Kavli Institute for Theoretical Physics UCSB, 25 November 2009

Modelling Excitations in Biological Chromophores: from TDDFT to GW+BSE

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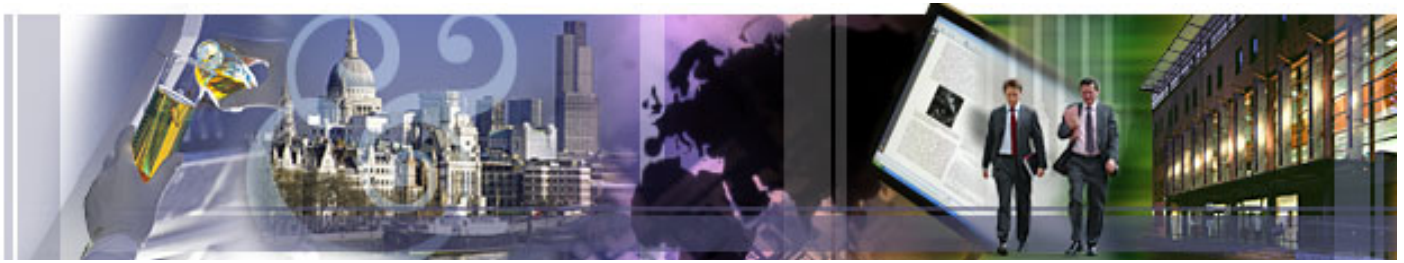


PHOTOACTIVE PROTEINS

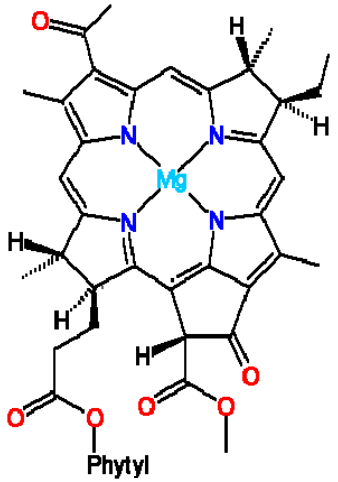
- Protein photoreceptors use bound organic molecules (**chromophores**) to detect light

- Light can be used for **photosynthesis, photoprotection and photosensing**

- Light absorption induce either **excitation transfer, electron transfer or photoisomerisation**

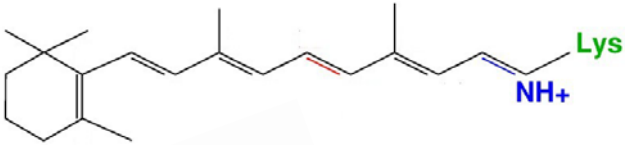
EXAMPLES of BIOLOGICAL CHROMOPHORES

TETRAPYRROLES



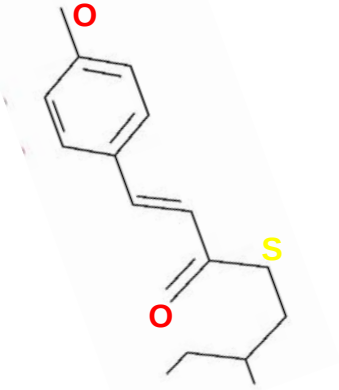
CHLOROPHYLL

POLYENES



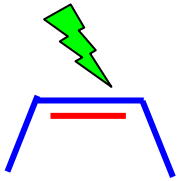
RETINAL

AROMATICS



p-COUMARIC ACID

- In a **PHOTOISOMERISATION** process, a specific **double bond** within the chromophore is **isomerised by light** triggering slower changes in the protein



- Given the short time of the initial photoreaction (**hundreds of femtoseconds**), it is experimentally difficult to see how this isomerisation proceeds and how it is converted into a protein-wide structural change

- A detailed molecular knowledge of the mechanism of photosensing is limited in most cases (Help from first principles simulations?)

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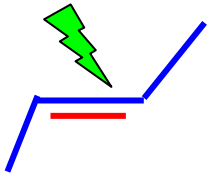
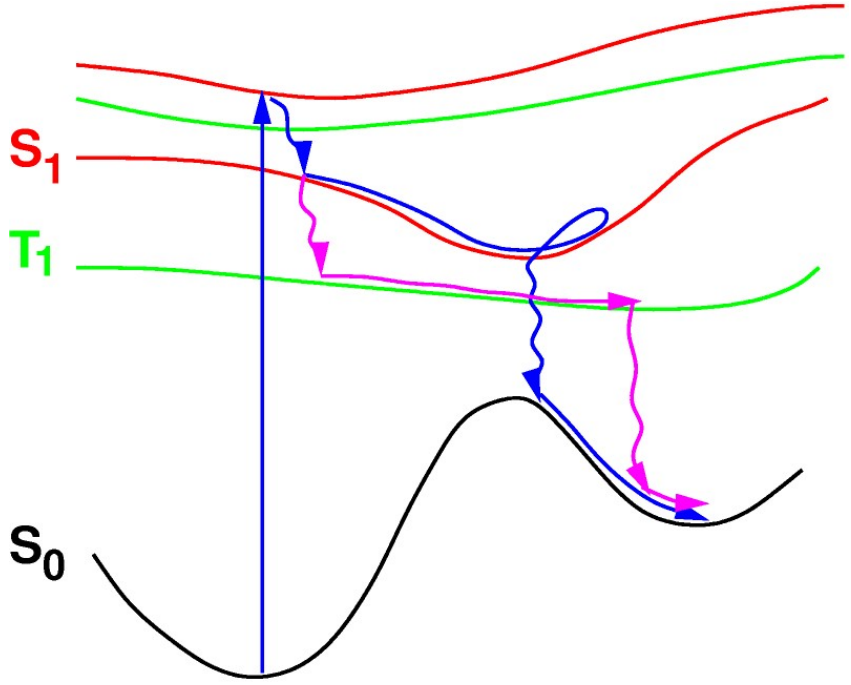


- Given the short time of the initial photoreaction (**hundreds of femtoseconds**), it is experimentally difficult to see how this isomerisation proceeds and how it is converted into a protein-wide structural change

- A detailed molecular knowledge of the mechanism of photosensing is limited in most cases (Help from first principles simulations?)

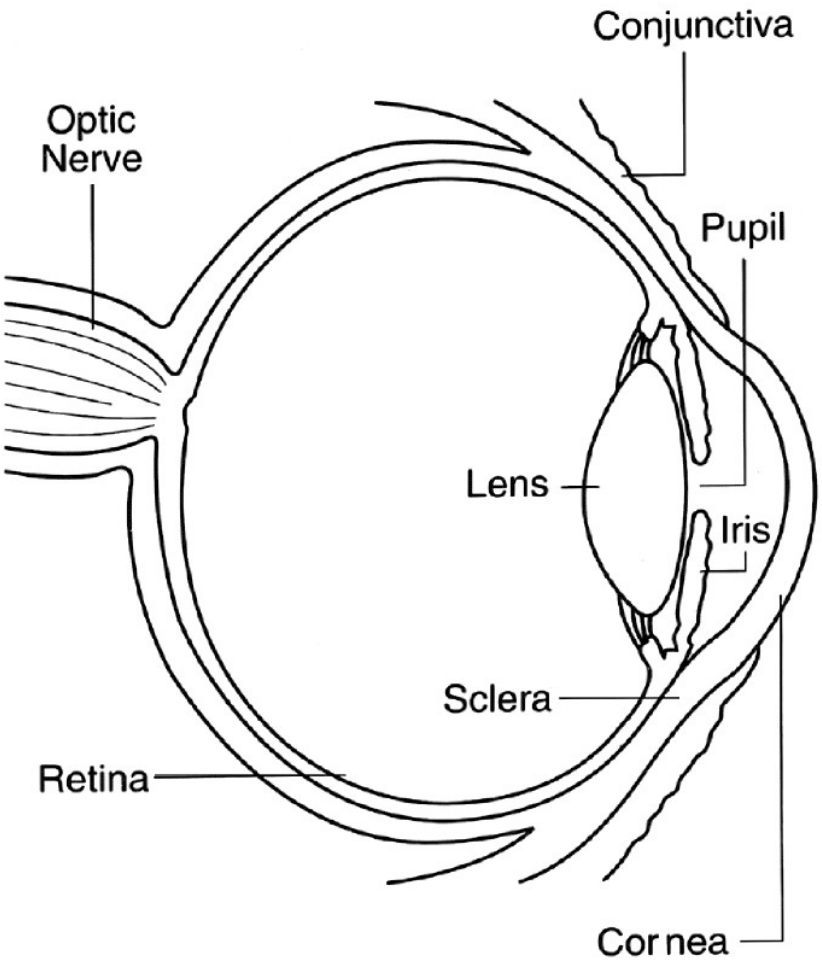
IDEAL GOAL

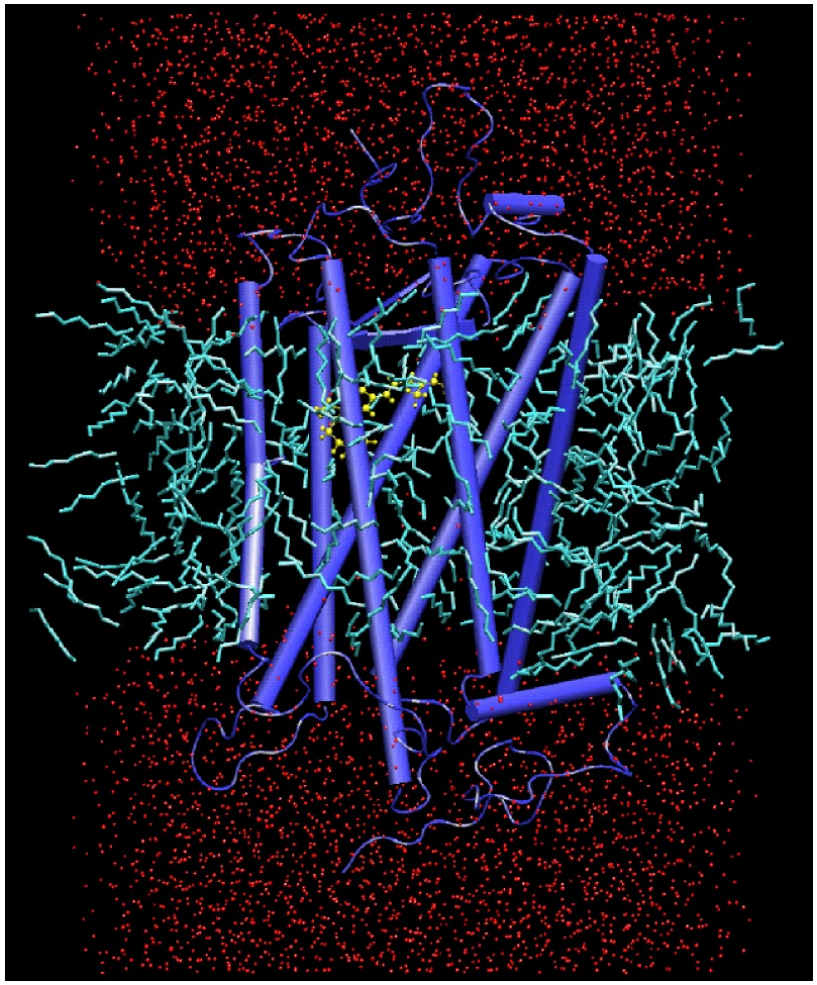
To study chromophore isomerization within the protein with a first principles method that combines high accuracy and low computational cost for an efficient evaluation of excited state energies and dynamics



Has such a method been developed?

RHODOPSIN

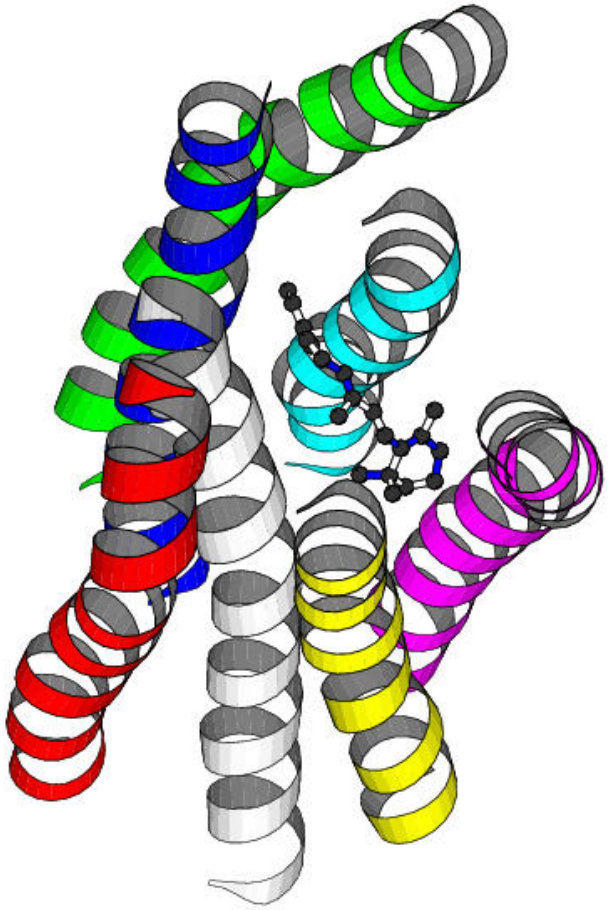




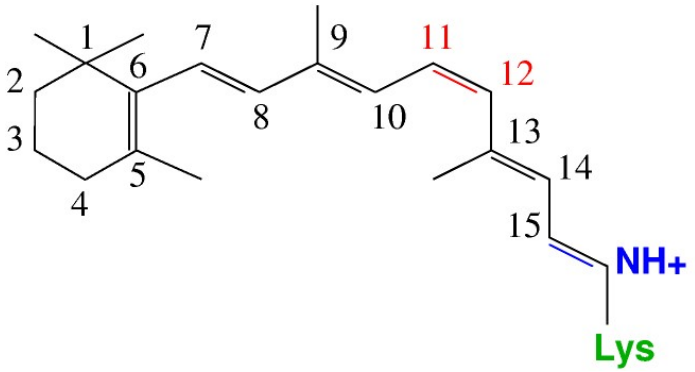
National Eye Institute,
National Institute of Health

U. Rohrig et al., Biochemistry 41, 10799 (2002)

VISION (first step)

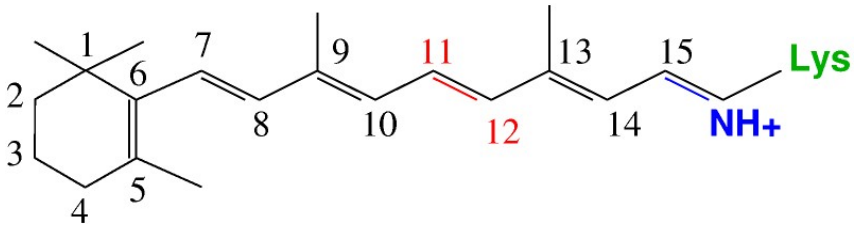


11-cis



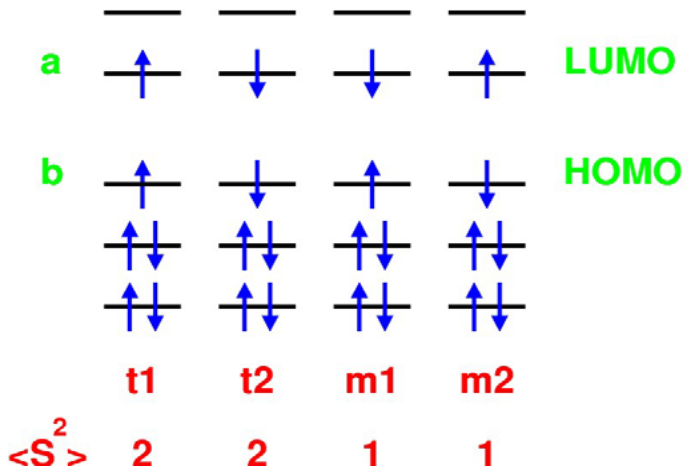
~ 200 fs ↓ *hν*

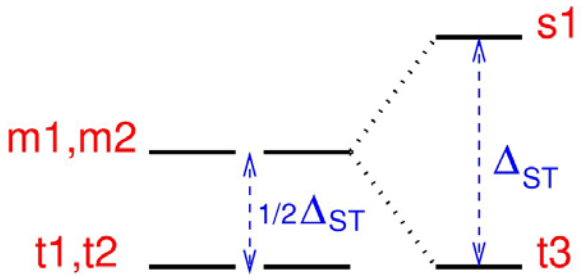
all-trans



Cis-trans isomerization

ROKS
Restricted Open Shell Kohn Sham method





$$E(s) = 2E(m) - E(t)$$

Ansatz:

$\{\psi_i(\mathbf{r})\}_{i=1,n+1}$ single set of spin-restricted orbitals **MINIMIZING** E(s)

$$E(s) = 2\left\langle m[\psi_i(\mathbf{r})]\middle|H_m\middle|m[\psi_i(\mathbf{r})]\right\rangle - \left\langle t[\psi_i(\mathbf{r})]\middle|H_t\middle|t[\psi_i(\mathbf{r})]\right\rangle$$

S_1 ENERGY

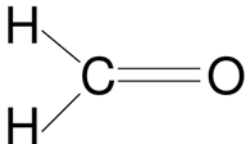
$$\left|s[\psi_i(\mathbf{r})]\right\rangle = \sqrt{2}\left|m[\psi_i(\mathbf{r})]\right\rangle - \left|t[\psi_i(\mathbf{r})]\right\rangle$$

S_1 WAVEFUNCTION

I. Frank et al. J. Chem. Phys. 108, 4060 (1998)

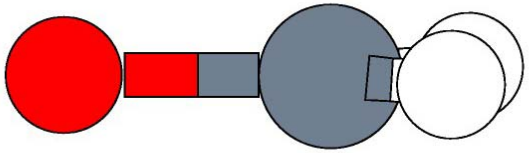
Does ROKS work?

