The Abdus Salam
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15th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

13 - 15 January 2011

Computational study of optical and structural properties of an organic dye sensitized solar cell

Ralph Gebauer

ICTP
Trieste
Italy

Strada Costiera 11, 34151 Trieste, Italy - Tel.+39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it

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Thursday, January 13th, 2011

Overview

- Nanostructured photovoltaic devices (Grätzel cells)

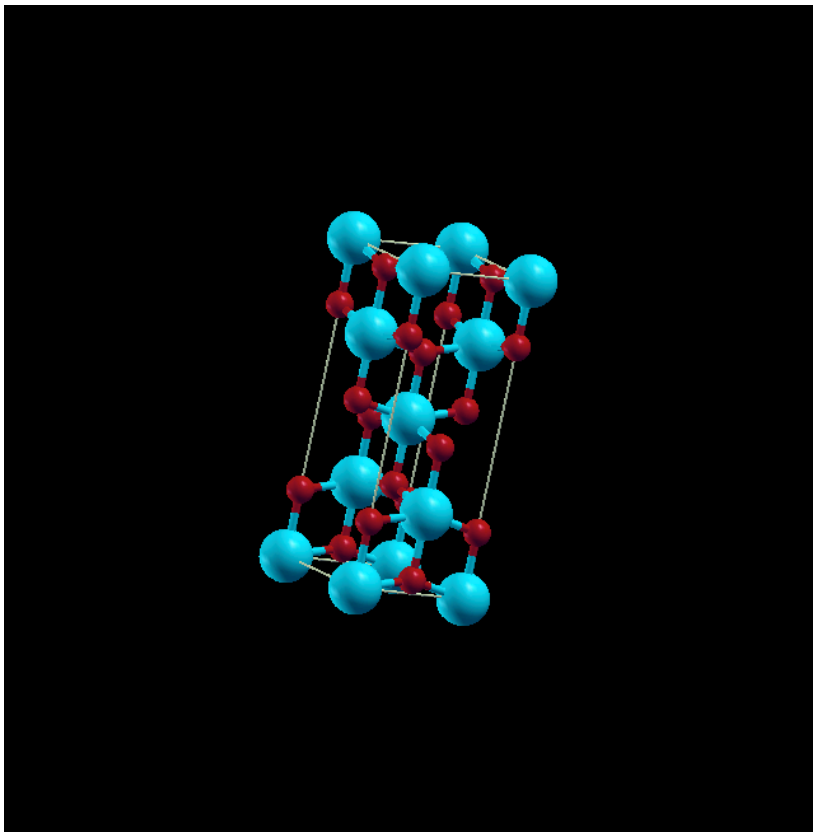
- Application of TDDFT to such systems
-

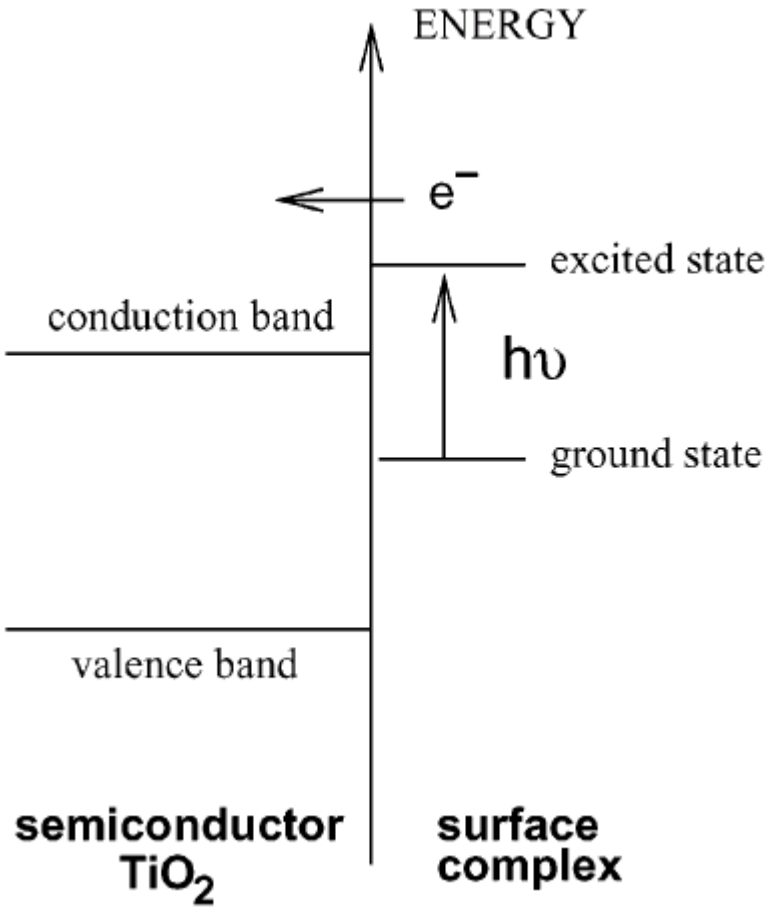
  computational approach
  dry system
  including (explicit) solvent
  averaging over MD in presence of solvent

- Dye adsorption/desorption in presence of explicit solvent

Sensitized semiconductor surfaces as photovoltaic devices

Idea (Graetzel solar cells):





Functioning of a Grätzel cell

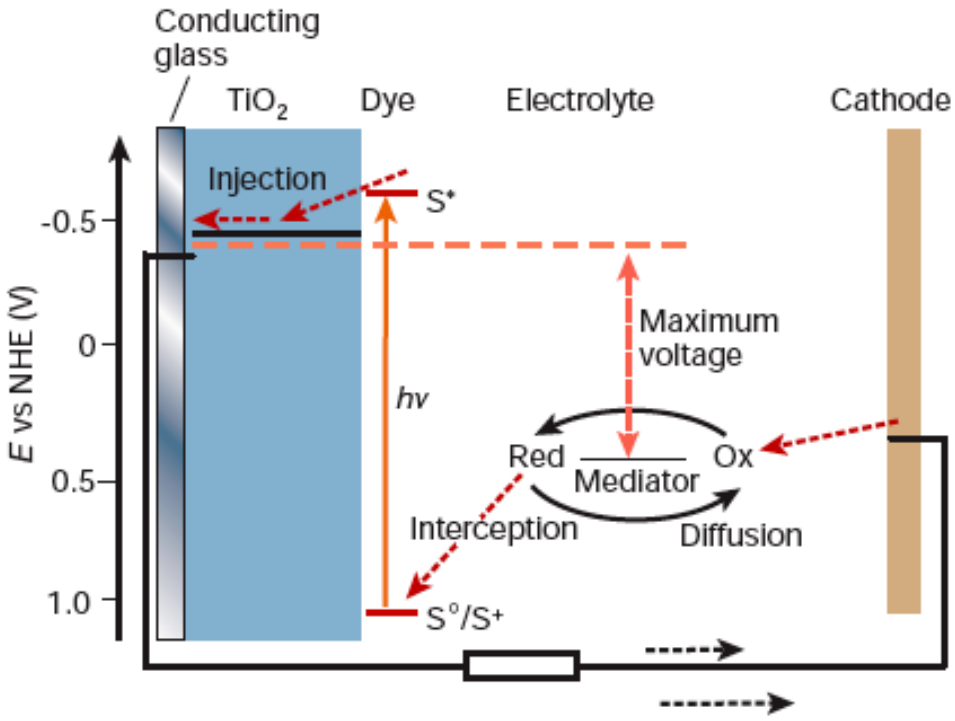


Figure 3 Schematic of operation of the dye-sensitized electrochemical photovoltaic cell. The photoanode, made of a mesoporous dye-sensitized semiconductor, receives electrons from the photo-excited dye which is thereby oxidized, and which in turn oxidizes the mediator, a redox species dissolved in the 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

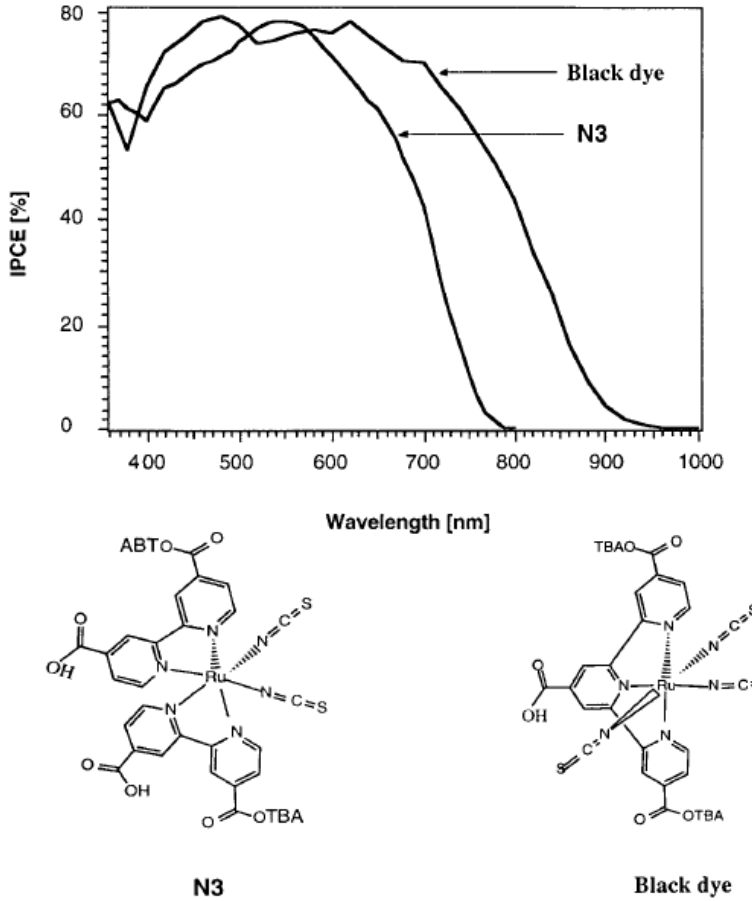
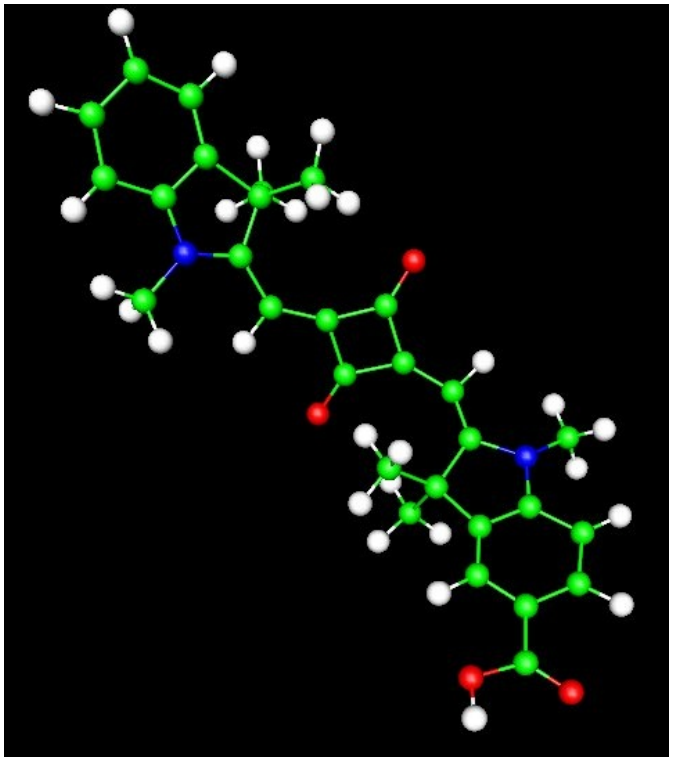


