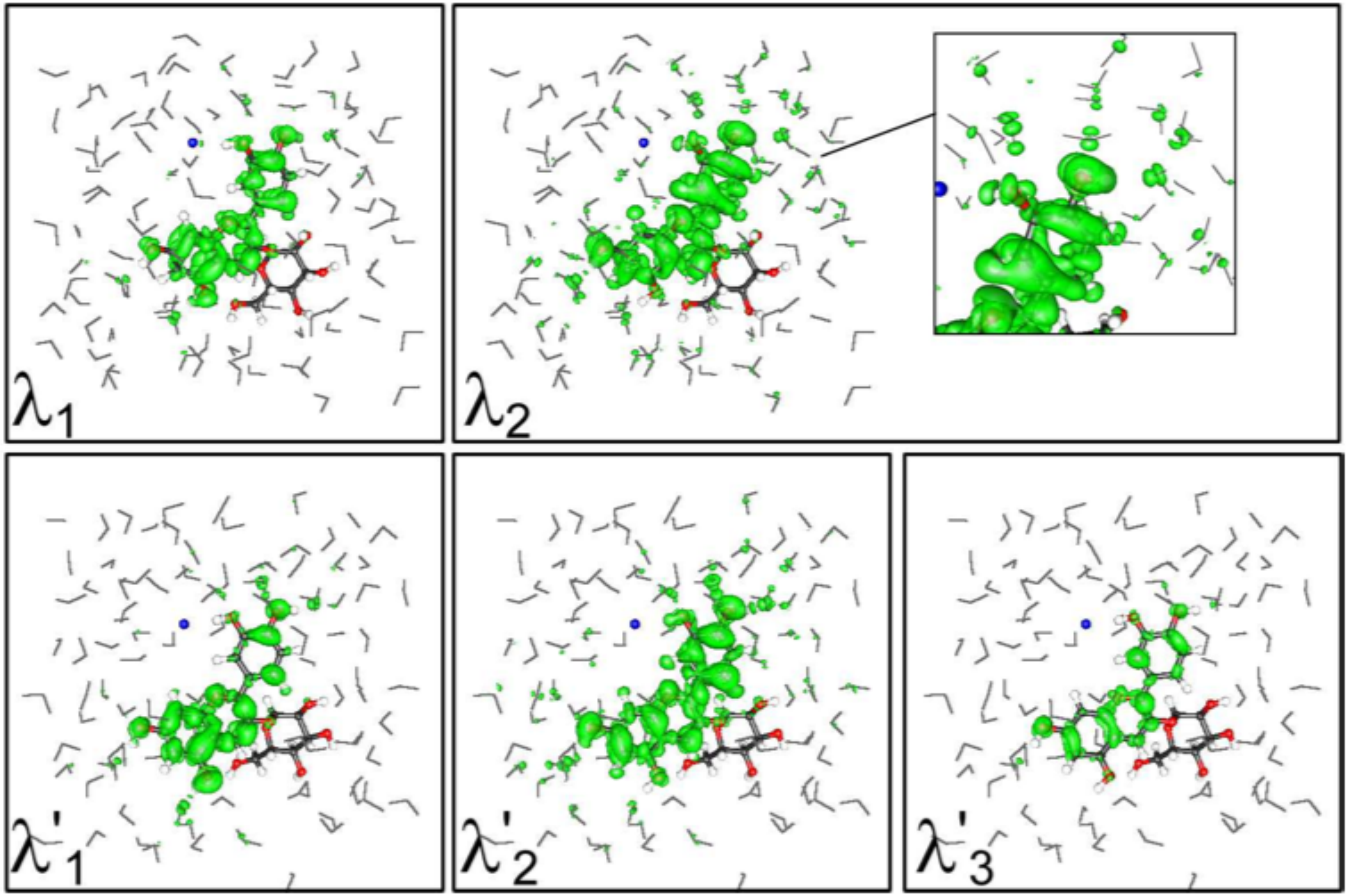


Analyzing configurational snapshots

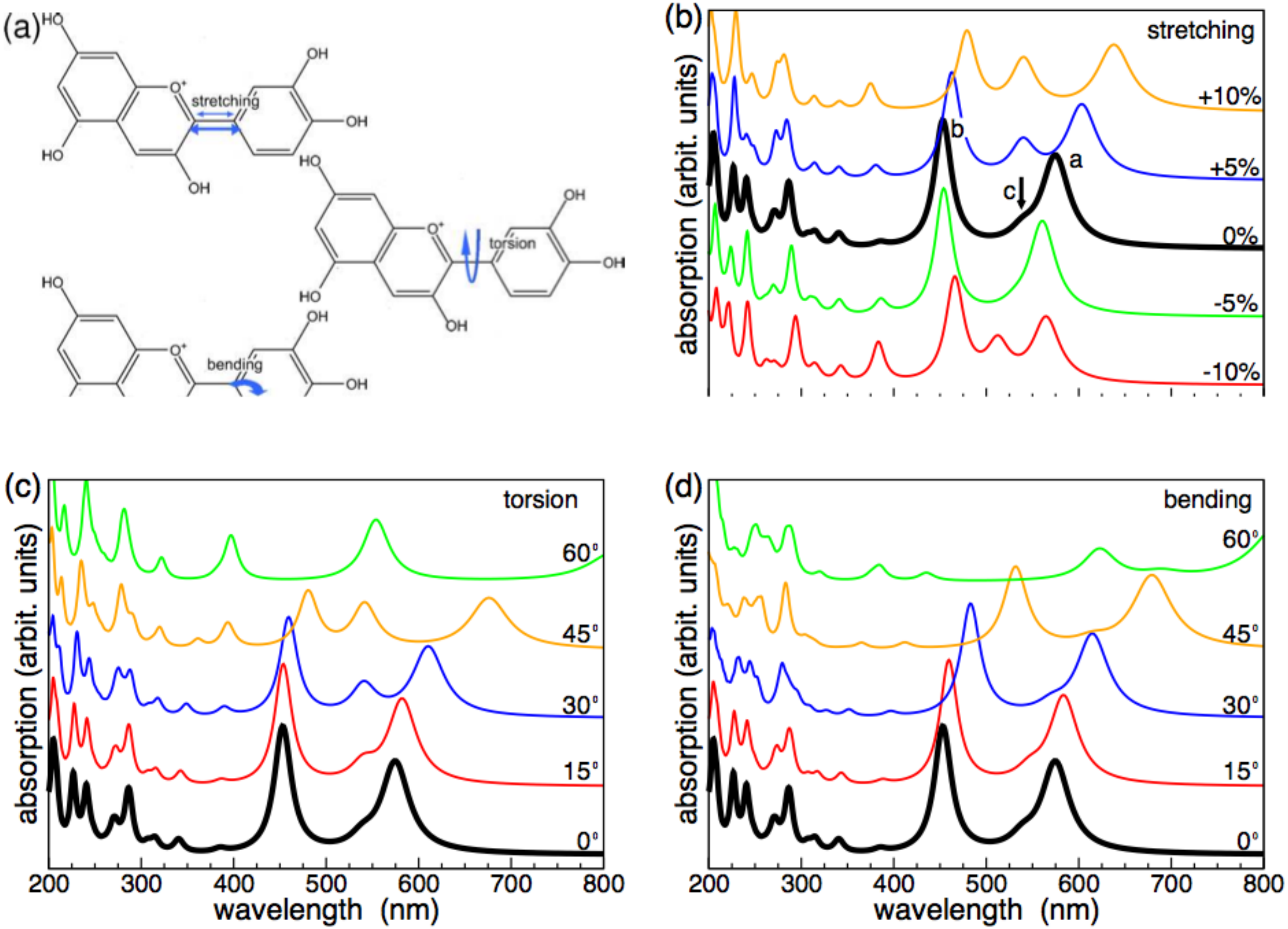




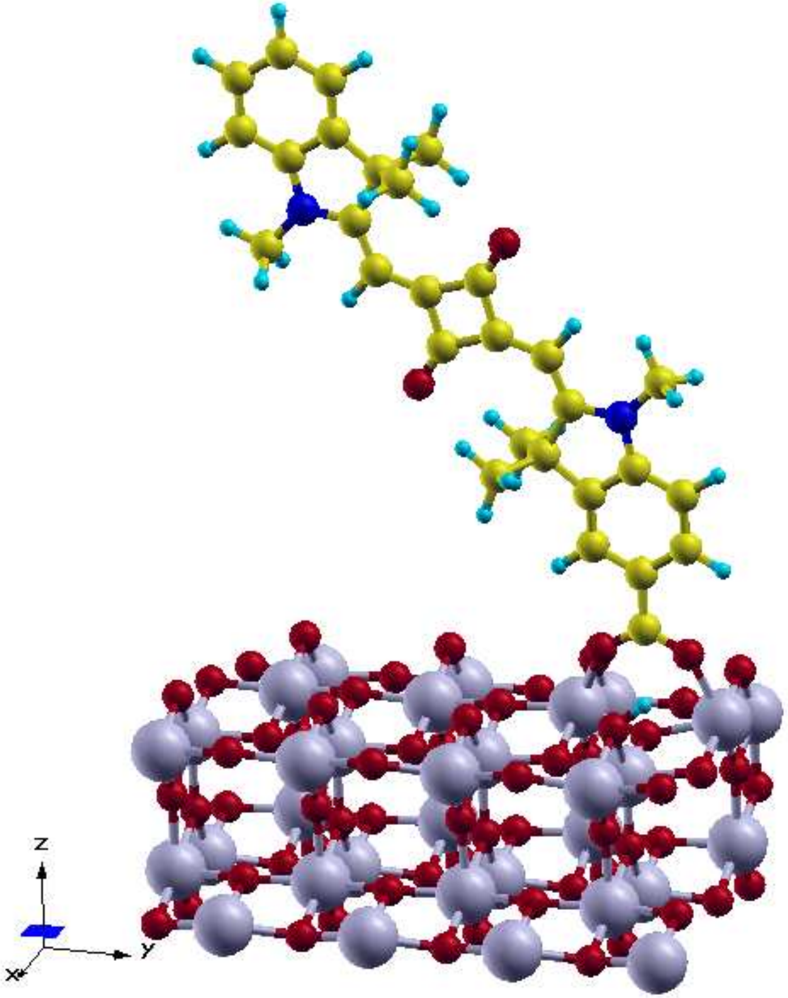
Response charge density at selected frequencies



Influence of various geometrical distortions



Model of a photovoltaic device: Squaraine on TiO_2 slab

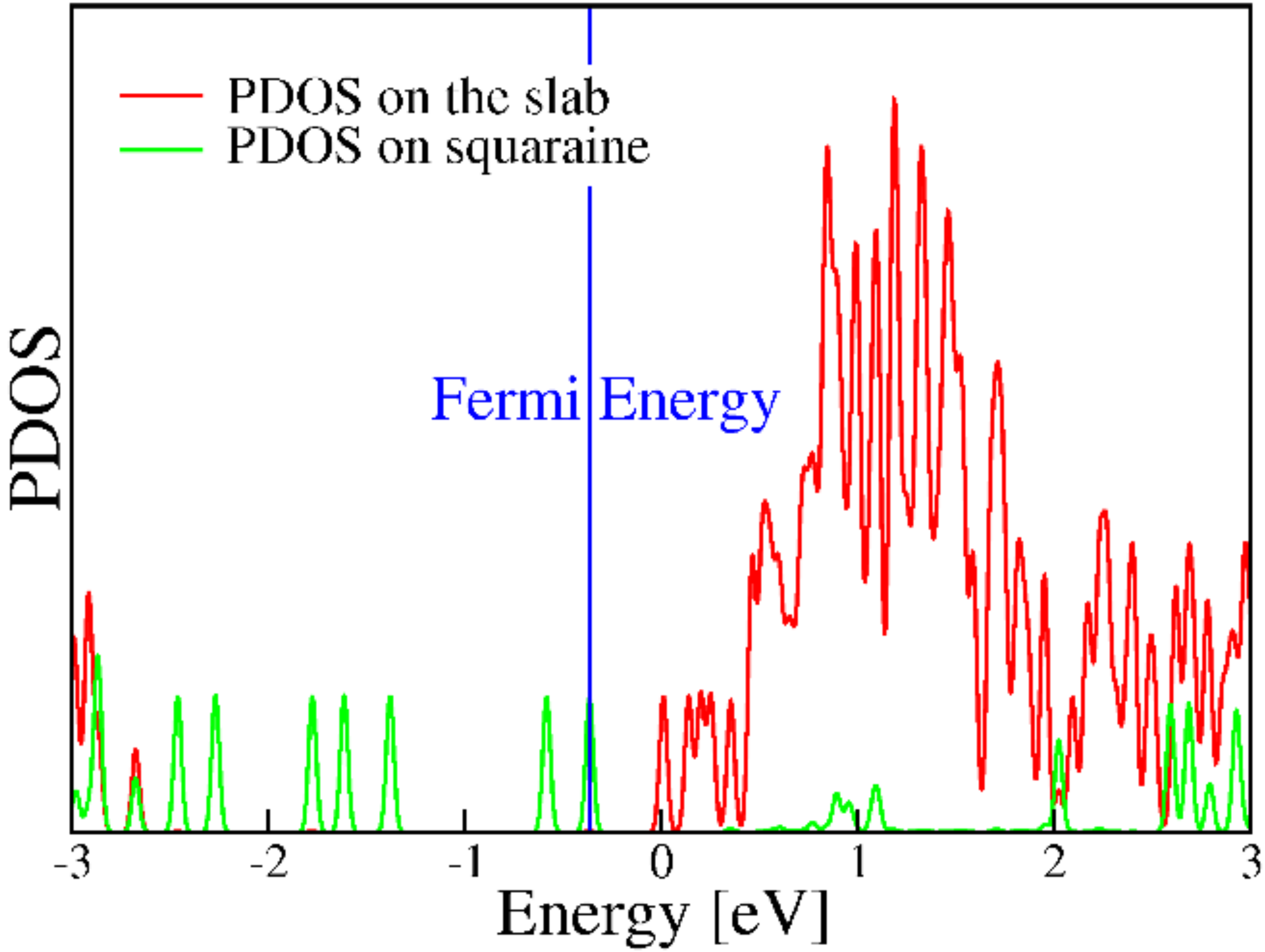


Slab geometry:
1x4 TiO2 anatase slab,
Exposing (101) surface

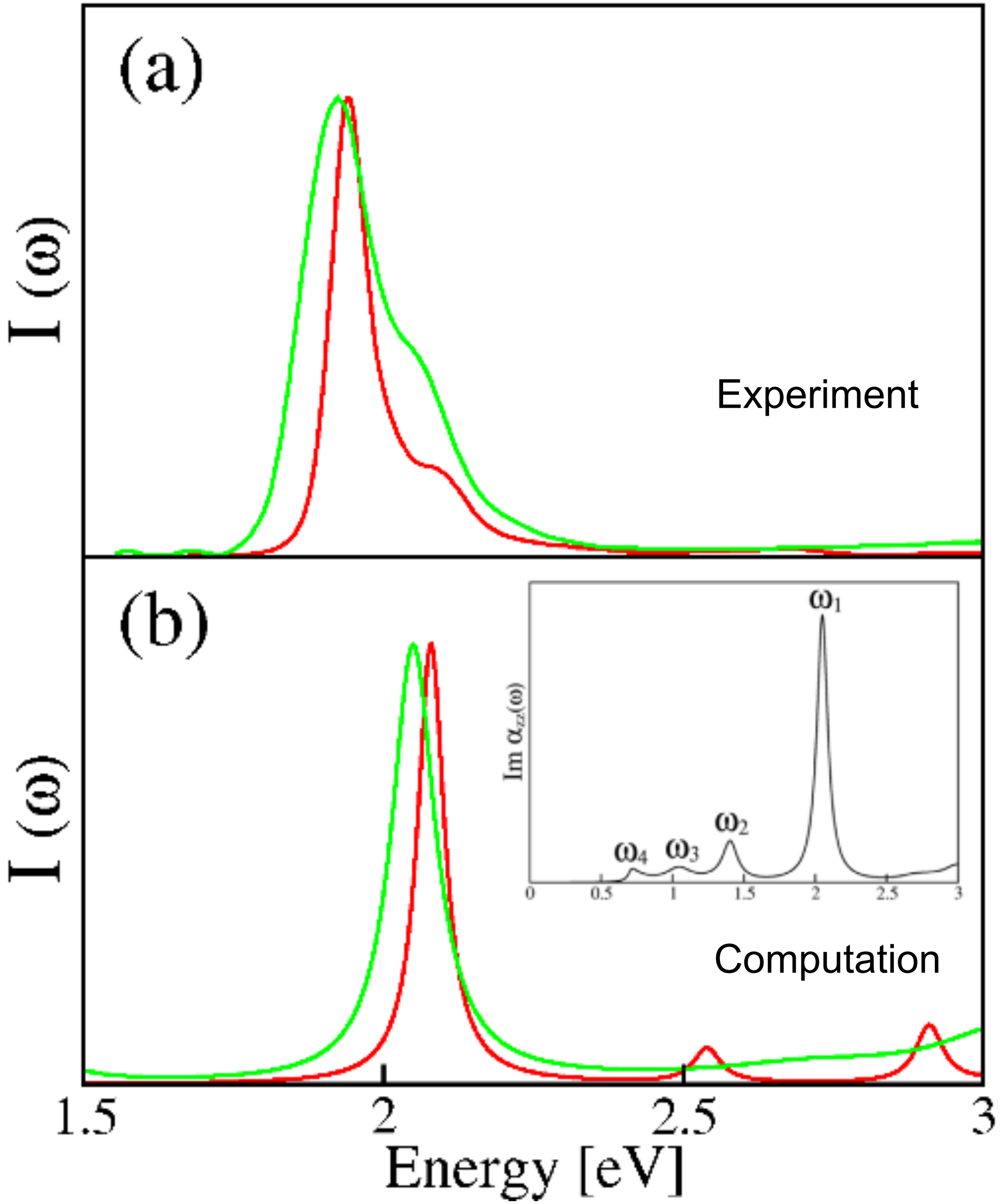
PBE functional, PW basis set
(Quantum-ESPRESSO code)

