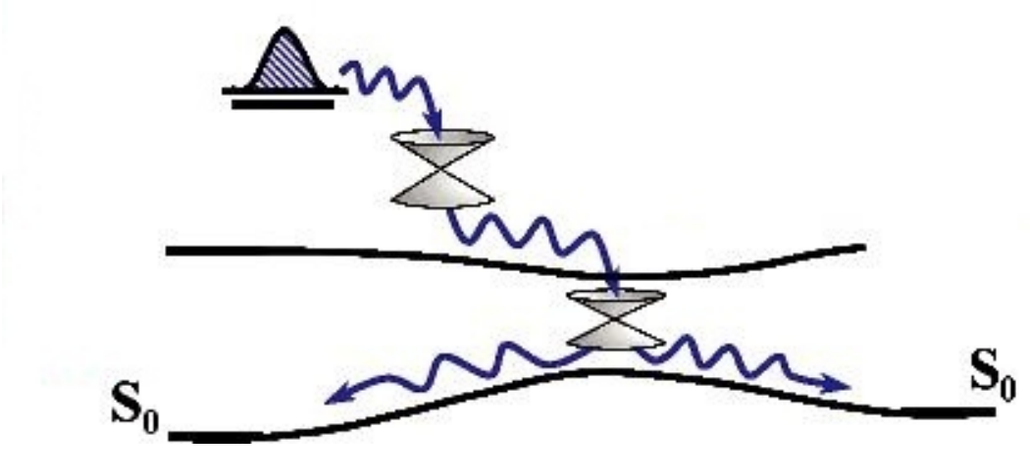
Theoretical Photochemistry WiSe 2016/17

Lecture 5



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http://www.theochem.uni-frankfurt.de/teaching/ $\longrightarrow$ Theoretical Photochemistry

Topics

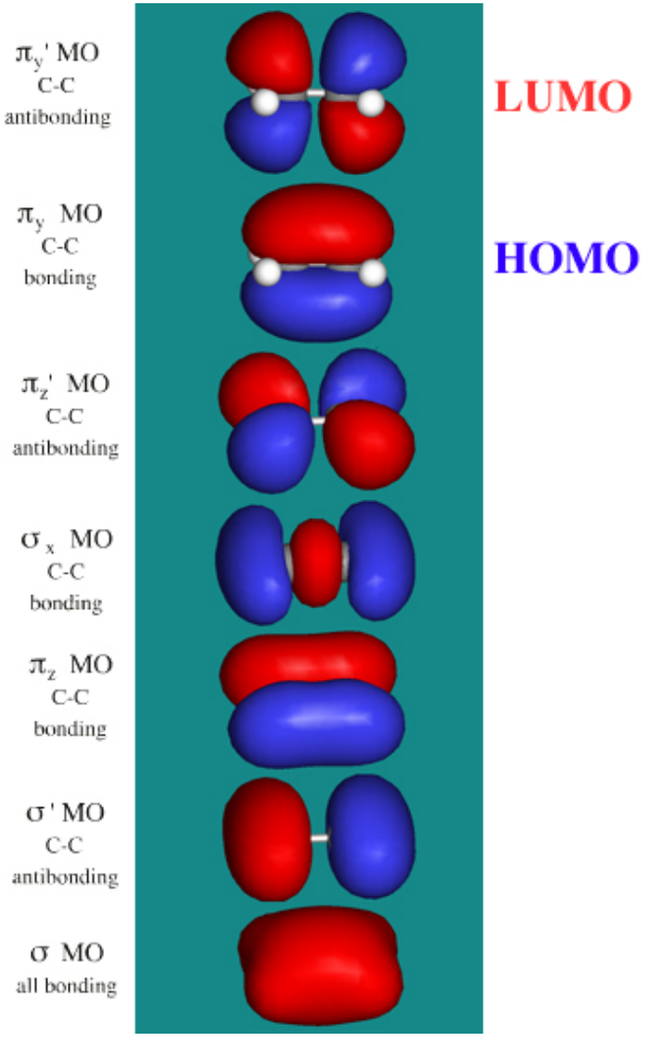
1. Photophysical Processes
3. Wavepackets
5. The Franck-Condon picture of electronic transitions
6. What do we measure experimentally?
2. The Born-Oppenheimer approximation
4. Beyond Born-Oppenheimer – non-adiabatic transitions
7. Conical intersections
8. Some electronic structure & dynamics aspects
9. Examples: Ethene, PYP
10. More on dynamics: trajectories or wavefunctions?
11. Wavefunction propagation techniques

12. **Trajectory surface hopping techniques**
13. **Non-linear optical spectroscopy: calculation of spectroscopic signals**
14. **Extended systems: Excitons, light-harvesting, etc.**
15. **Solvent/environmental effects**