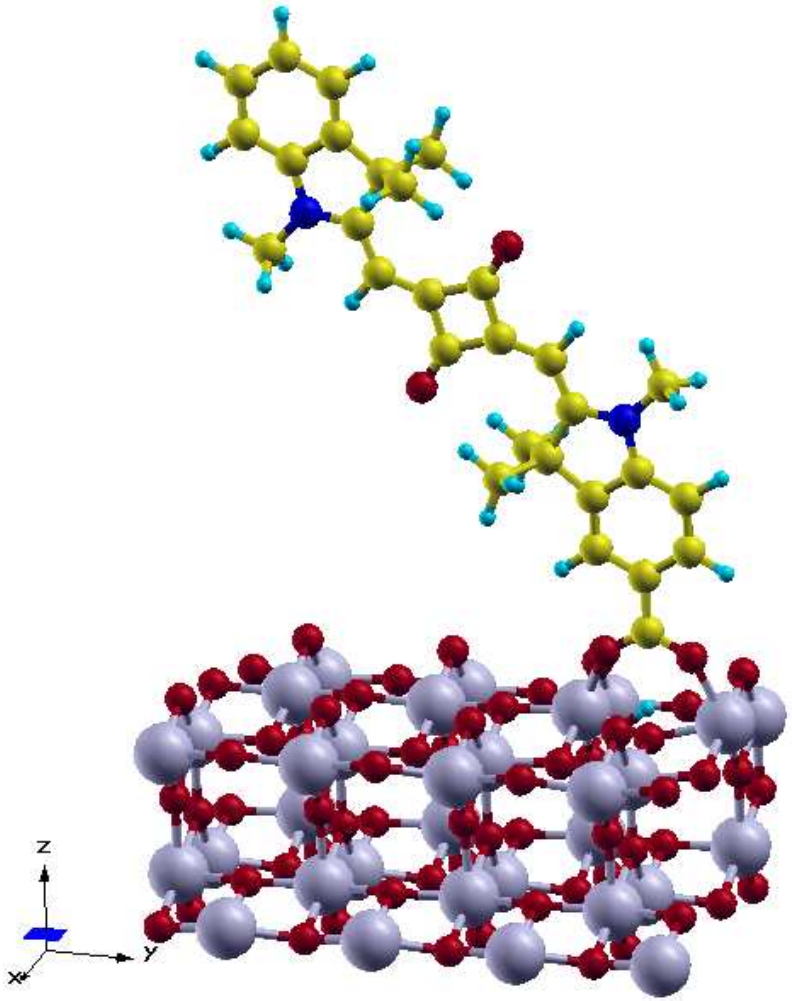
Figure 3. Spectral response curve of the photocurrent for the DYSC sensitized by N3 and the black dye. The incident photon to current conversion efficiency is plotted as a function of wavelength

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



Squaraine dye

Our system: Squaraine on TiO_2 slab

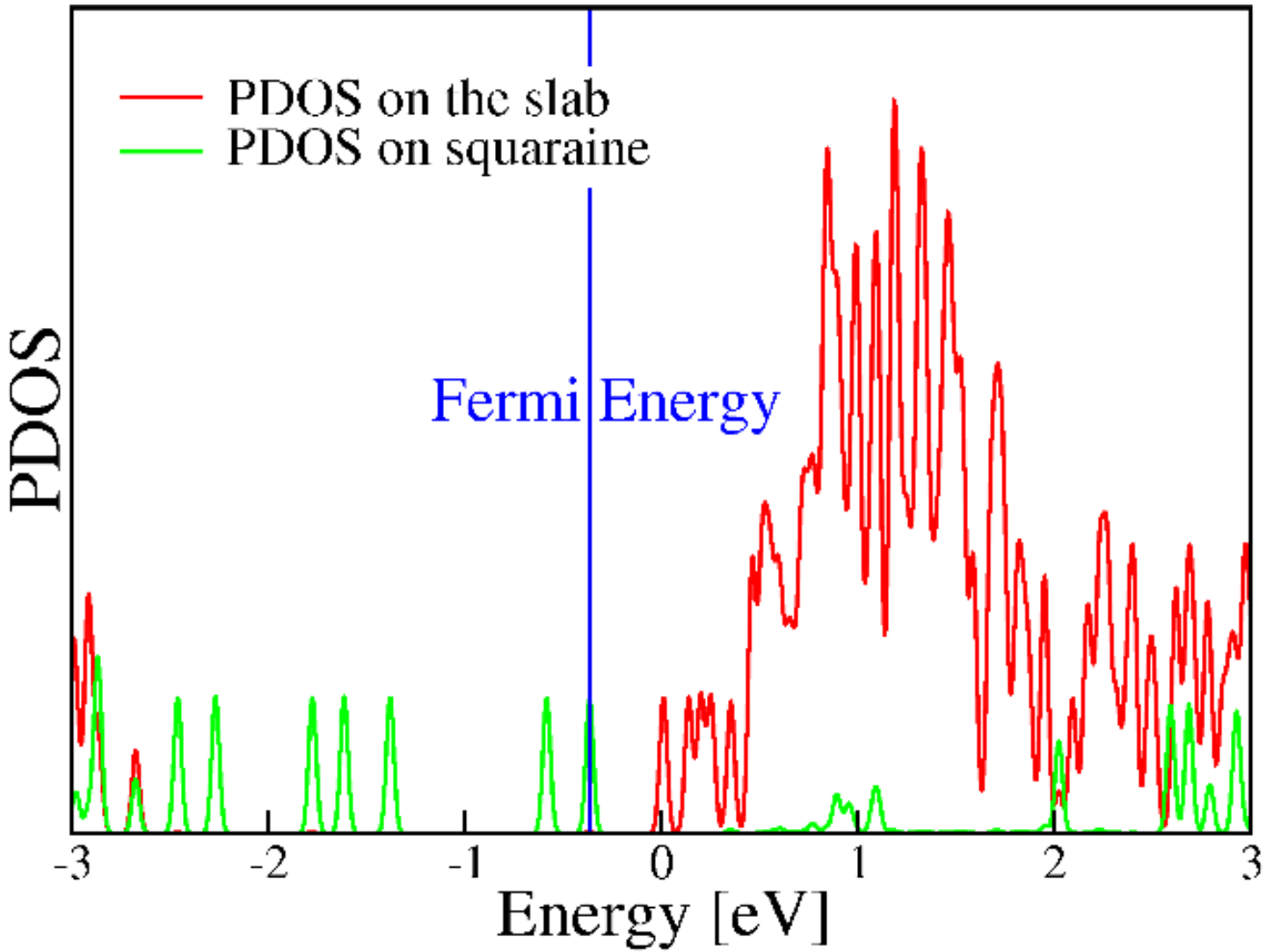


Slab geometry:
1x4 TiO2 anatase slab,
Exposing (101) surface

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

Shown here: minimum energy
configuration

TiO2 slab with squaraine dye



TDDFT treatment of model system

- Adiabatic PBE functional

- Recursive Lanczos algorithm for TDDFT:

  Ideally suited for
  - large systems
  - broad spectral region,
  - large basis set

Linear response formalism in TDDFT:

$$\omega\delta\psi_v^+(\boldsymbol{r}) = \left(H_{KS}^0 - \epsilon_v^0\right)\delta\psi_v^+ + \hat{P}_c\left(\delta V_{SCF}^+(\boldsymbol{r}) + V_{pert}(\boldsymbol{r})\right)\psi_v^0(\boldsymbol{r})$$

$$-\omega\delta\psi_v^-(\boldsymbol{r}) = \left(H_{KS}^0 - \epsilon_v^0\right)\delta\psi_v^- + \hat{P}_c\left(\delta V_{SCF}^-(\boldsymbol{r}) + V_{pert}(\boldsymbol{r})\right)\psi_v^0(\boldsymbol{r})$$

Now define the following linear combinations:

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

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

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

With the following definitions:

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

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

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:

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

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

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 $(\omega - \mathcal{L})^{-1}$.

Use a recursion to represent L as a tridiagonal matrix:

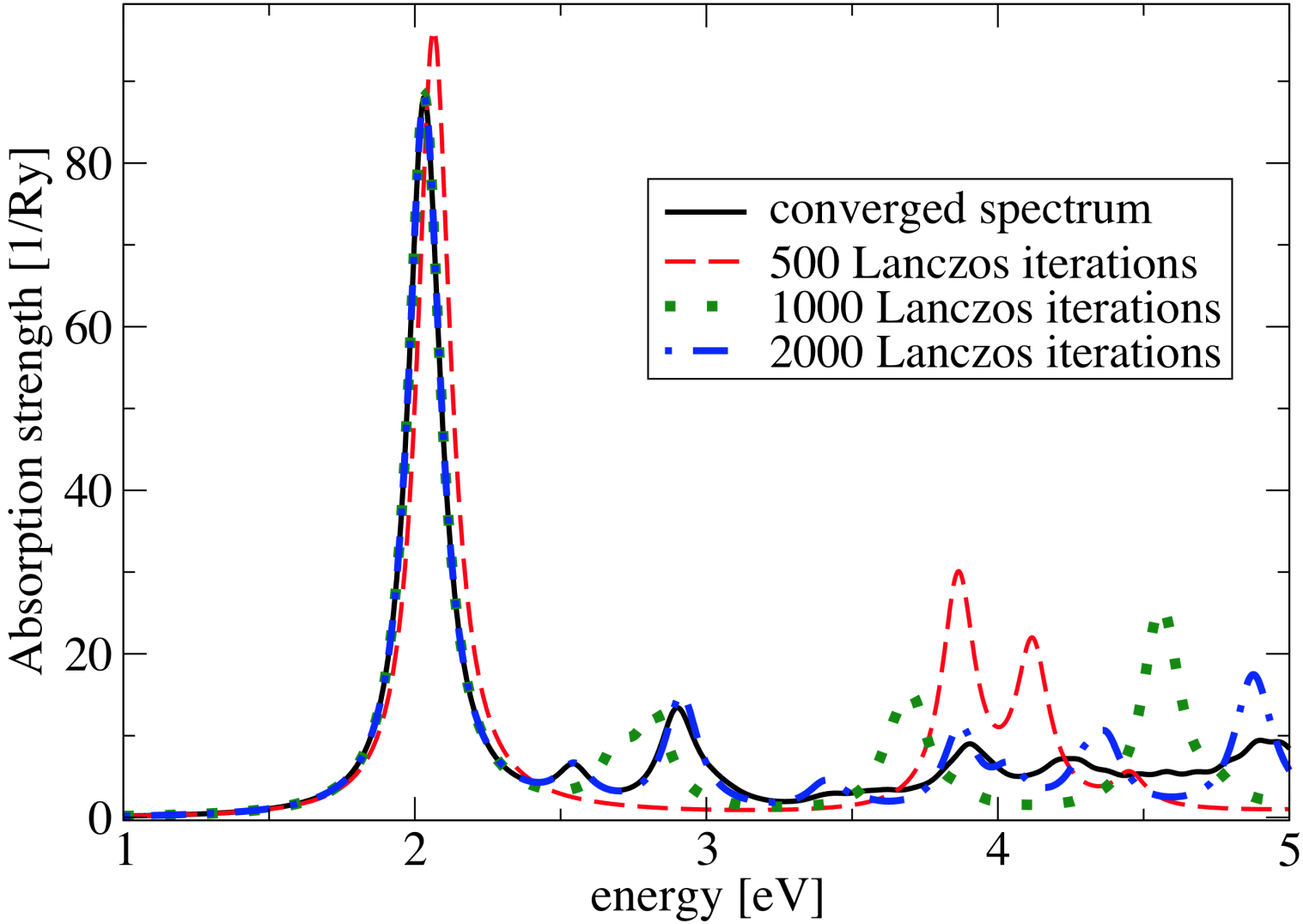
$$\mathcal{L} = \begin{pmatrix} a_1 & b_1 & 0 & & & & \\ c_1 & a_2 & b_2 & & & & \\ 0 & c_2 & a_3 & b_3 & & & \\ & & \ddots & \ddots & \ddots & b_{N-1} & \\ & & & & c_{N-1} & a_N & \end{pmatrix}$$

And the response can be written as a continued fraction!