	BLYP	EXP
C-O(A)	1.217	1.208
C-H (A)	1.111	1.116
H-C-H (deg)	116	116.5
α (deg)	0	0.0
μ(D)	2.34	2.33
C-O (A)	1.329	1.323
C-H (A)	1.102	1.103
H-C-H (deg)	115	118.1
α (deg)	38	34.0
μ(D)	1.46	1.56
Vertical (eV)	3.51	4.07
Adiabatic (eV)	3.16	3.50



formaldehyde

S_0



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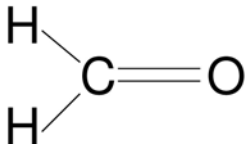
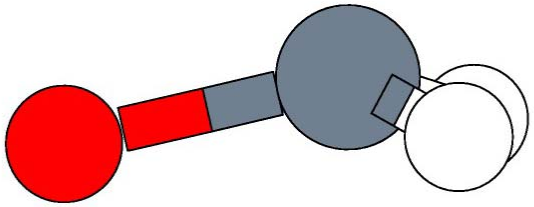


formaldehyde

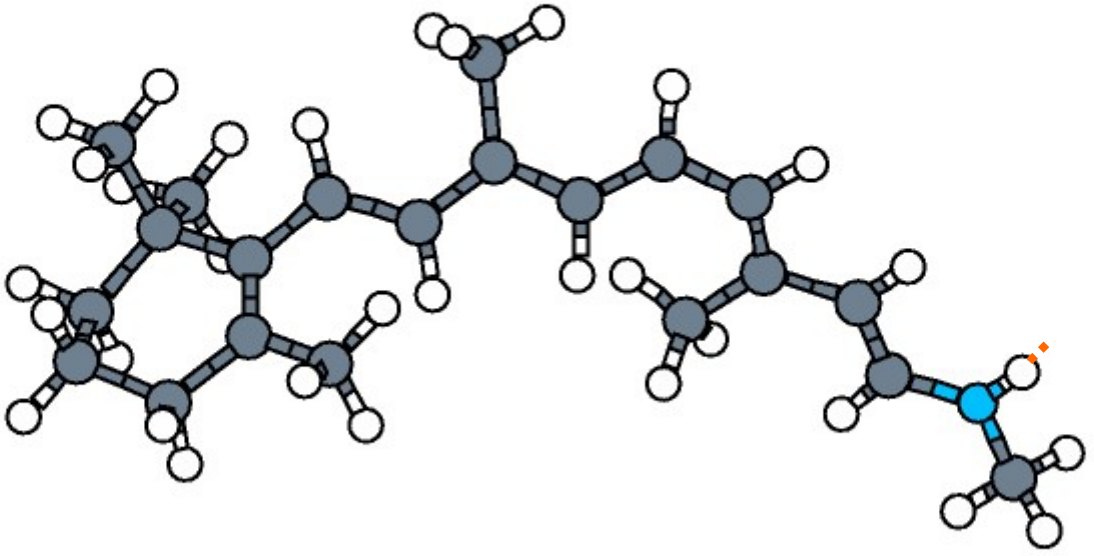


S_1

I. Frank et al.
J. Chem. Phys. 108, 4060 (1998)

"ENVIRONMENT" EFFECTS

protonated Schiff base of retinal



C. Molteni, I. Frank and M. Parrinello, J. Am. Chem. Soc. 121, 12177 (1999)

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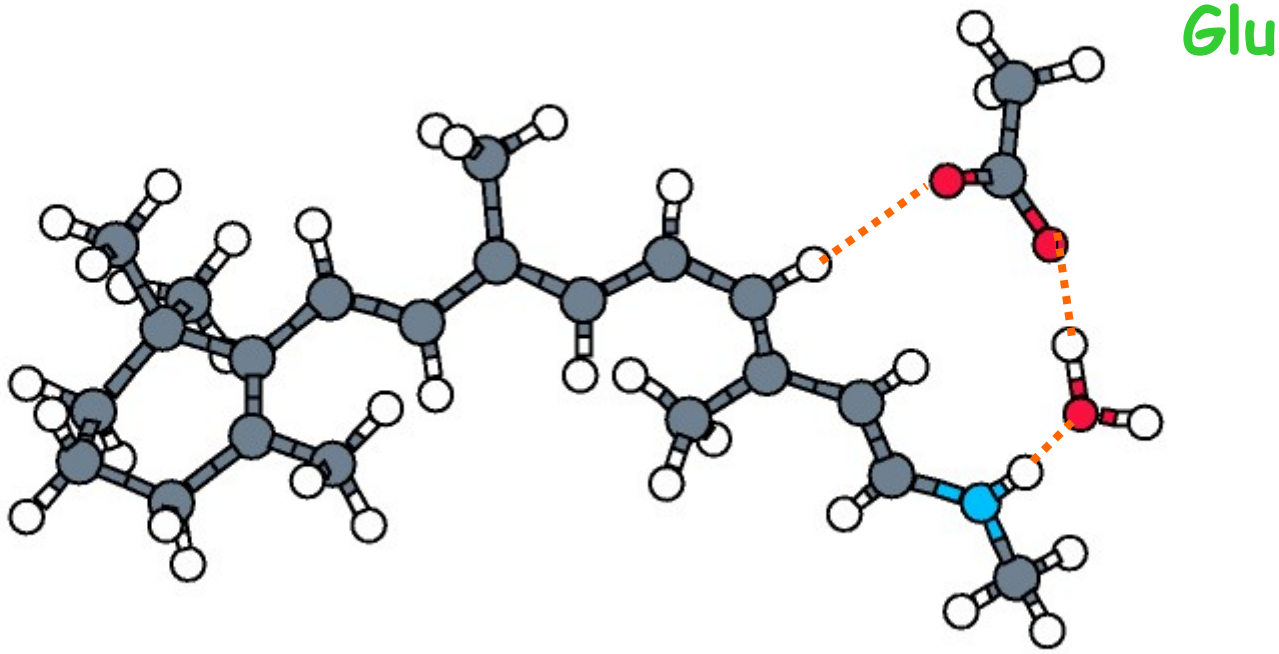
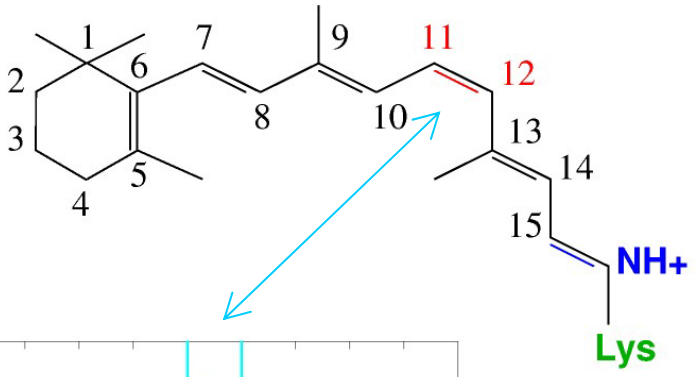
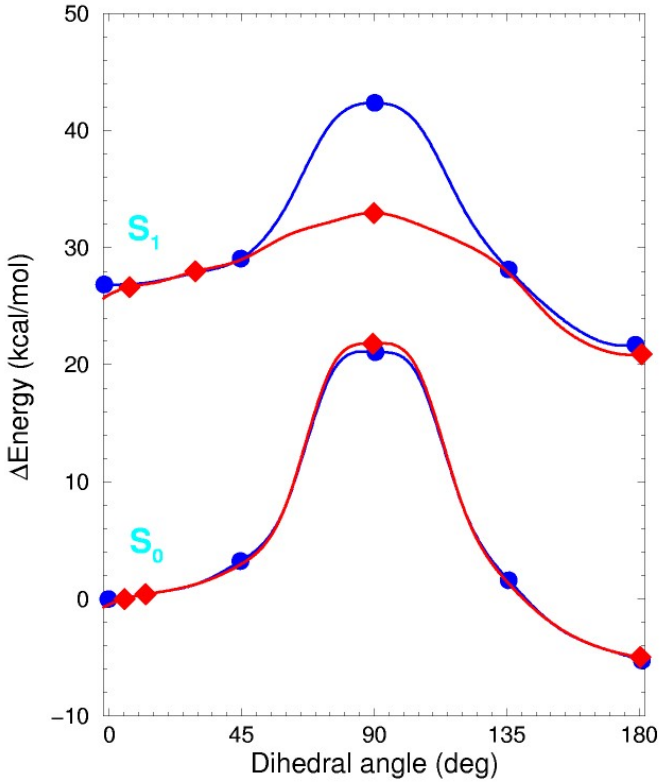
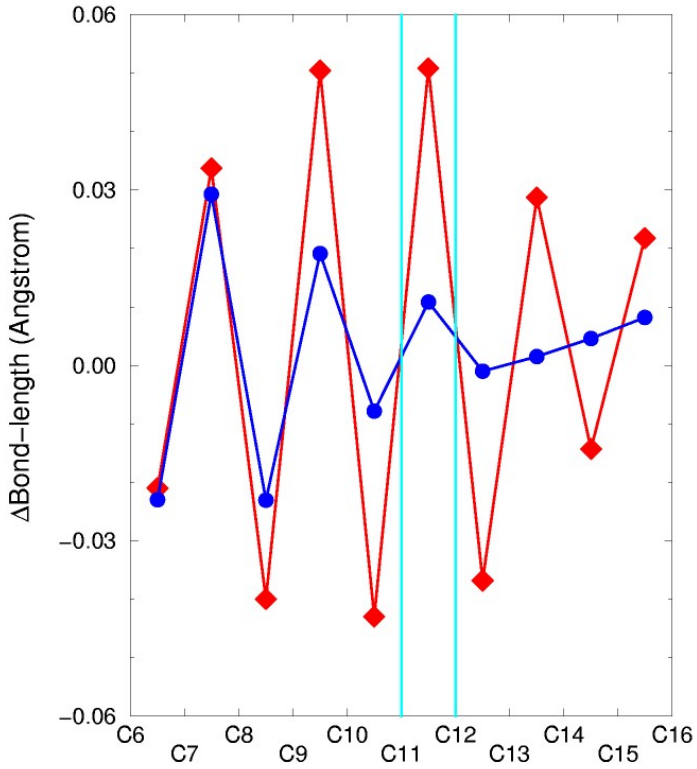


C. Molteni, I. Frank and M. Parrinello, J. Am. Chem. Soc. 121, 12177 (1999)



cis *trans*





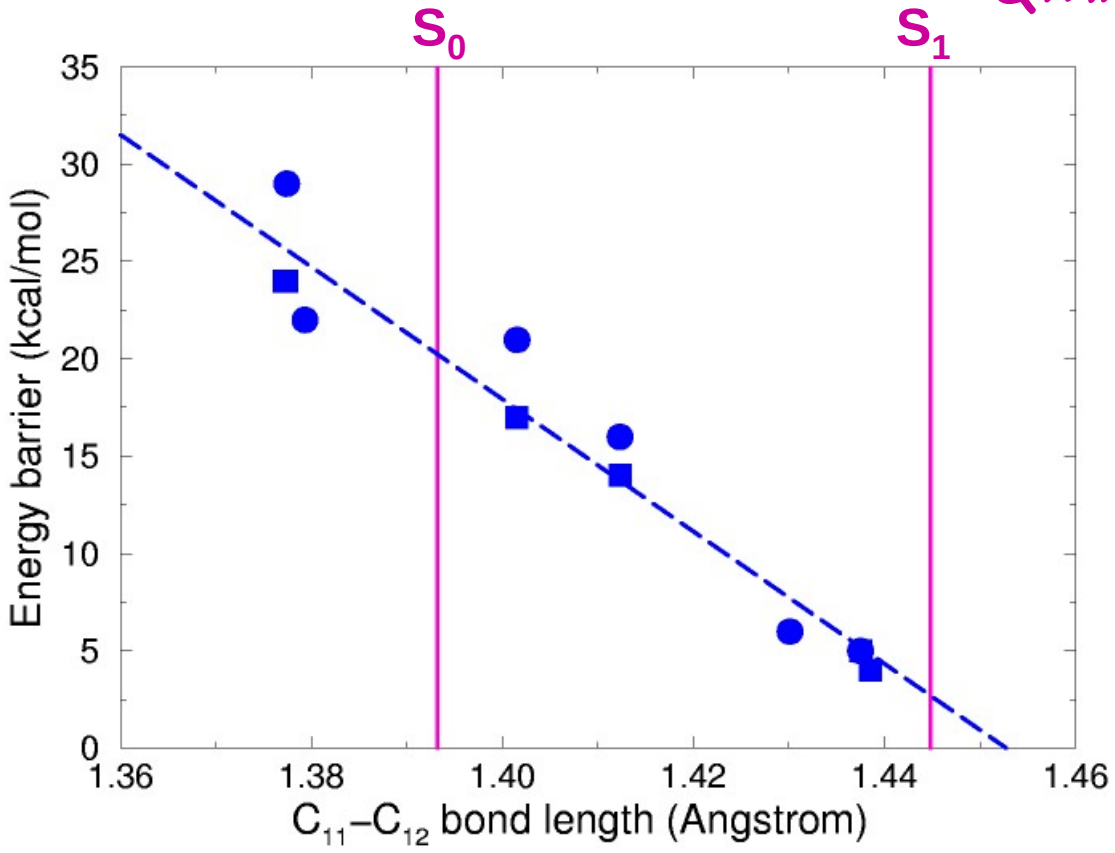
protonated Schiff base of retinal

protonated Schiff base of retinal + counterion + water

C. Molteni, I. Frank and M. Parrinello, J. Am. Chem. Soc. 121, 12177 (1999)

"ENVIRONMENT" EFFECTS

QMMM

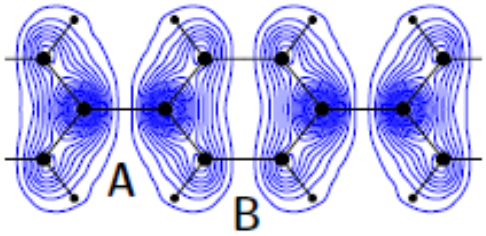


C. Molteni, I. Frank and M. Parrinello, Comp. Mat. Sci, 20, 311 (2001)

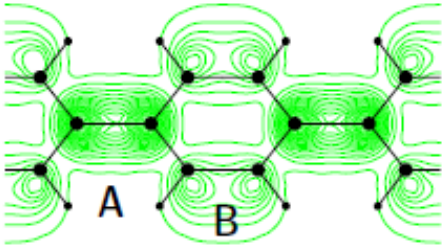
PPP Poly-Para-Phenylene $(C_6H_4)_n$

Ground state geometry

HOMO / VBM (at Γ):



LUMO / CBM (at Γ):