Literature

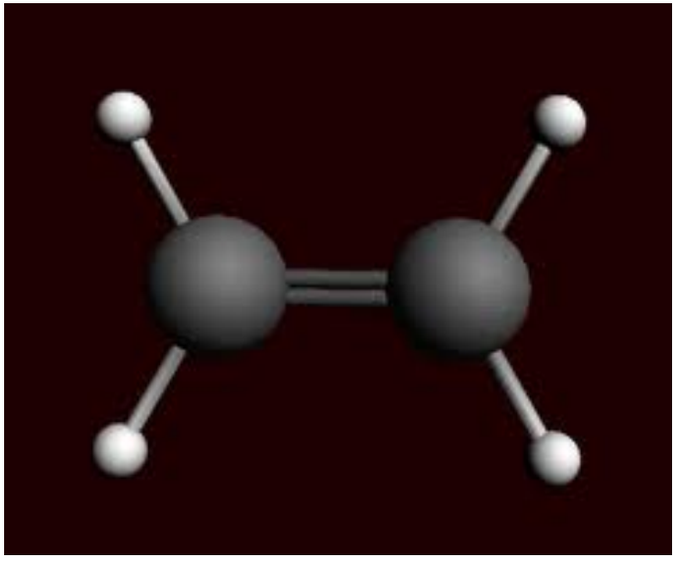
1. P. W. Atkins and R. Friedman, Molecular Quantum Mechanics, 5th Edition, Oxford University Press (2011).
2. D. Tannor, Introduction to Quantum Mechanics: A Time-Dependent Perspective, University Science Books (2006).
3. M. Klessinger, J. Michl, Excited States and Photochemistry of Organic Molecules, VCH-Wiley (1995).
4. I. N. Levine, Quantum Chemistry, 6th Edition, Pearson International Edition (2009).
5. F. Jensen, Introduction to Computational Chemistry, 2nd Edition, Wiley (2007).
6. C. J. Cramer, Essentials of Computational Chemistry – Theories and Models, 2nd Edition, Wiley (2004).

How does ethylene isomerize?



LUMO

HOMO



Singlet electronic states

Omitting σ framework, consider only "Hückel-type" π and π^* configurations:

$N(\pi^2)$ = **"Normal"**

$V(\pi\pi^*)$ = **"Valence"**

$Z(\pi^{*2})$ = **"Zwitterionic"**

experimental observation: V lifetime around 20-100 femtoseconds

Normal Modes

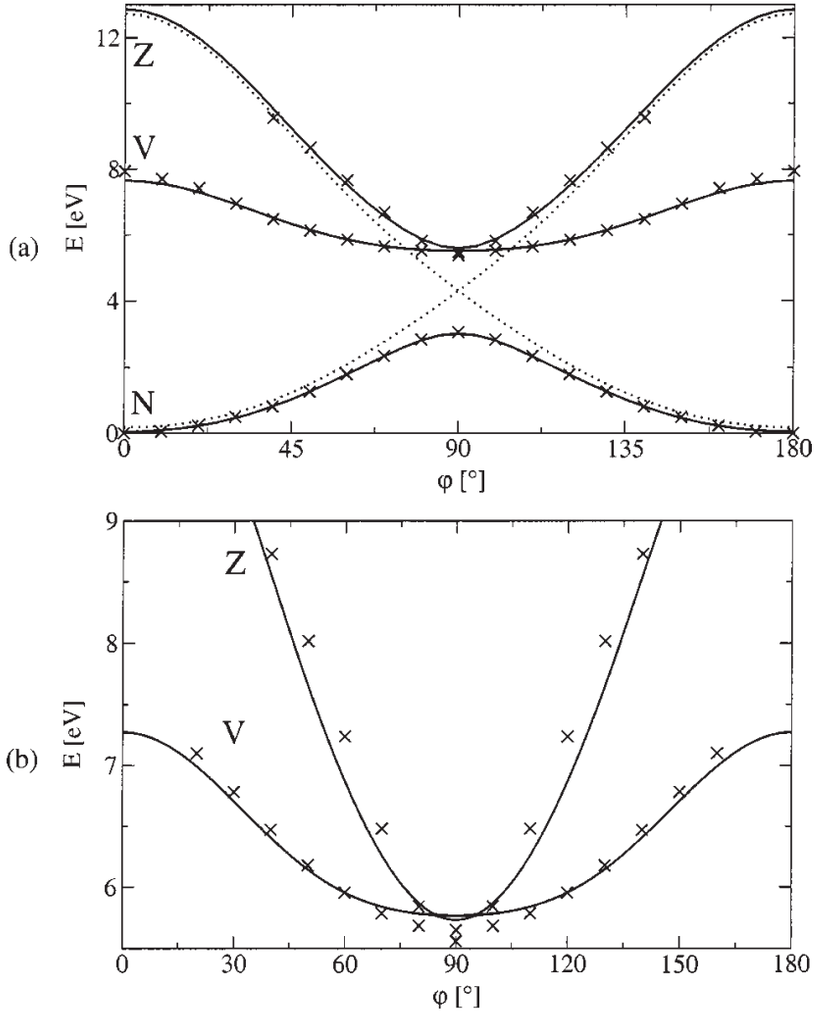
TABLE I. Ground-state harmonic frequencies of ethene (in cm^{-1}).

