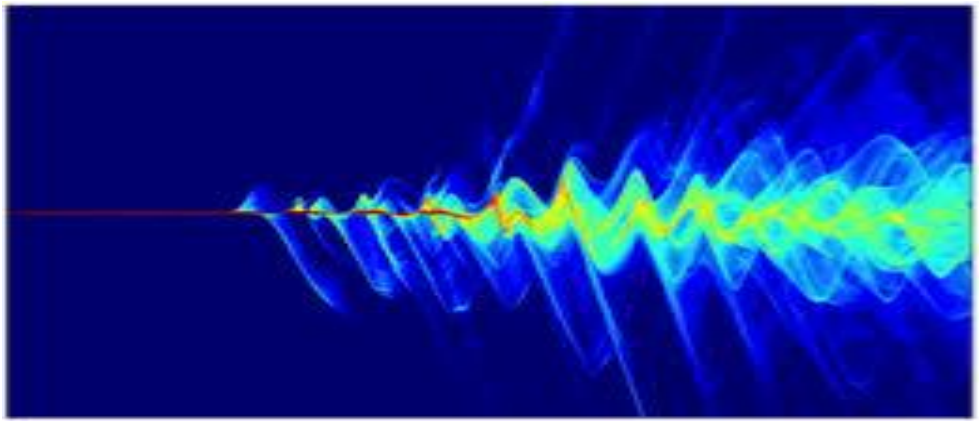
RHODES UNIVERSITY

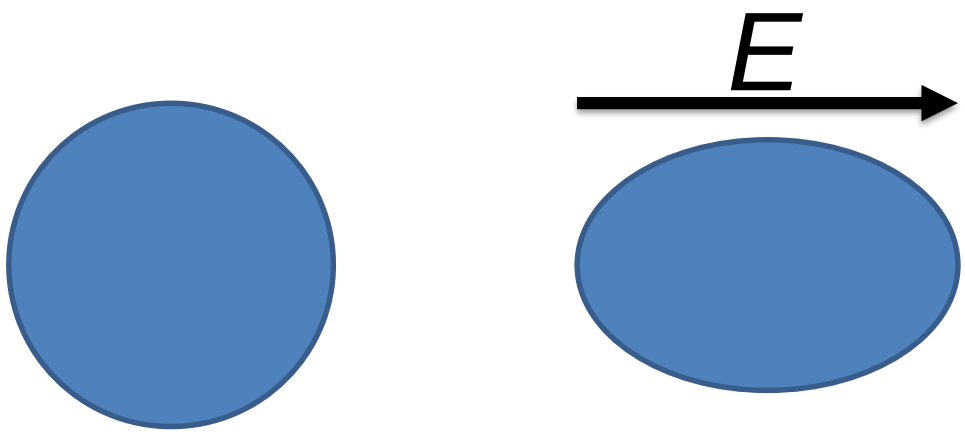
Basics DFT Calculation of Z-Scan Properties.

Marcel Louzada

Aviwe #1

Non-Linear Optics (NLO)