Shown here: minimum energy
configuration

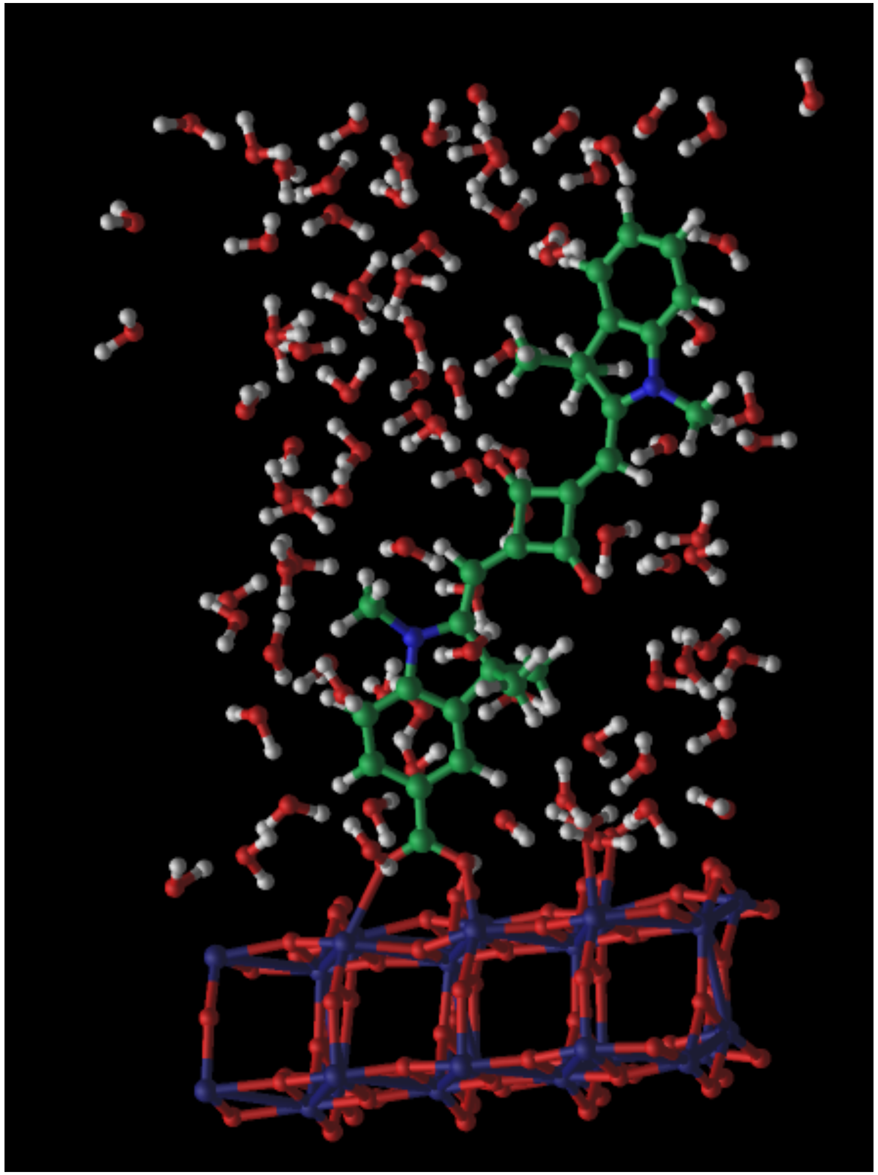
TiO2 slab with squaraine dye



Experimental and TDDFT absorption spectra



A more realistic system: Including the solvent



TDDFT calculation of optical spectra and related quantities

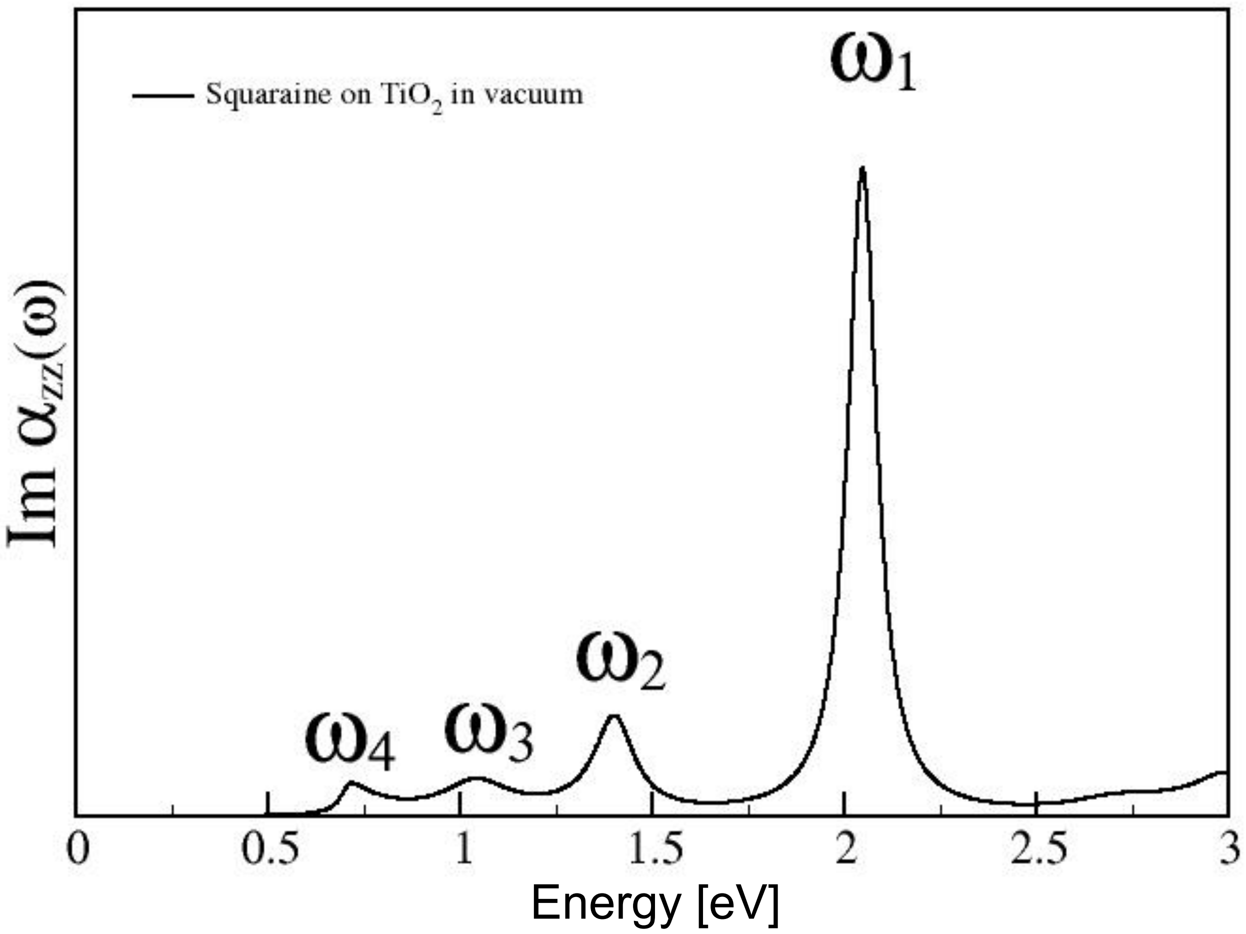
Various challenges:

- 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

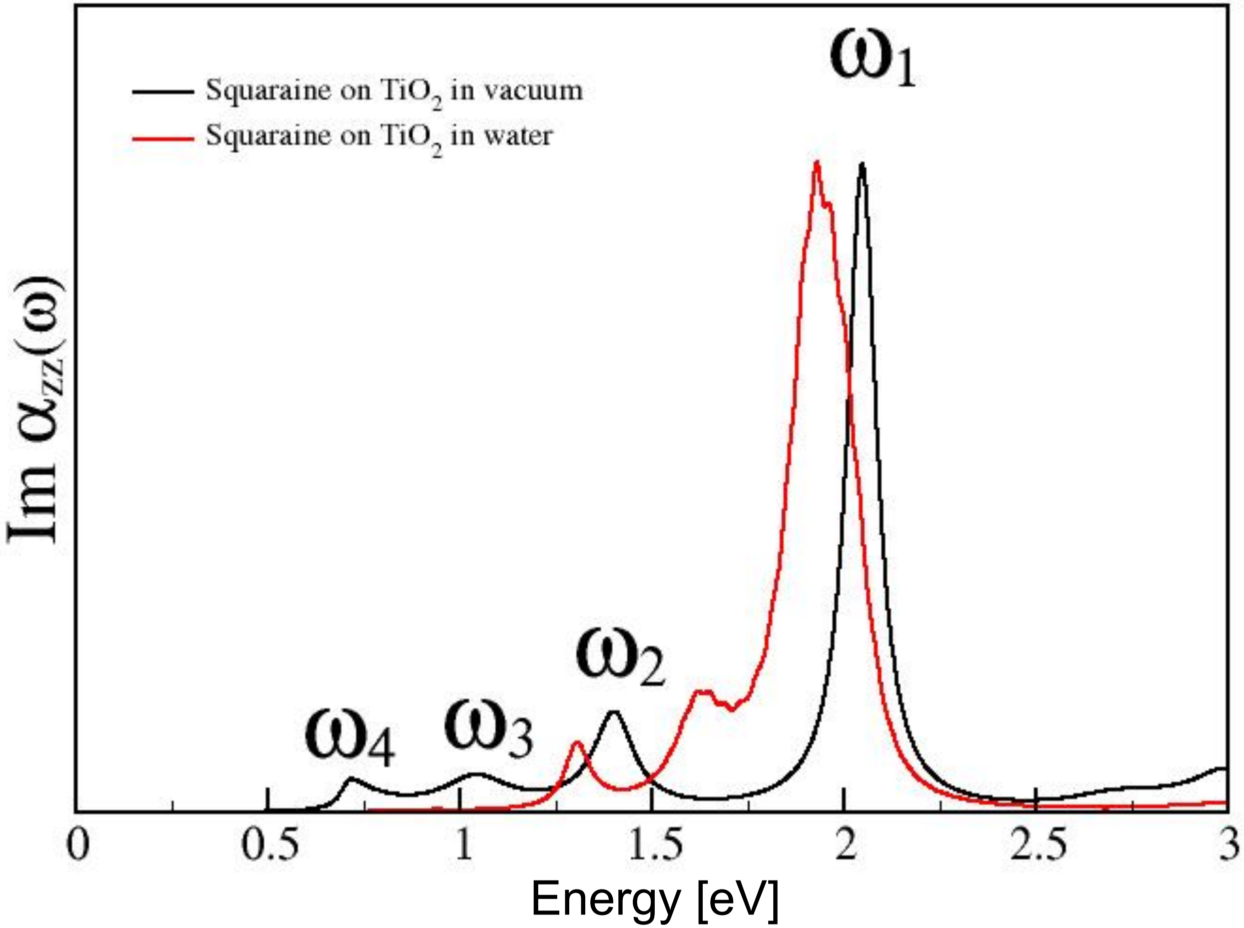
Computational tool:

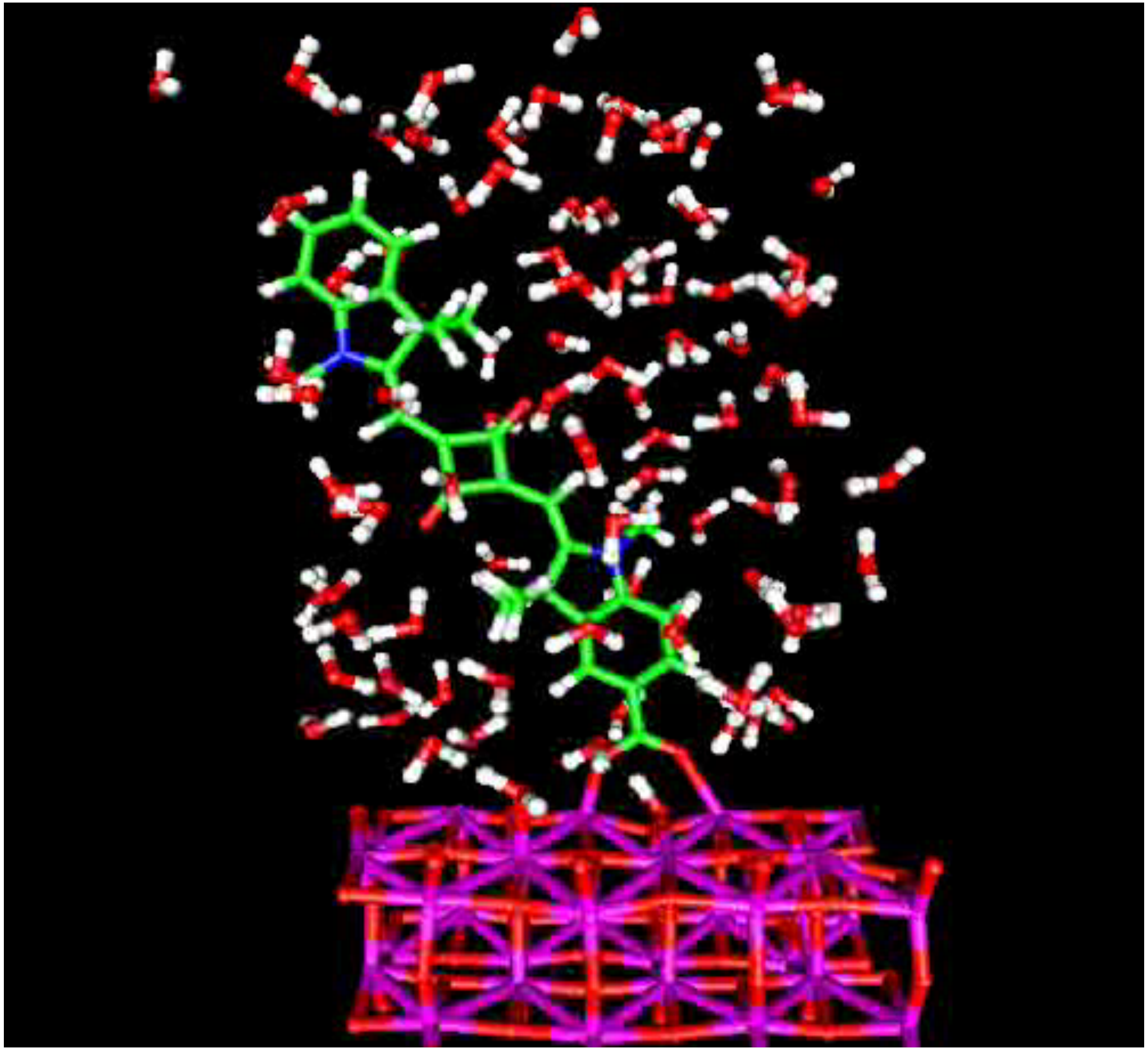
- Recursive Lanczos algorithm for TDDFT

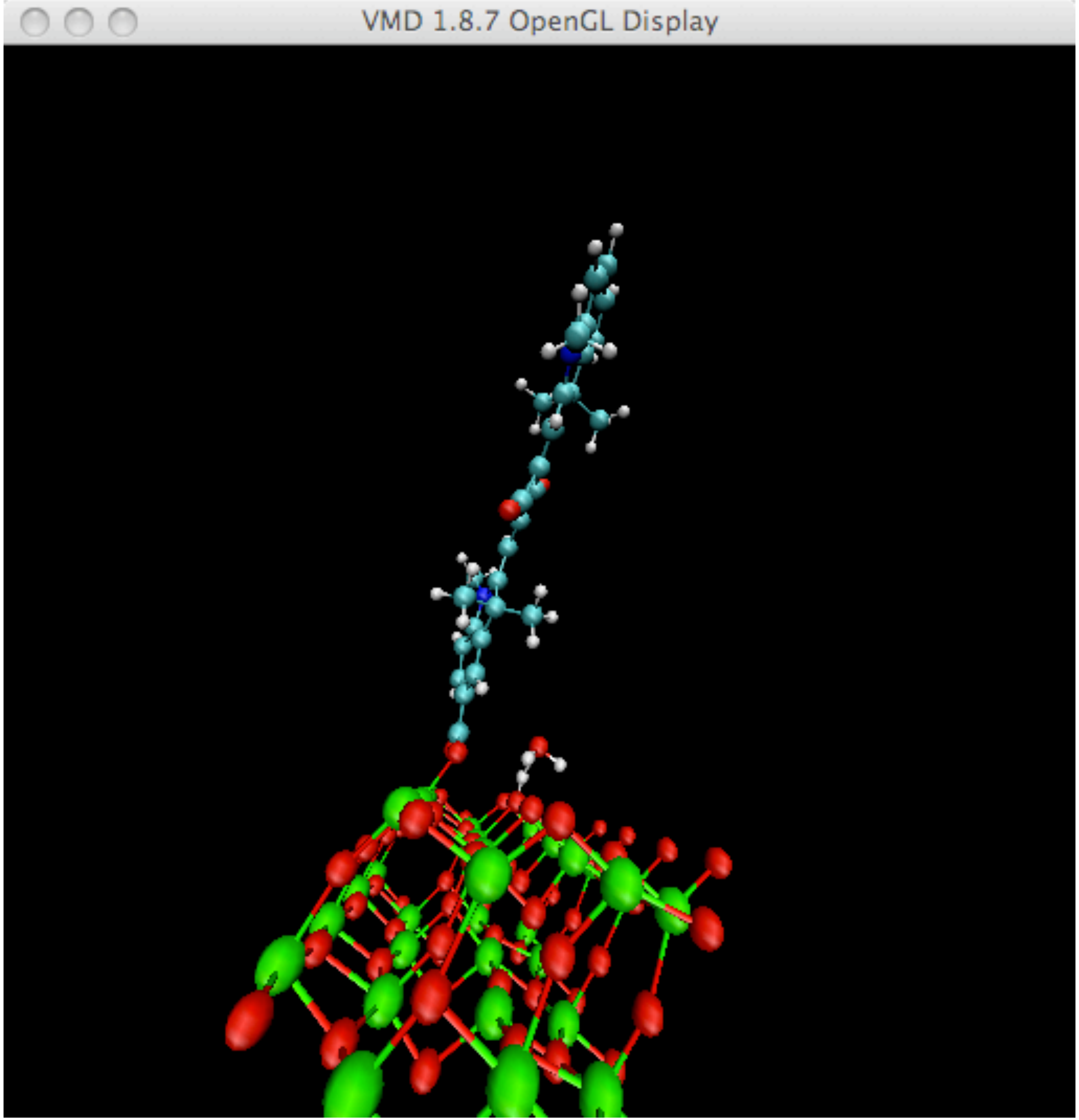
TDDFT optical spectrum: dry system

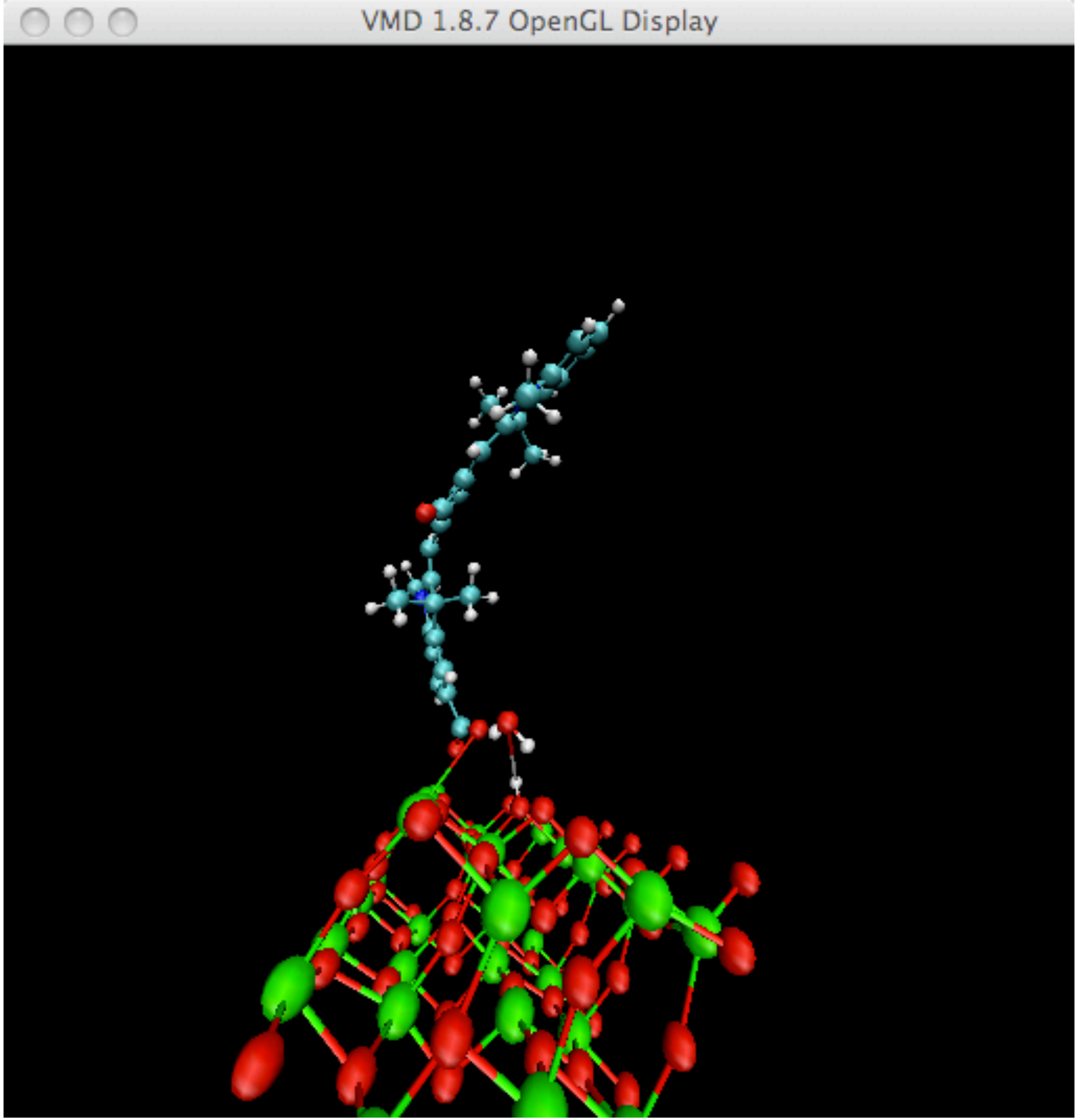


TDDFT optical spectrum including solvent



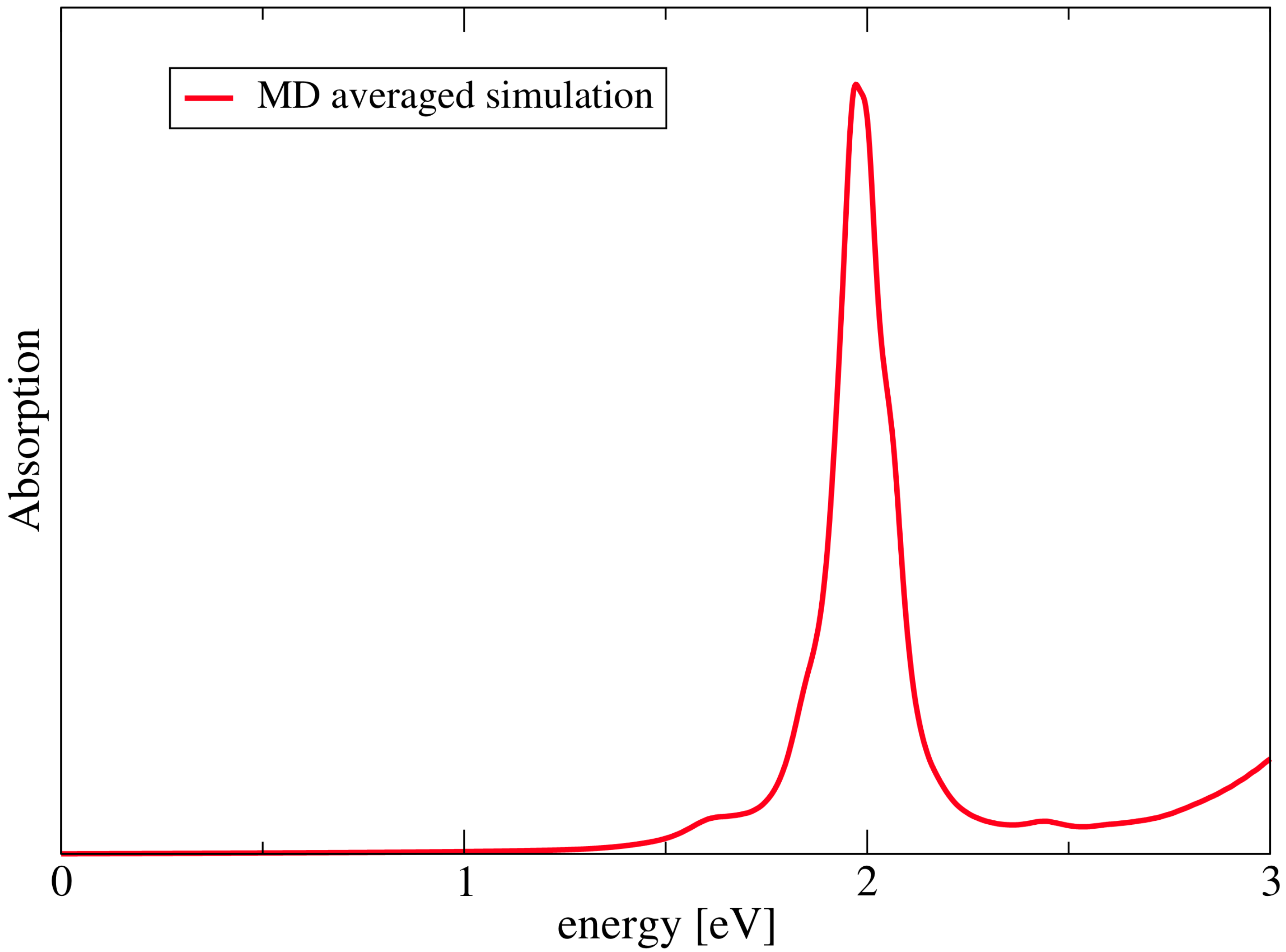



VMD 1.8.7 OpenGL Display


VMD 1.8.7 OpenGL Display

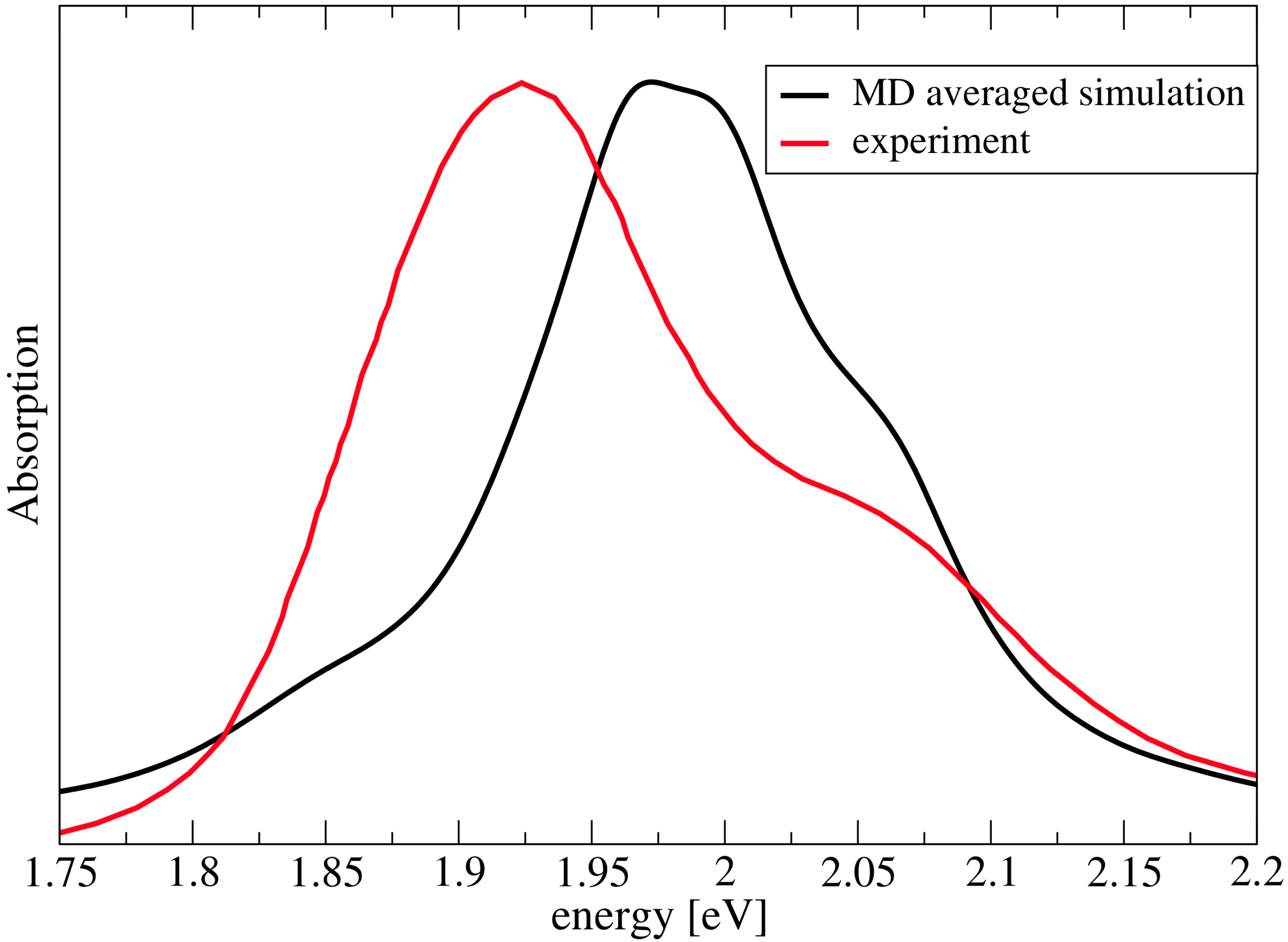
Squaraine on TiO_2