Symmetry	Mode	Frequency MP2 (this work)	CCSD(T)[a]	Expt.[b]	Description
a_g	ν_1	3196	3157	3156	C–H sym. stretch
	ν_2	1684	1672	1656	C–C stretch
	ν_3	1384	1369	1372	CH_2 sym. scissor
a_u	ν_4	1076	1044	1045	torsion
b_{1u}	ν_5	3178	3139	3130	C–H sym. stretch
	ν_6	1485	1479	1472	CH_2 antisym. scissor
b_{2g}	ν_7	960	942	960	CH_2 pyramid. (wagging)
b_{2u}	ν_8	3293	3246	3239	C–H antisym. stretch
	ν_9	828	823	844	CH_2 sym. rocking
b_{3g}	ν_{10}	3266	3219	3207	C–H antisym. stretch
	ν_{11}	1247	1242	1249	CH_2 antisym. rocking
b_{3u}	ν_{12}	984	967	968	CH_2 pyramid. (wagging)

[a]Reference 71.
[b]Reference 74.

NB. Symmetry determines vibronic coupling!

Zeroth-order picture: torsion only



large $V - N$ gap!

CASSCF/CASPT2 calc's

Krawczyk et al., JCP 119, 1397 (2003)

Torsion plus pyramidalization

- **There is a CoIn if the pyramidalization mode is added to the picture!**

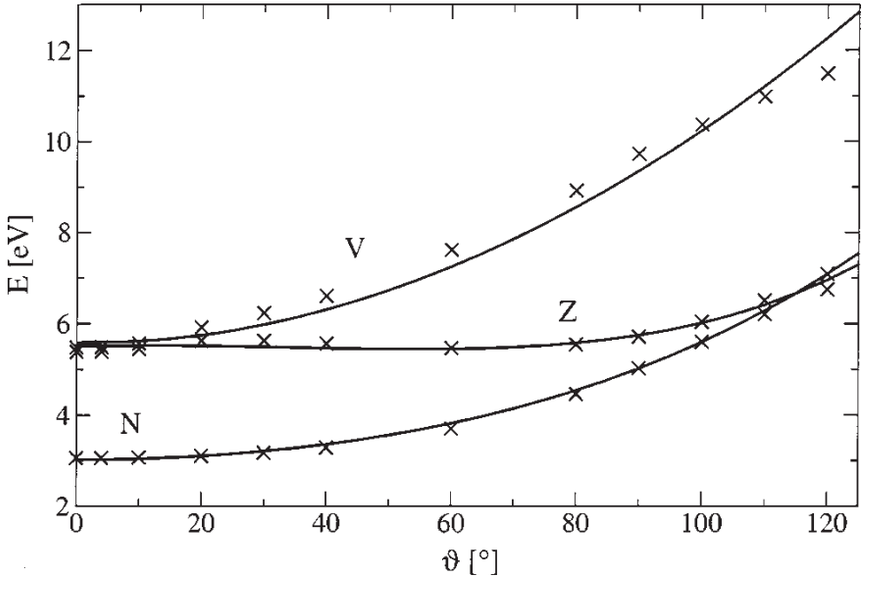


FIG. 3. Adiabatic PEs of the valence states of perpendicular ethene ($r = 1.332$ Å) as a function of the one-sided pyramidalization angle ϑ. Crosses: *ab initio* data; full lines: global analytic fit (see text).