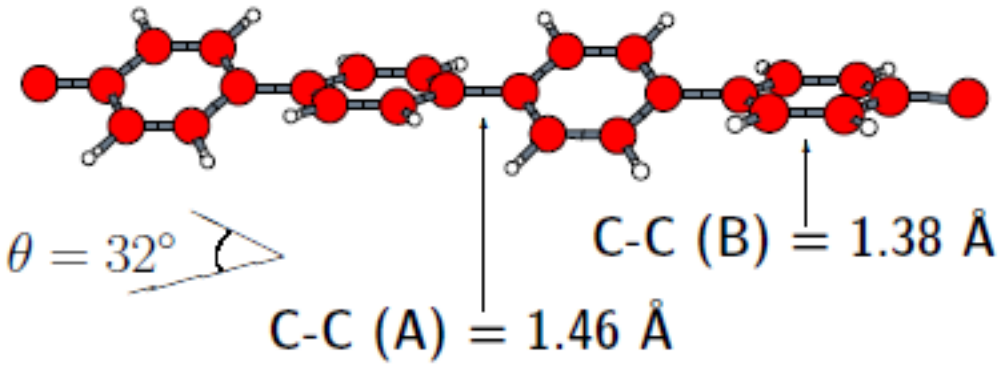
Excited state geometry

Exciton wavefunction

Self-trapping

E. Artacho, M. Rohlfing, M. Cote', P.D. Haynes, R.J. Needs and C. Molteni, PRL 93, 116401 (2004)

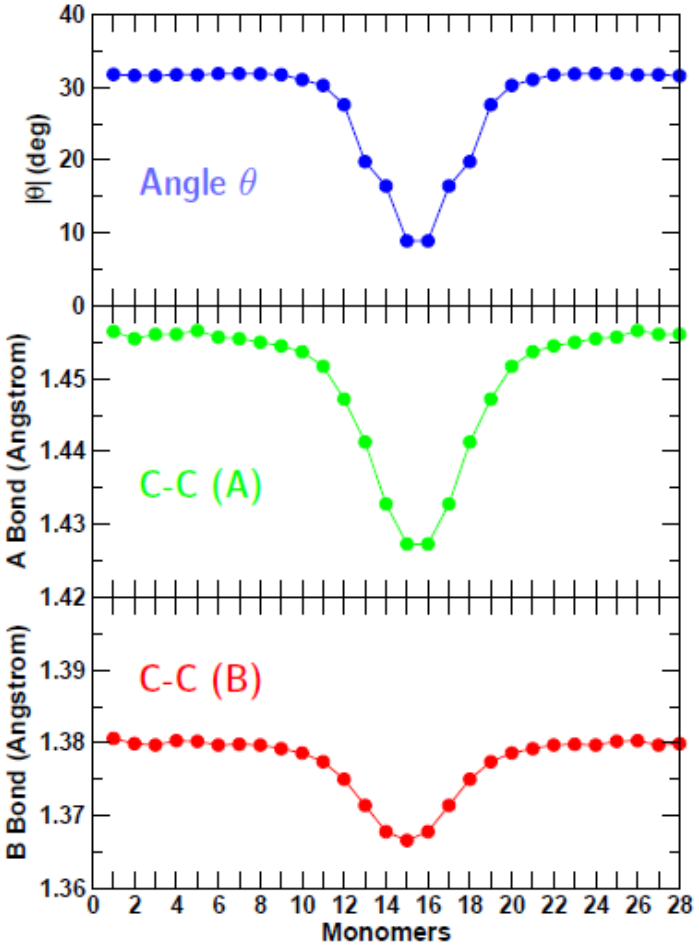
PPP Poly-Para-Phenylene $(C_6H_4)_n$



28 C_6H_4 rings / 280 atoms

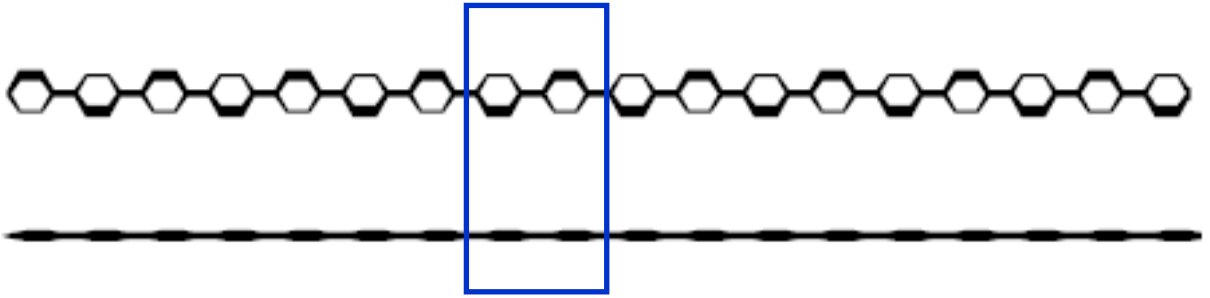
Constrained DFT

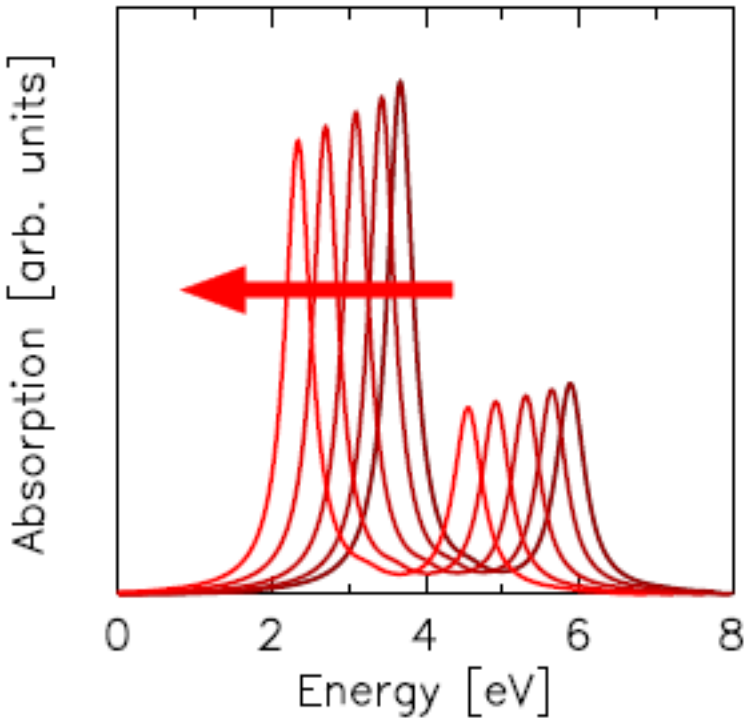
HOMO-LUMO excitation

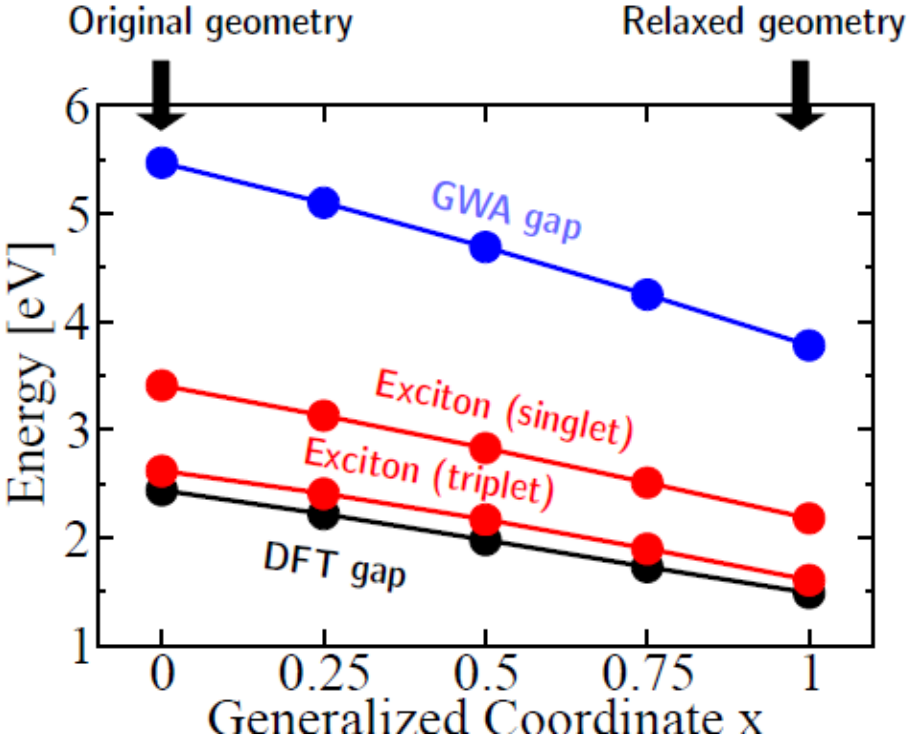


E. Artacho, M. Rohlfing, M. Cote', P.D. Haynes, R.J. Needs and C. Molteni, PRL 93, 116401 (2004)

…it always need validation

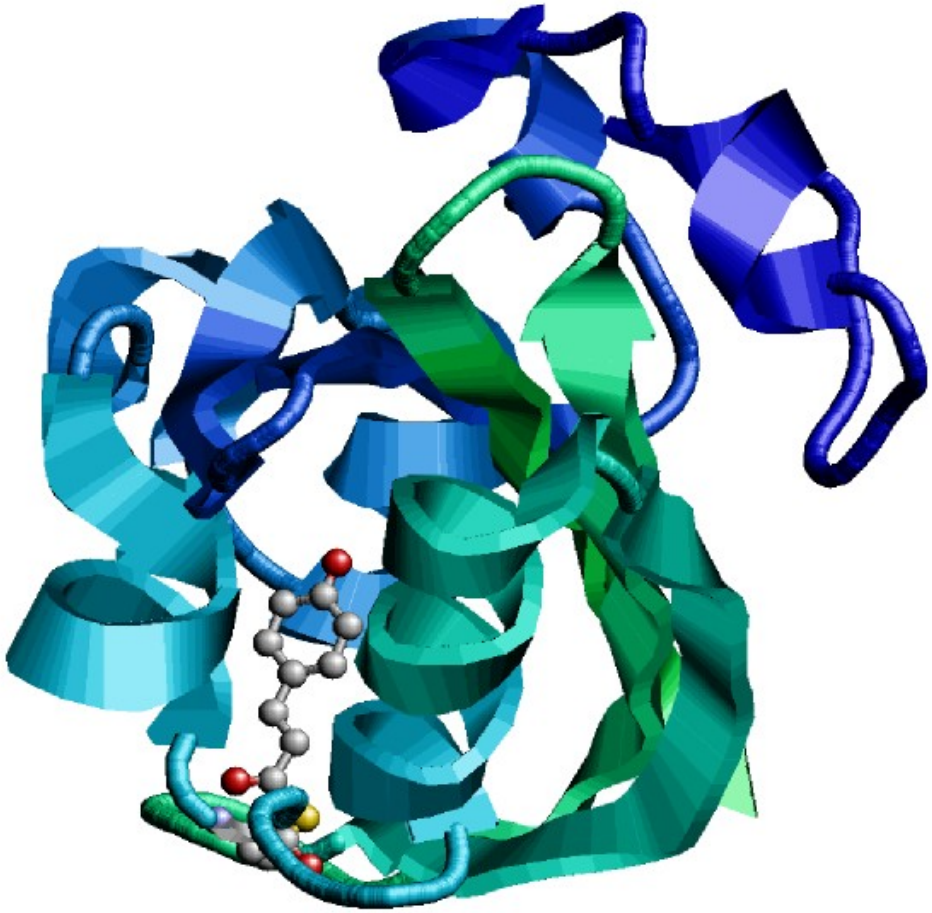






E. Artacho, M. Rohlfing, M. Cote', P.D. Haynes, R.J. Needs and C. Molteni, PRL 93, 116401 (2004)

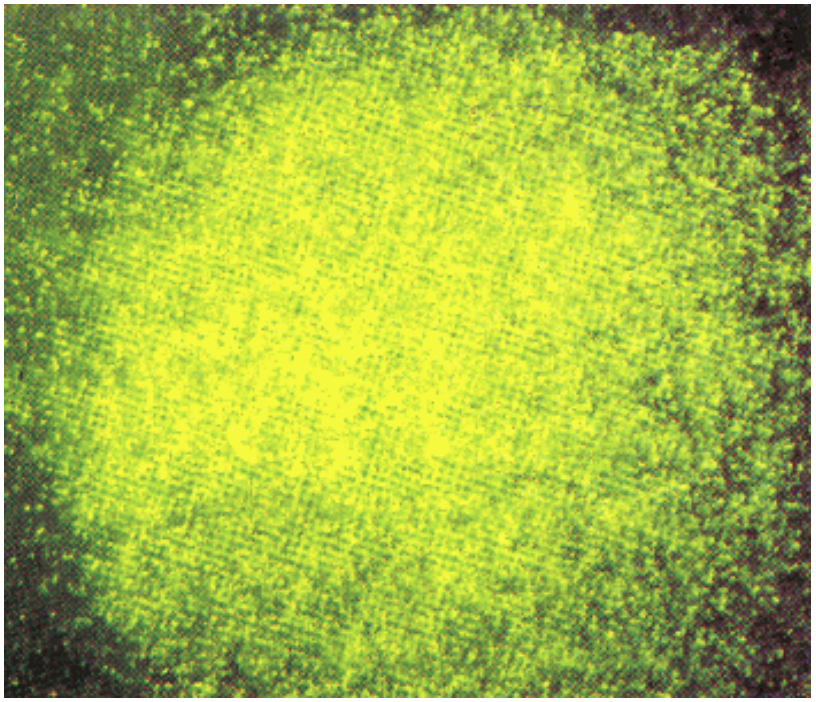
PHOTOACTIVE YELLOW PROTEIN



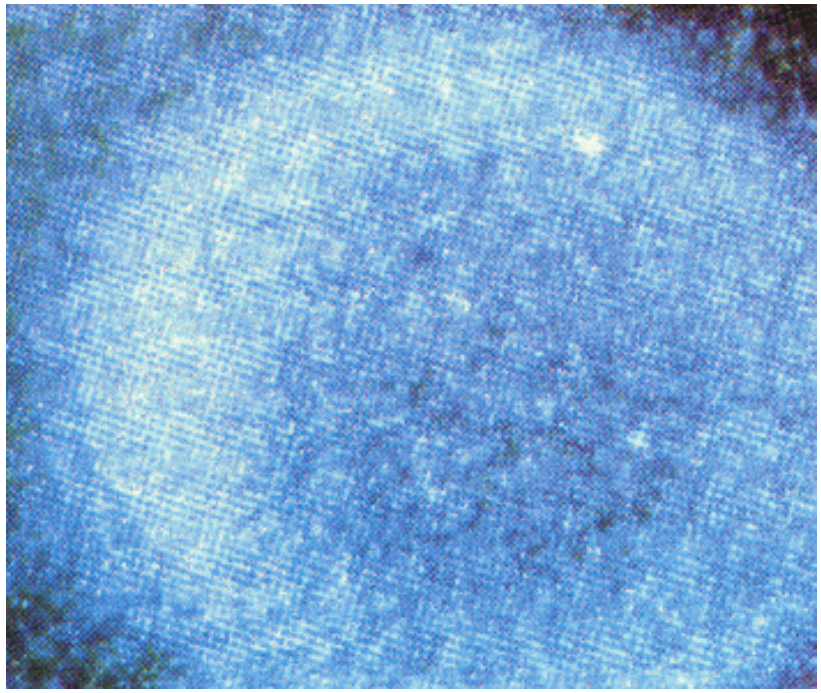
Small (125-residues) water-soluble protein,
from Ectothiorhodospira Halophila

T.E. Meyer, Biochim. Biophys. Acta 806, 175 (1985)