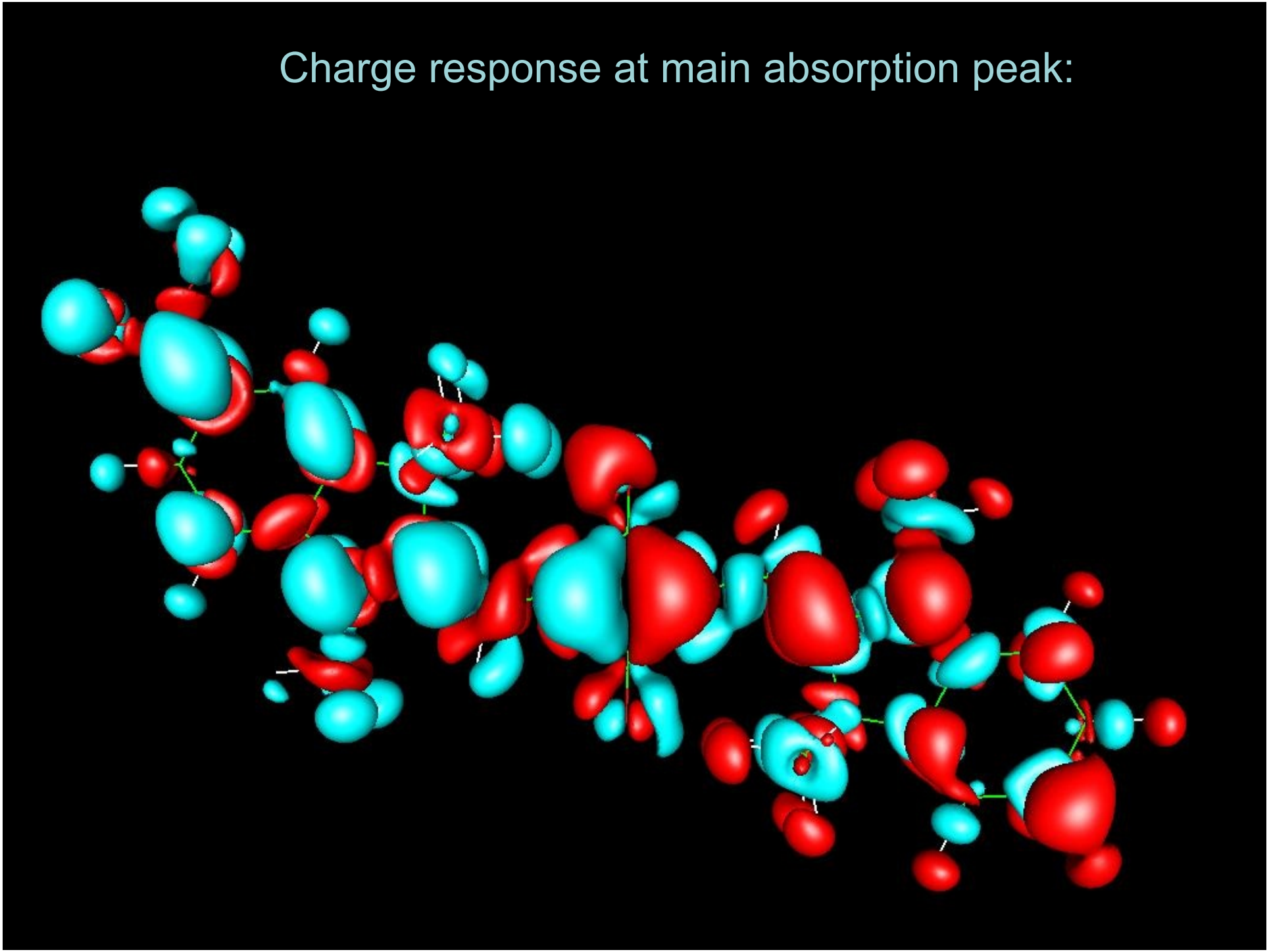
$$\begin{aligned} \tilde{A}(\omega) &= 2\left\langle \boldsymbol{a}, \mathbf{0} \middle| (\omega - \mathcal{L})^{-1} \middle| \mathbf{0}, \boldsymbol{v} \right\rangle \\ &= \cfrac{1}{\omega - a_1 + b_2 \cfrac{1}{\omega - a_2 + \cdots} c_2} \end{aligned}$$

Convergence of the TDDFPT spectrum

Isolated squaraine molecule



Charge response at main absorption peak:



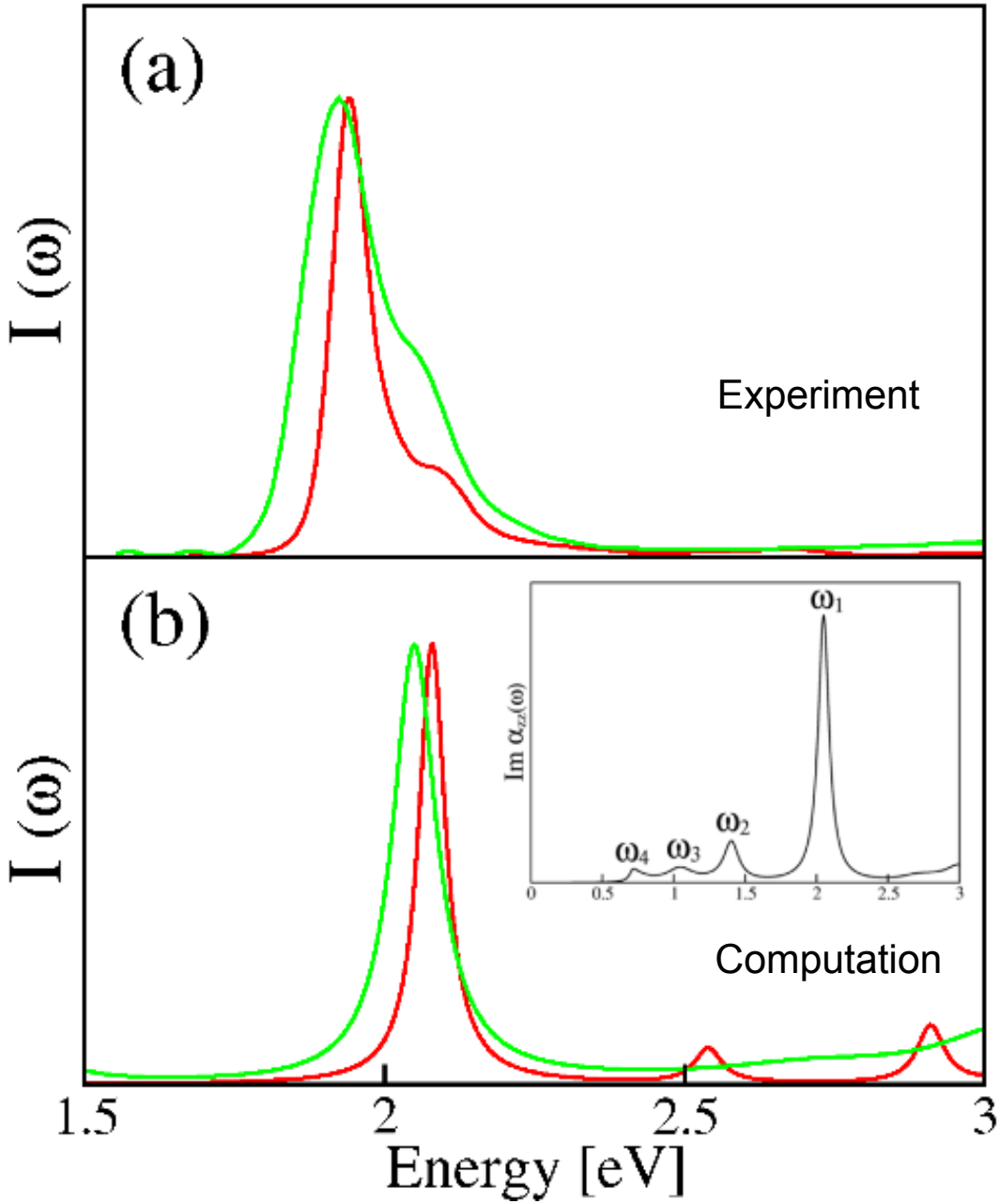
Main features:

Recursive Lanczos technique allows to compute TDDFT spectra:

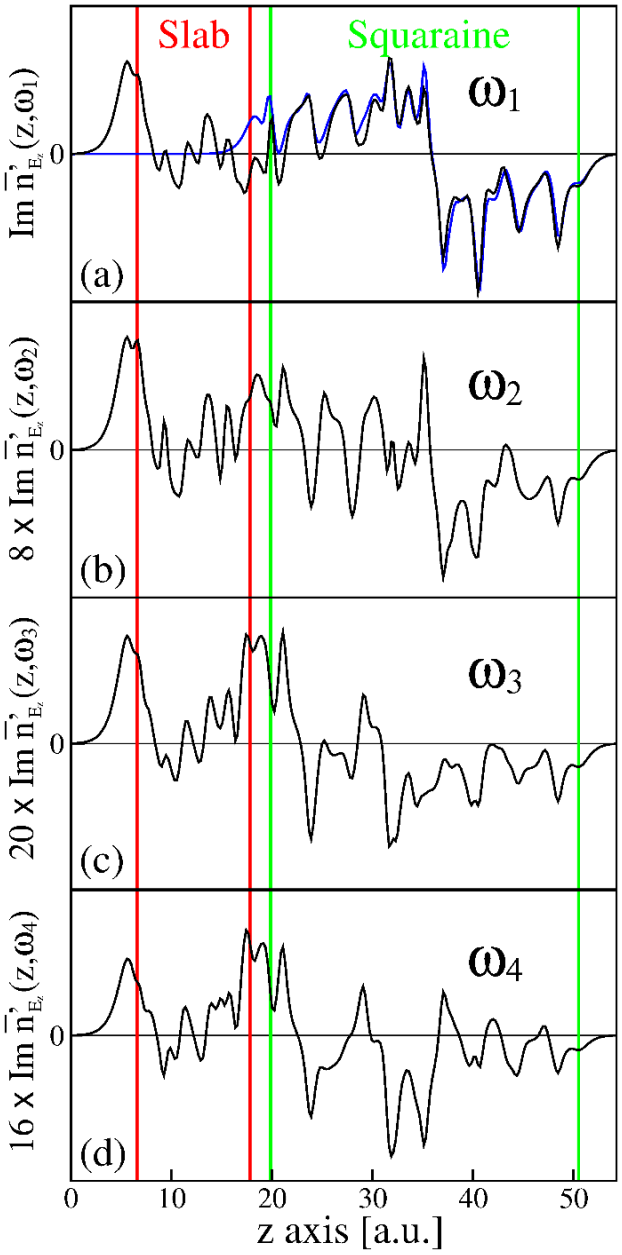
- Rather fast (even in large systems)
- Over broad spectral region
- No virtual KS states required
- Allows to analyze particular features of a spectrum