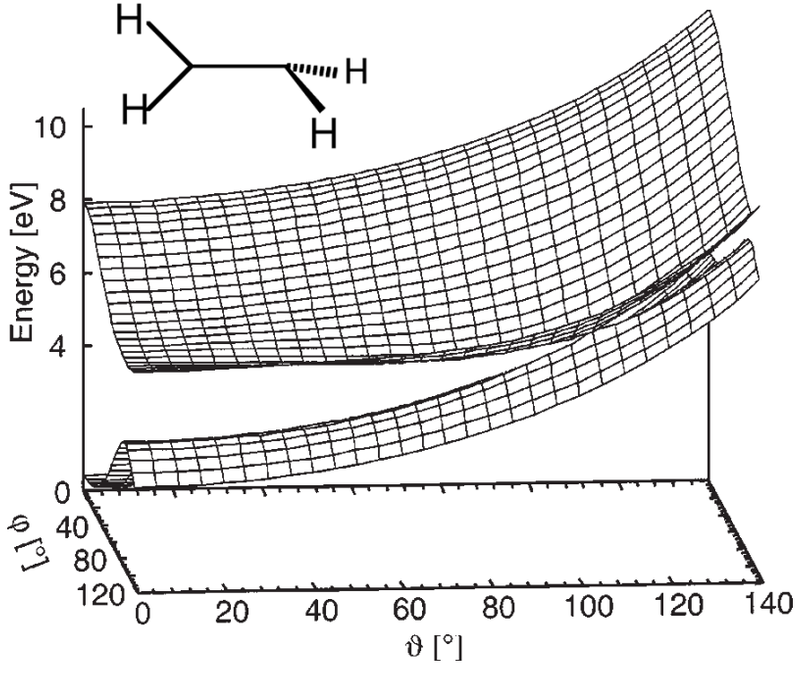
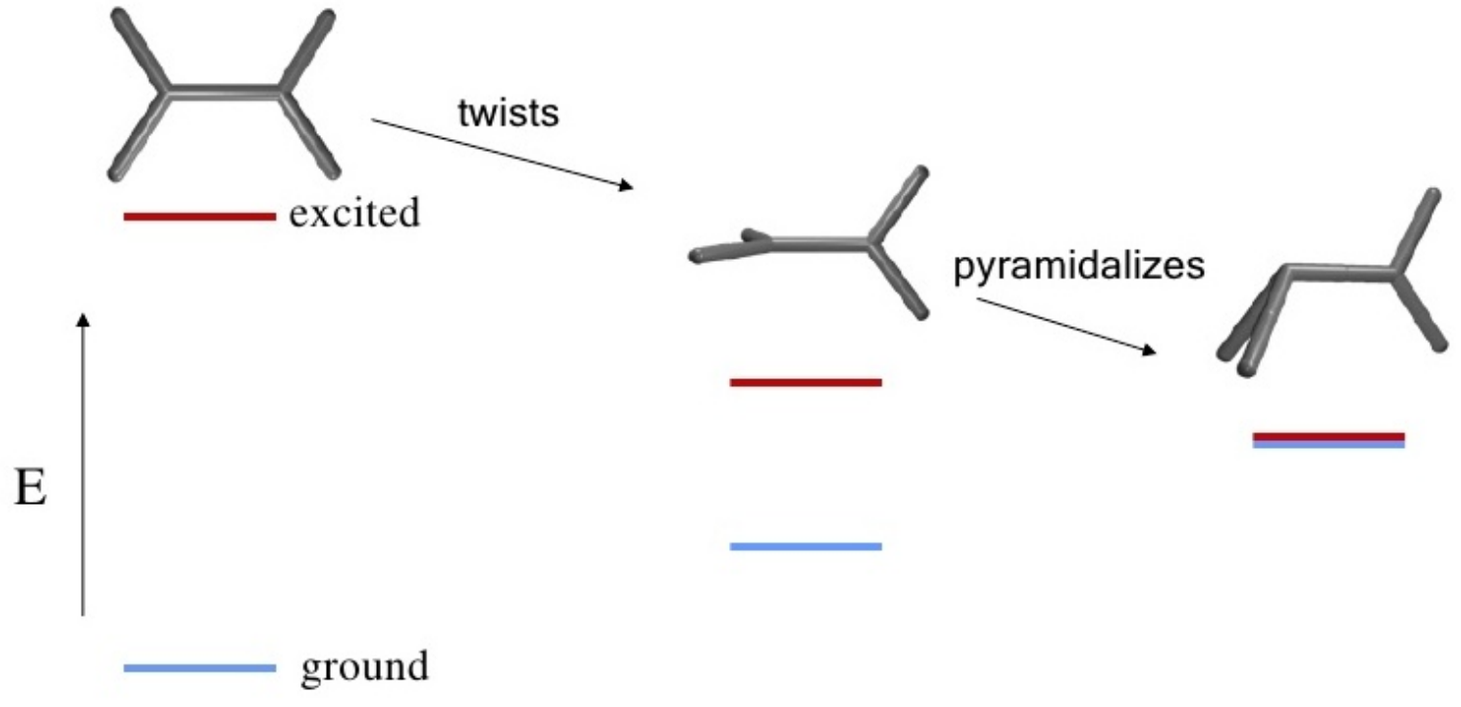


FIG. 9. Conical intersection of the S_0 and S_1 surfaces of ethene in φ,ϑ space. The other coordinates (r,α_s,α_a) have been relaxed to minimize the energy of the intersection.

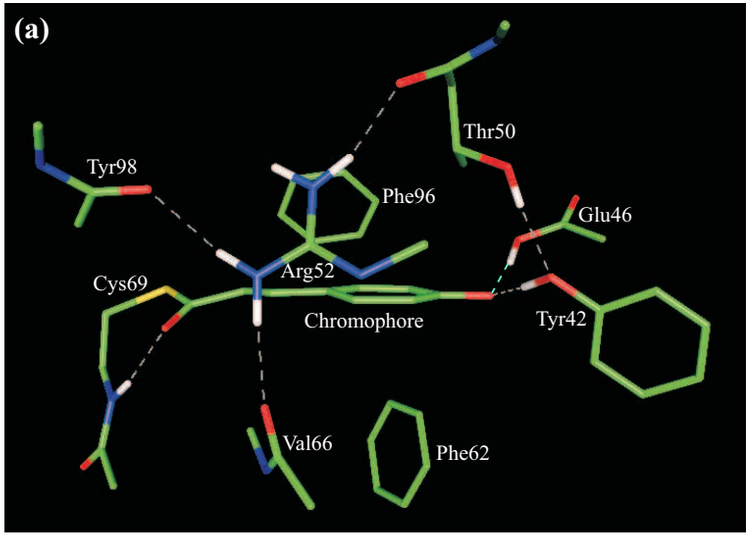
Krawczyk et al., JCP 119, 1397 (2003)