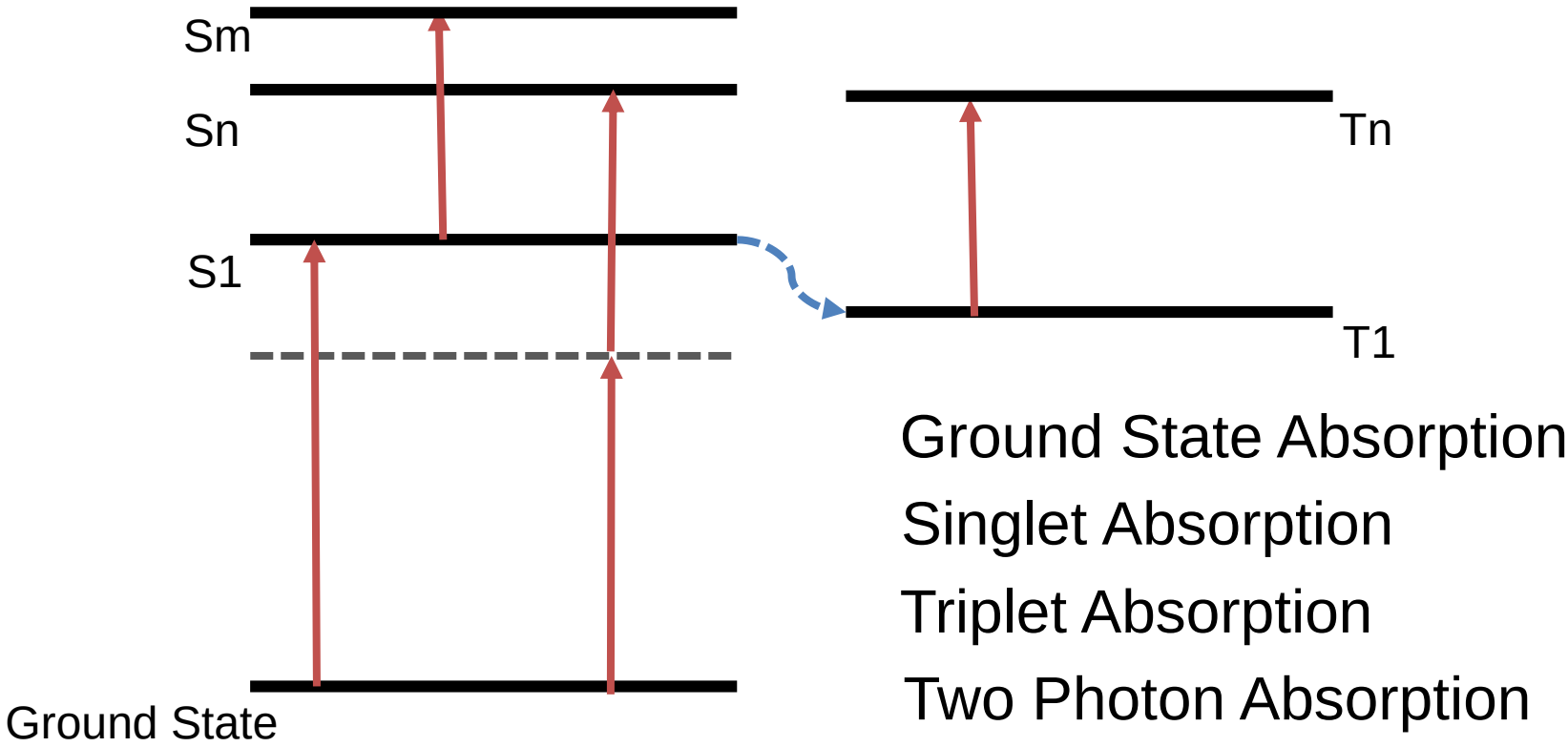




$$P = \mu_0 + \varepsilon_0(E\chi^{(1)} + E^2\chi^{(2)} + E^3\chi^{(3)} + \ldots)$$

http://www.ictp-saifr.org/?page_id=3616

Imaginary Components



Ground State Absorption

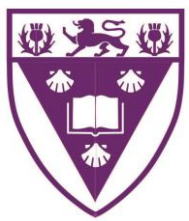
Singlet Absorption

Triplet Absorption

Two Photon Absorption

2PA Methods

- A *posteriori* Tamm–Dancoff Approximation (ATDA) [*modified* Gaussian09]
- Equation Of Motion-Coupled Clusters Including Single and Double Substitution (EOM-CCSD) [Orca, Dalton, QChem or GAMES]
- Intermediate Neglect of Differential Overlap Combined-Multireference Configuration Interactions (INDO-MRCI) [GAMES or Molpro]
- Quadratic Response Double Residue (QRDR) [Dalton]
- Sum Over State Couple Perturbation HF (CPHF) [Most Programs]



2PA Methods

- Sum Over State Couple Perturbation HF (CPHF) [Most Programs]

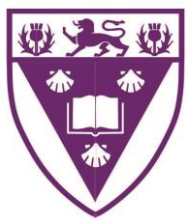
Basis and Functionals

6-311g/B3LYP

No Diffusion

Situational Polarization

Avoid long range exchange



CPHF

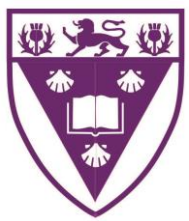
6-311g/B3LYP CPHF= RdFreq Polar=(DCSHG,Cubic)

H2O Gamma Calculation

0 1

O	-0.26315789	-1.06015034	0.00000000
H	0.69684211	-1.06015034	0.00000000
H	-0.58361248	-0.15521451	0.00000000

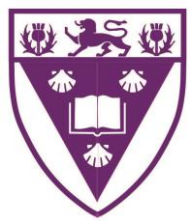
532nm



Results

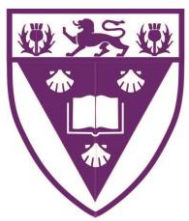
$$\gamma \approx \frac{1}{6}\left[\left(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}\right) + 2\left(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}\right)\right]$$