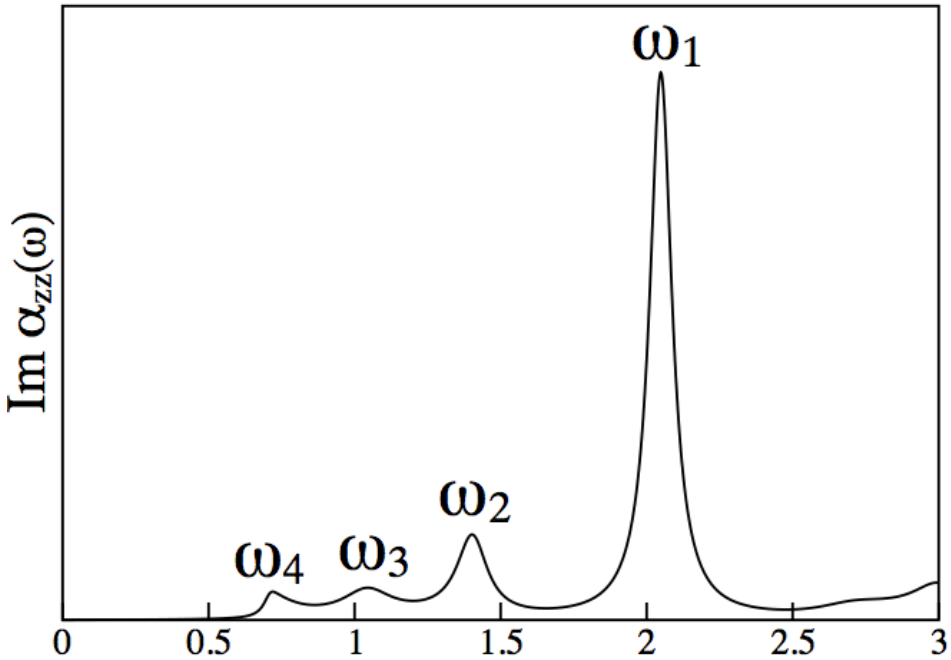
(use of this "turboTDDFT" code will be part of next week's hands-on tutorial)

Experimental and TDDFT absorption spectra

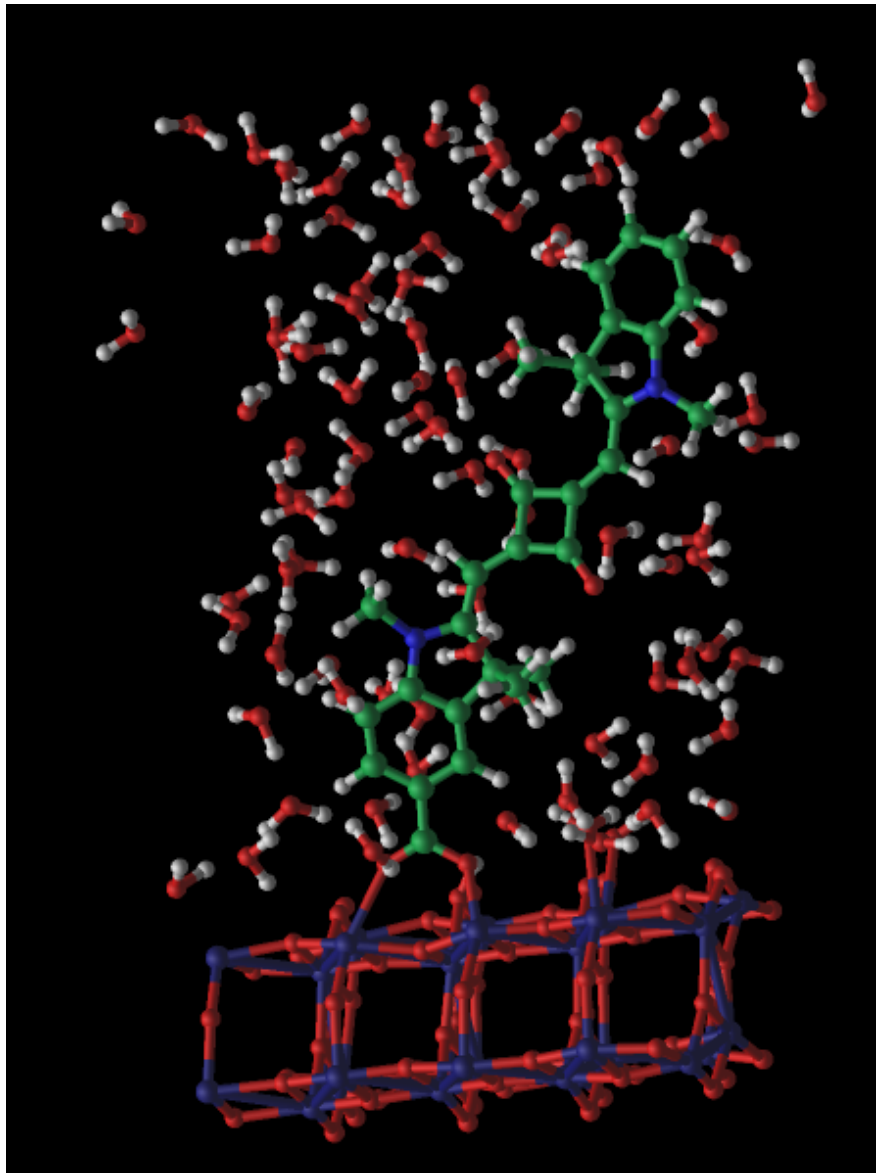


Analyzing the various transitions





A more realistic system: Including the solvent



TDDFT calculation of optical spectra and related quantities

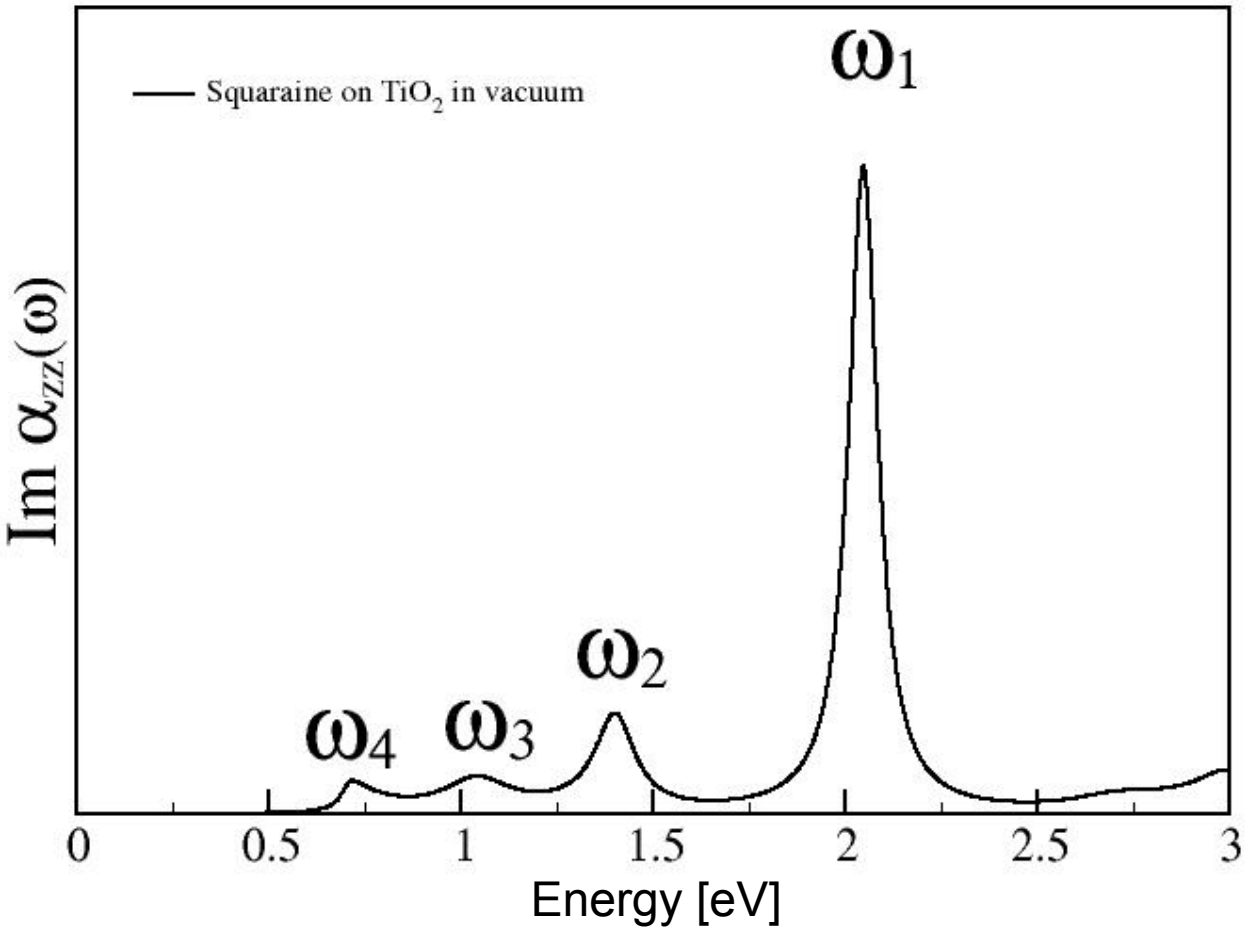
Various challenges:

- 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

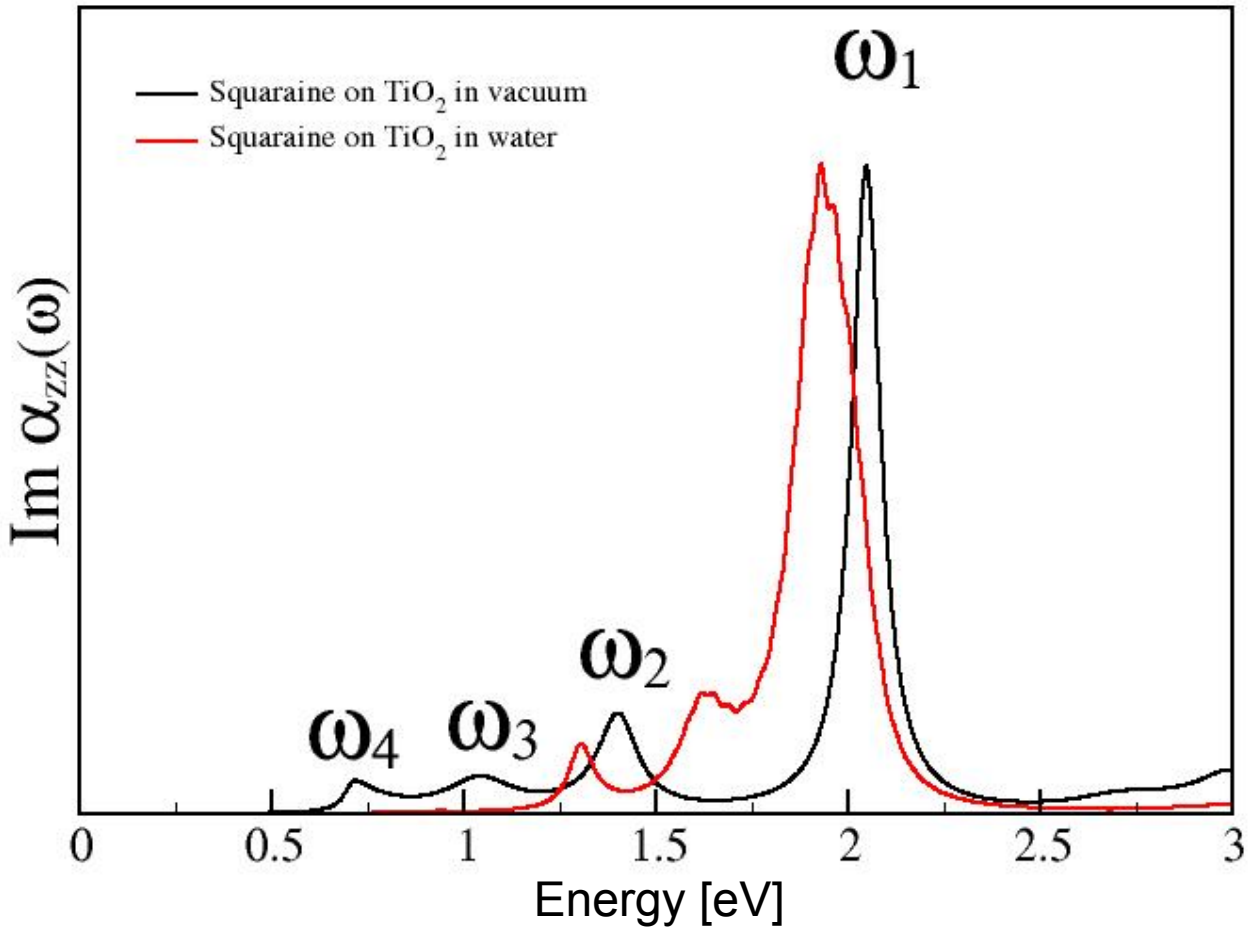
Computational tool:

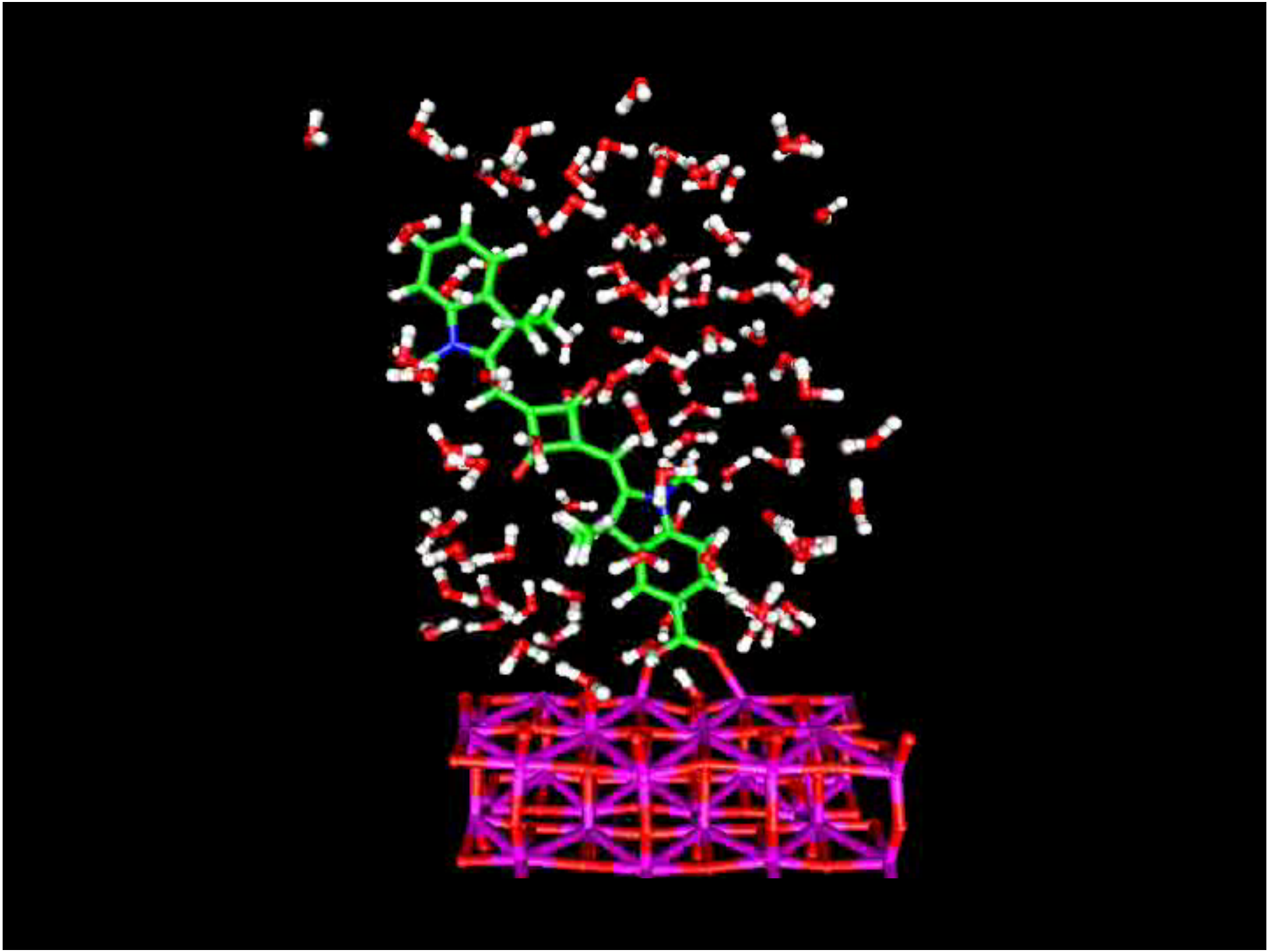
- Recursive Lanczos algorithm for TDDFT

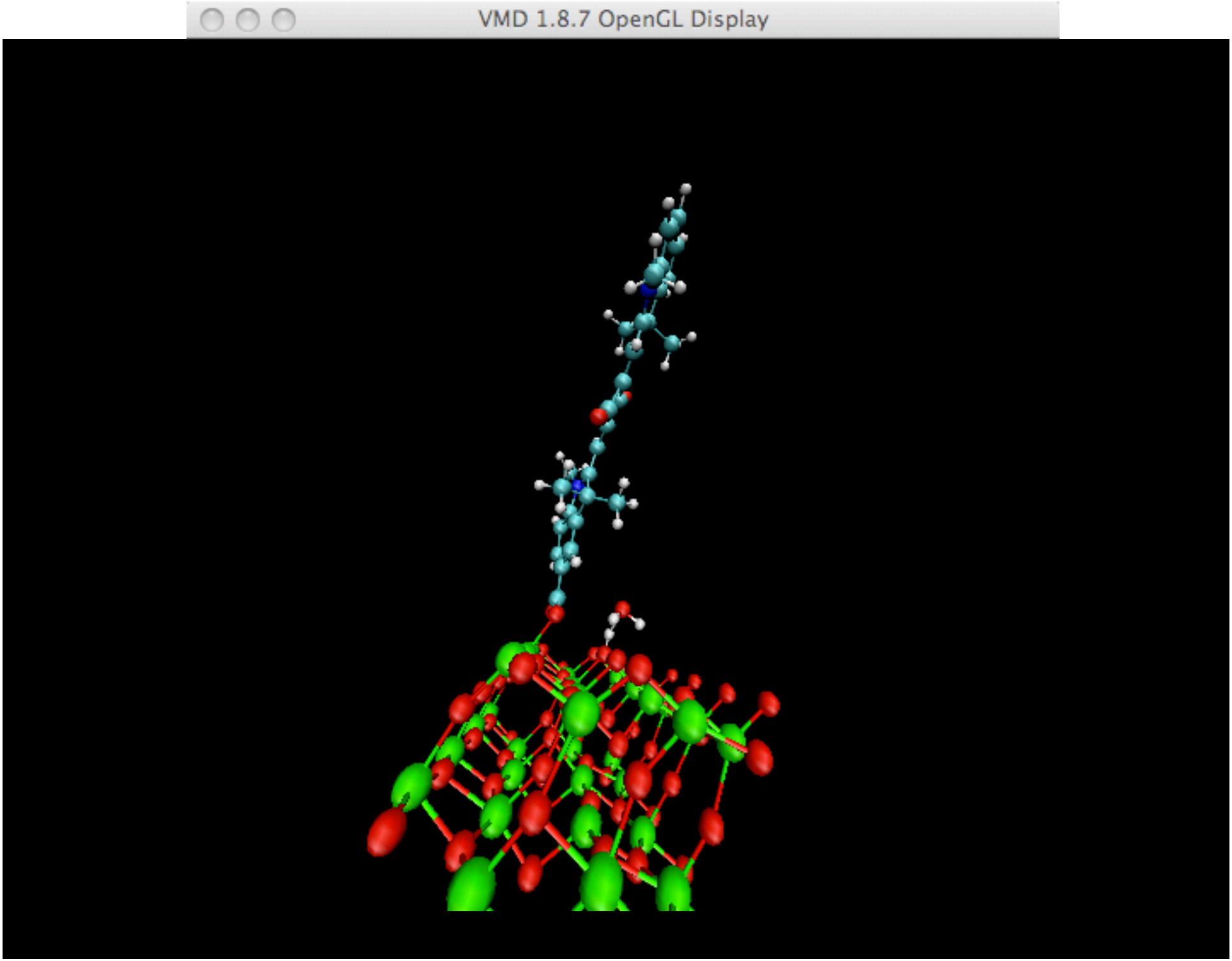
TDDFT optical spectrum: dry system

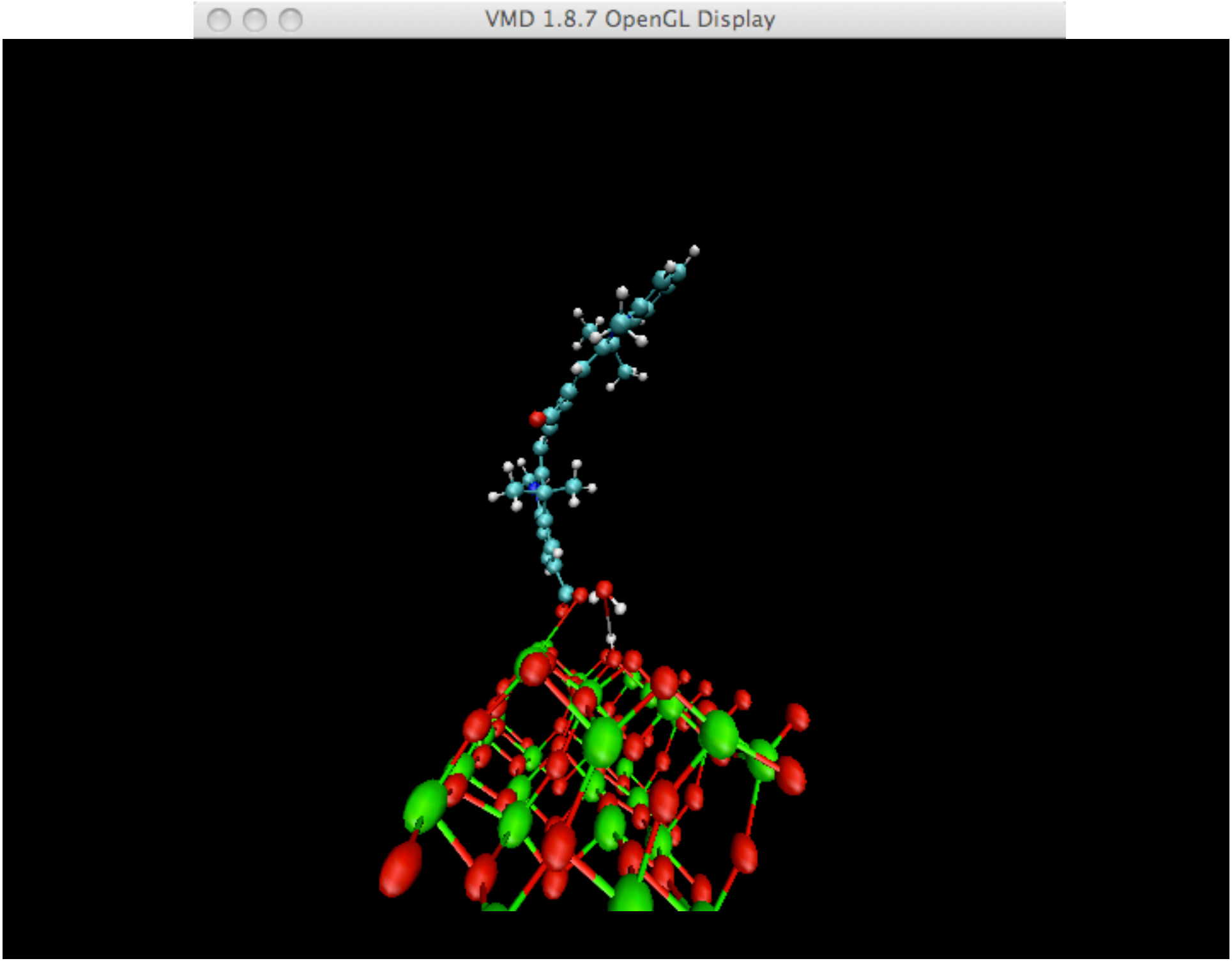


TDDFT optical spectrum including solvent



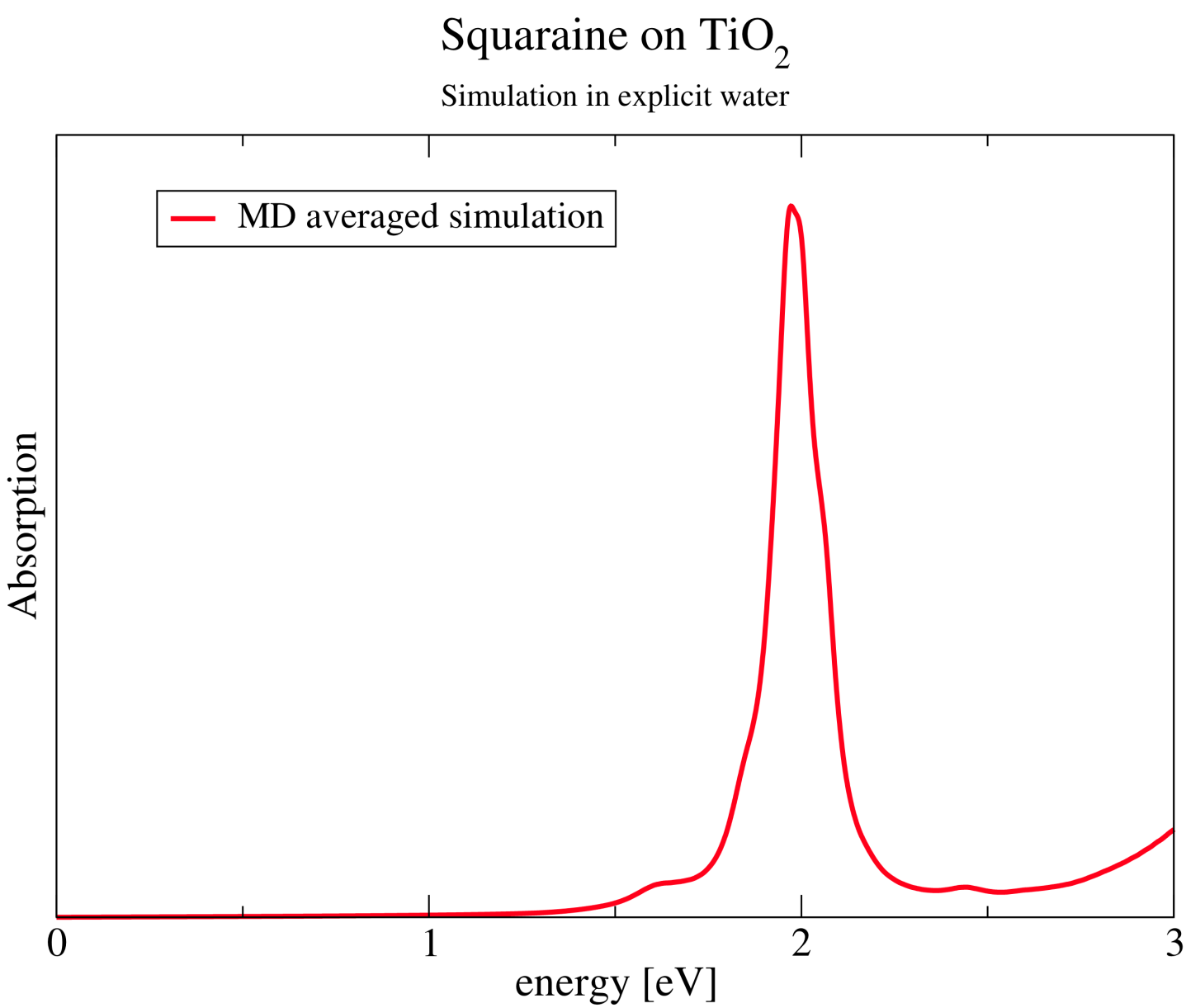


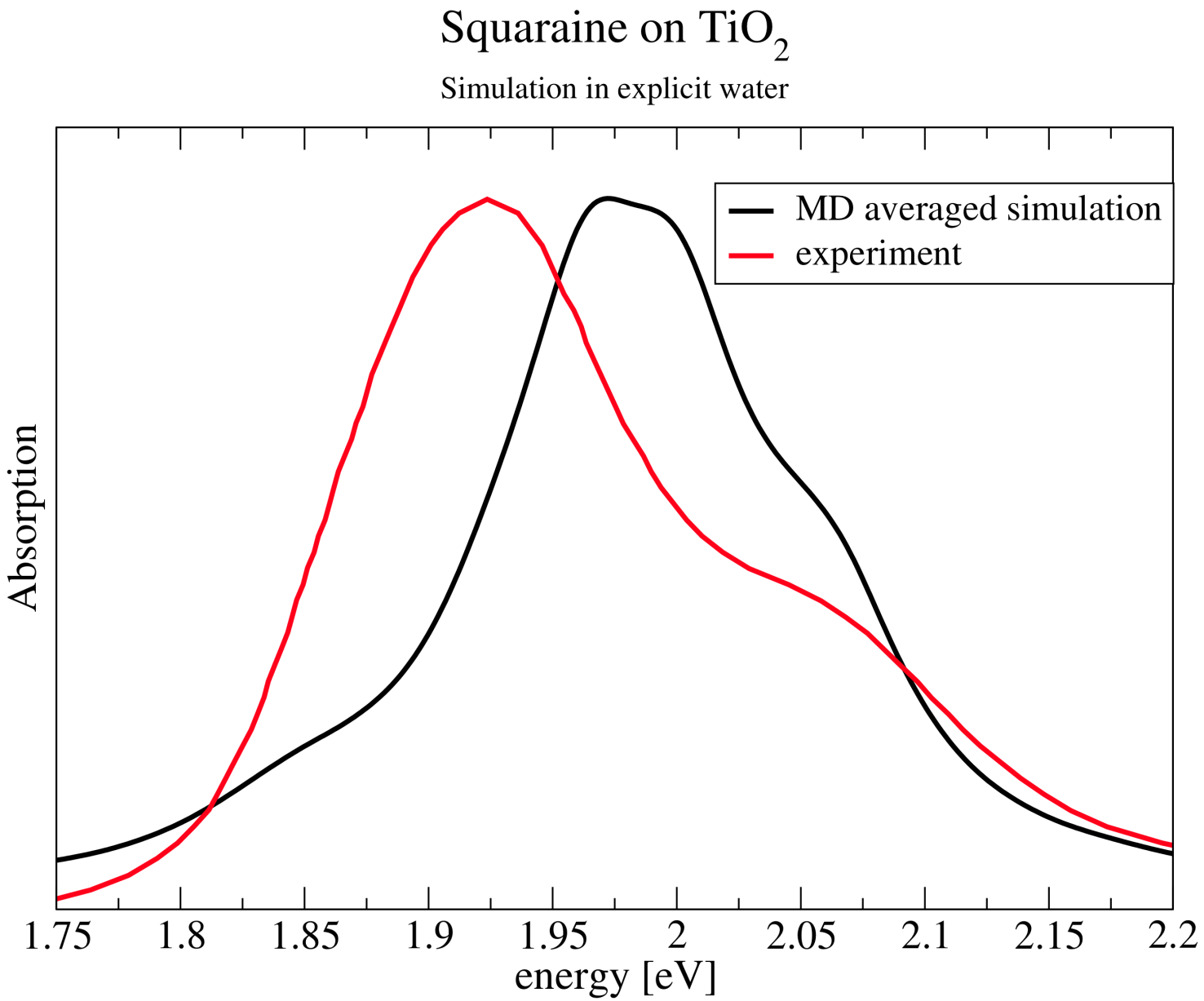

VMD 1.8.7 OpenGL Display

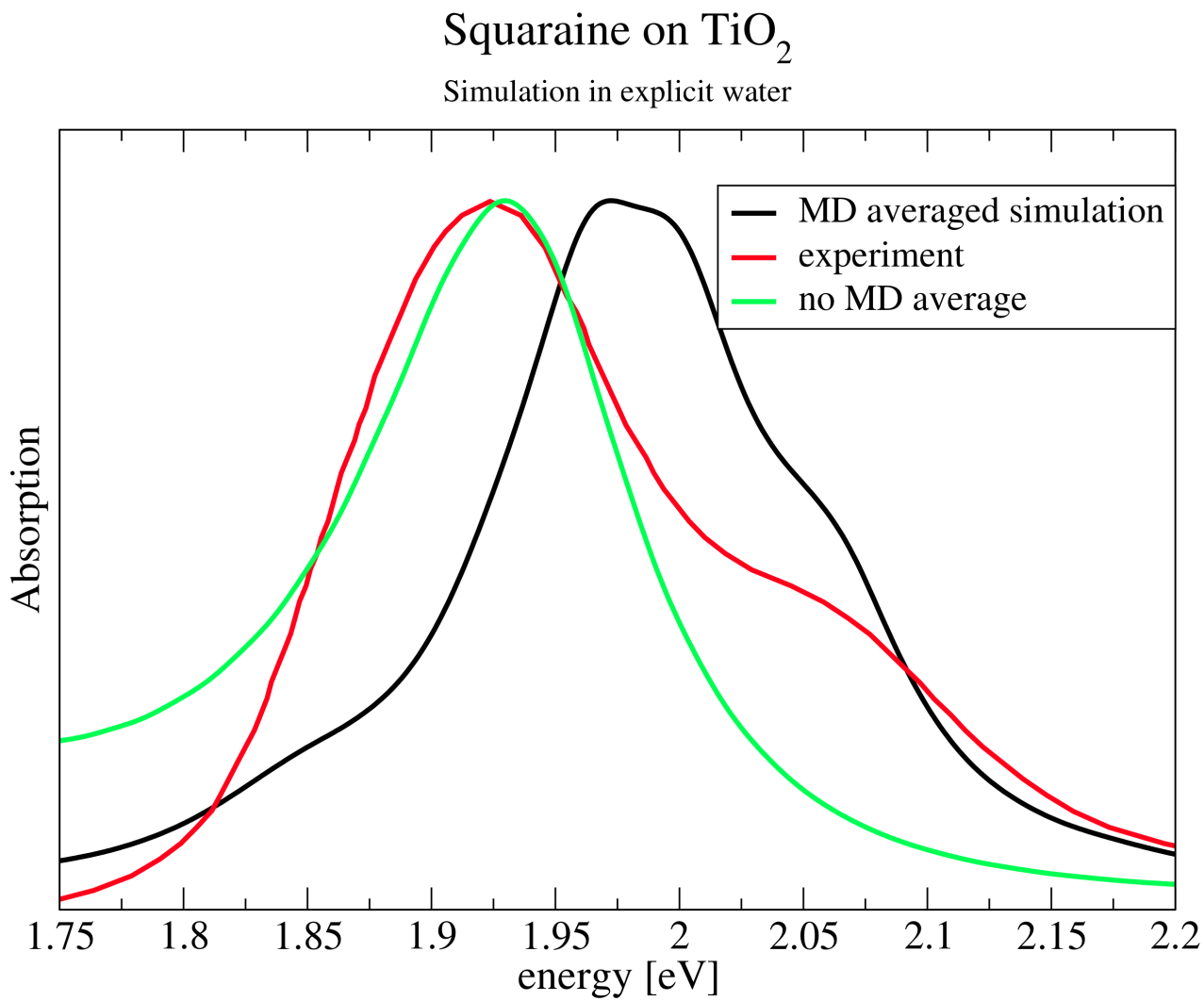

VMD 1.8.7 OpenGL Display

Including the solvent in MD and TDDFT computations

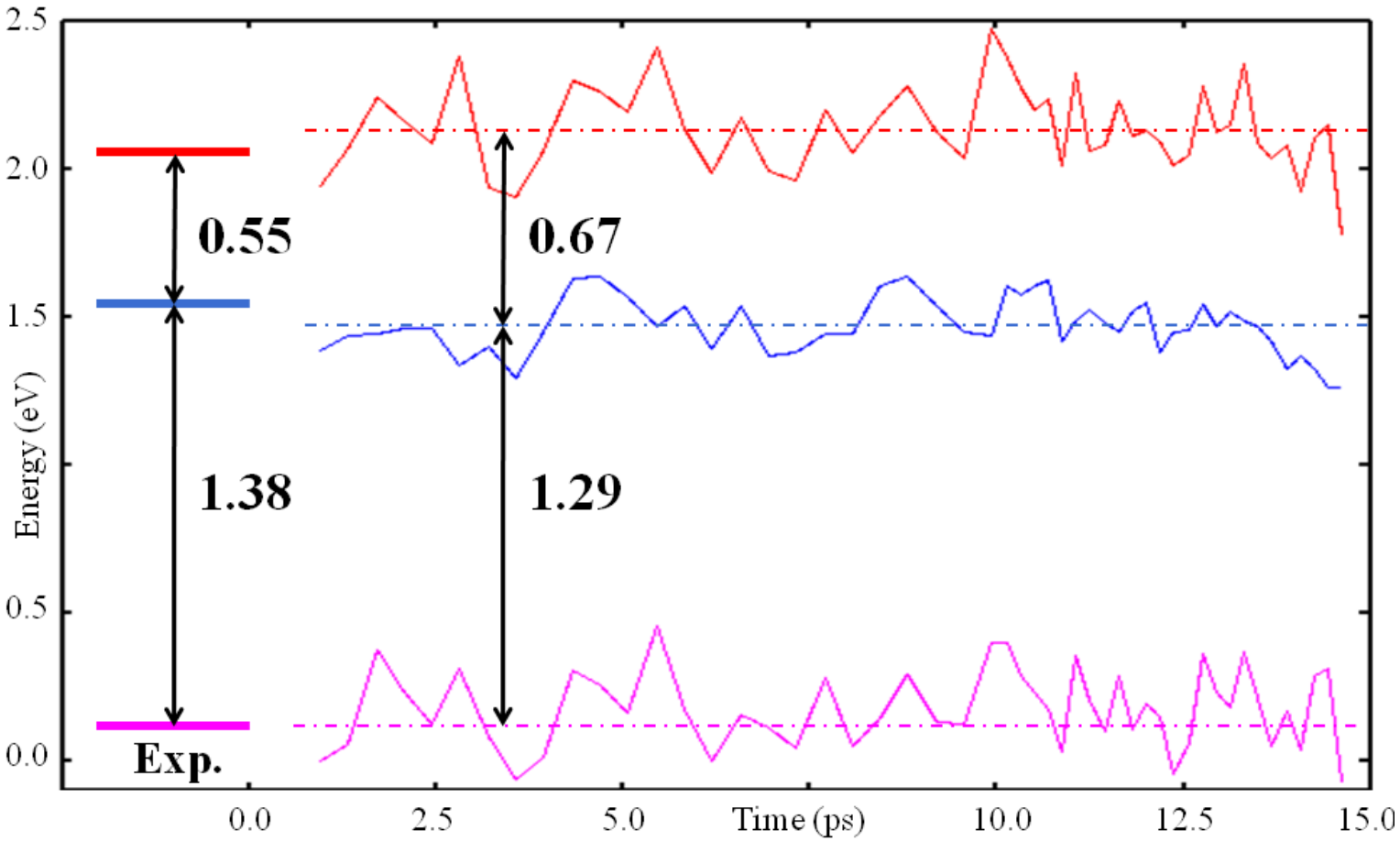