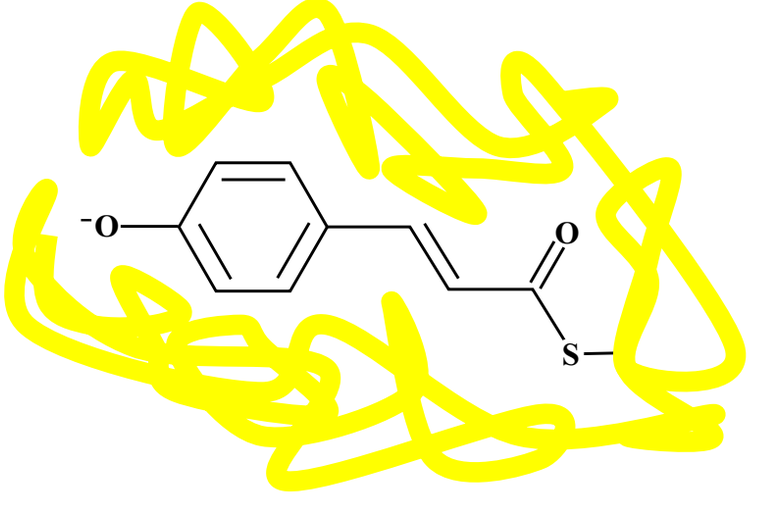
Torsion plus pyramidalization



- . . . and that's far from the whole story: complex CoIn seam
- ethylidene formation is another pathway (via H migration)

Photoactive Yellow Protein (PYP)

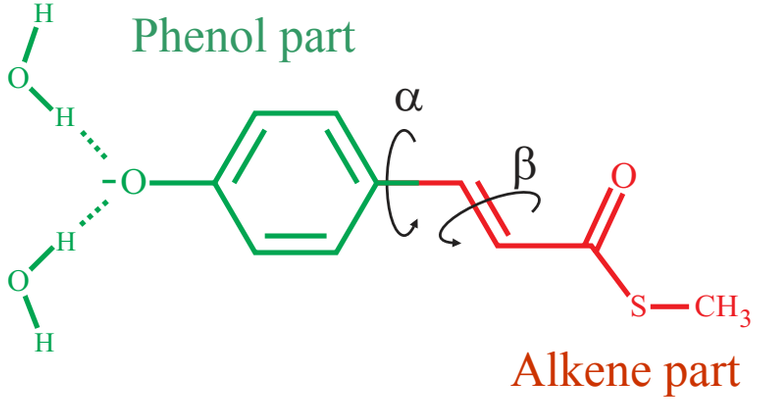


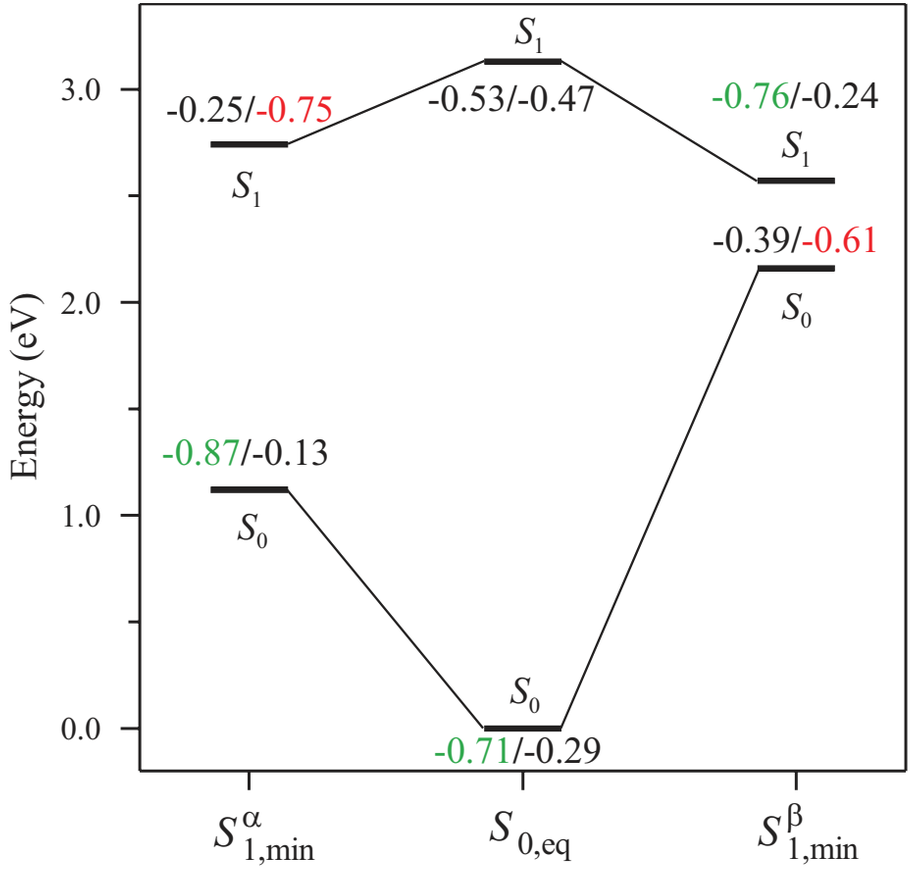


Gromov, Burghardt, Köppel, Cederbaum, JACS, 129, 6798 (2007)

- biological local environments (e.g., individual amino acids) can be of key importance
- how is the chromophore's quantum dynamics concerted with the environmental dynamics/fluctuations?