$$|\gamma| = \sqrt{(Im[\gamma])^2 + (Re[\gamma])^2}$$



Excited state Absorption

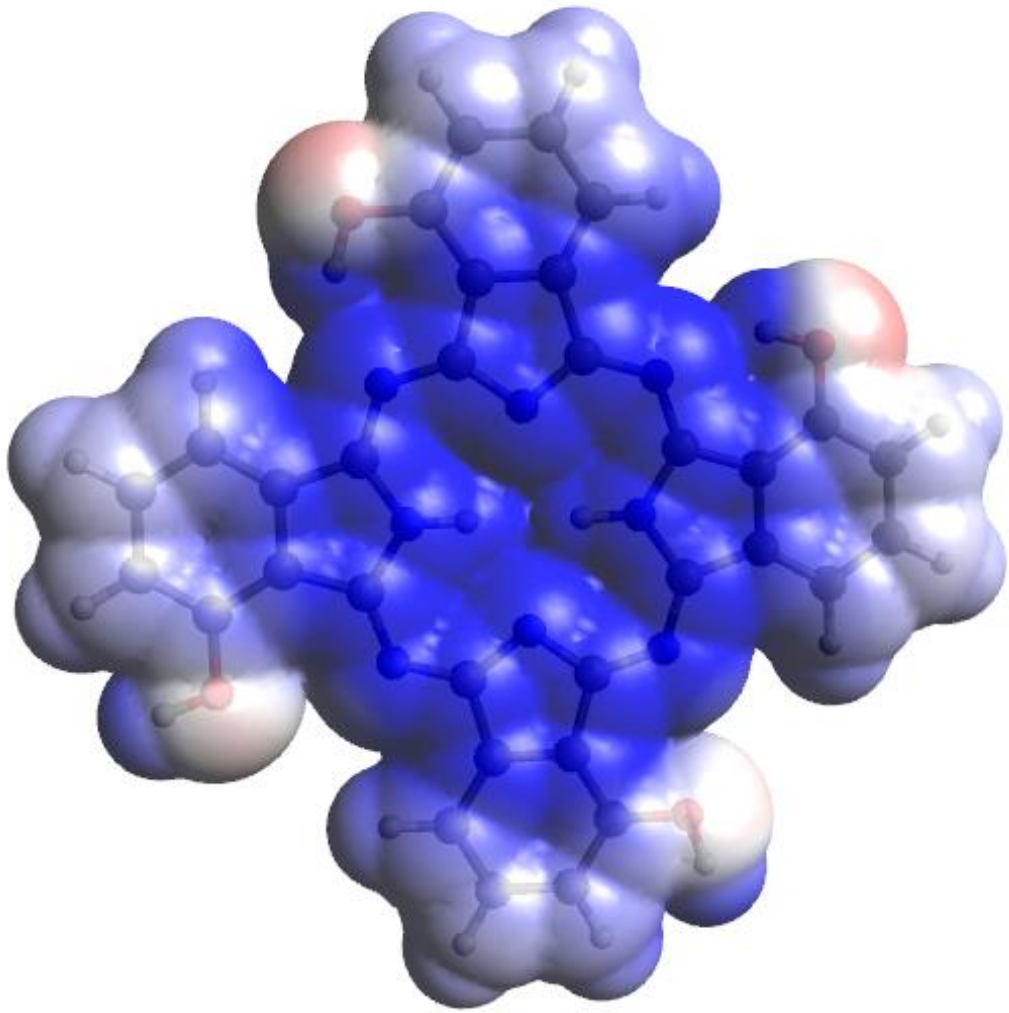
- Equation Of Motion-Coupled Clusters Including Single and Double Substitution (EOM-CCSD) [Orca, Dalton, QChem or GAMES]
- Linear Response DFT (LR-DFT) [Most Programs]
- Real Time TD-DFT (RTTD-DFT) [NWChem or Qchem]