PHOTOTAXIS
in Ectothiorhodospira Halophila



POSITIVE

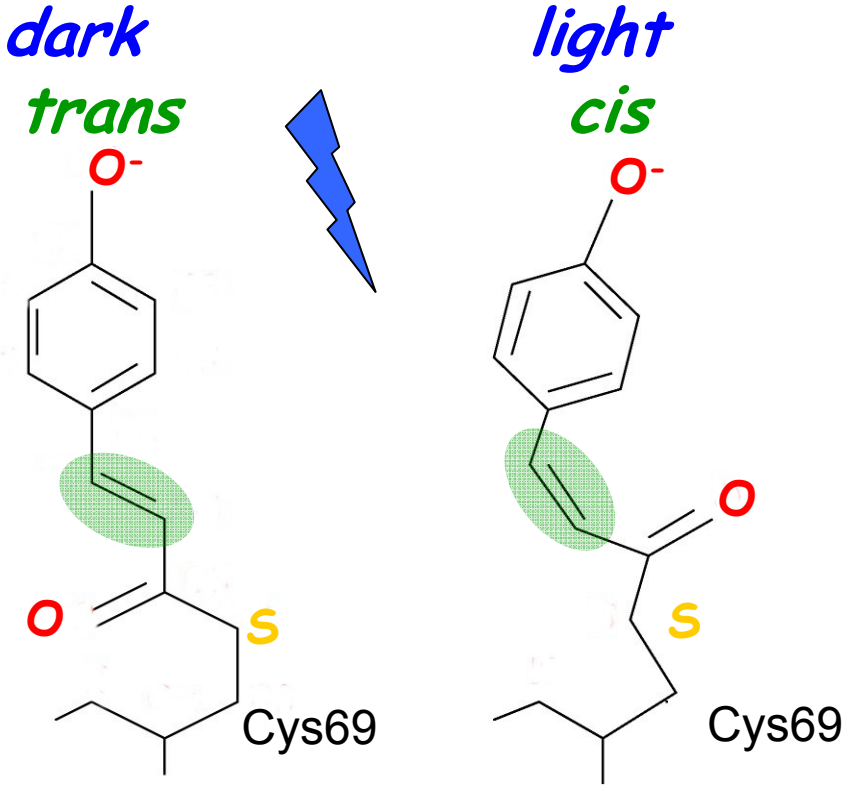


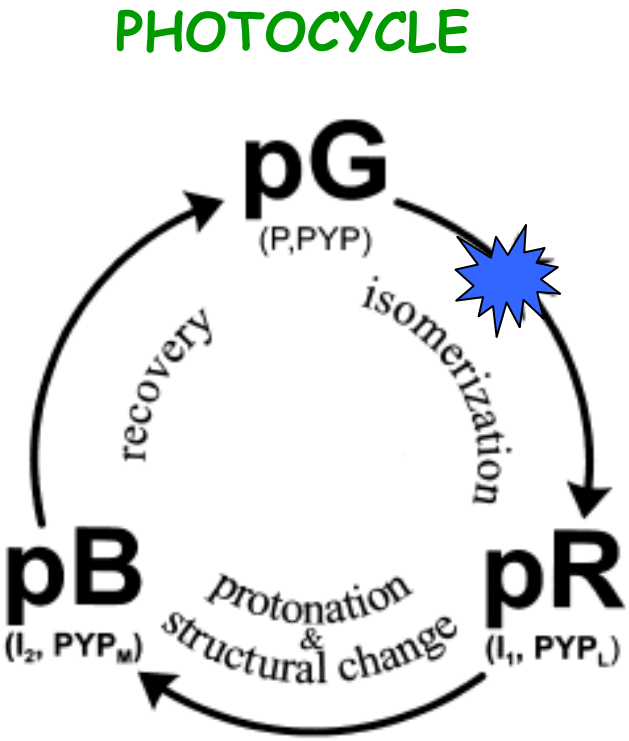
NEGATIVE

W.W. Sprenger et al., J. Bacteriol. 175, 3099 (1993)

PYP CHROMOPHORE

p-coumaric acid

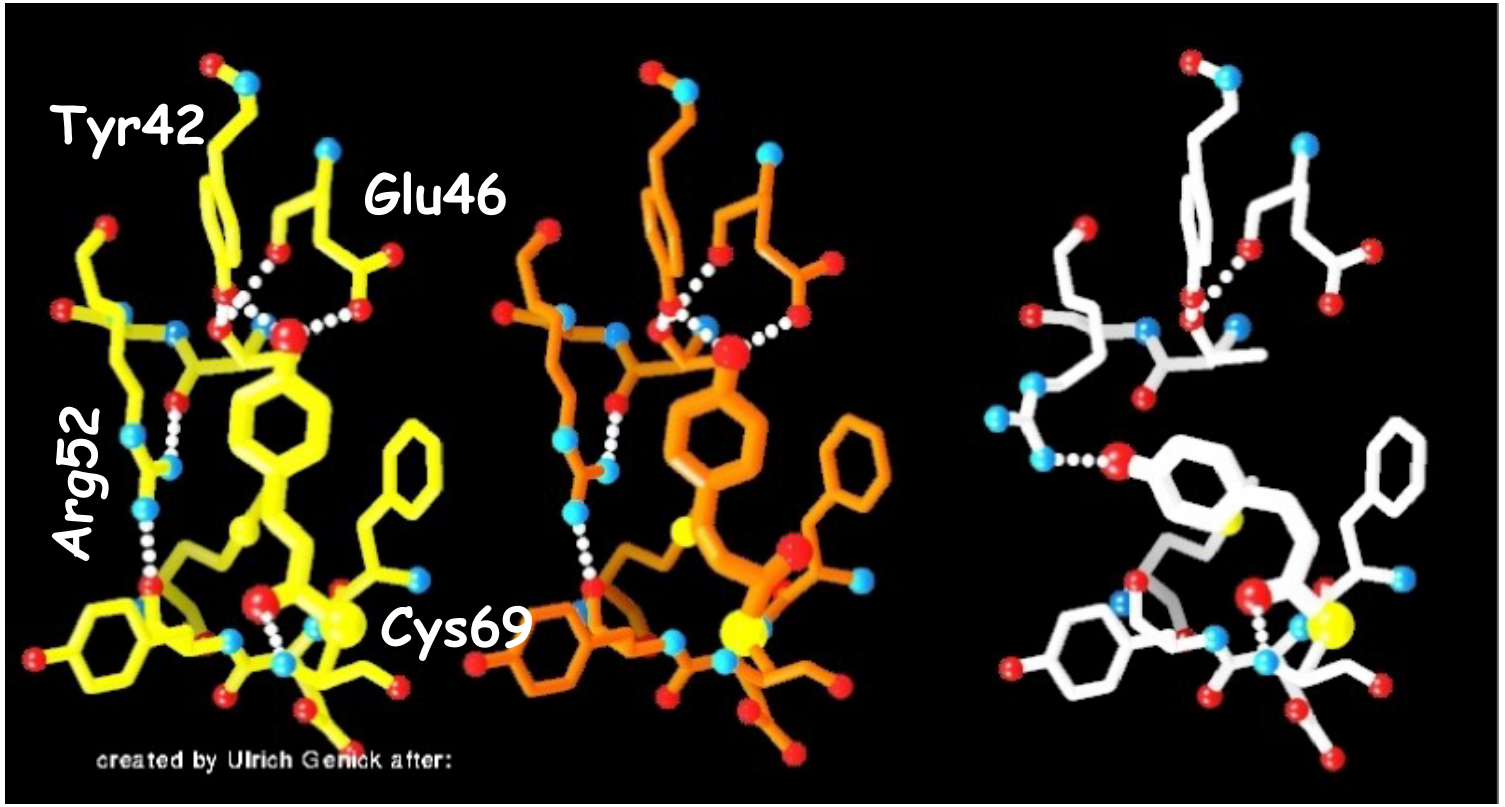




K.J. Hellingwerft et al. J. Phys. Chem. A 107, 1082 (2003)

APPARENTLY SIMPLE

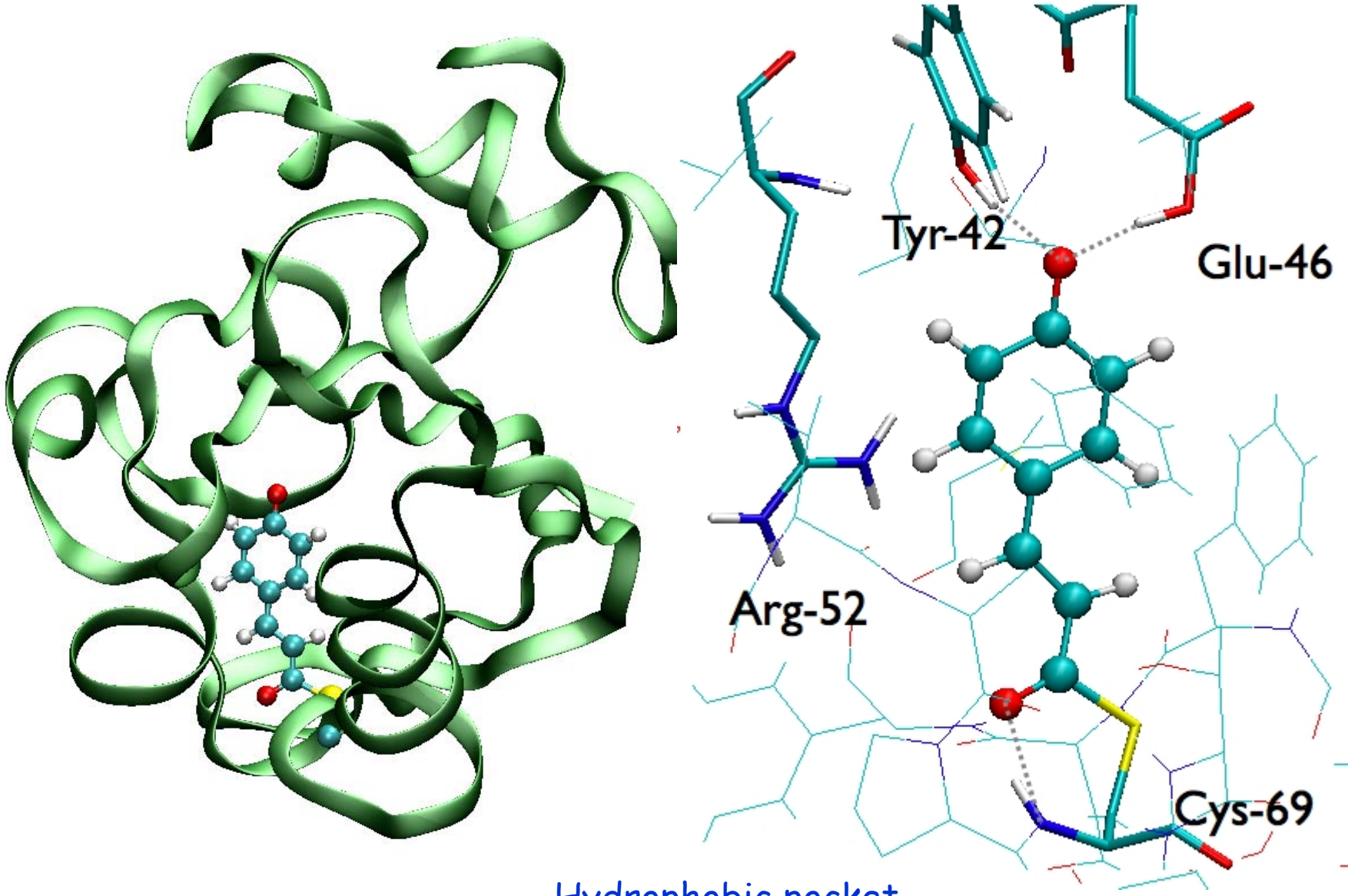
HIGH RESOLUTION (<1 Å) CRYSTAL STRUCTURES FOR DIFFERENT INTERMEDIATES



Ground state Early intermediate Bleached state

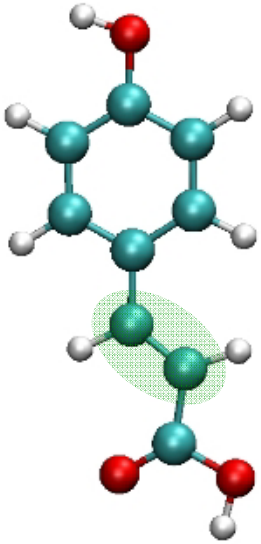
U.K. Genick et al., Science 275, 1471 (1997);
U.K. Genick et al., Nature 392, 206 (1998)

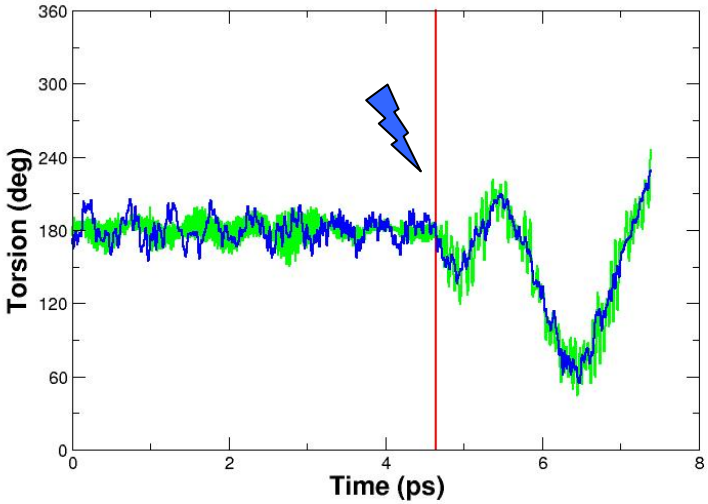
Binding site

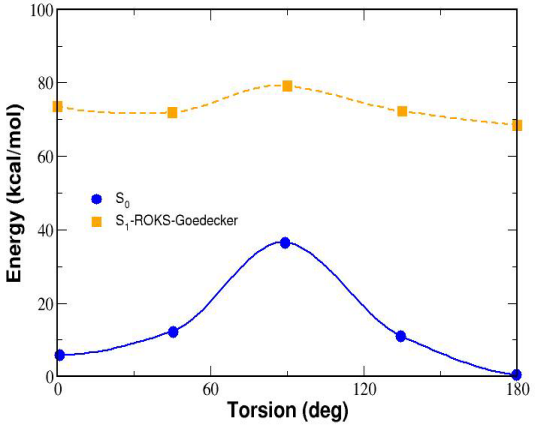


Hydrophobic pocket

ROKS ISOMERIZATION?







Underestimated energies

Only HOMO-LUMO excitations

Reliability?

CAN WE DO BETTER?

TDDFT?

TDDFT ASSESSMENT PLAN
PYP

Plan:

- test the performance of TDDFT in describing the low-lying excited states of PYP chromophore models in vacuo against reference data (experiments and high level theory)

- evaluate protein environment effect

PYP CHROMOPHORE MODELS IN VACUO

SIMULATION DETAILS

LR-TDDFT

- **CPMD**:

  Plane waves + Martins-Troullier pseudopotentials (70 Ry cutoff); Tamm Dancoff approximation; xc functionals PBE, PBE0

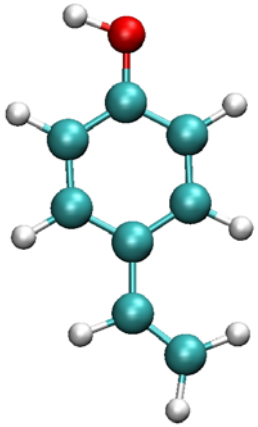
- **GAUSSIAN**:

  Localised basis set (CC-pVTZ); xc functionals BLYP, B3LYP

PYP CHROMOPHORE MODELS

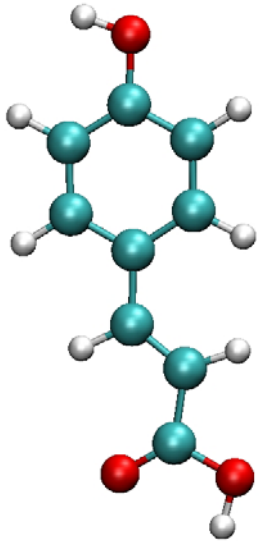
NEUTRAL

ANIONS



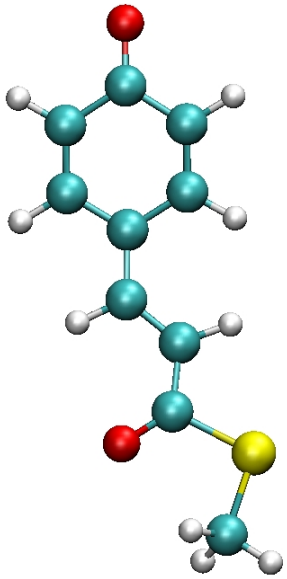
p-vinylphenol E T

pVP



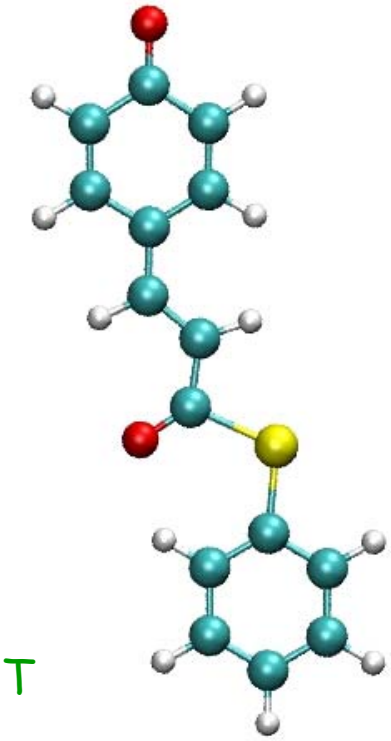
p-coumaric acid T

pCA



Phenolate anion of thiomethyl-*p*-coumaric acid T

$TMpCA^-$

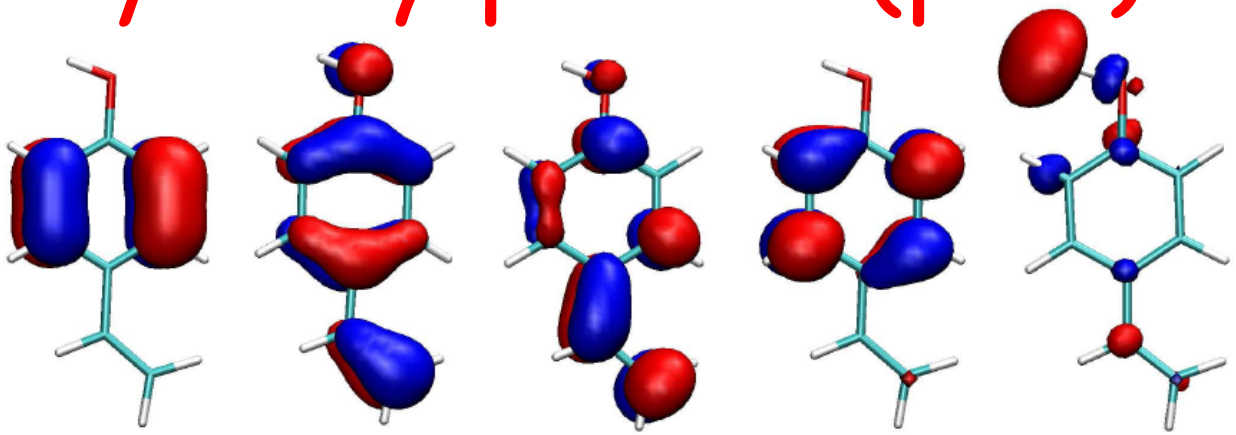


Phenolate anion of thiophenyl-*p*-coumarate E

pCT^-

p-vinylphenol (pVP)

eV



HOMO-1 HOMO LUMO LUMO+1 LUMO+2

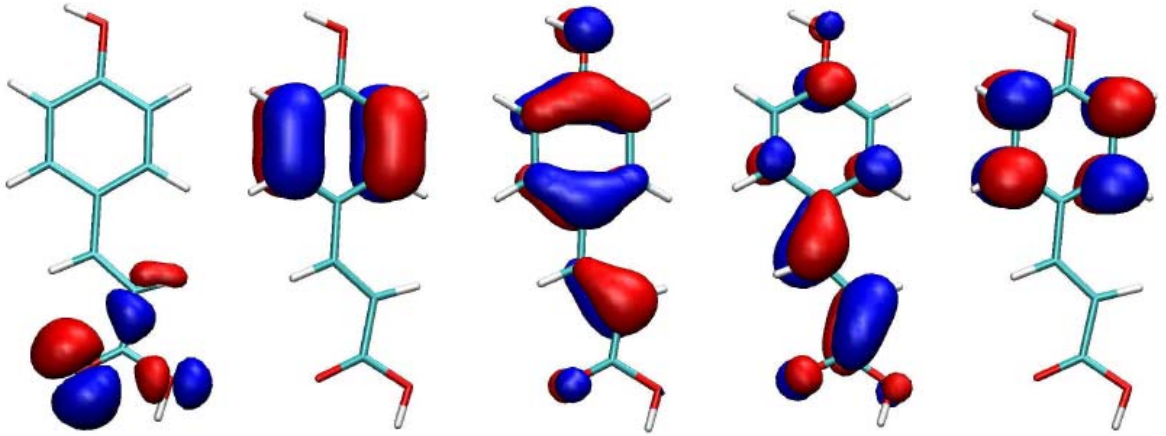
-	PBE(TD)	BLYP	PBE0(TD)	B3LYP	CCSD[a]	Exp.[b]	
S_1	4.20 (0.028) H→L+1 H→L H-1→L	4.17 (0.075) H→L+1 H→L H-1→L	4.68 (0.066) H→L+1 H→L H-1→L	**4.57 (0.118)** **H→L+1** **H→L** **H-1→L**	4.66 (0.016) H→L+1 H→L H-1→L	4.12	π→π*
S_2	4.39 (<0.01) H→L+2	**4.50 (0.334)** **H→L** **H→L+1** **H-1→L**	4.93 (<0.01) H→L+2	**4.89 (0.347)** **H→L** **H→L+1** **H-1→L**	**5.43 (0.469)** **H→L** **H→L+1** **H-1→L**	-	π→π*
S_3	**4.63 (0.193)** **H→L** **H→L+1** **H-1→L**	5.03 (<0.01) H→L+2	**5.07 (0.297)** **H→L** **H→L+1** **H-1→L**	5.69 (<0.01) H→L+2	5.47 (<0.01) H→L+2	-	

[a] *M. de Groot et al., J. Chem. Phys. 125, 204302 (2006) - EOM-CCSD*
[b] *W.L. Ryan et al. J. Am. Chem. Soc. 124, 6194 (2004)*

E. Muguruza
PhD thesis KCL

p-coumaric acid (pCA)

Energy underestimation?



HOMO-2 HOMO-1 HOMO LUMO LUMO+1

Exp for OMpCA

-	PBE(TD)	BLYP	PBE0(TD)	B3LYP	CCSD[a]	CASPT2[b]	
4.06 S_1	3.56 (<0.01) H-2→L	3.63 (<0.01) H-2→L	**4.46 (0.375) H→L**	**4.20 (0.653) H→L**	4.84 (0.061) H→L+1	**4.93 H→L**	π→π*
4.37 S_2	**4.01 (0.267) H→L**	**3.80 (0.574) H→L**	4.57 (<0.01) H-2→L	4.48 (<0.01) H-2→L	**5.13 (0.739) H→L**	5.17 H-1→L H→L+1	π→π*
S_3	4.14 (0.046) H-1→L H→L+1	4.11 (0.015) H-1→L H→L+1	4.73 (0.050) H→L+1 H-1→L	4.61 (0.028) H→L+1 H-1→L	5.30 (<0.01) H-2→L	5.33 H-2→L	n→π*

[a] *E .V. Gromov et al., J. Phys. Chem. A 109, 4623 (2005)*

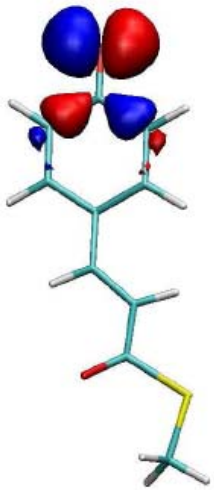
[b] *C. Ko et al. J. Am. Chem. Soc. 125, 12710 (2003)*

Sergi et al. J. Phys. Chem. B 105, 4386 (2001) TDDFT-PBE-triple ζ localized basis set 3.76 eV

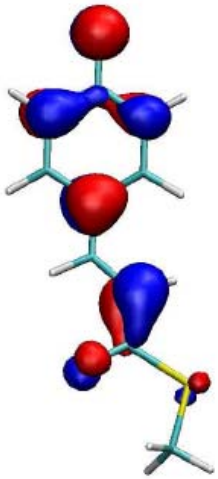
Exp de Groot et al., J. Phys. Chem. B 112, 4427 (2008)

Phenolate anion of thiomethyl-*p*-coumaric acid (TMpCA$^-$)

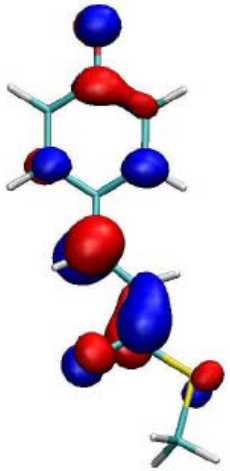
Energy overestimation!



HOMO-1



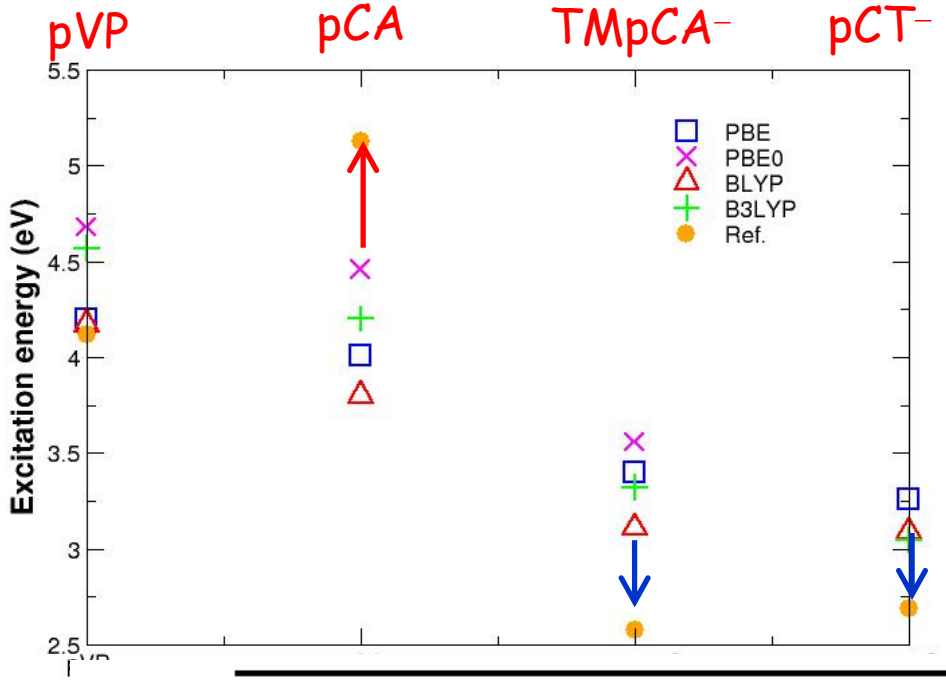
HOMO



LUMO

	-	PBE(TD)	BLYP	PBE0(TD)	B3LYP	CASPT2[b]
n→π*	S_1	2.24 (<0.01) H-1→L	2.37 (<0.01) H-1→L	3.37 (<0.01) H-1→L	3.25 (<0.01) H-1→L	**2.58 (0.567)** $\pi \rightarrow \pi^*$
π→π*	S_2	**3.40 (0.444) H→L**	**3.11 (0.934) H→L**	**3.56 (0.857) H→L**	**3.32 (1.0) H→L**	2.95 (<0.01) $n \rightarrow \pi^*$

[b] *V. Molina et al., PNAS 98, 4299 (2001) for the crystallographic structure*
L.L. Premvardhan et al., J. Phys. Chem. B 108, 5138 (2004) - TDDFT BLYP 3.08 eV



TDDFT SUMMARY

References (reliable?)

[a] Ryan et al. JACS124, 6194 (2004)
[b] Ko et al. JACS. 125, 12710 (2003)
[c] de Groot et al., J. Phys. Chem. B 112, 4427 (2008)
[d] Molina et al., PNAS 98, 4299 (2001)
[e] Nielsen et al., Biophys. J. 89, 2597 (2005)

	Excitation energy/eV				
Molecule	PBE	PBE0	BLYP	B3LYP	Ref.
pVP	4.20 [3.38]	4.68	4.17	4.57	4.12[a]
pCA	4.01 [2.89]	4.46	3.80	4.20	4.93[b], 4.95[c]
$TMpCA^-$	3.40 [1.91] (3.24[f])	3.56	3.11	3.32	2.58[d]
pCT^-	3.28 [1.88]	3.34	3.09	3.05	2.70[e]

[a] Experiments.[47] [b] CASPT2.[6] [c] EOM-CCSD.[7] [d] CASPT2.[19] [e] Experiments.[14] [f] Calculation for the crystallographic structure.

E. Muguruza Gonzalez, L. Guidoni and C. Molteni, PCCP 11,4556 (2009)

TDDFT SUMMARY

Non-trivial system dependency

pVP … it depends on what we compare

pCA and pCTA energy underestimation (charge transfer?)

pCA^- $TMpCA^-$ and PCT^- energy overestimation

THE PROBLEM WITH ANIONS…

	VDE (eV)	ES(eV)
$TMpCA^-$	3.04	3.32
pCT^-	3.16	3.05

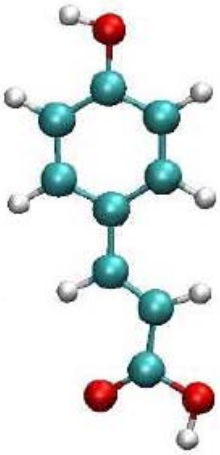
VDE Vertical Detachment Energy

E. Muguruza Gonzalez, L. Guidoni and C. Molteni, PCCP 11,4556 (2009)

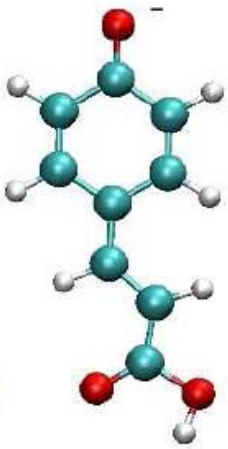
SPECTRAL TUNING

$$\Delta E = \Delta E_{chemical} + \Delta E_{protein}$$

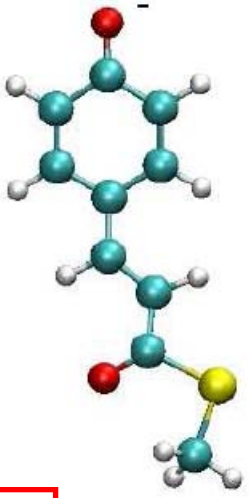
SPECTRAL TUNING
CHEMICAL MODIFICATION



deprotonation
of phenyl oxygen
Red shift



thioester bond
with Cys69
Red shift



Spectral shift

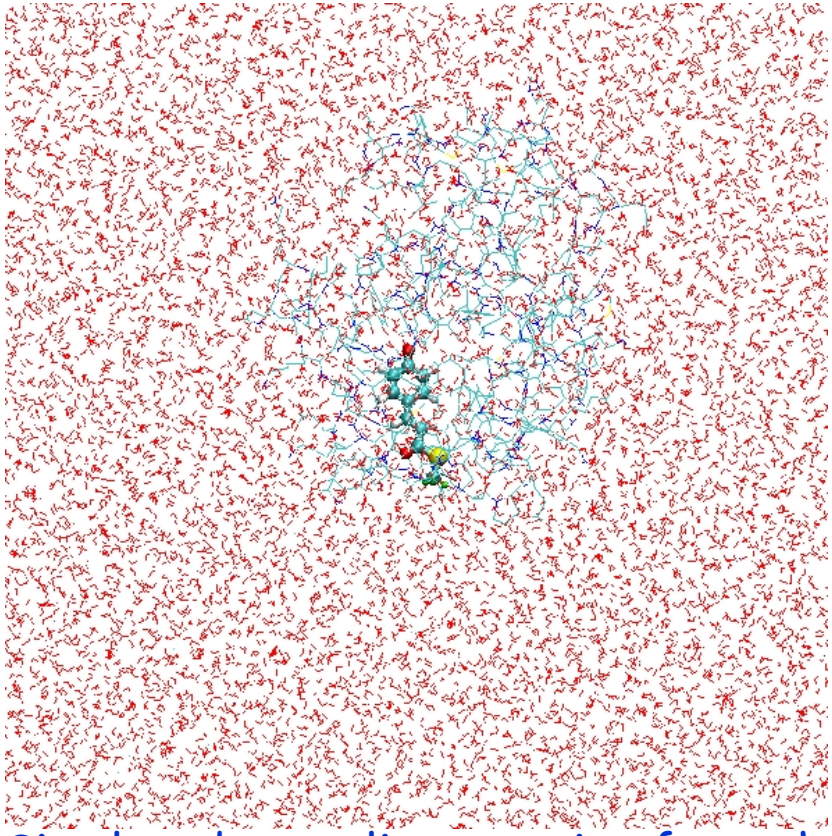
(absorption)