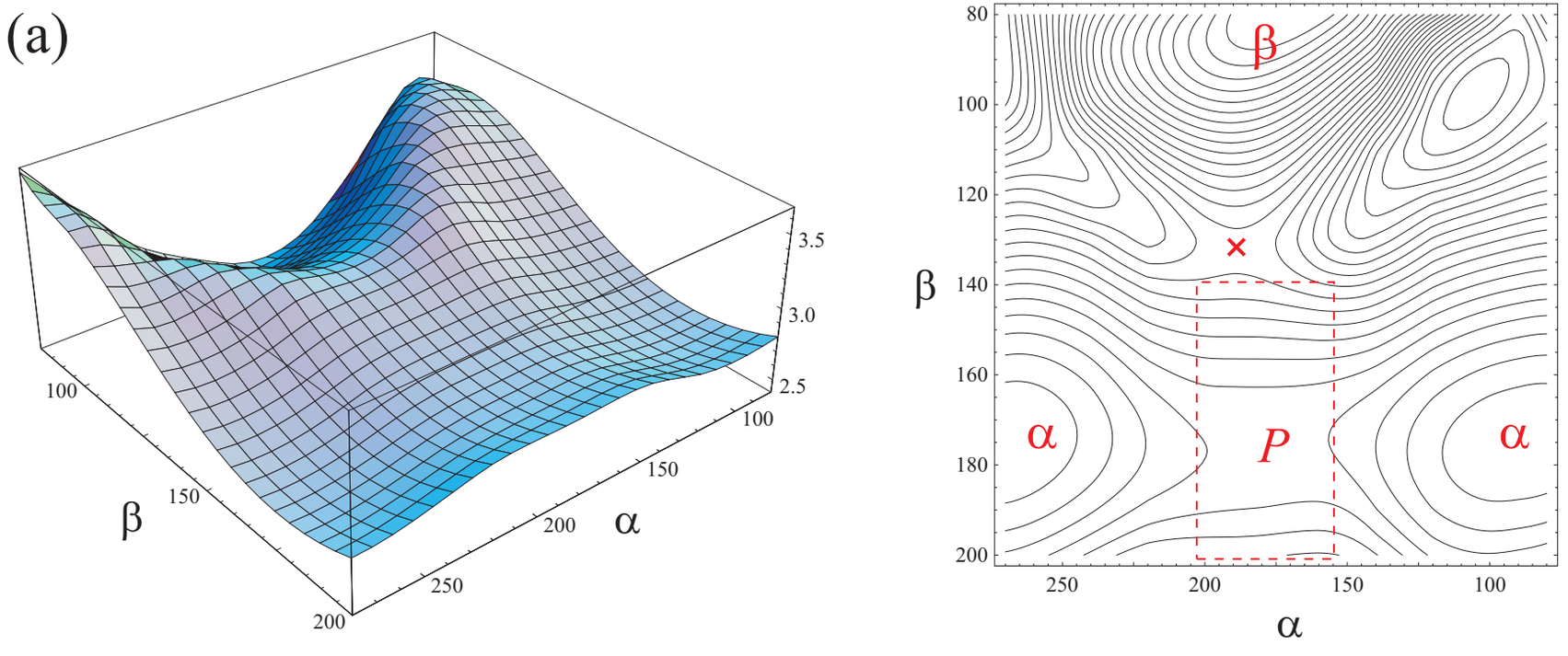
PYP chromophore: A complicated photoswitch!