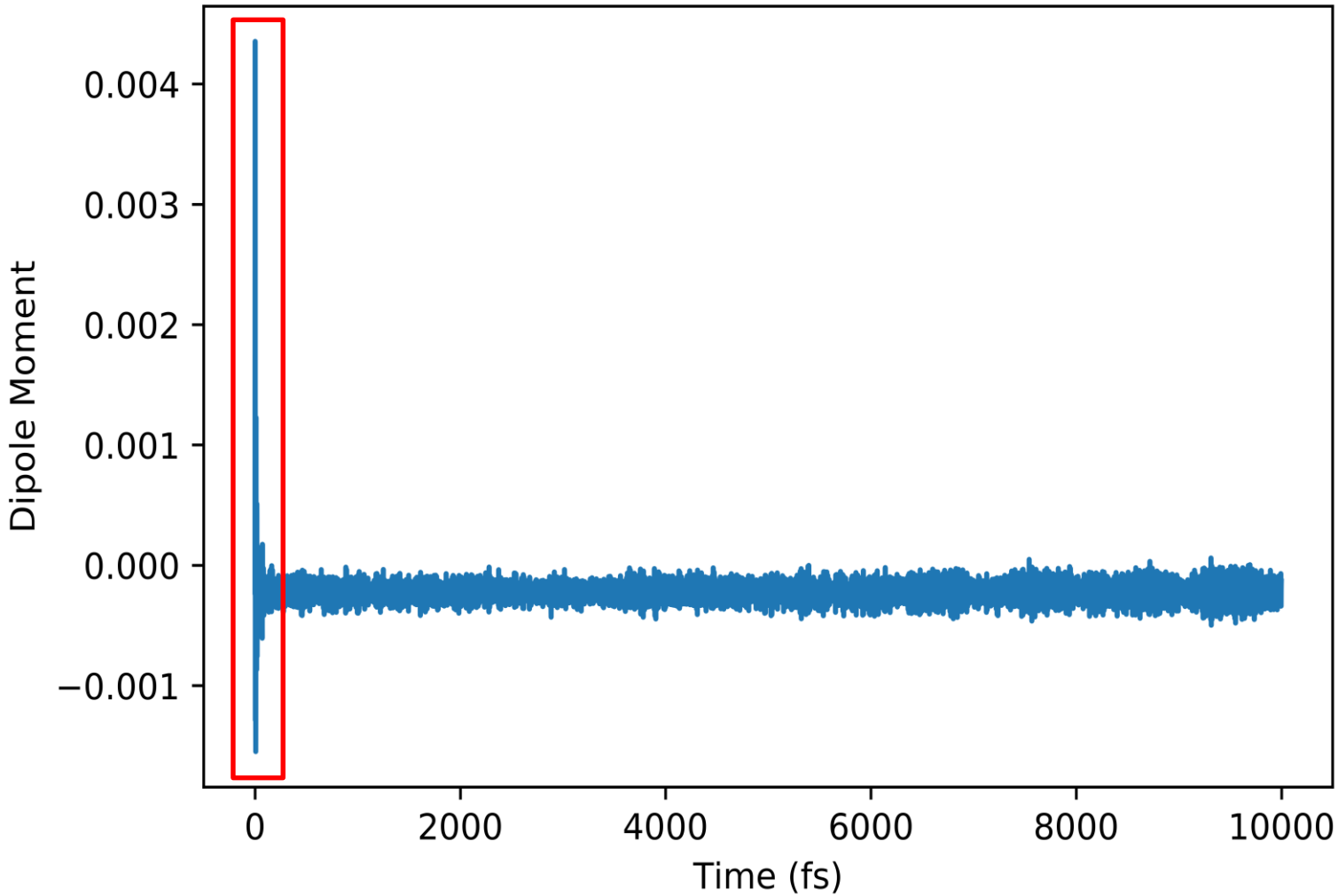
Excited state Absorption

- Real Time TD-DFT (RTTD-DFT) [NWChem or Qchem]