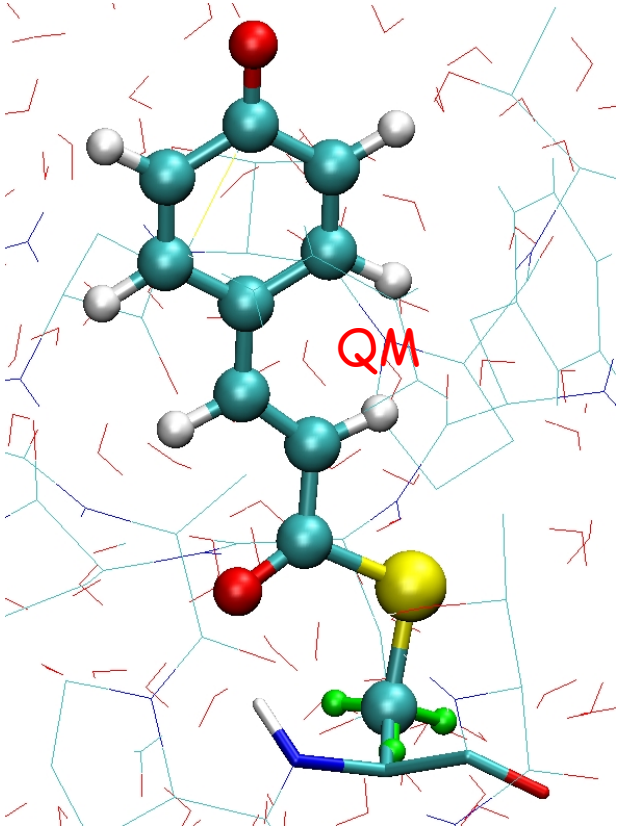
$$\Delta E_{chemical} = \Delta E_{deprot} + \Delta E_{thiol}$$

	E(eV)	pCA	pCA^-	$TMpCA^-$	ΔE_{deprot}	ΔE_{thiol}	ΔE_{chem}
PBE	BLYP	3.80	3.26	3.11	-0.54	-0.15	-0.69 -0.61
PBE0	B3LYP	4.20	3.48	3.32	-0.72	-0.16	-0.88 -0.90

Changenet-Barret et al., Chem. Phys. Lett. 365, 285 (2002) with respect to solution 0.6 eV(dep)+0. 55eV(thio); Kroon et al., J. Biol. Chem. 271, 31949 (1996) (0.58+0.74); Nielsen et. al Biophys. J. (2005) with respect to vacuum 0.19 eV

TMpCA$^-$ in the PROTEIN





Simulated annealing starting from the crystallographic structure for PYP[a]

in a physiological water solution after equilibration MD

GROMOS96 force-field + PW-PBE-DFT (QMMM in CPMD)

[a] *E.D. Getzoff et al., Nat. Str. Mol. Biol. 10, 663 (2003) [0.82 Å] - 1NWZ*

SPECTRAL SHIFTS

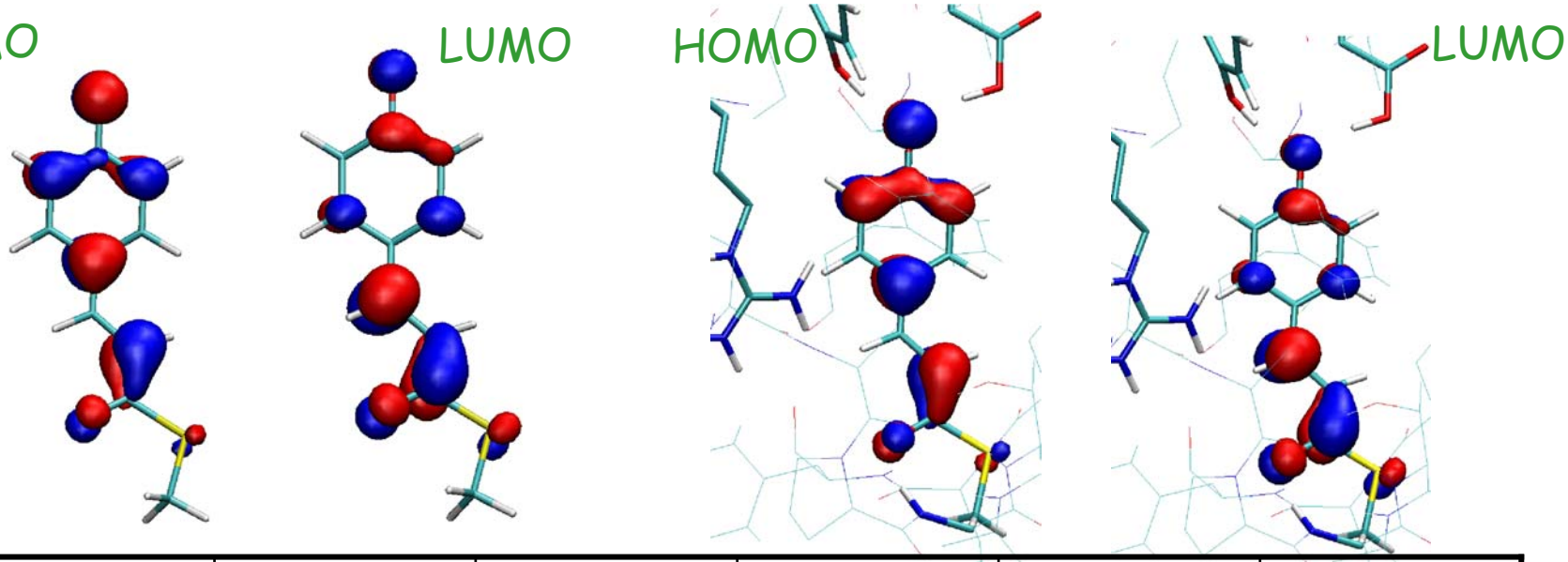
	ΔE_{chem} (eV)	ΔE_{prot} (eV)	ΔE (eV)
PBE	-0.61	0.05	-0.56
PBE0	-0.90	-0.05	-0.95
BLYP	-0.69	-0.05	-0.74
B3LYP	-0.88	-0.11	-0.99
Experiment	-0.19[a], -1.66[b], -1.15[c]	0.08	-0.11[a],-1.58, -1.07[c]
Other theories	-0.76[d]	-0.04[d], 0.20[e]	-0.80[d]

a. In vacuo calculated using as refs pCT- and the carboxylate anion of pCA-
b. In vacuo calculated using as refs pCT- and 4-hydroxycinnamate
c. In aqueous solution
d. TDDFT
e. MS-CASPT2

E. Muguruza Gonzalez, L. Guidoni and C. Molteni, PCCP 11,4556 (2009)

TMpCA- in the PROTEIN

HOMO LUMO HOMO LUMO



	VDE(eV)	ES(eV)		VDE(eV)	ES(eV)
vacuum	3.04	3.32	PYP	6.22	3.45

The lowest excitations in the protein are **non-ionizing bound states** unlike in vacuo.

The protein environment prevents radical formation (experimental evidence)*.

* I.-R Lee, W. Lee and A.H. Zewail, Proc. Natl. Acad. Sci. U.S.A. 103, 258 (2006)

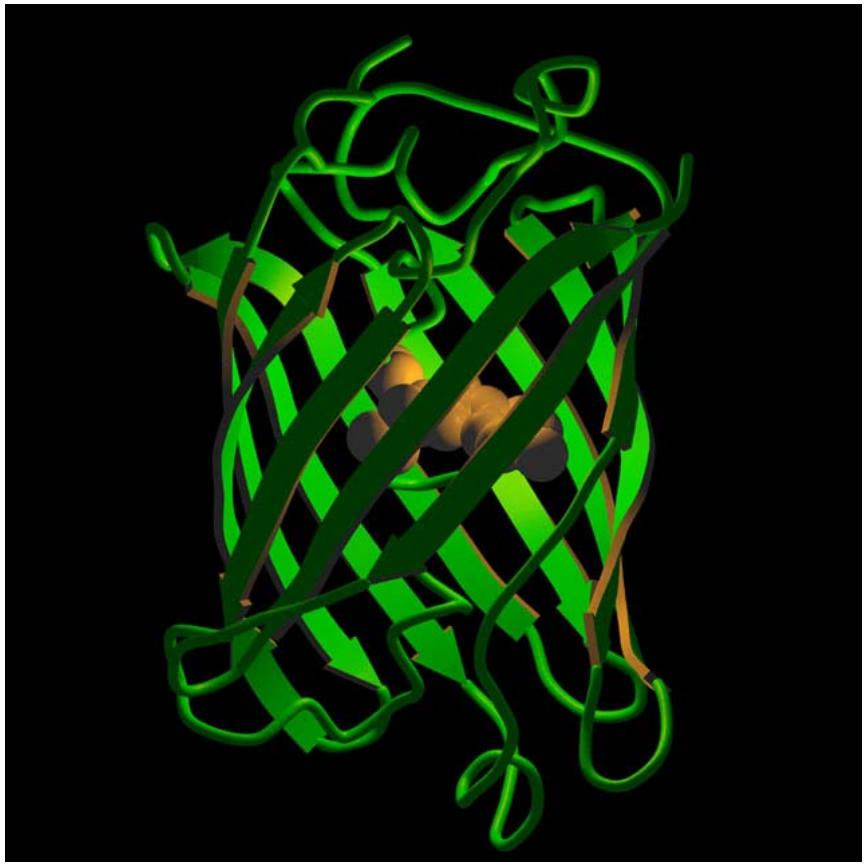
SPECTRAL TUNING

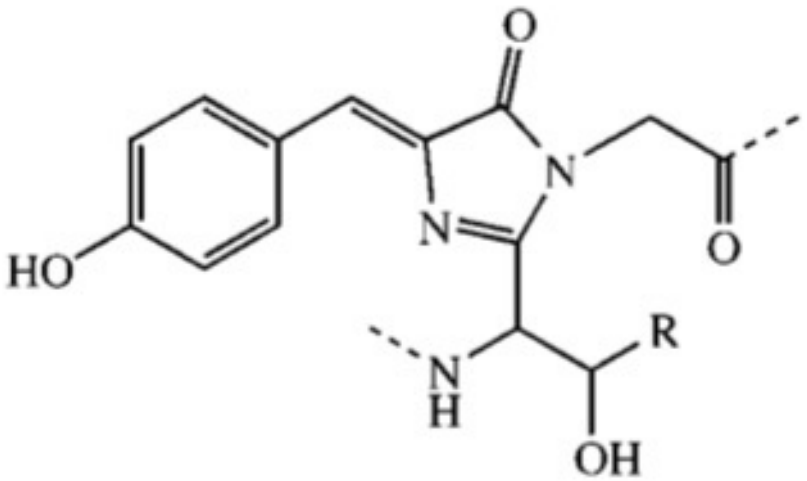
- Small protein shift calculated with TDDFT
- The protein shields the chromophore from the solvent thus preventing a significant shift
  (Nielsen et al. Biophys. J. 2005)
- The protein environment prevents radical formation
  (Lee et al, PNAS 2006)
- Or is TDDFT unable to feel the protein environment?

CAN WE DO BETTER?

GW+BSE?

Green Fluorescent Protein



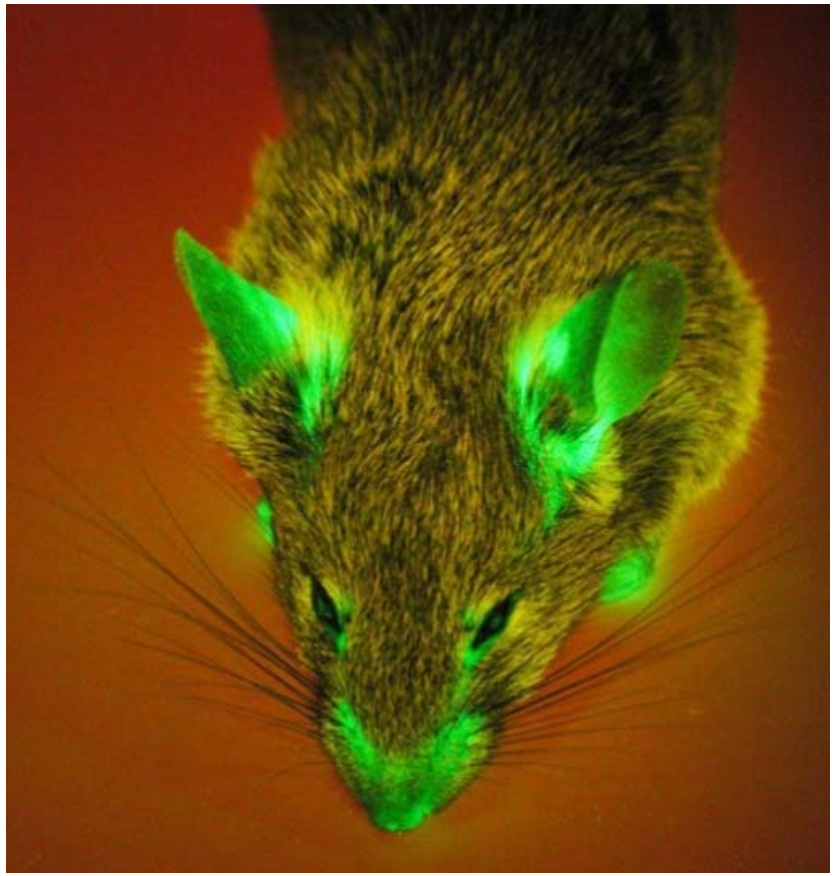


p-hydroxybenzylideneimidazolinone
(*p*-HBDI)

Nobel Prize in Chemistry 2008 awarded to O. Shimomura, M. Chalfie and R. Tsien "for the discovery and development of the green fluorescent protein, GFP" (D. Prasher)

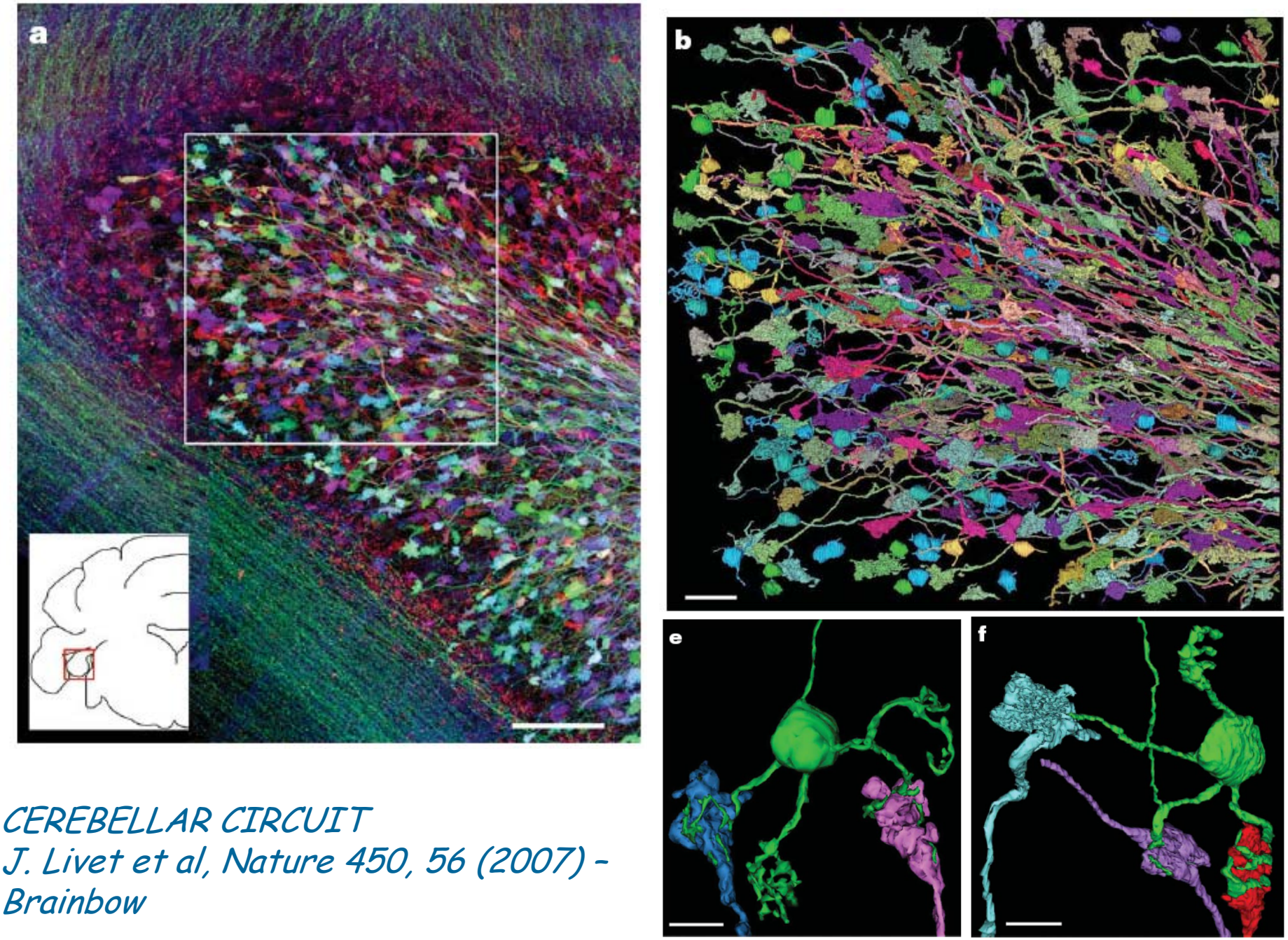
http://brainwindows.wordpress.com/2008/10/08/2008-nobel-prize-in-chemistry-to-gfp/