- Solvent is treated at the same level of theory as molecule and surface slab
- Solvent changes electrostatic conditions (dielectric constant …)
- Solvent participates actively:
  - in formation surface dipoles, etc.
  - hydrogen bonding networks
  - is essential for geometry of solute

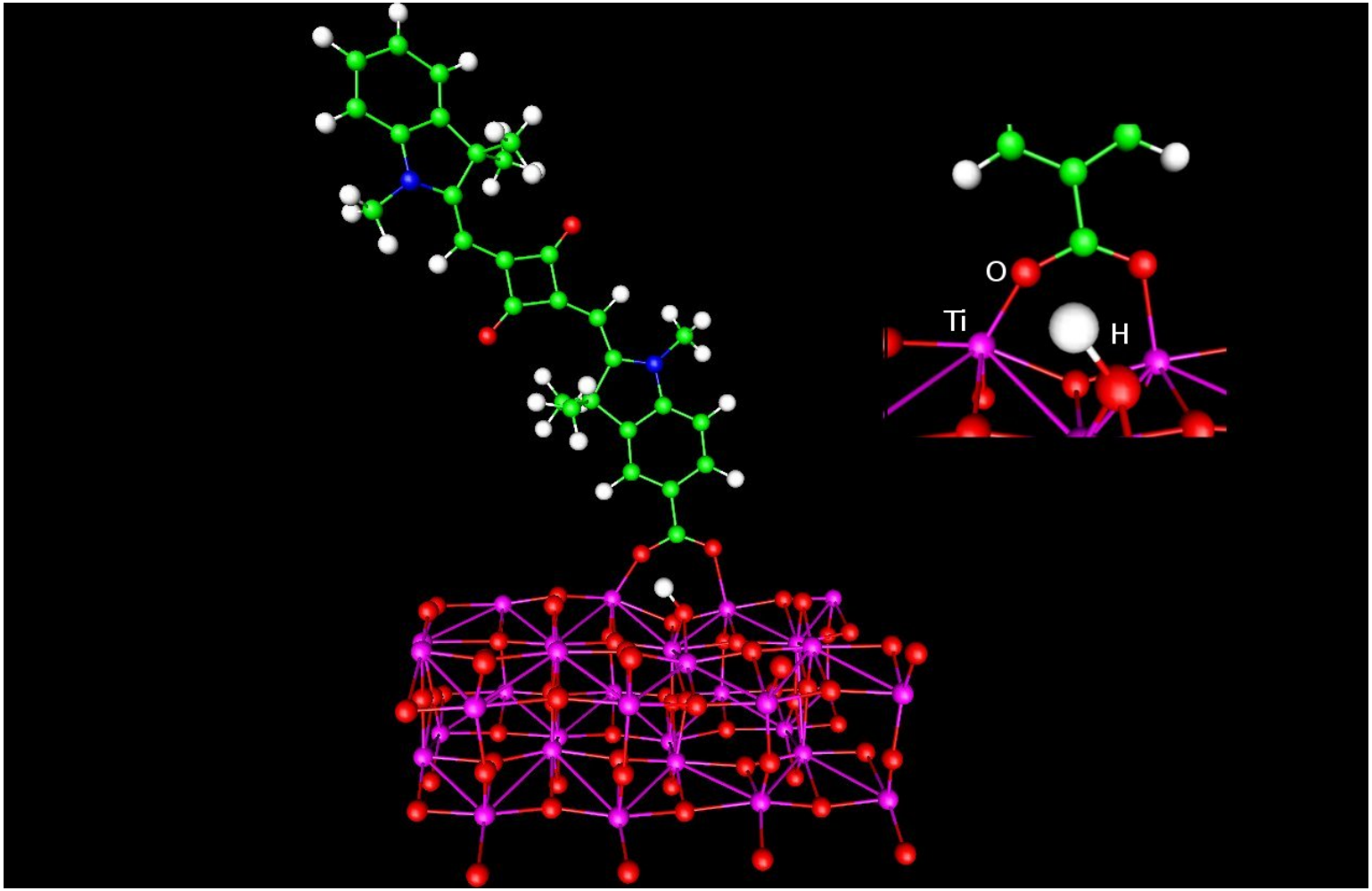

Squaraine on TiO2
Simulation in explicit water
MD averaged simulation
Absorption
0
1
2
3
energy [eV]


Squaraine on TiO2
Simulation in explicit water
MD averaged simulation
experiment
Absorption
1.75
1.8
1.85
1.9
1.95
2
2.05
2.1
2.15
2.2
energy [eV]