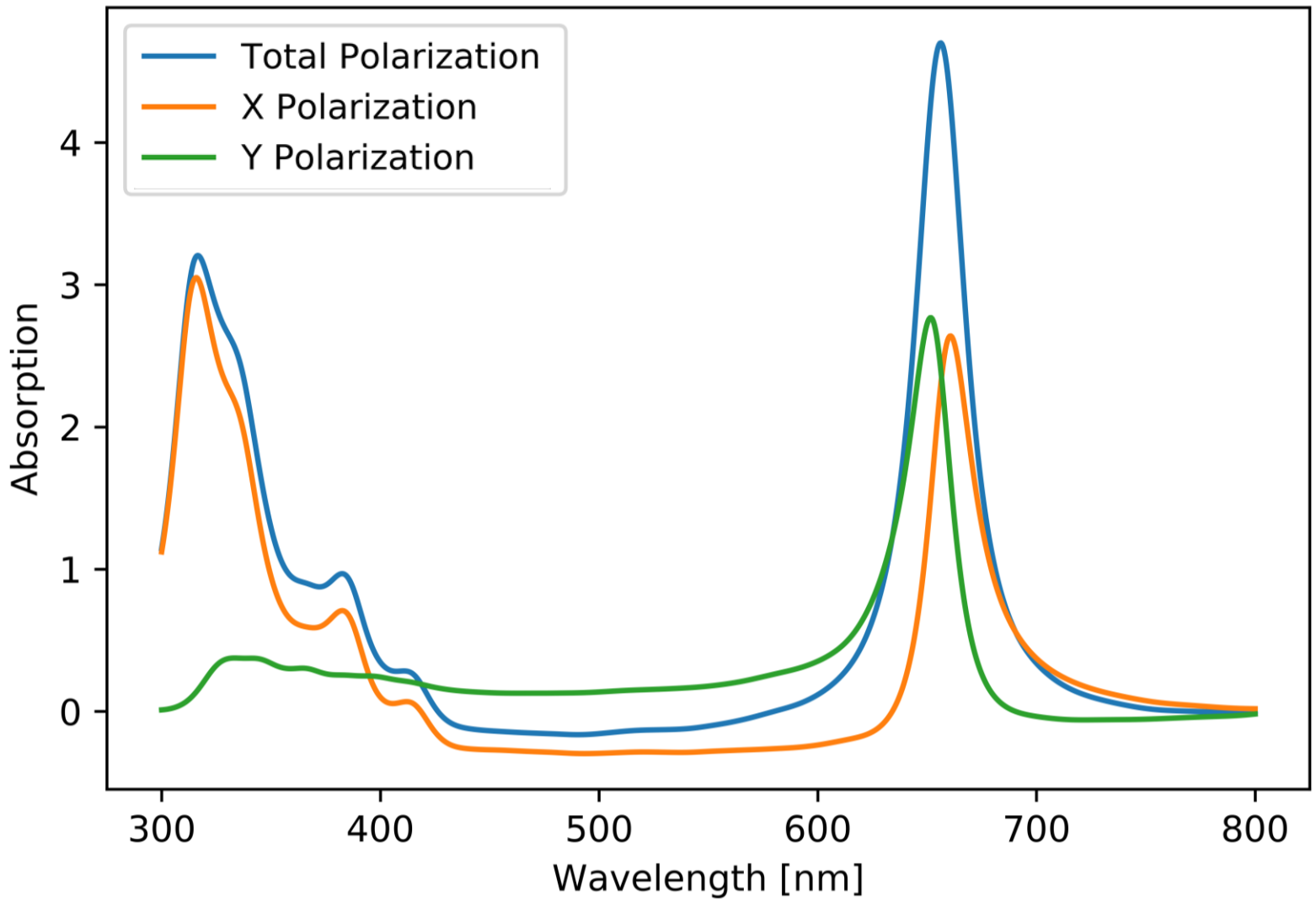
Electrostatic Potential from SCF



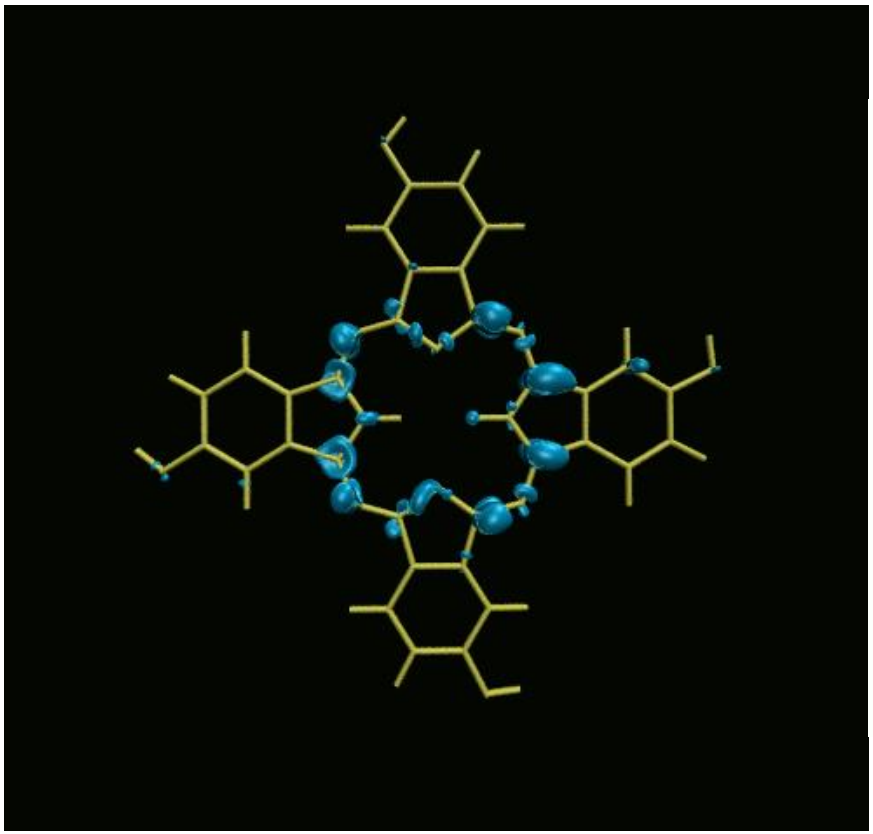
Broad Spectrum
Dipole(x)