Green Fluorescent Protein
a molecular tag



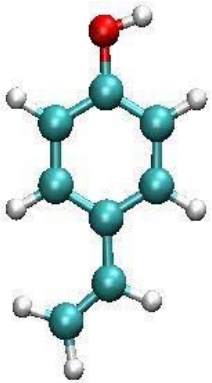
Aequorea Victoria

http://brainwindows.wordpress.com/2008/10/08/2008-nobel-prize-in-chemistry-to-gfp/

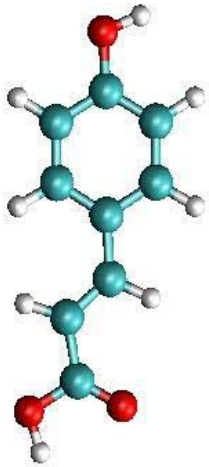


CEREBELLAR CIRCUIT
J. Livet et al, Nature 450, 56 (2007) – Brainbow

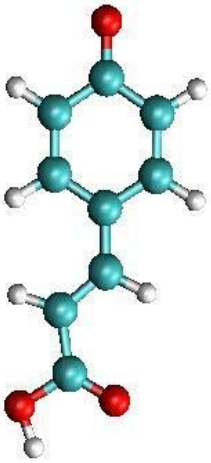
PYP



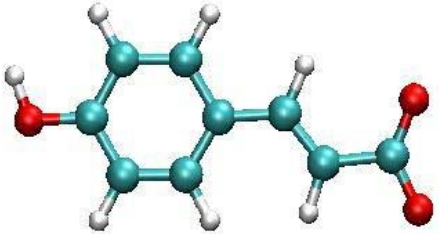
pVP (a)



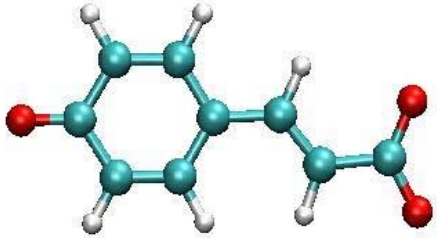
p*CA* (b)



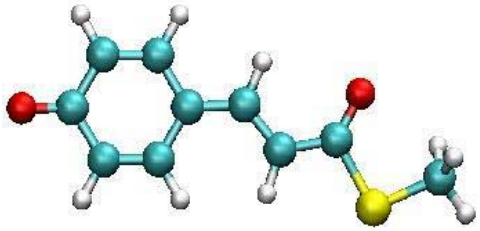
p*CA*$^{-\prime}$ (c)



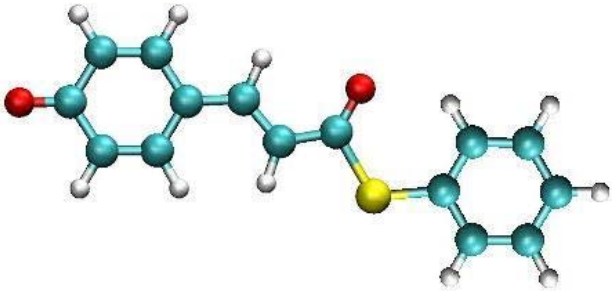
p*CA*$^{-\prime\prime}$ (d)



p*CA*$^{2-}$ (e)

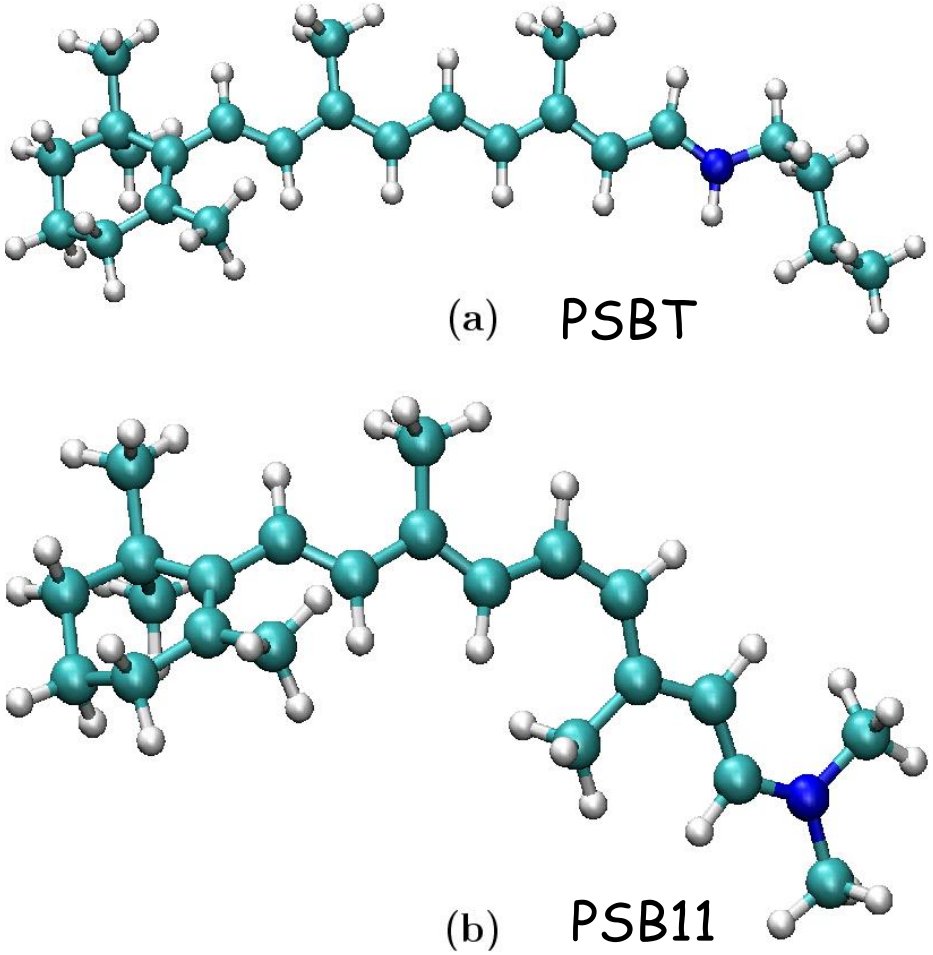


TMp*CA*$^{-}$ (f)



p*CT*$^{-}$ (g)

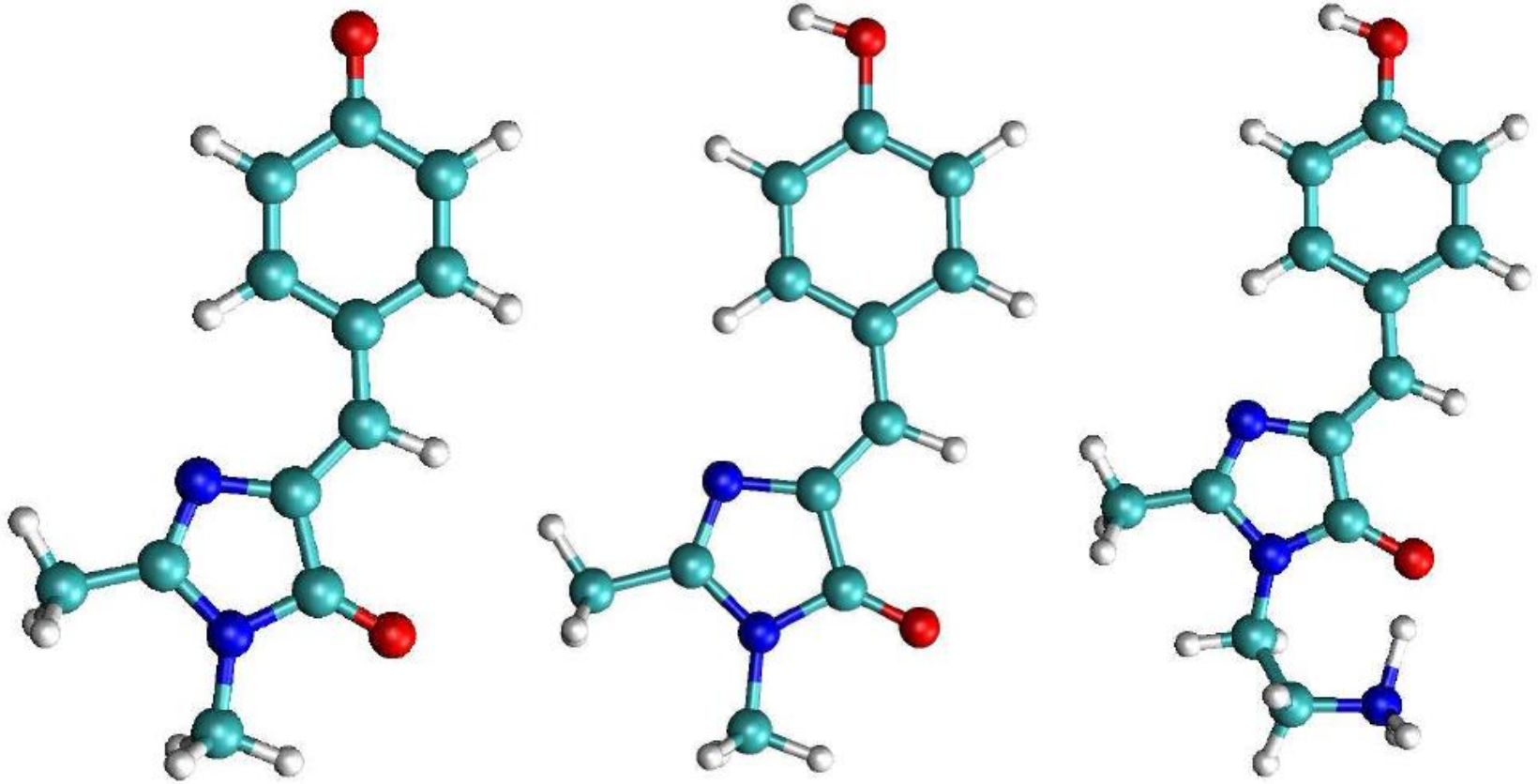
RHODOPSIN



(a) PSBT

(b) PSB11

GFP



p-HBDI^{-} (a) *p*-HBDI (b) *p*-HBDI^{+} (c)

Molecules vs extended systems

At variance from excitons in three-dimensional extended systems where the electron and hole are loosely bound, excitons (Coulomb correlated *e-h* pair created by a Photon) in chromophores are confined to a quasi-zero dimensional space, where the *e-e* and *e-h* exchange and correlation interactions and the excitonic binding energy are large.

Review: "Excitons in nanoscale systems", GD Scholes and G Rumbles, Nat. Mat. 5,683 (2006).

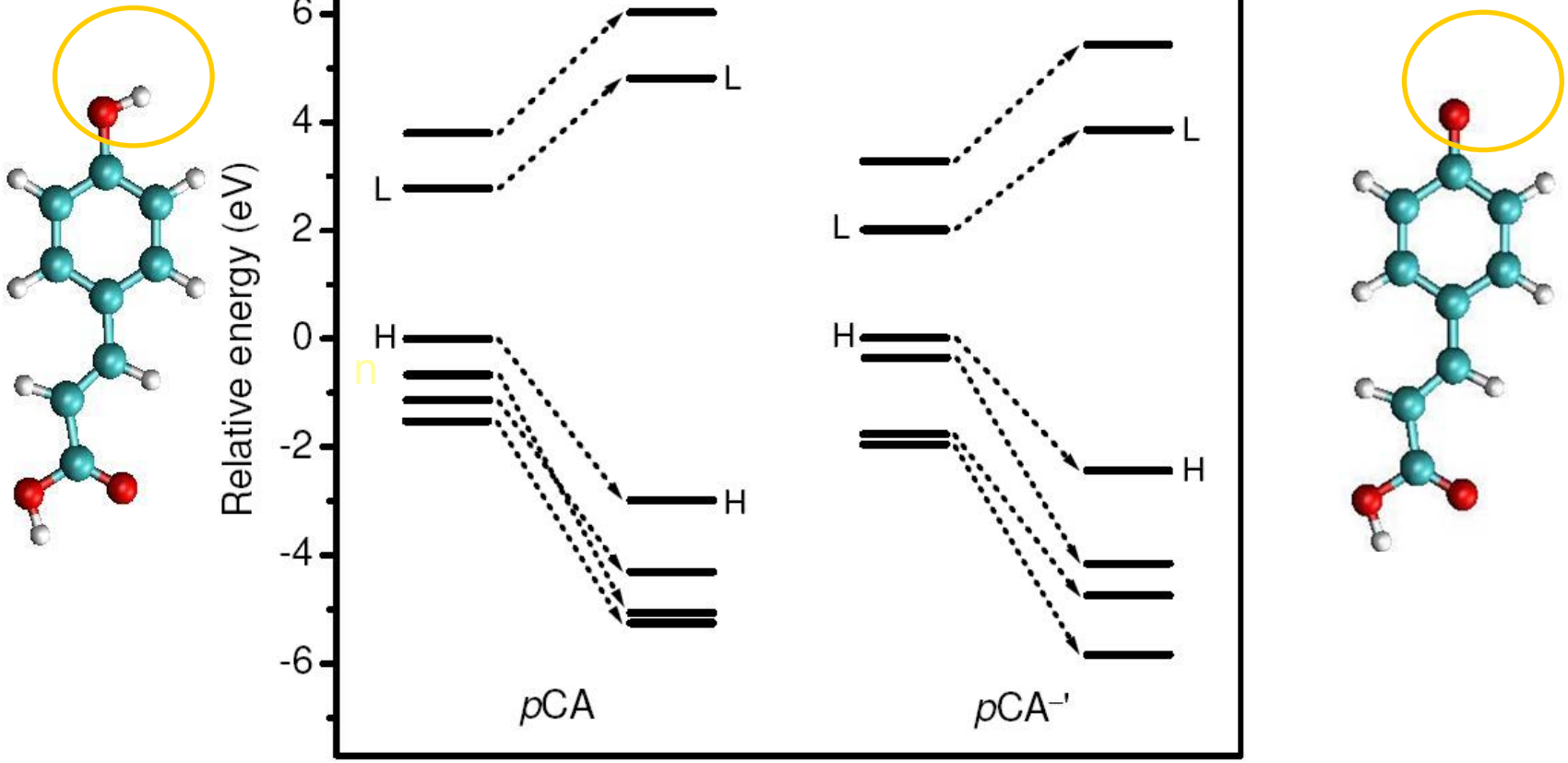
GW+BSE Calculation details

- Ground-state geometries DFT
- Vertical excited states GW+BSE
  - PBE xc-functional, Martins-Trouillier psp
  - Basis set: atom-centered Gaussian orbitals

    $\phi_{ijk}(r)=A_{ijk}\exp(-\alpha r^2)$ *s*, *p*, *d* and *s** symmetry
    4 decay constants (α) for *C*, N, *O* and S
    (0.2, 0.5, 1.25 and 3.2 a_0^{-2})
    3 decay constants for H (0.1, 0.4 and 1.5 a_0^{-2})
    Gaussian orbitals with
    40 Gaussians/atom for *C*, N, *O*, S and 30 for H

  - Full BSE (beyond Tamm-Dancoff approximation)
  - Dynamical screening effects included