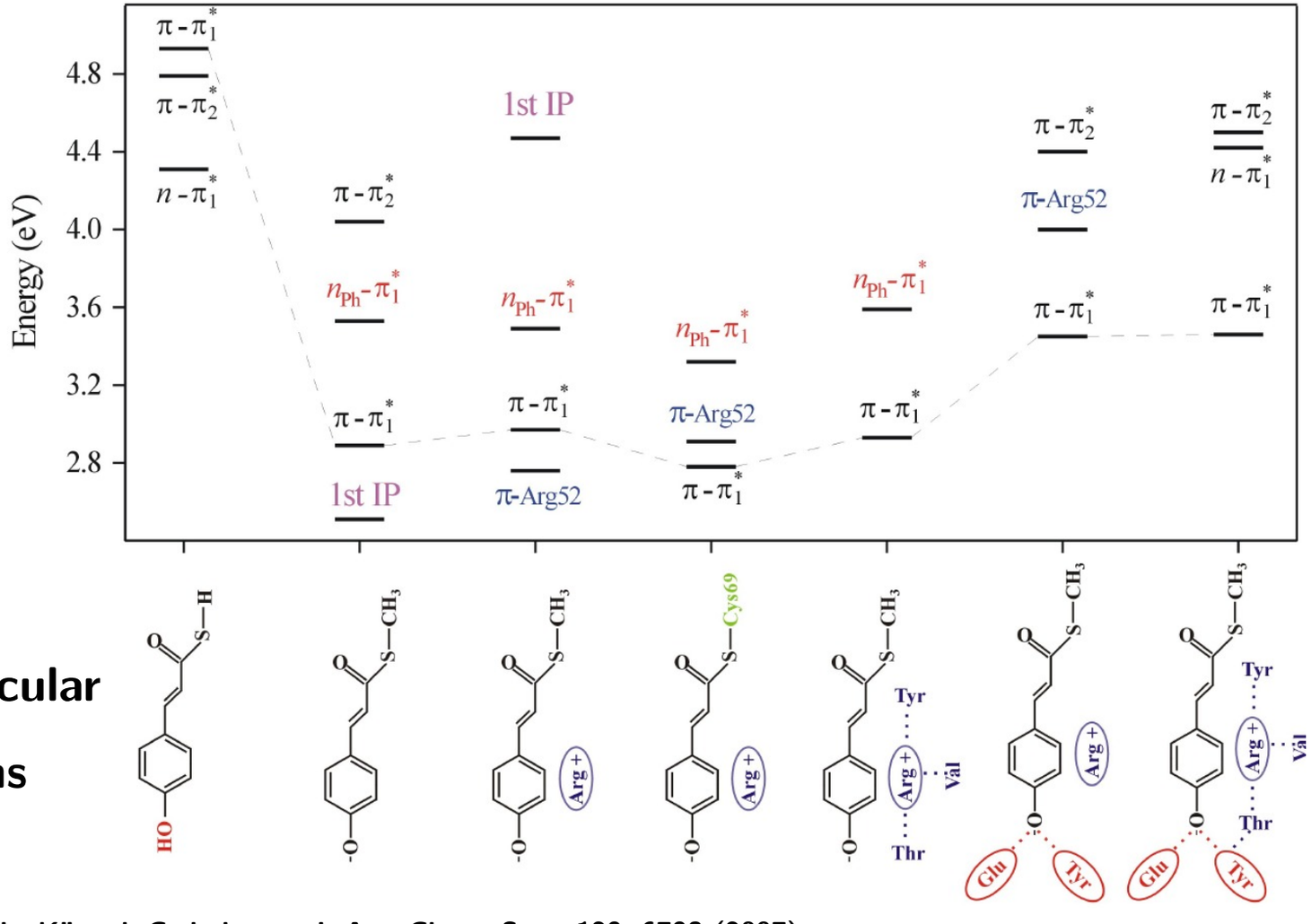
- **double and single-bond isomerisation**

PYP chromophore: S_1 potential surface



- **CC2 calculations**
- **barrier towards double-bond isomerisation but essentially no barrier to single-bond isomerisation**
- **another important mode: hydrogen-out-of-plane (HOOP) mode**