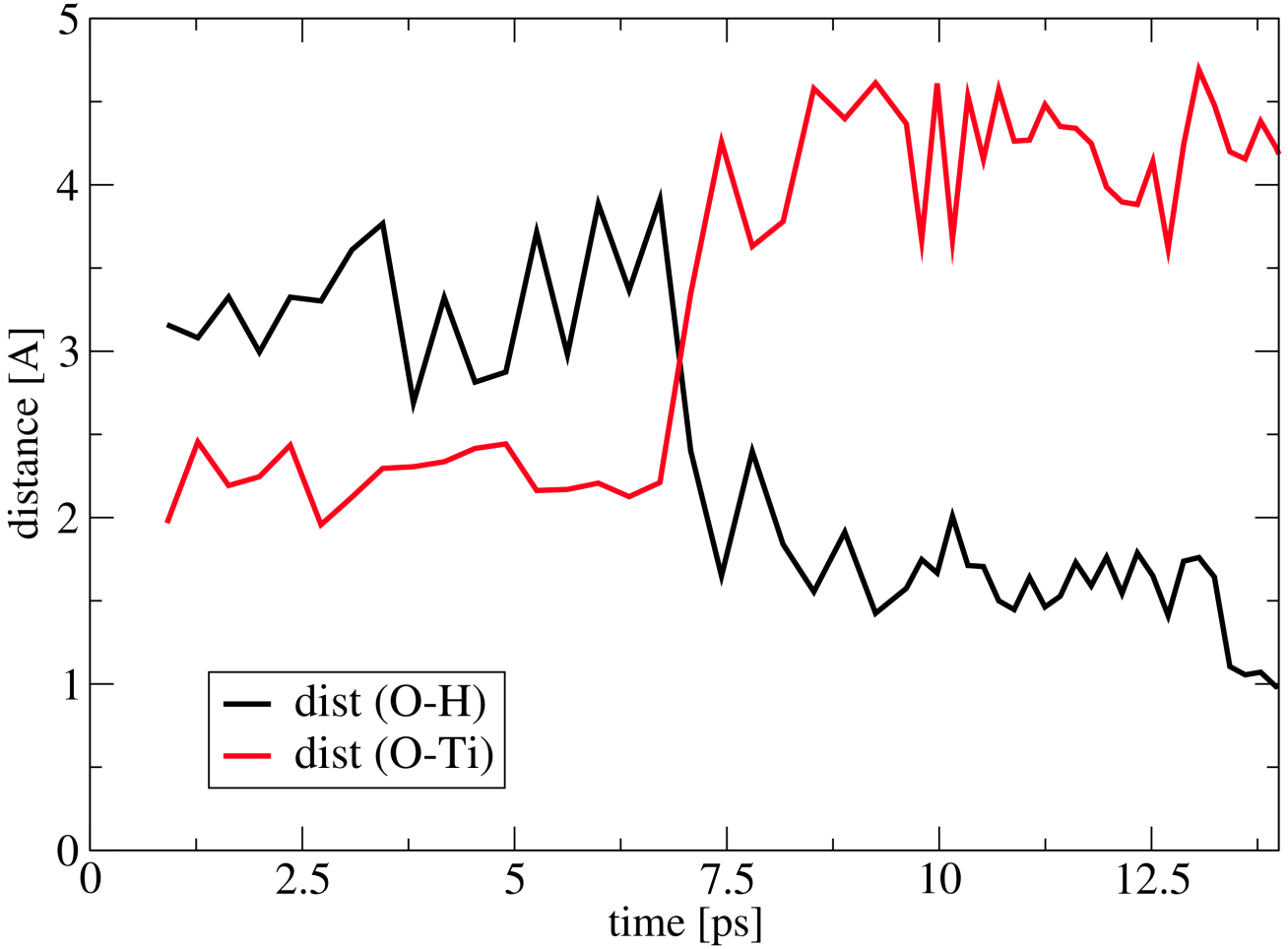

Squaraine on TiO2
Simulation in explicit water
MD averaged simulation
experiment
no MD average
Absorption
1.75
1.8
1.85
1.9
1.95
2
2.05
2.1
2.15
2.2
energy [eV]

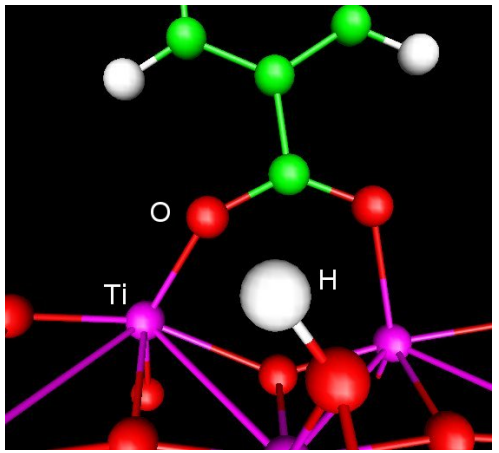
Energy level fluctuations and electron injection driving force



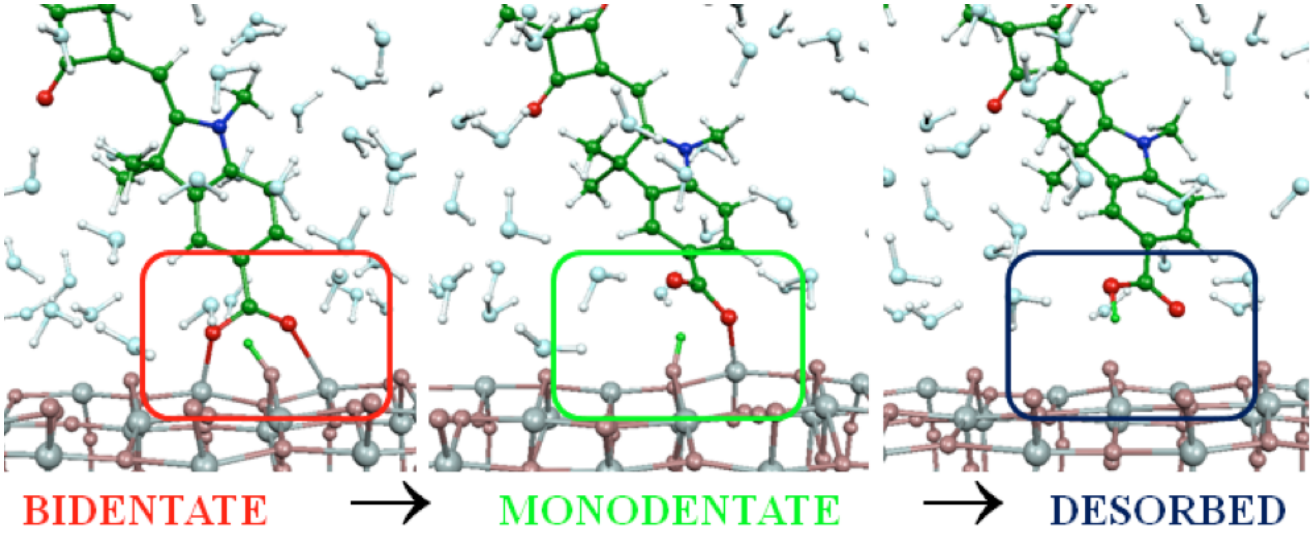

O
Ti
H

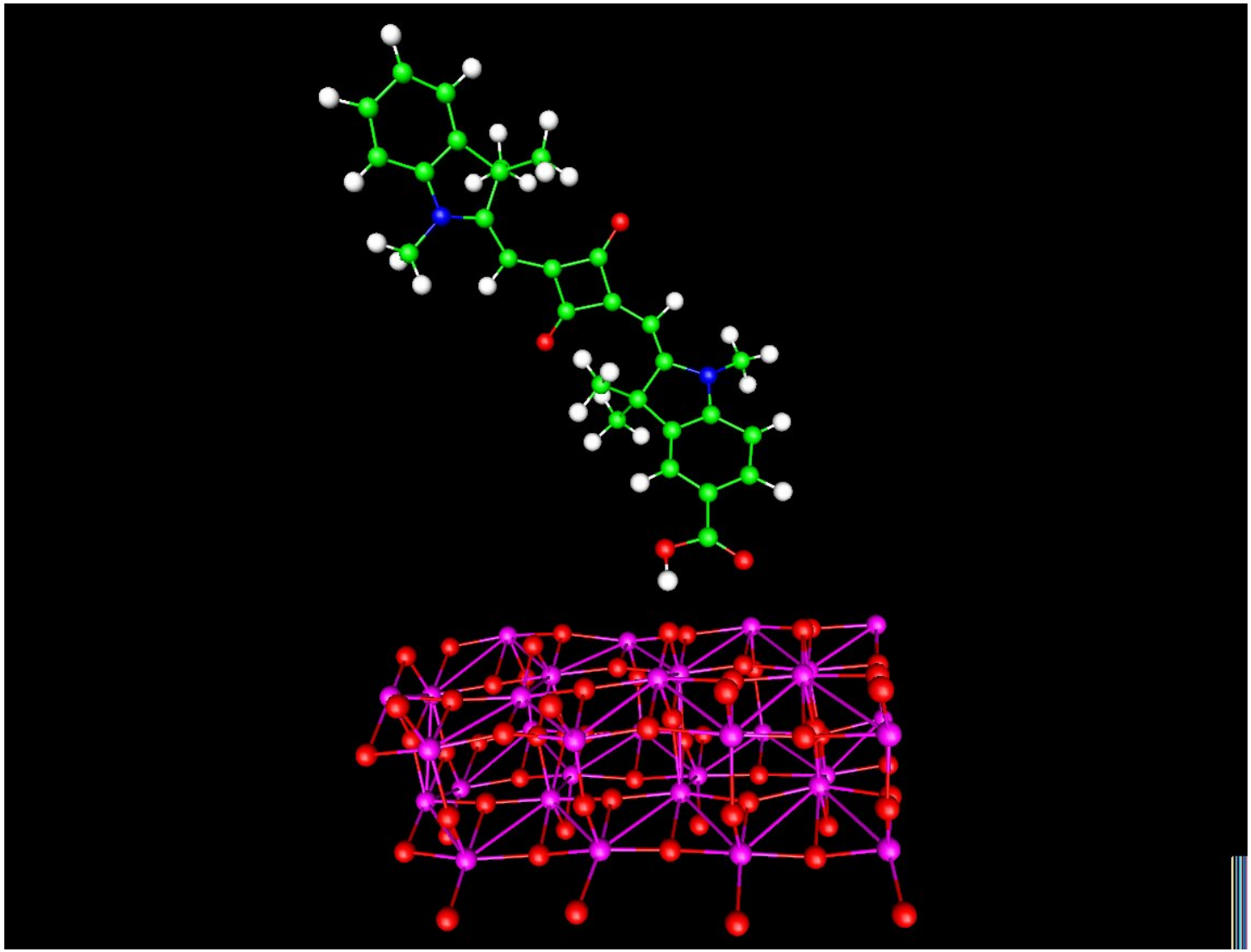
Squaraine adsorption on TiO_2





Dye desorption steps:





Conclusions

- TD-DFT study of squaraine dye adsorbed on TiO_2 slab

  Fair agreement with experiment in absence of solvent in computation

- Including the solvent explicitly

  Improvement of computed spectrum, but important features are not reproduced (shoulders, etc.)

- Molecular dynamics of dye sensitized slab with explicit solvent

  Averaging of optical properties over many configurations leads to a description of optical properties in good agreement with experiment

- Very efficient implementation of TD-DFT for large systems/basis sets

  Recursive Lanczos TDDFT based on time-dependent DFPT for a system composed of 429 atoms and described by ≈ 200,000 PWs

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)
- Quantum ESPRESSO and its community

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)