DFT vs GW


DFT
GWA
DFT
GWA
Relative energy (eV)
8
6
4
2
0
-2
-4
-6
L
L
L
L
H
H
H
H
pCA
pCA⁻'

model	Exp. (eV)		GW+BSE (eV)
pVP	4.12	S_1	4.17
	4.75	S_2	4.60
pCA	4.06*,4.00^{sol}	S_1	3.94
	4.37*	S_2	4.20
$pCA^{-'}$	2.88	S_1	2.95
$pCA^{-''}$	4.36^{sol},4.39^{sol}	S_4	4.37
pCA^{2-}	3.69^{sol},3.72^{sol}	S_2	3.73
$TMpCA^{-}$	2.78^{prot}	S_1	2.80
pCT^{-}	2.70	S_1	2.75
$p\text{-}HBDI^{-}$	2.59,2.60^{prot}	S_1	2.67
P-HBDI	3.12^{prot}	S_1	3.17
$P\text{-}HBDI^{+}$	2.99	S_1	2.93
PSBT	2.00,2.03	S_1	2.09
	3.22	S_2	3.10
PSB11	2.03	S_1	2.04
	3.18	S_2	3.01

*OMpCA

Y. Ma, M. Rohlfing and C. Molteni, J. Chem. Theor. Comp. (2009)
ASAP article http://pubs.acs.org/doi/full/10.1021/ct900528h

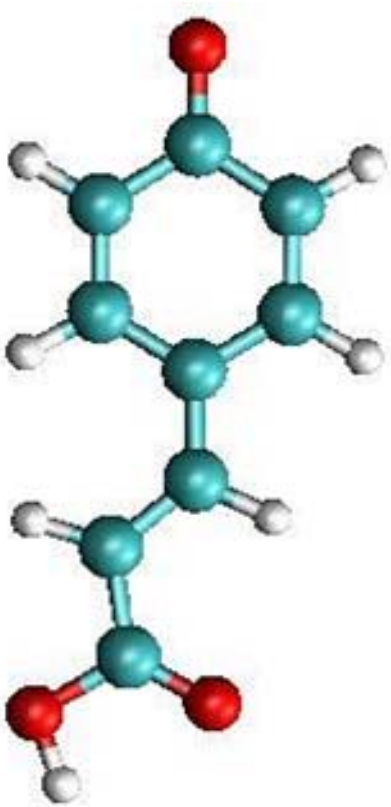
Table 1. Selected Excitation Energies (in eV) of PYP, GFP, and Retinal Chromophore Models Calculated by Many-Body Green's Function Theory and Their Comparison with Reference Experimental Data and a Selection of Theoretical Values[a]

model	experiment	MBGFT		other theory
*p*VP	4.12 (ref 4)	S_1	4.17	4.19 (ref 4)[b], 4.57 (ref 11)[c], 4.66 (ref 4)[d]
	4.75 (ref 4)	S_2	4.60	4.52 (ref 4)[b], 5.43 (ref 4)[d]
*p*CA	4.06 (ref 5)[e], 4.00 (ref 44)[f]	S_1	3.94	3.78 (ref 12)[g], 4.15 (ref 5)[h], 4.20 (ref 11)[c], 4.69 (ref 5)[d], 4.92 (ref 17)[i]
	4.37 (ref 5)[e]	S_2	4.20	4.58 (ref 5)[h], 4.95 (ref 5)[d], 5.14 (ref 17)[i], 5.22 (ref 12)[g]
$pCA^{-\prime}$	2.88 (refs 8, 10)	S_1	2.95	2.79 (ref 10)[j], 2.82 (ref 10)[k], 3.10 (ref 10)[l], 3.24 (ref 12)[g], 3.40 (ref 10)[m]
$pCA^{-\prime\prime}$	4.36 (ref 8)[f], 4.39 (ref 44)[f]	S_4	4.37	2.85 (ref 30)[k], 4.70 (ref 10)[m], 4.79 (ref 10)[l], 5.17 (ref 27)[j]
pCA^{2-}	3.69 (ref 8)[f], 3.72 (ref 44)[f]	S_2	3.73	
$TMpCA^-$	2.78 (ref 20)[n]	S_1	2.80	2.58 (ref 20)[o], 2.89 (ref 15)[p], 3.18 (ref 15)[q], 3.32 (ref 11)[c]
pCT^-	2.70 (ref 8)	S_1	2.75	2.71 (ref 30)[k], 3.01 (ref 12)[g], 3.05 (ref 11)[c]
$p\text{-HBDI}^-$	2.59 (ref 7)	S_1	2.67	2.52 (ref 30)[r], 2.66 (ref 18)[s,t], 2.92 (ref 25)[u], 3.12 (ref 18)[s,v], 2.93 (ref 25)[w], 3.04 (ref 25)[x]
p-HBDI	3.12 (ref 45)[n]	S_1	3.17	3.46 (ref 6)[y], 3.85 (ref 18)[s,t], 3.58 (ref 25)[u], 4.21 (ref 18)[s,v], 3.20 (ref 25)[w]
$p\text{-HBDI}^+$	2.99 (ref 6)	S_1	2.93	3.34 (ref 6)[y], 3.21 (ref 25)[u], 3.21 (ref 25)[w], 3.36 (ref 25)[x]
PSBT	2.00 (ref 9), 2.03 (ref 3)	S_1	2.09	2.03 (ref 30)[z], 2.07 (ref 22)[aa], 2.28 (ref 51)[ab], 2.32 (ref 19)[ac]
	3.22 (ref 9)	S_2	3.10	2.85 (ref 22)[aa], 3.12 (ref 51)[ab], 3.51 (ref 19)[ac]
PSB11	2.03 (ref 9)	S_1	2.04	2.07 (ref 23)[z], 2.05 (ref 22)[aa], 2.27 (ref 51)[ab], 2.32 (ref 19)[ac], 2.14 (ref 16)[ad]
	3.18 (ref 9)	S_2	3.01	2.84 (ref 22)[aa], 3.10 (ref 51)[ab], 3.49 (ref 19)[ac], 3.21 (ref 16)[ad]

[a] Details of the theoretical methodologies and basis sets used for the calculation of the excited-state energies//ground-state geometries for the theoretical results are given. [b] TDDFT(BP86)/def-TZVP//DFT(BP86)/def-TZVP. [c] TDDFT(B3LYP)/cc-PVTZ//DFT(B3LYP)/cc-PVTZ. [d] EOM-CCSD/6-31+G*//CCSD/cc-pVDZ. [e] OMpCA. [f] In solution. [g] TDDFT(BP86)/TZP//DFT(BP86)/PW. [h] TDDFT(B3LYP)/def-TZVP//DFT(B3LYP)/def-TZVP. [i] EOM-CCSD/6-31G*//DFT(B3LYP)/6-31G**. [j] MRMP2/CASSCF(14,12)/(p-type d-aug)-cc-pVDZ//DFT(PBE0)/cc-pVDZ. [k] aug-MCQDPT2/CASSCF(14,12)/(p-type d-aug)-cc-pVDZ//DFT(PBE0)/cc-pVDZ. [l] RI-CC2/aug-cc-pVTZ//DFT(PBE0)/aug-cc-pVDZ. [m] TDDFT(CAM-B3LYP)/aug-cc-pVTZ//DFT(PBE0)/aug-cc-pVDZ. [n] In the protein. [o] MS-CASPT2/CASSCF(12,10)/ANO//CASSCF(12,10)/ANO. [p] CC2/SV(P)//HF/6-31G*. [q] EOM-CCSD/6-31G*//HF/6-31G*. [r] aug-MCQDPT2/CASSCF(16,14)/(p-type d-aug)-cc-pVDZ//DFT(PBE0)/cc-pVDZ. [s] A 2,3-dimethyl model. [t] SA-2-CAS(2,2)PT2/6-31G//SA-2-CAS(2,2)/6-31G. [u] CASPT2/CASSCF(14,14)/cc-pVDZ//DFT(BLYP)/cc-pVTZ. [v] EOM-CCSD/6-31G//SA-2-CAS(2,2)/6-31G. [w] TDDFT(SAOP)/ET-pVQZ//DFT(BLYP)/cc-pVTZ. [x] Diffusion Quantum Monte Carlo/cc-pVDZ//DFT(BLYP)/cc-pVTZ. [y] TDDFT(B3LYP)/6-311++G*//MP3. [z] aug-MCQDPT2/CASSCF(12,12)/(p-type d-aug)-cc-pVDZ//DFT(PBE0)/cc-pVDZ. [aa] CASPT2/CASSCF(12,12)/ANO//MP2/6-31G**. [ab] TDDFT(B3LYP)/6-311++G(d)//DFT(B3LYP)/6-31G(d). [ac] CASPT2/CASSCF(12,12)/6-31G*//CASSCF(12,12)/6-31G*. [ad] CC2/def2-TZVPP//MP2/TZVP.

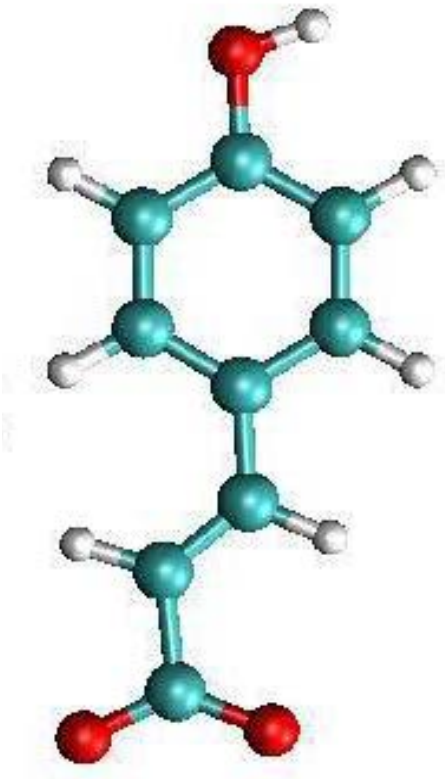
Y. Ma, M. Rohlfing and C. Molteni, J. Chem. Theor. Comp. (2009)
ASAP article http://pubs.acs.org/doi/full/10.1021/ct900528h

pCA$^{-\prime}$



in vacuo

pCA$^{-\prime\prime}$



in solution

RESONANT-ANTIRESONANT COUPLING

$R \simeq C$

$$\begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = \Omega \begin{pmatrix} A \\ B \end{pmatrix}$$

non-Hermitian Hamiltonian

$C \ll R$ $\qquad$ $C \simeq 0$

Tamm-Dancoff approximation: neglecting coupling term

DYNAMICAL SCREENING

$R = D + 2K^{R,x} + K^{R,d}$ $C = 2K^{C,x} + K^{C,d}$ $D : E_c^{QP} - E_v^{QP}$

$K^{R,x}\left(K^{C,x}\right)$: bare exchange term of the e–h interaction kernel for the resonant transition (coupling term)

$K^{R,d}\left(K^{C,d}\right)$: screened direct term of the e–h interaction kernel for the resonant transition (coupling term)

$$K^{R,d}_{vc,v'c'}(\Omega) = -\sum_l \int d\mathbf{x}d\mathbf{x}' \psi_c^*(\mathbf{x})\psi_{c'}(\mathbf{x})\psi_v(\mathbf{x}')\psi_{v'}^*(\mathbf{x}')$$

$$\times W_l(\mathbf{r},\mathbf{r}')\frac{\omega_l}{2}\left(\frac{1}{\omega_l - \left(\Omega - \left(E_{c'}^{QP} - E_{v'}^{QP}\right)\right)} + \frac{1}{\omega_l - \left(\Omega - \left(E_c^{QP} - E_v^{QP}\right)\right)}\right)$$

$\Omega - \left(E_{c'}^{QP} - E_{v'}^{QP}\right) \ll \omega_l$

$$K^{R,d}_{vc,v'c'}(static) = -\sum_l \int d\mathbf{x}d\mathbf{x}' \psi_c^*(\mathbf{x})\psi_{c'}(\mathbf{x})\psi_v(\mathbf{x}')\psi_{v'}^*(\mathbf{x}')W_l(\mathbf{r},\mathbf{r}',\omega=0)$$

otherwise

$$\delta\Omega = \sum_{vc,v'c'} A_{vc}^* \left[K^{R,d}_{vc,v'c'}(\Omega) - K^{R,d}_{vc,v'c'}(static)\right]A_{v'c'}$$

Effects of resonant-antiresonant coupling & dynamical screening

Model	State	GW+BSE	eV	
		TDA	Full BSE	
		Stat	Stat	Dyn
pCA	S_1 $\pi\rightarrow\pi^*$	4.25	4.06	3.94
	S_2 $\pi\rightarrow\pi^*$	4.46	4.33	4.20
TMpCA$^-$	S_1 $\pi\rightarrow\pi^*$	3.34	2.91	2.80
	S_2 $n\rightarrow\pi^*$	3.44	3.44	3.19
PSB11	S_1 $\pi\rightarrow\pi^*$	2.61	2.13	2.04
	S_2 $\pi\rightarrow\pi^*$	3.29	3.05	3.01

*OMpCA

___ predominantly HOMO-LUMO

Y.Ma, M. Rohlfing and C. Molteni, Phys. Rev. B (2009)

	v	c	E_c^{QP}-E_v^{QP}	$K^{R,d}$	$K^{C,d}$	$K^{R/C,x}$	R	C
TMpCA–	H-1 n	L π*	7.81	-4.23	-0.08	0.10	3.78	0.12
	H π	L π*	6.03	-4.53	-0.56	1.50	4.50	2.44
PSB11	H-1 π	L π*	5.62	-3.58	-0.34	0.97	3.98	1.60
	H π	L π*	4.50	-3.58	-0.45	1.19	3.30	1.93

TDA OK for n→π*

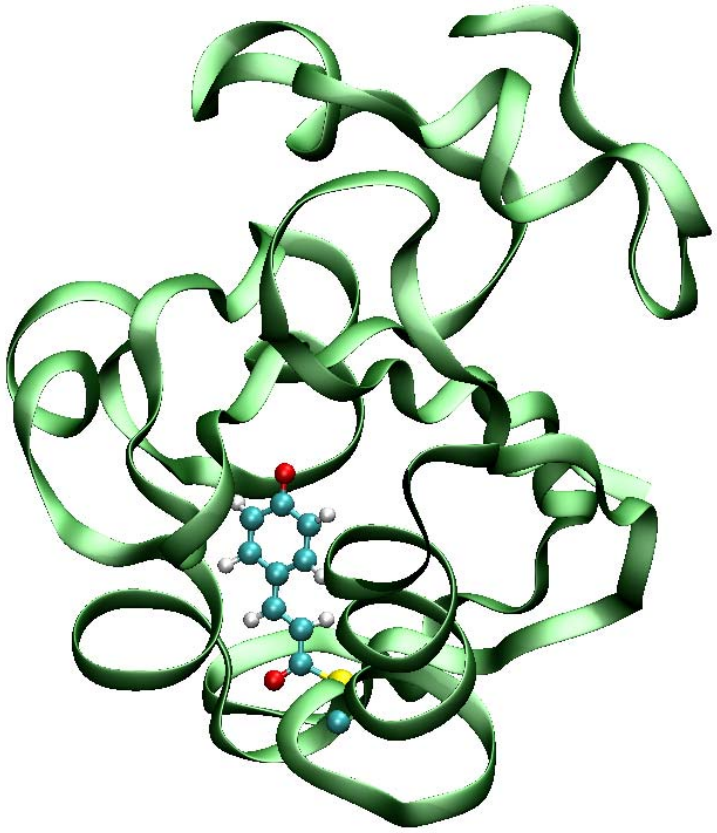
RARC important for π→π*of short polyene chains

v	c	v'	c'	A_{vc}	$A_{v'c'}$	$K^{R,d}_{vcv'c'}$	$\delta K^{R,d}_{vcv'c'}$
H-1	L	H-1	L	0.95	0.95	-4.23	-0.05
H-1	L	H-1	L+5	0.95	-0.27	0.80	0.21

TMpCA⁻ S_2 n→π*

Dynamical screening effects important for n→π* excitation

SPECTRAL SHIFTS



pCA in vacuo: 4.06

$TMpCA^-$
In vacuo: 2.80 eV
Protein structure/no field: 2.84 eV
Protein: 3.07 eV [exp 2.78 eV]

ΔE_{chem}=–1.26
ΔE_{prot} =+0.27 eV

ΔE= –0.99 eV

CONCLUSIONS

- GW+BSE for biological chromophores seems promising
- Alternative/complementary to TDDFT as in condensed matter?
- More tests necessary
- Forces in the excited states?

"How can the events in *space* and *time* which take place within the spatial boundary of a living organism be accounted for by physics and chemistry? …

…The obvious inability of present-day physics and chemistry to account for such events is no reason at all for doubting that they cannot be accounted for by those sciences."

Erwin Schroedinger, 'What is life?' (1943)

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CAN WE DO BETTER?

HOW?