FC geometry: combined effect of local AA environment



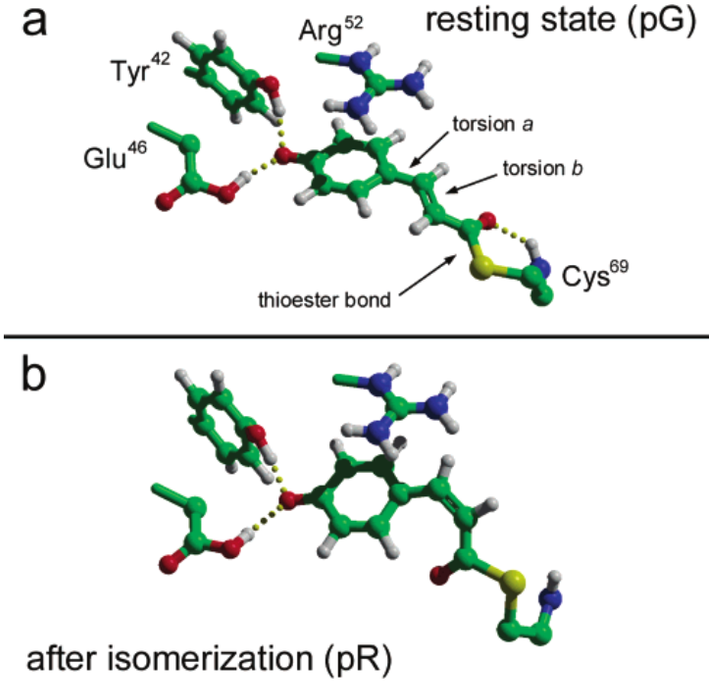
CC2

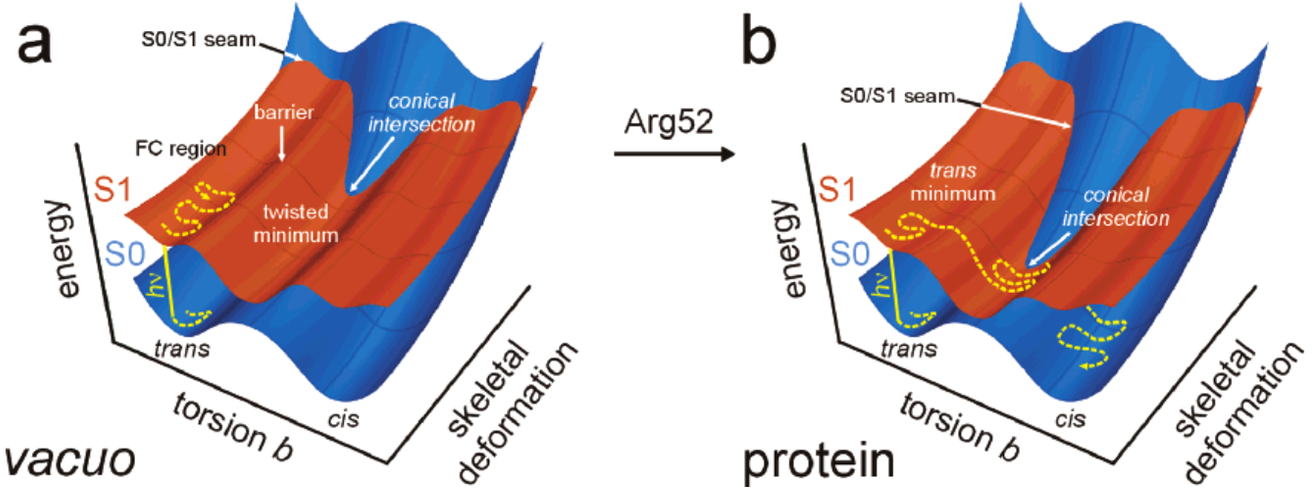
supermolecular

calculations

Gromov, Burghardt, Köppel, Cederbaum, J. Am. Chem. Soc., 129, 6798 (2007)

Influence of the protein environment on the CoIn (QM/MM)

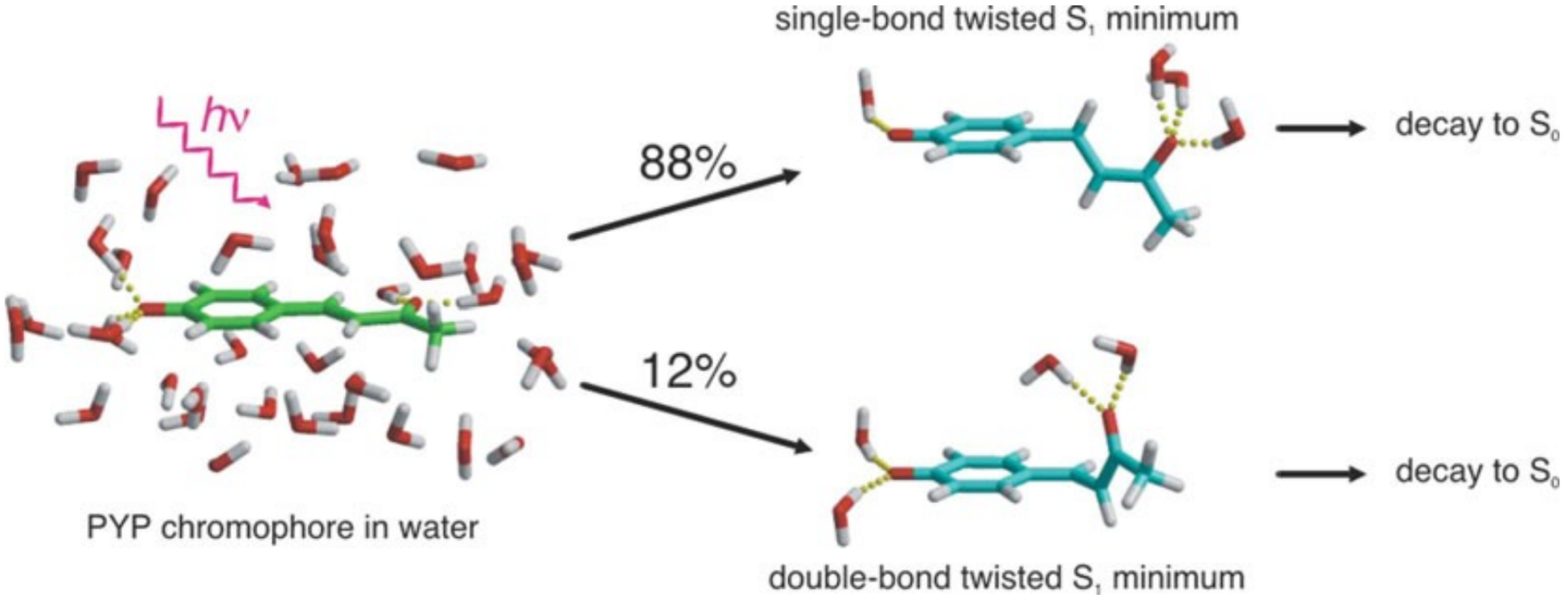




- **the CoIn can be significantly shifted due to the local protein environment**

Groenhof et al. JACS, 126, 4228 (2004)

Influence of water environment on the CoIn (QM/MM)



- **selective hydrogen bonding interactions determine the twisting pathway!**

Groenhof et al. Meth. Mol. Biol. (2013)