Simulation in explicit water



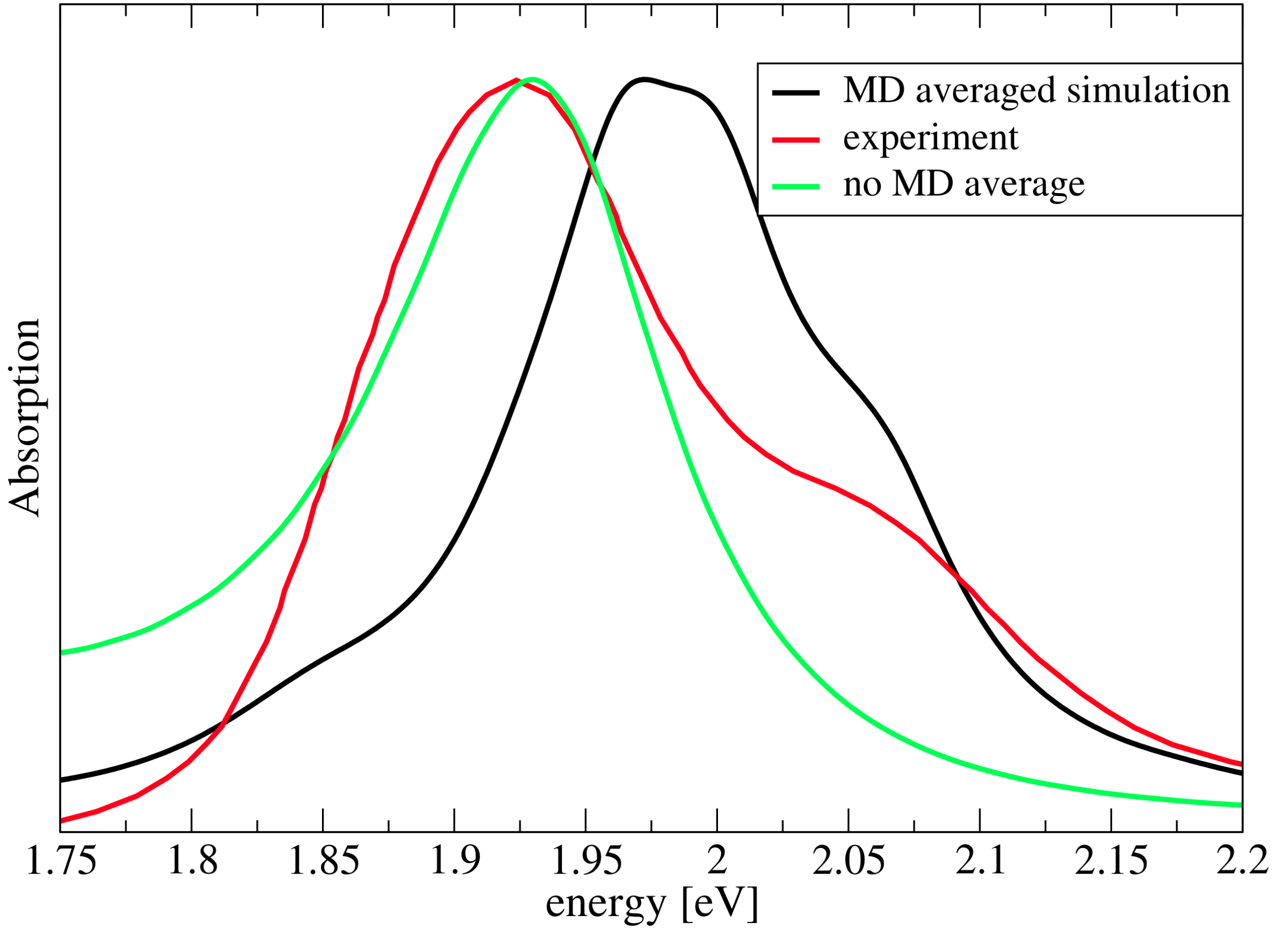
Squaraine on TiO_2

Simulation in explicit water

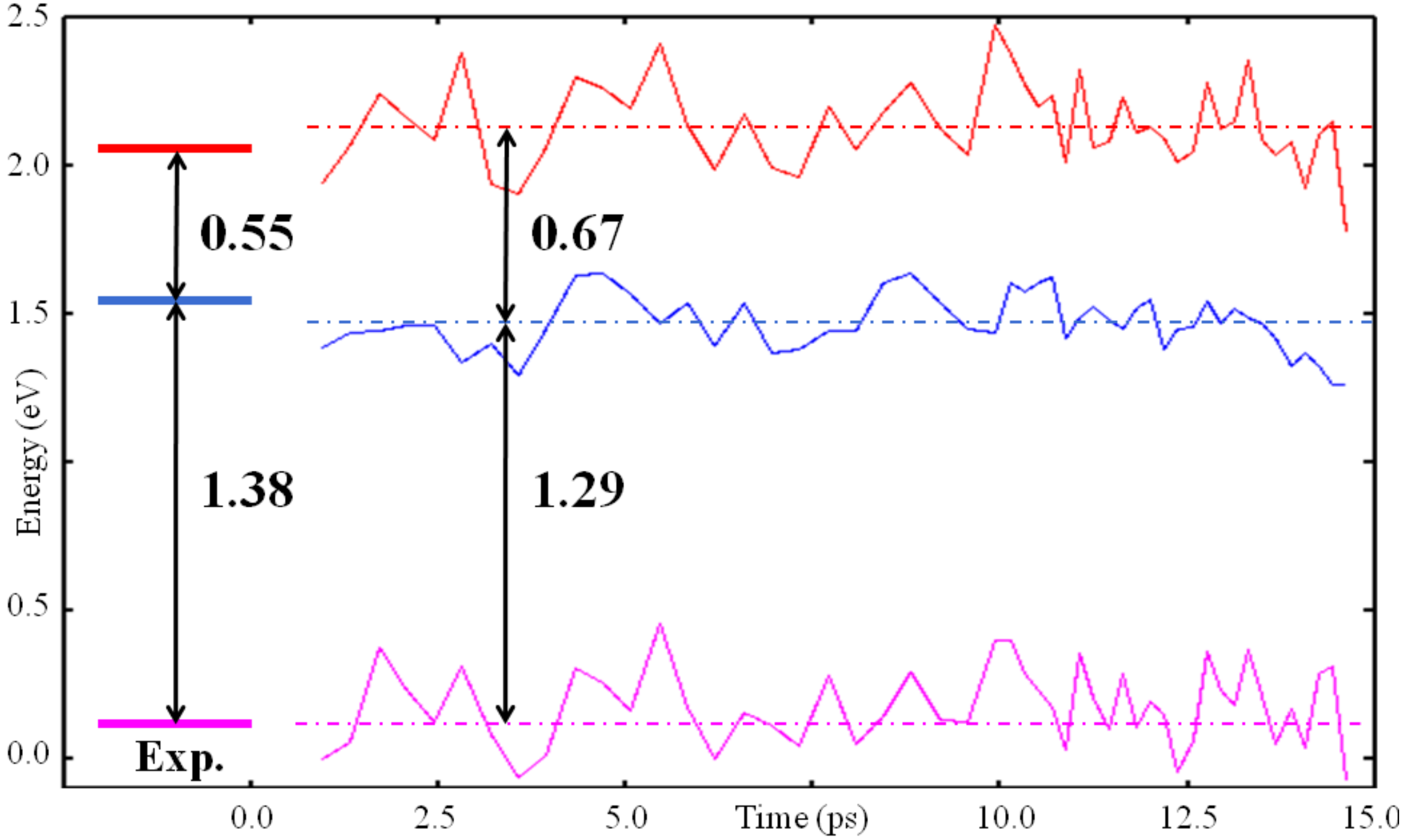


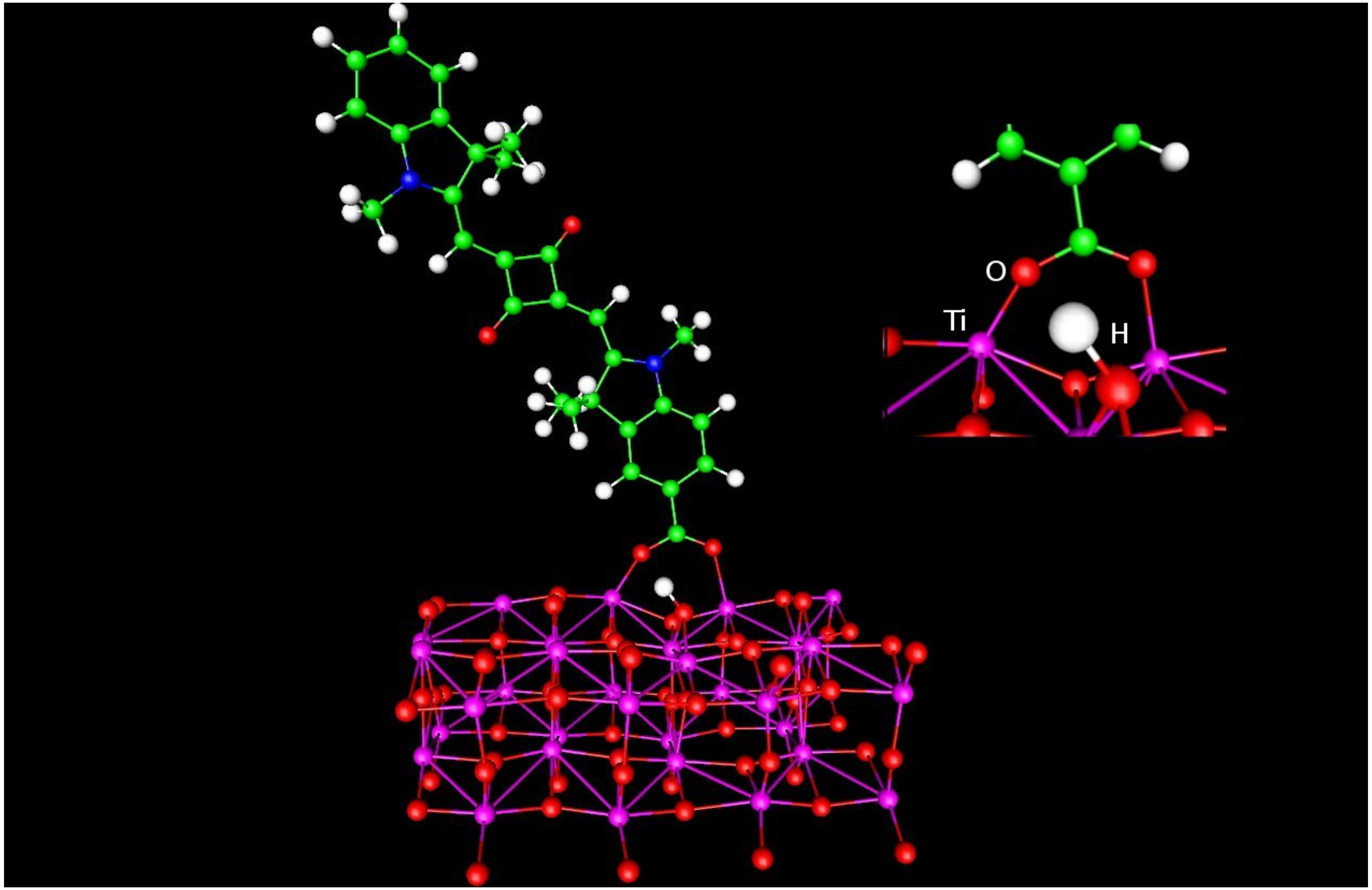
Squaraine on TiO_2

Simulation in explicit water

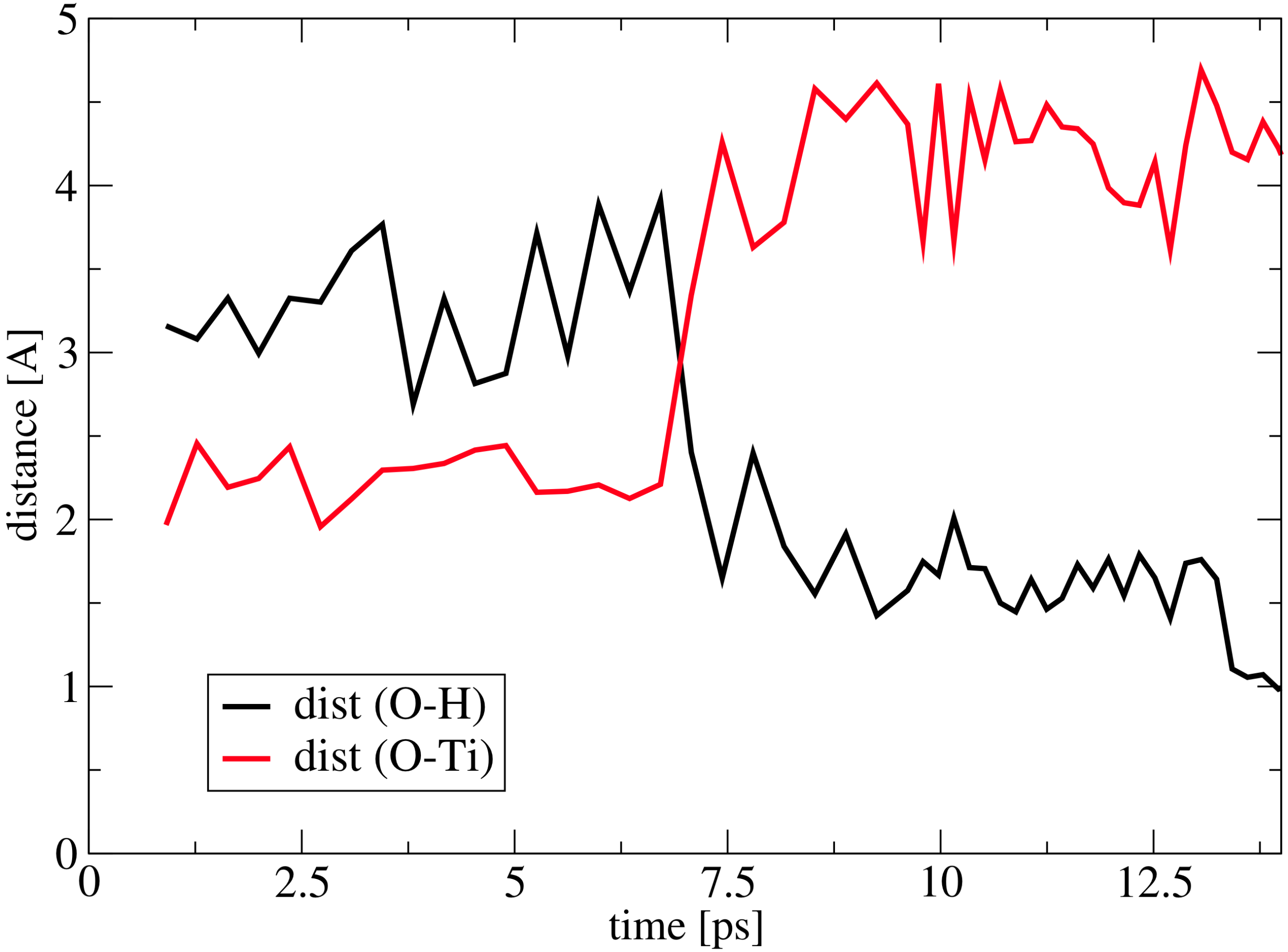


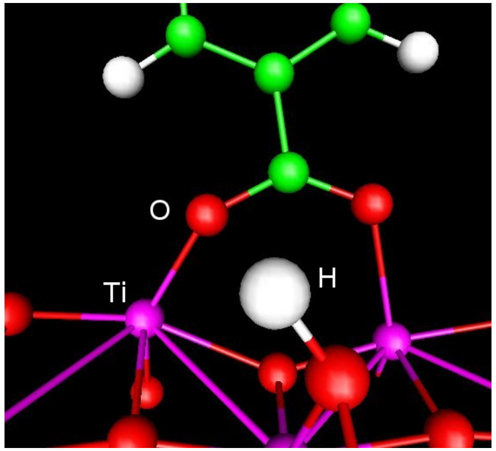
Energy level fluctuations and electron injection driving force