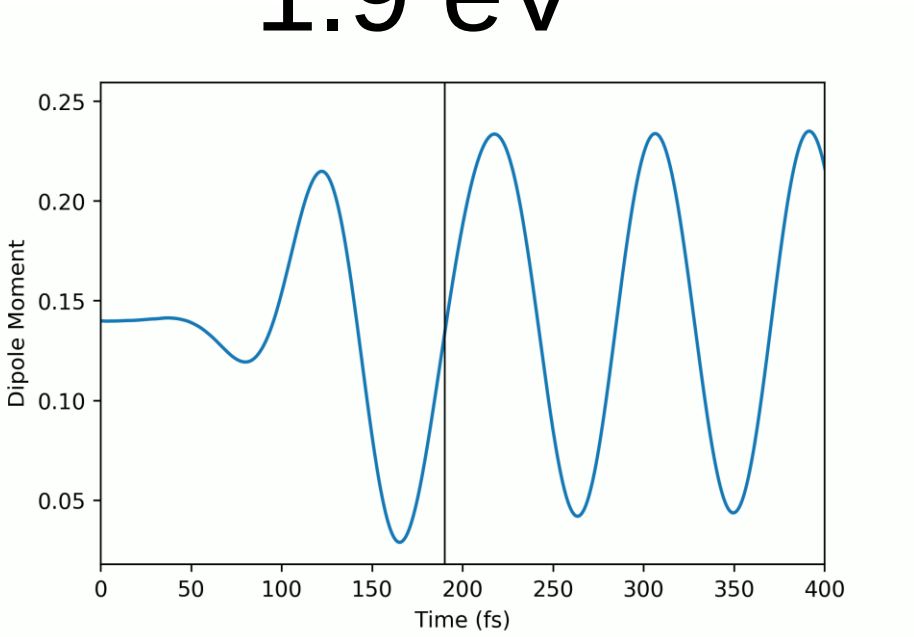
RTTD-DFT Calculated Absorption (GS)



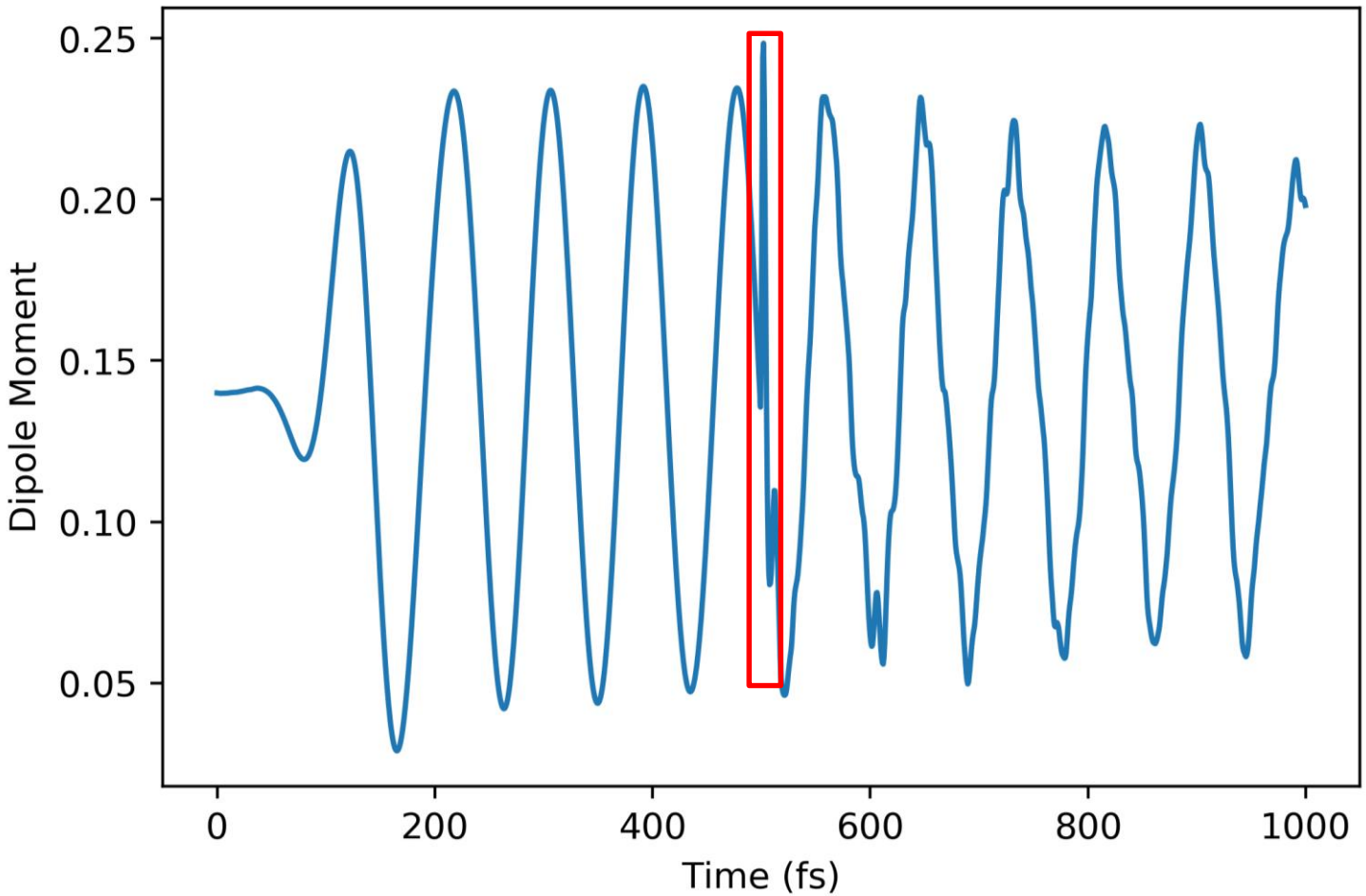
Perturbated SCF



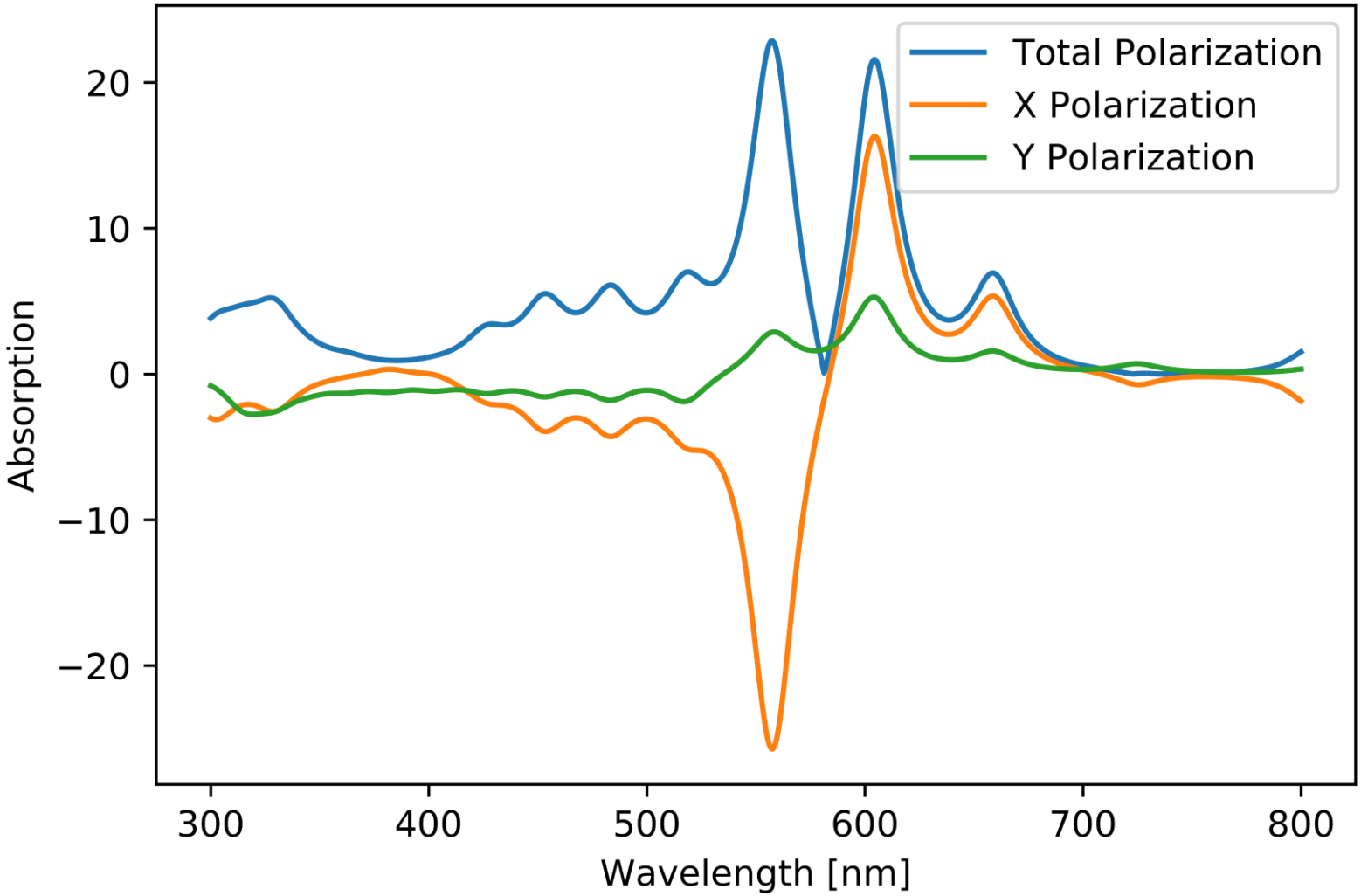
1.9 eV

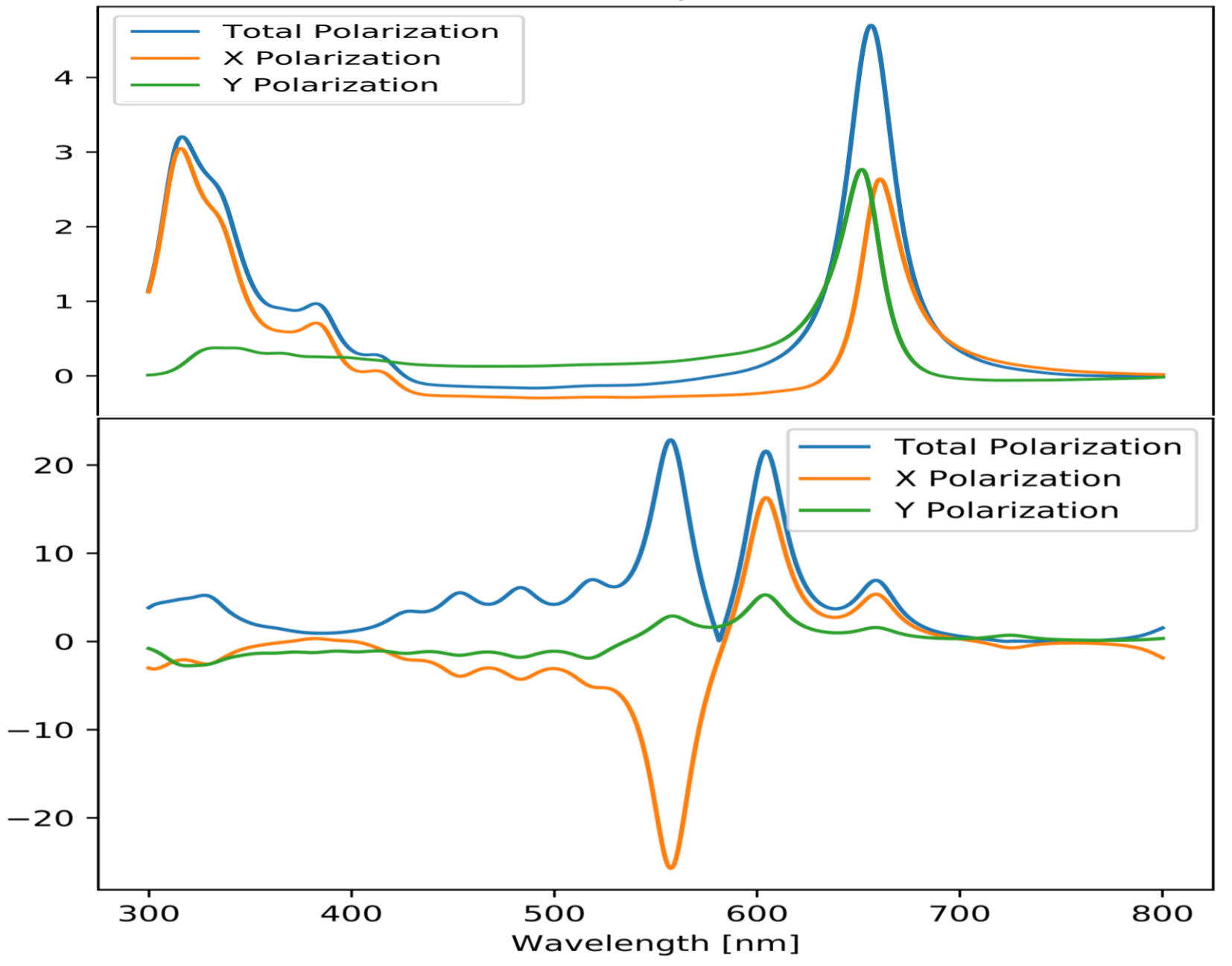


Driver + Excitation Dipole



Driver + Excitation Absorption (S1)




Total Polarization
X Polarization
Y Polarization
4
3
2
1
0
Total Polarization
X Polarization
Y Polarization
20
10
0
−10
−20
300
400
500
600
700
800
Wavelength [nm]


Thank
You