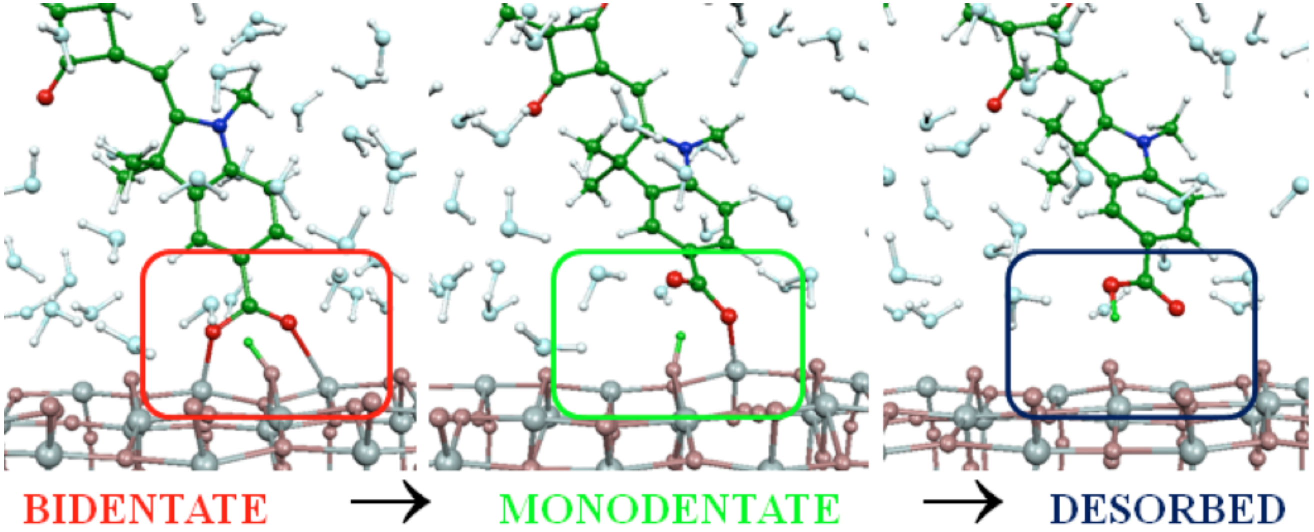

O
Ti
H

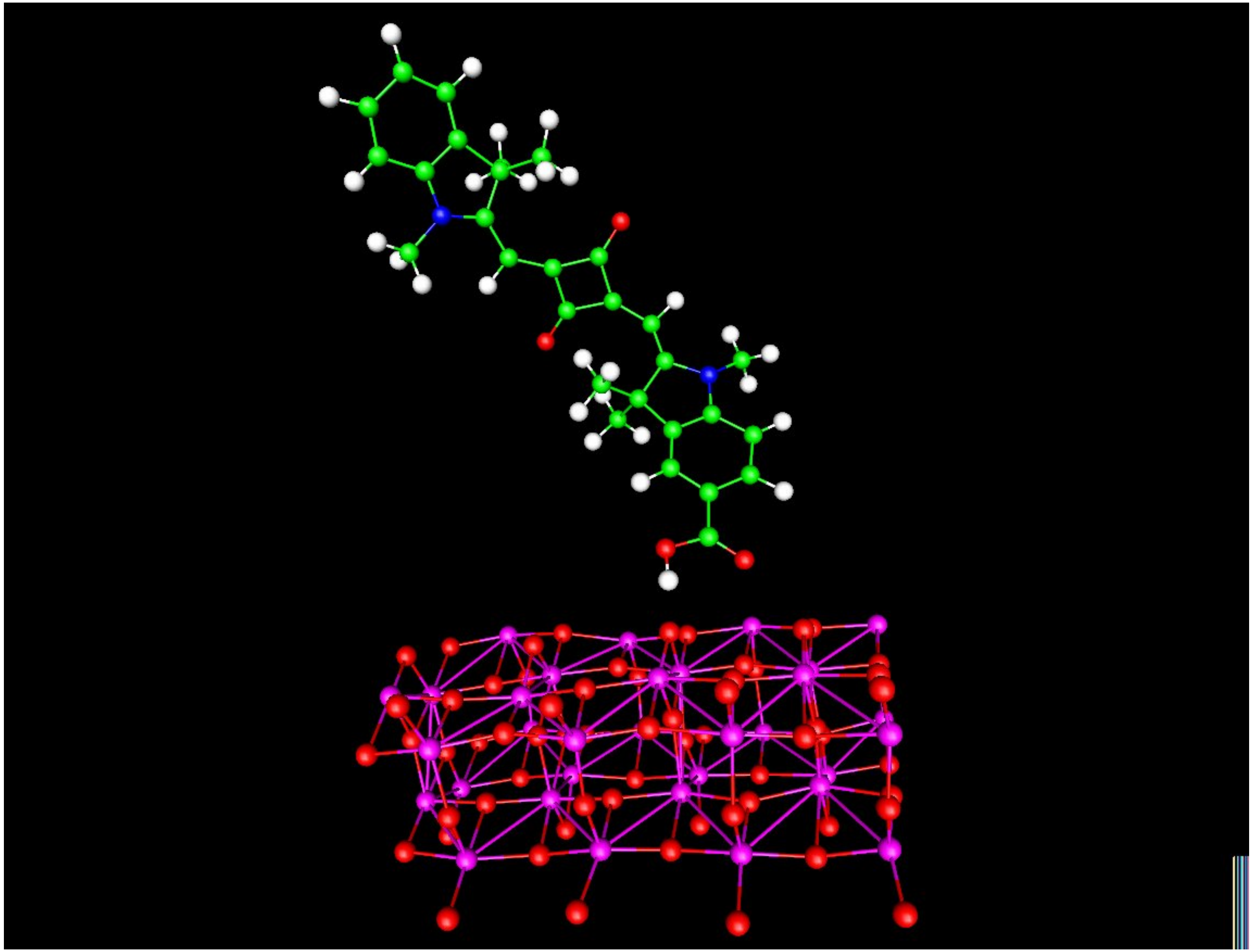
Squaraine adsorption on TiO_2





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

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

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

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

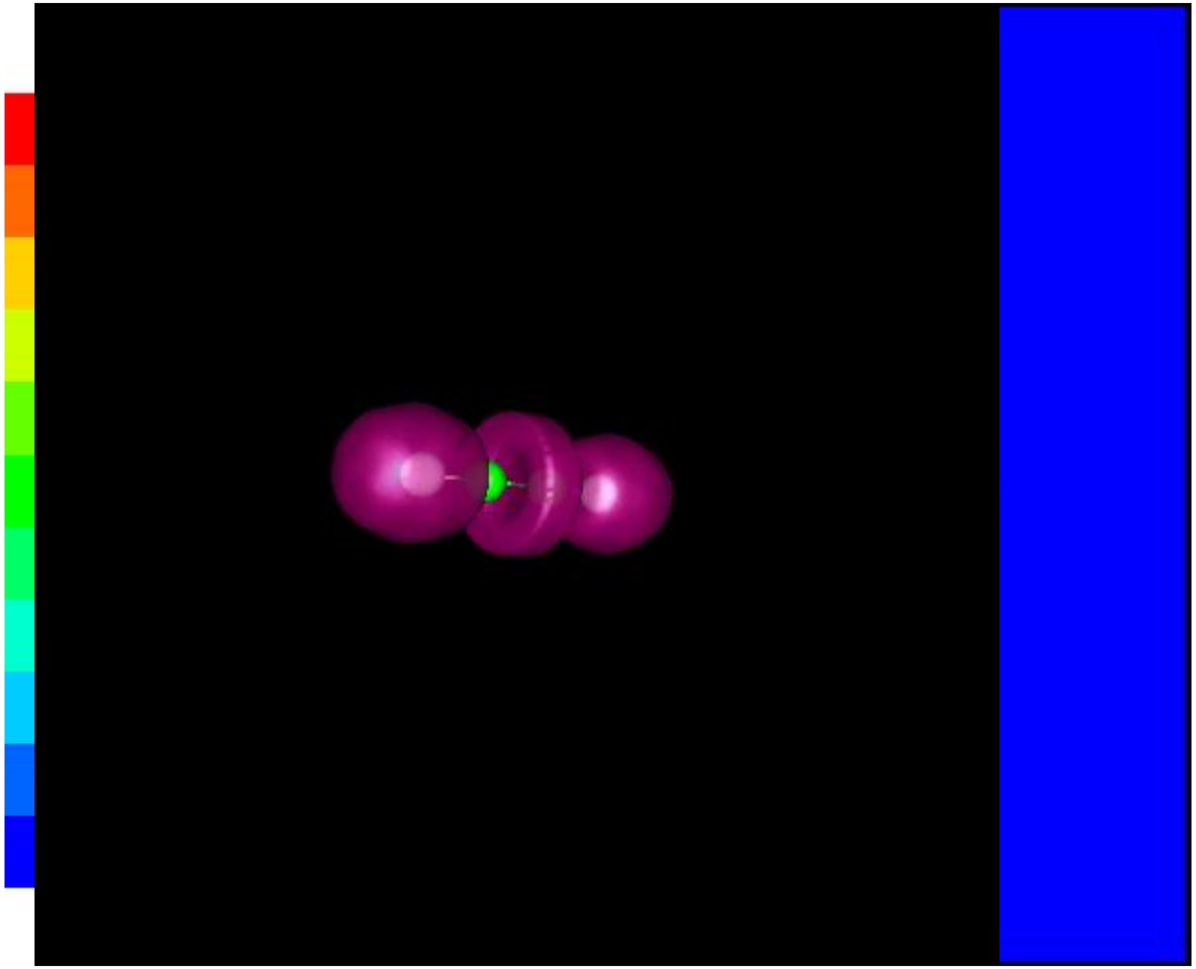
Nonlinear optical response

- Electron localization function:

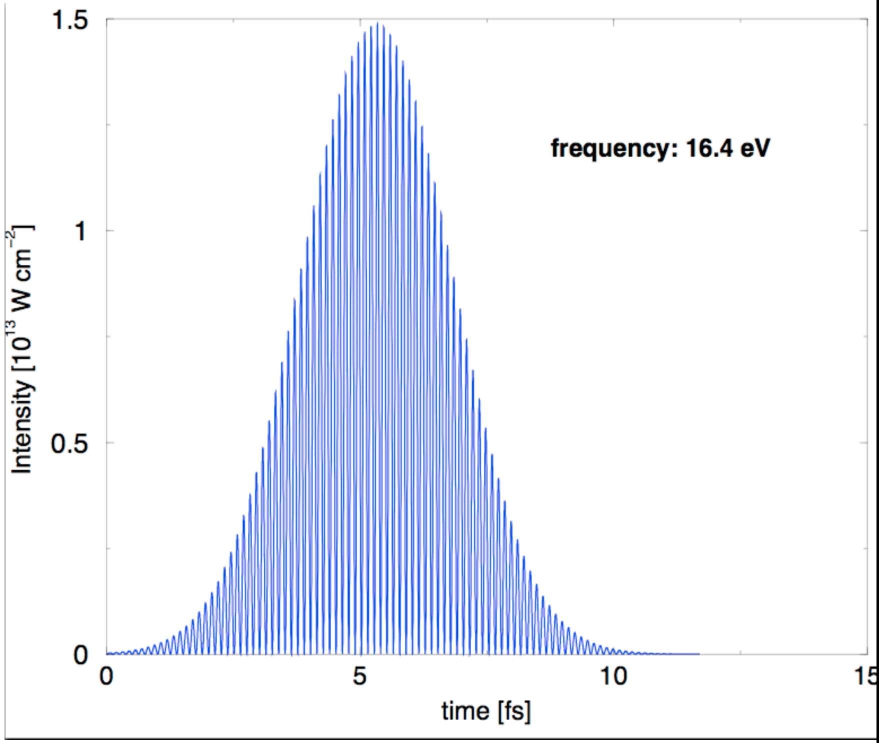
$$ELF(\boldsymbol{r},t) = \frac{1}{1+\left[D_\sigma(\boldsymbol{r},t)/D_\sigma^0(\boldsymbol{r},t)\right]^2}$$

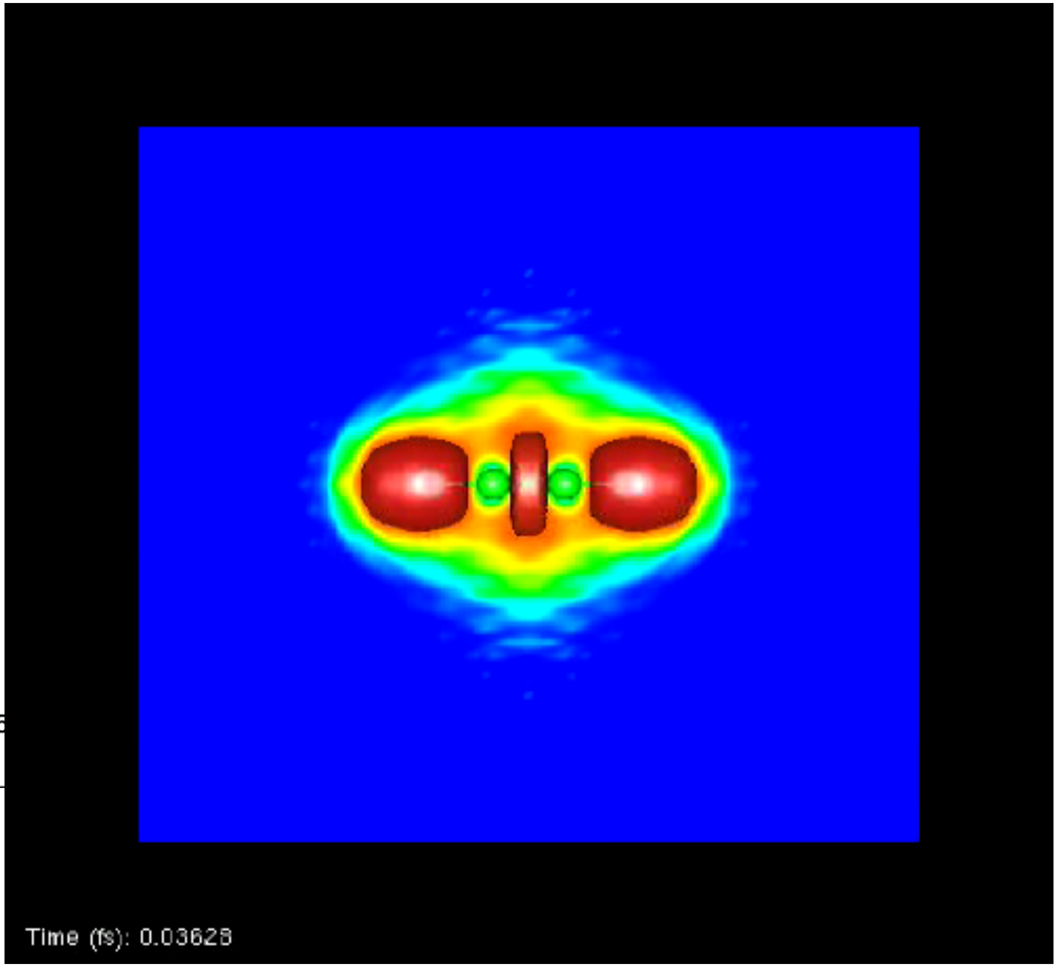
$$D_\sigma(\boldsymbol{r},t) = \tau_\sigma(\boldsymbol{r},t) - \frac{1}{4}\frac{\left[\nabla n_\sigma(\boldsymbol{r},t)\right]^2}{n_\sigma(\boldsymbol{r},t)} - \frac{j_\sigma^2(\boldsymbol{r},t)}{n_\sigma(\boldsymbol{r},t)}$$

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:

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

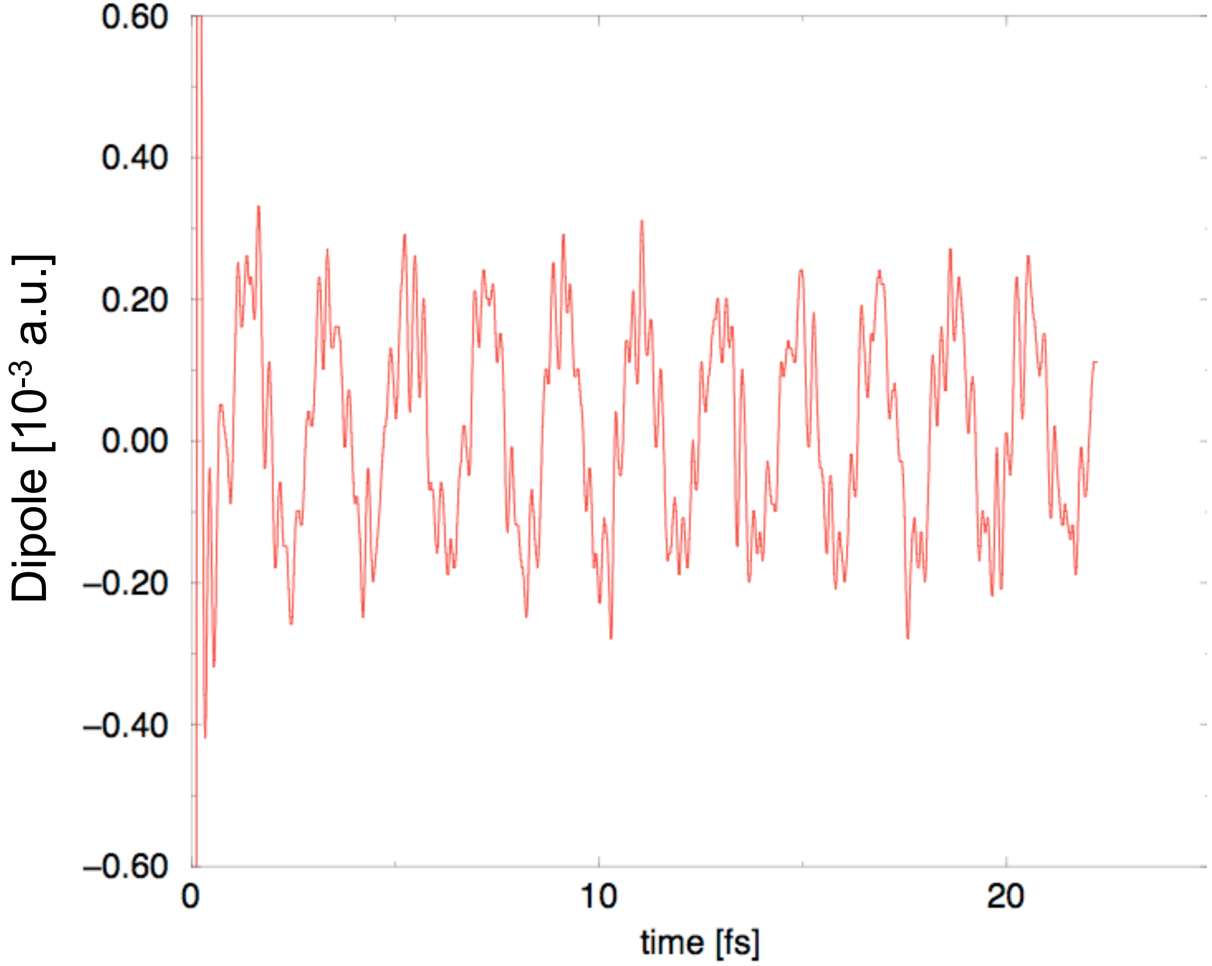
The experimentally measured strength function S is related to the Fourier transform of α:

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

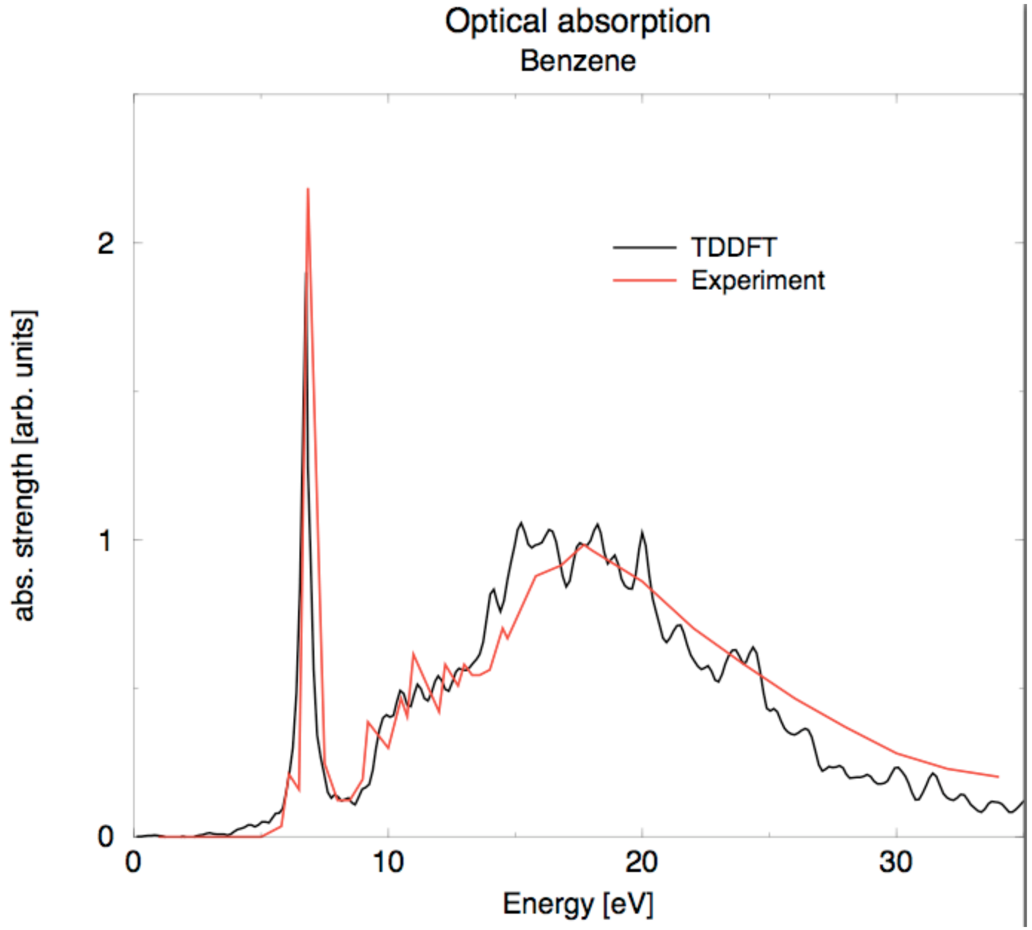
In practice: We take an E-field pulse $E_{ext} = E_0 \, \delta(t)$, calculate d(t), and obtain the spectrum $S(\omega)$ by calculating

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

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:

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

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

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:

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

Its Fourier transform is:

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

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

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

Therefore:

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

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 hermitean problem:

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

Build a Lanczos recursion chain:

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

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

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

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

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

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

Back to the calculation of spectra:

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

Therefore:

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

Use a recursion to represent L as a tridiagonal matrix:

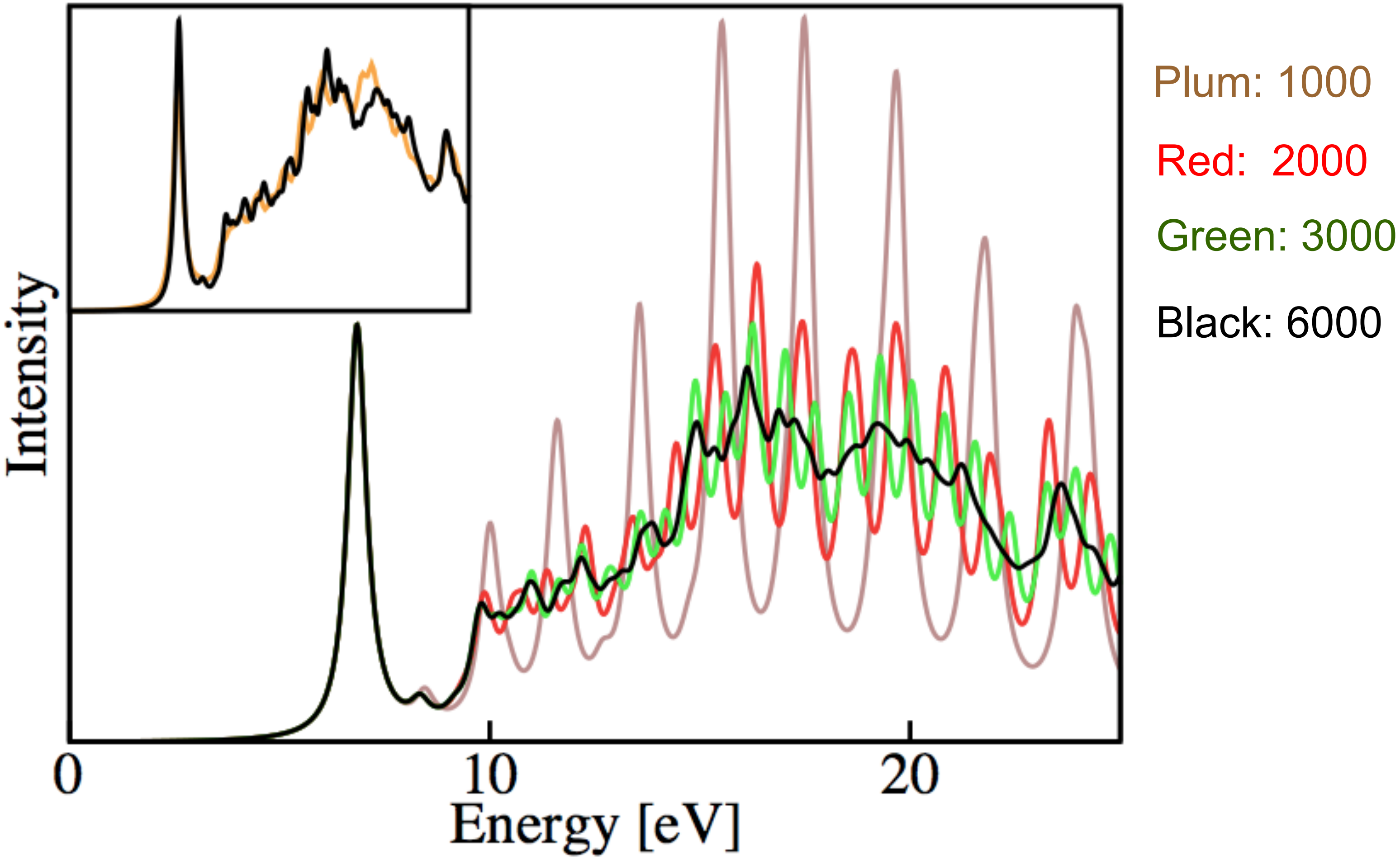
$$\mathcal{L} = \begin{pmatrix} a_1 & b_1 & 0 & & & & \\ c_1 & a_2 & b_2 & & & & \\ 0 & c_2 & a_3 & b_3 & & & \\ & & & \ddots & \ddots & \ddots & b_{N-1} \\ & & & & & c_{N-1} & a_N \end{pmatrix}$$

And the response can be written as a continued fraction!

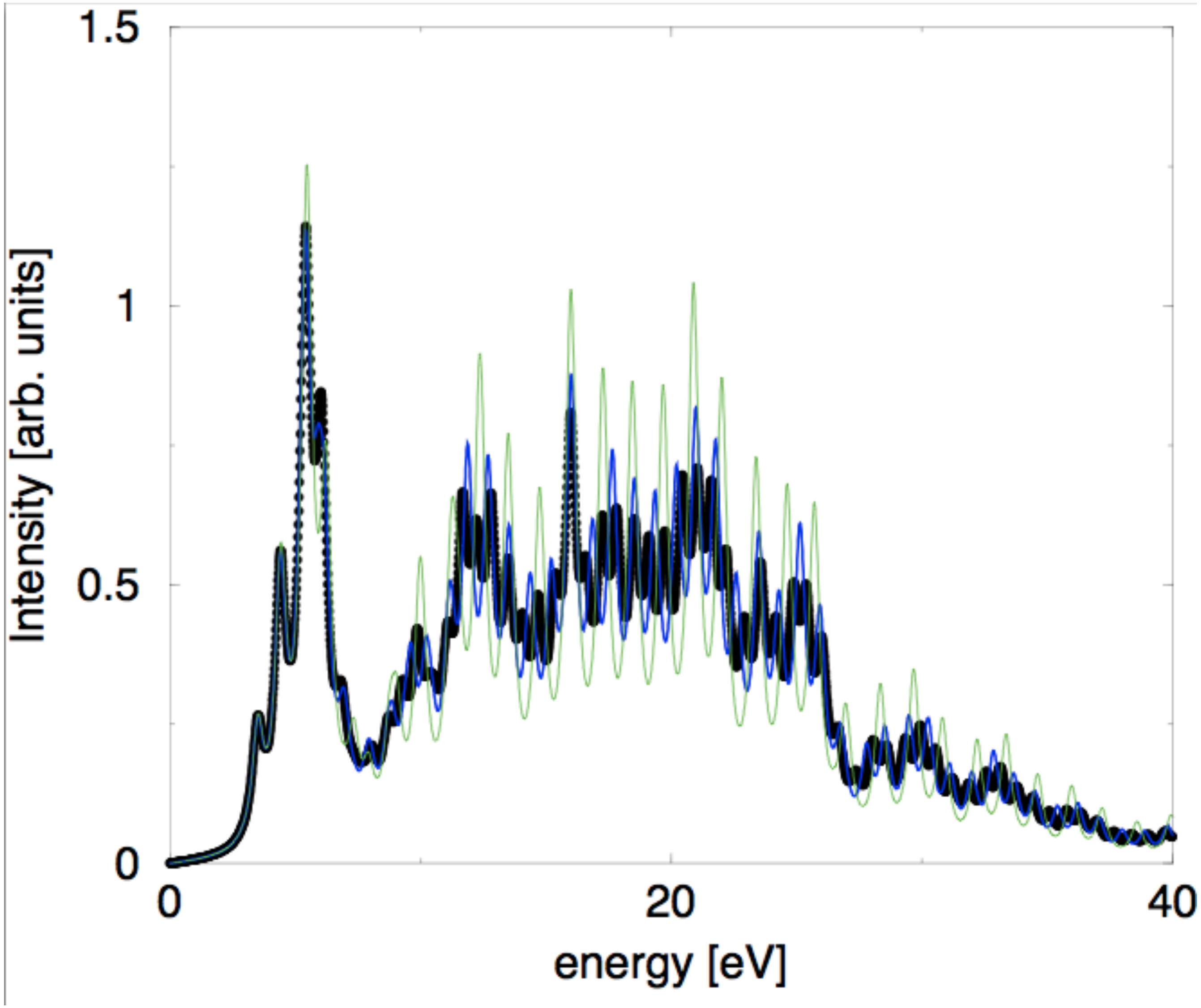
$$
\begin{aligned}
\tilde{A}(\omega) &= 2\left\langle \boldsymbol{a}, \boldsymbol{0} \middle| (\omega - \mathcal{L})^{-1} \middle| \boldsymbol{0}, \boldsymbol{v} \right\rangle \\
&= \frac{1}{\omega - a_1 + b_2 \frac{1}{\omega - a_2 + \cdots} c_2}
\end{aligned}
$$

How does it work?

Benzene spectrum



Spectrum of C_{60}

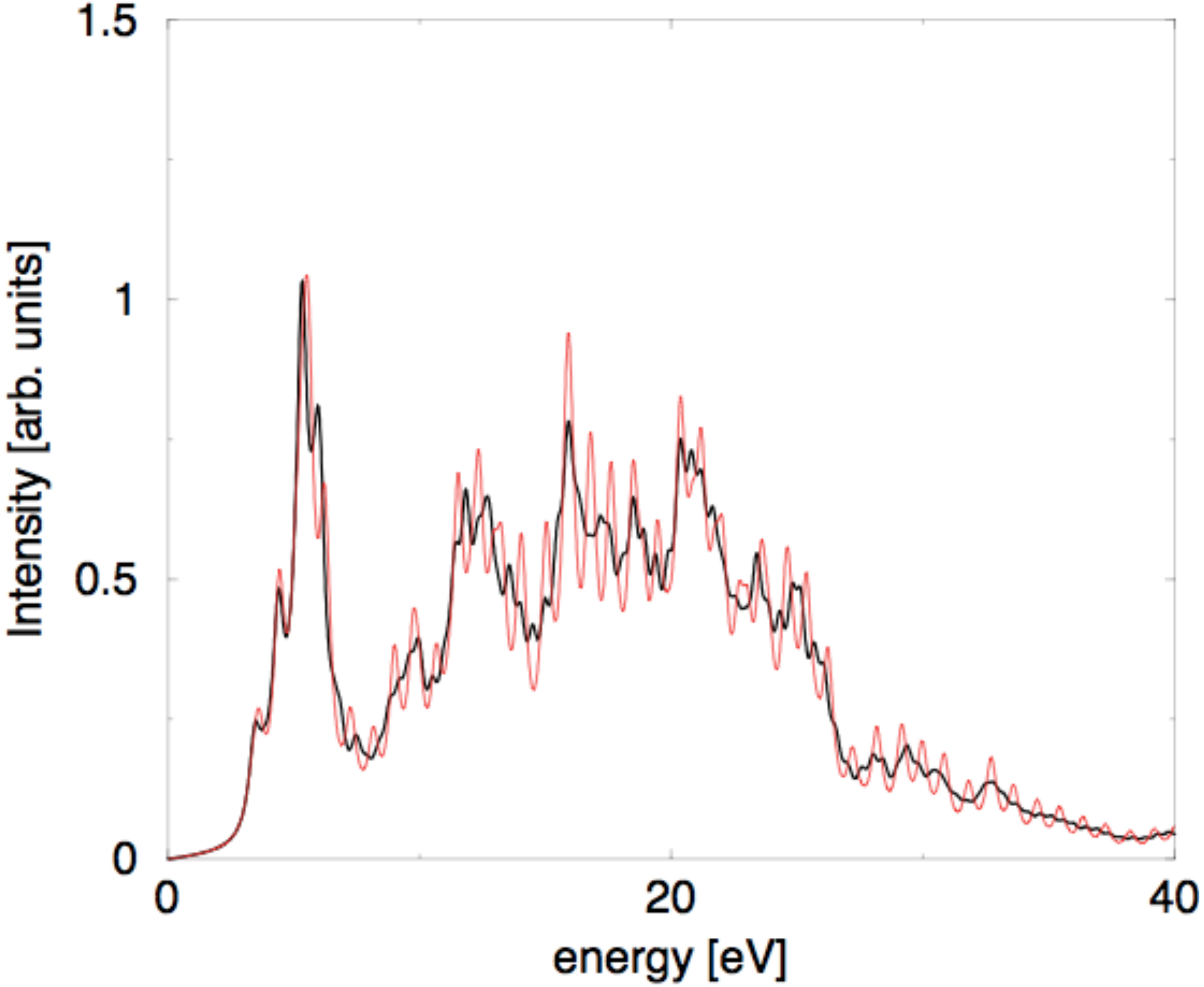


Black: 4000

Blue: 3000

Green: 2000

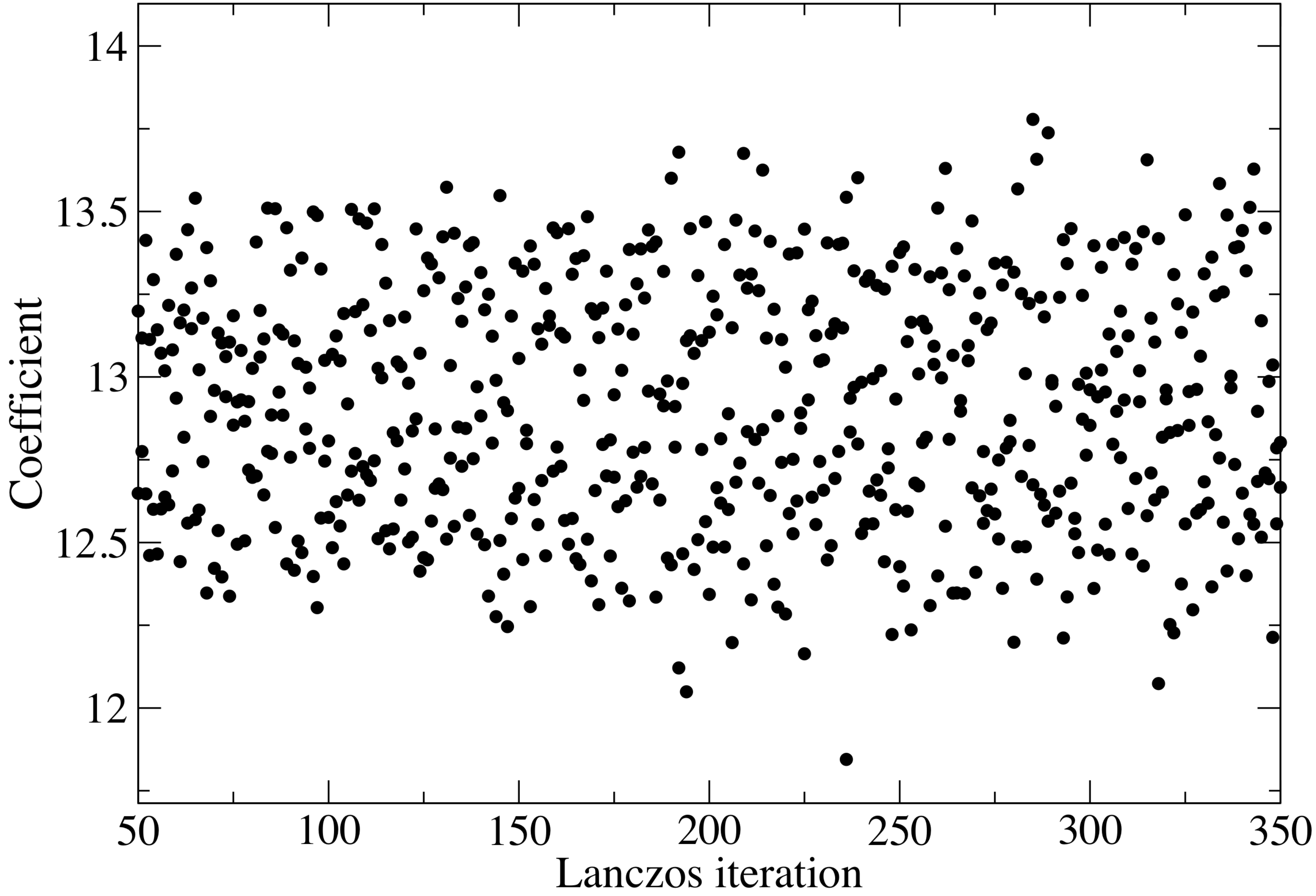
Spectrum of C_{60}: Ultrasoft pseudopotenitals



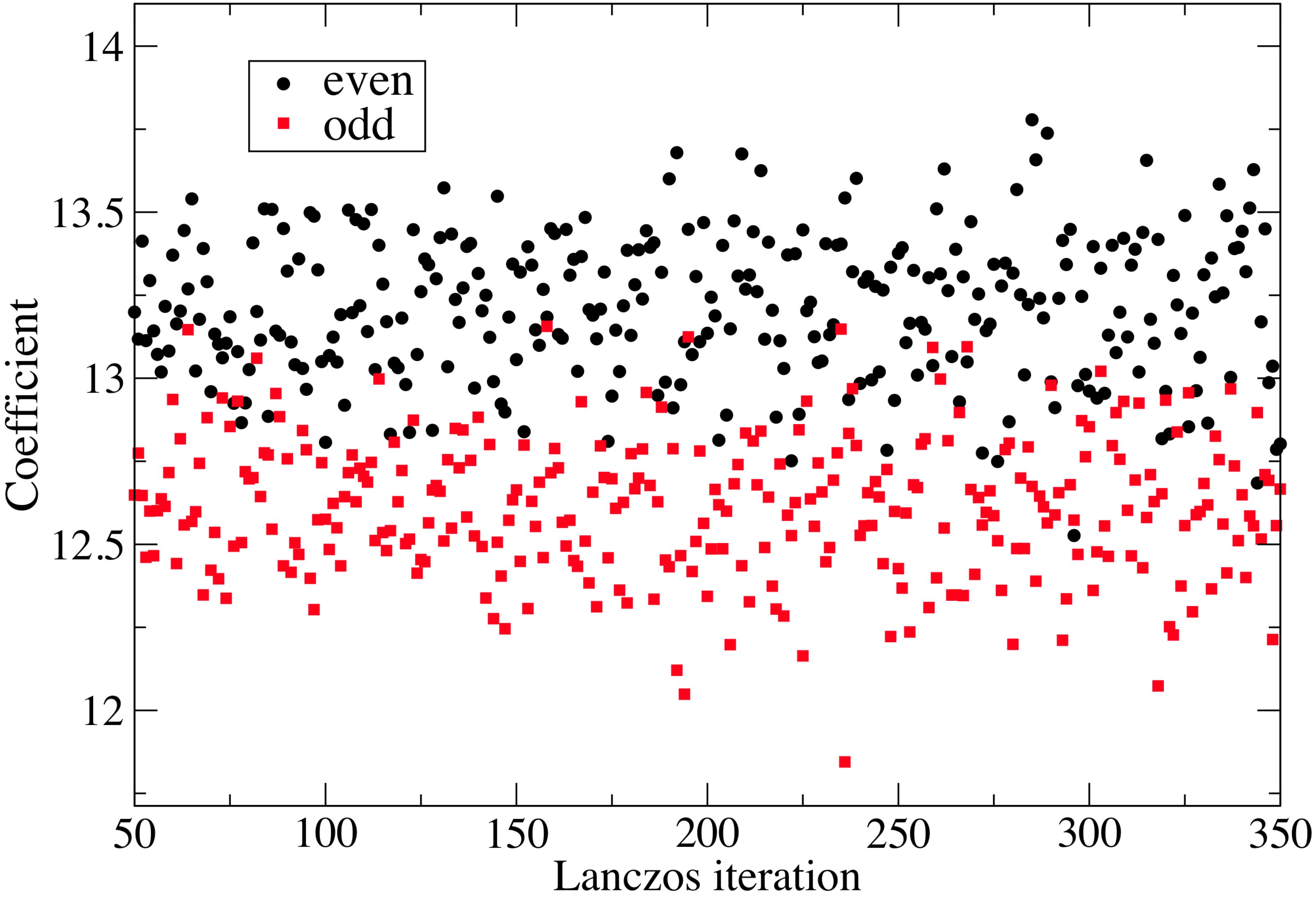
Black: 2000

Red: 1000

Speeding up convergence:
Looking at the Lanczos coefficients

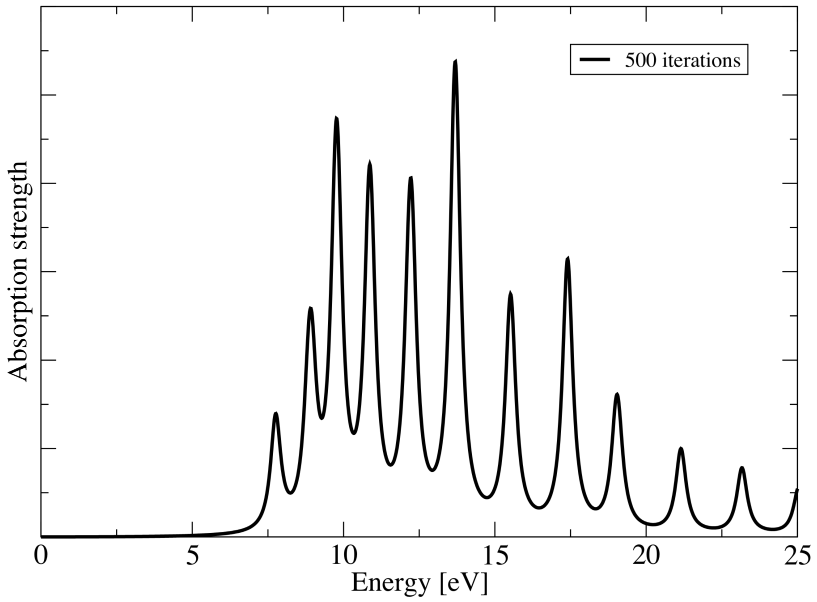


Speeding up convergence: Looking at the Lanczos coefficients



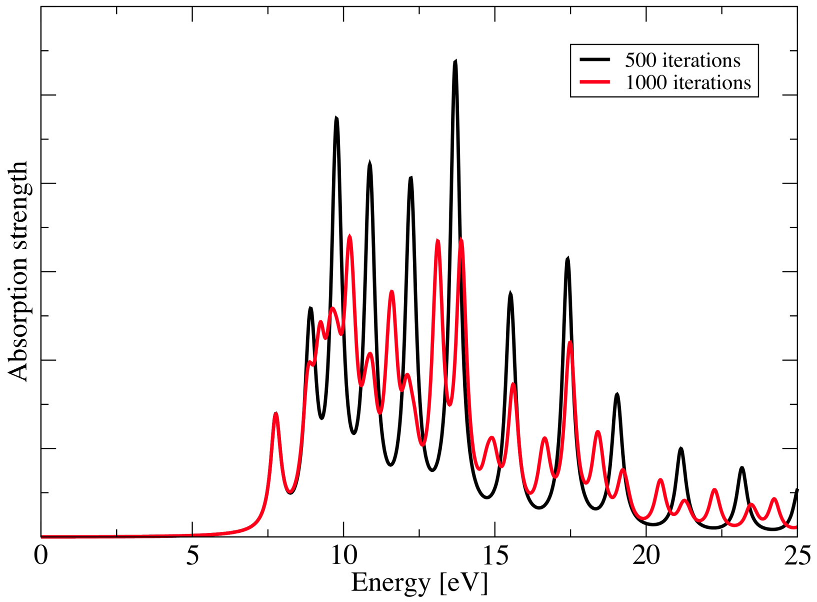
Effect of the terminator:

No terminator:



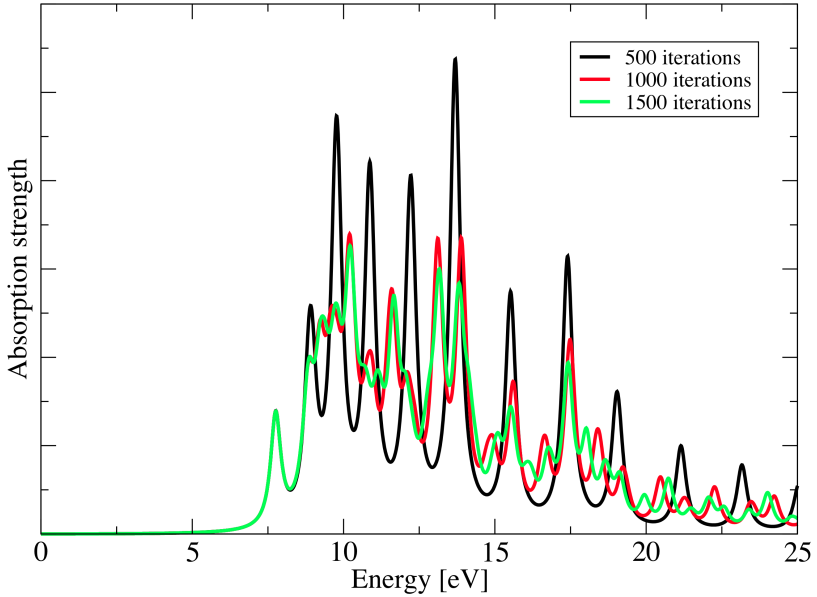
Effect of the terminator:

No terminator:



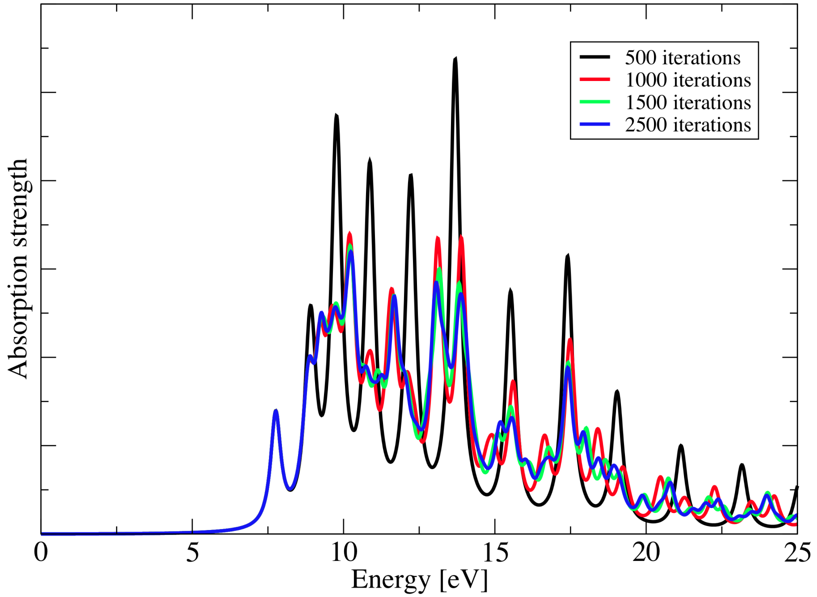
Effect of the terminator:

No terminator:



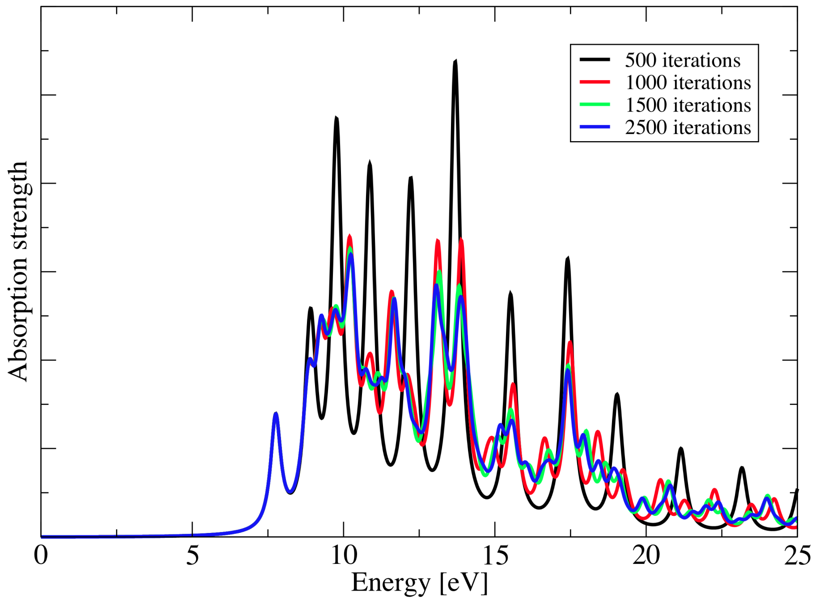
Effect of the terminator:

No terminator:

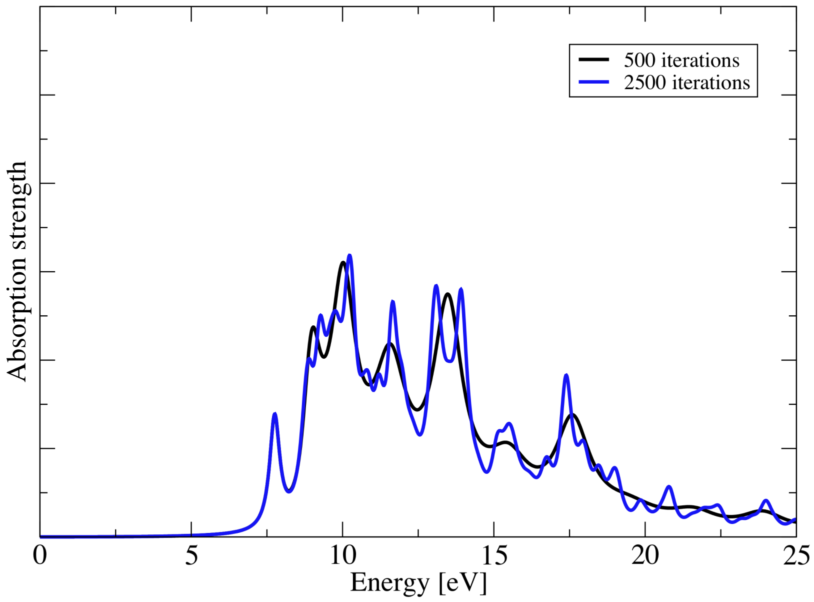


Effect of the terminator:

No terminator:

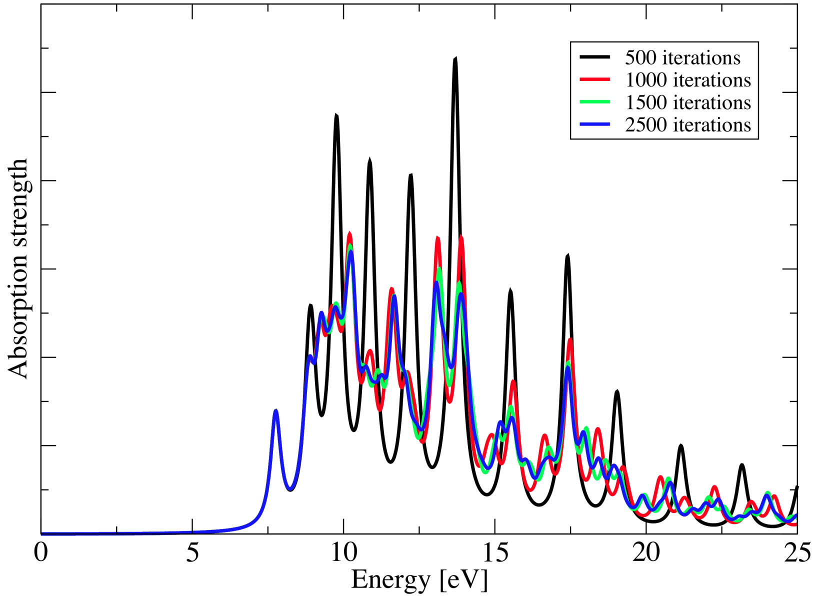


Terminator:

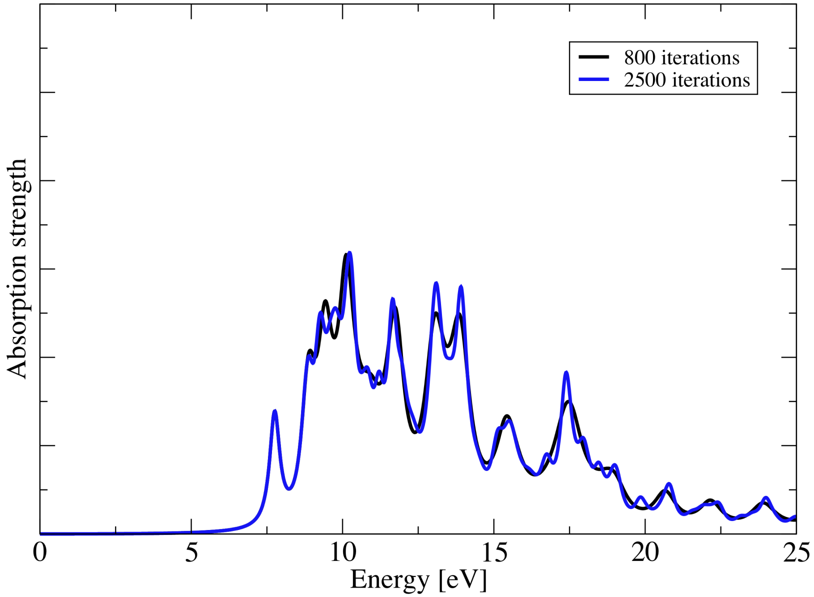


Effect of the terminator:

No terminator:

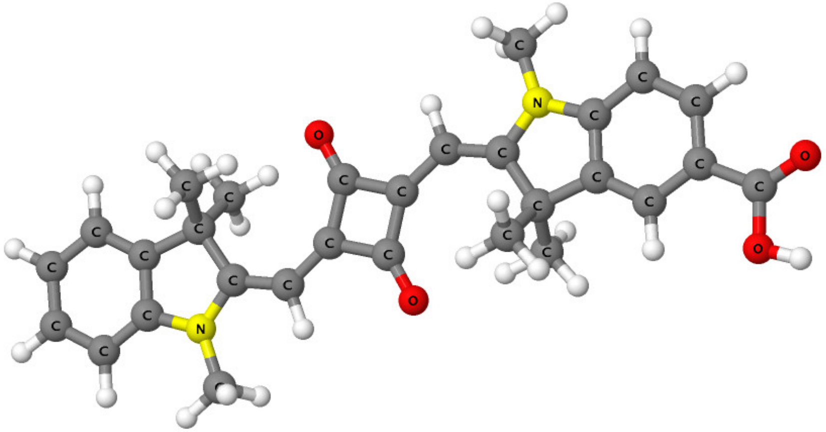


Terminator:



Analyzing the spectrum

Example of a squaraine dye:



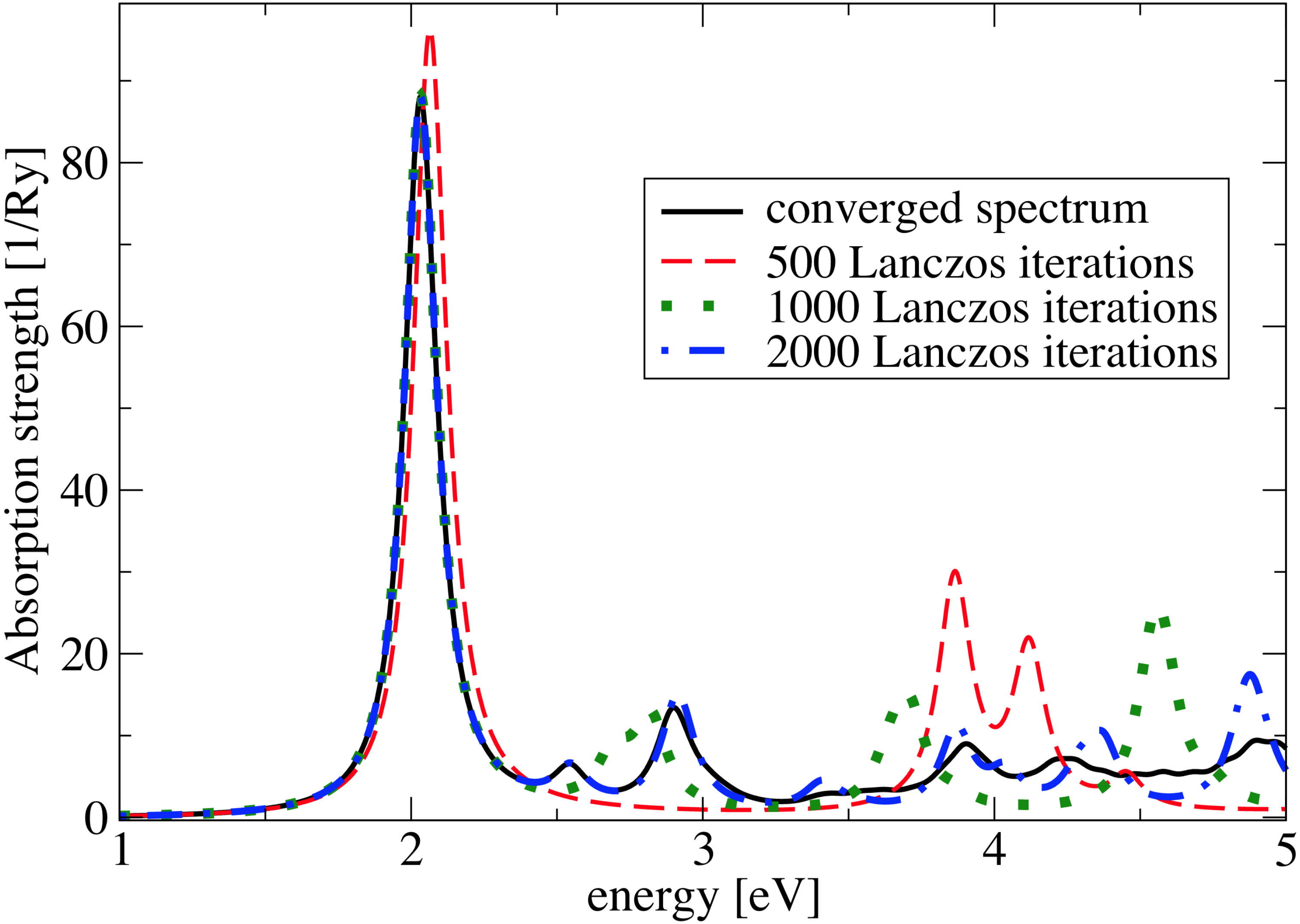
Can we analyze given features of the spectrum in terms of the electronic structure?

YES!

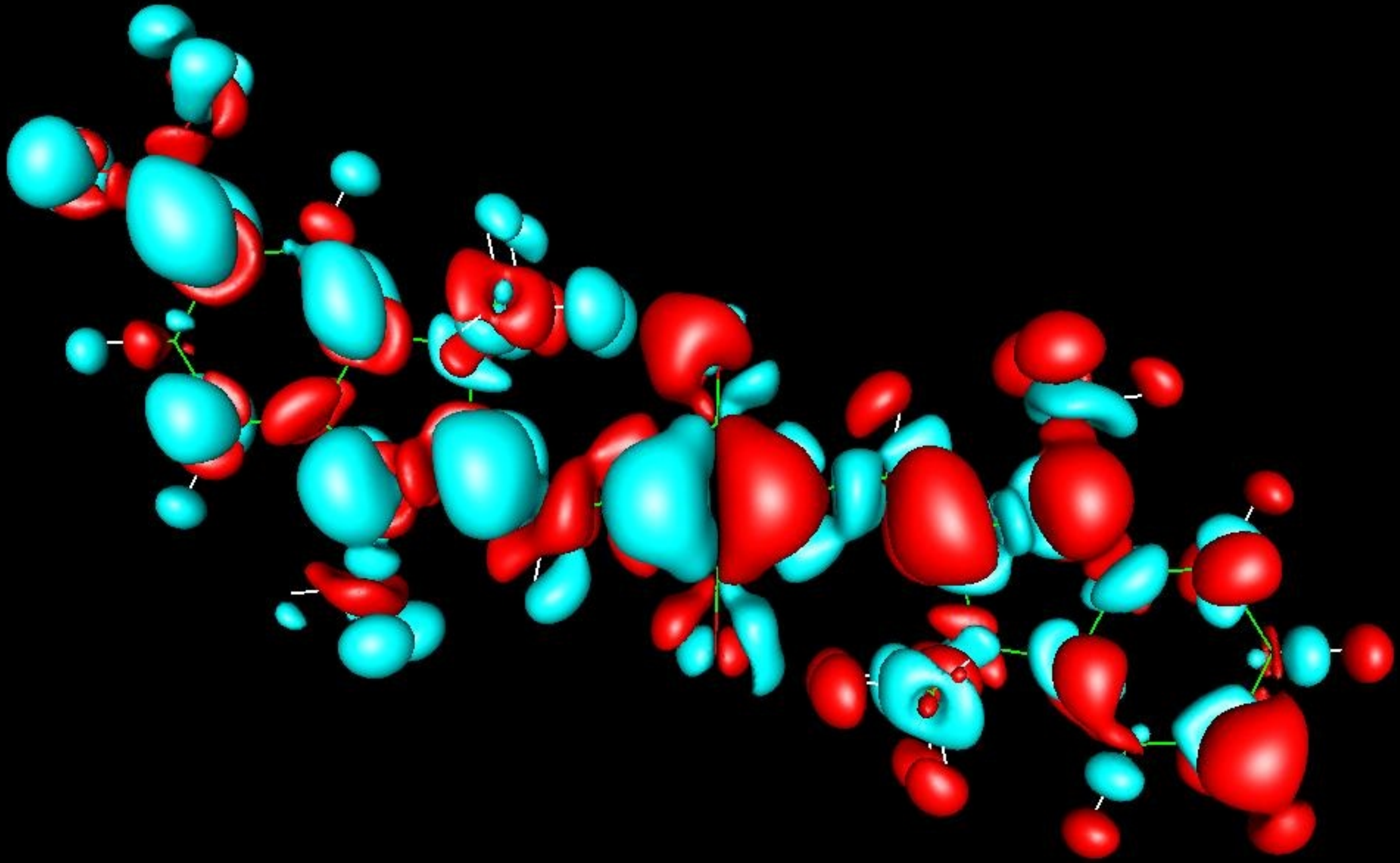
It is possible to compute the response charge density for any given frequency using a second recursion chain.

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)