How do conical intersections control photostability and photochemical reactivity?

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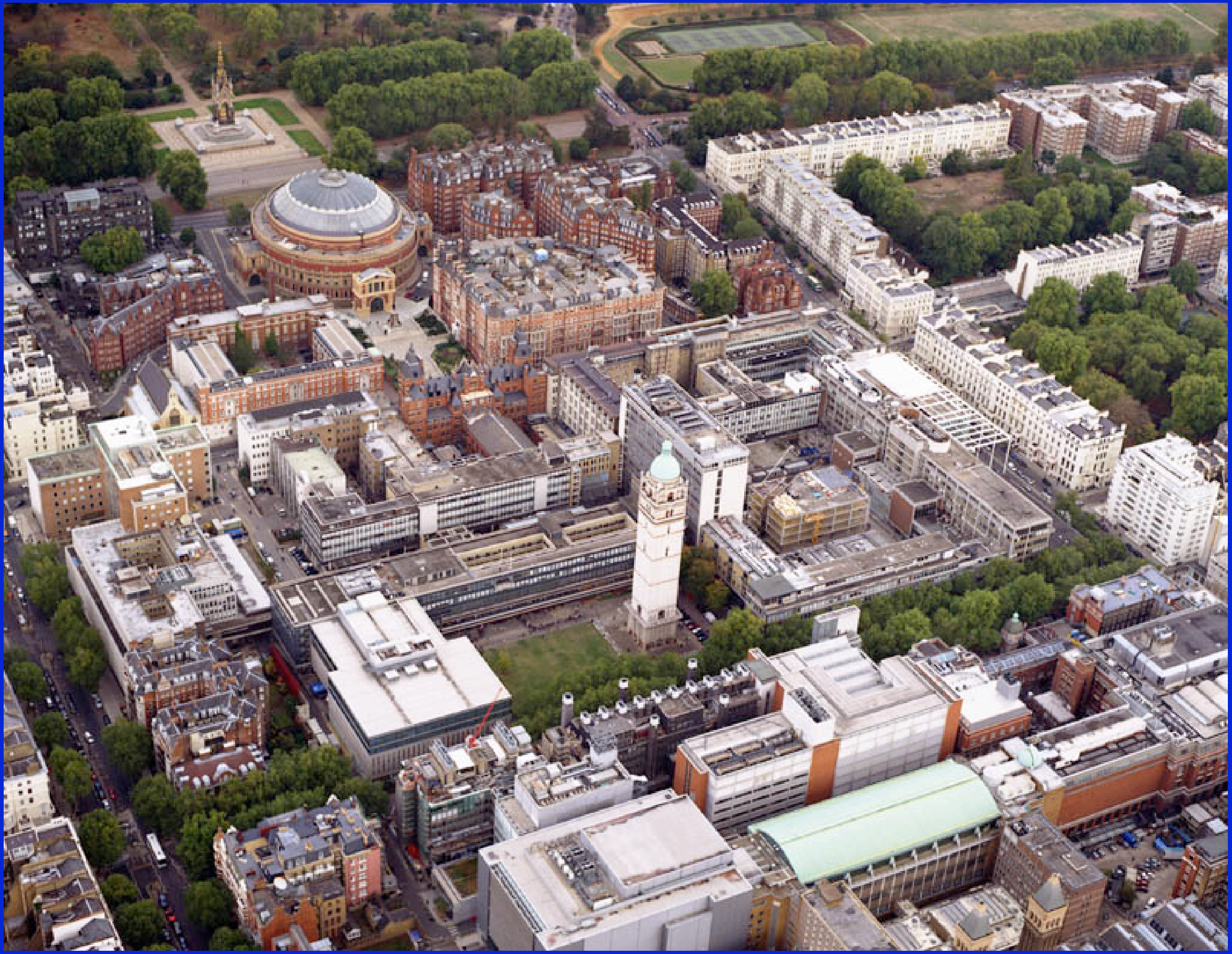


Contents

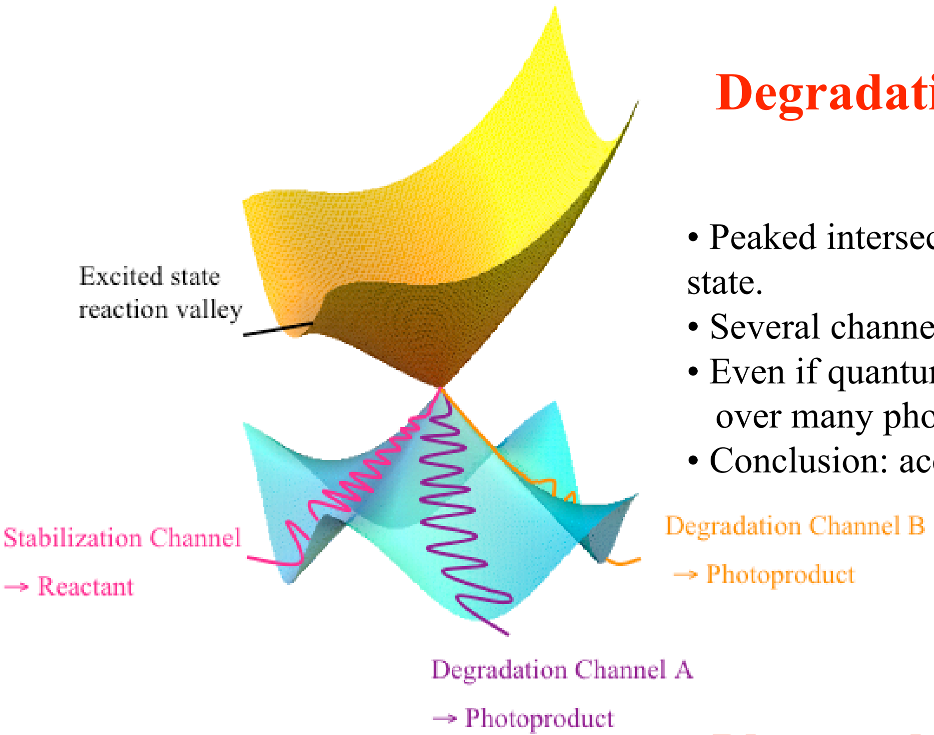
1. Important concepts in photochemistry: role of conical intersections and their topology in photostability and photoreactivity

    - Notion of peaked / sloped conical intersection
    - Importance of reaction path in non-adiabatic processes

2. Illustrations:

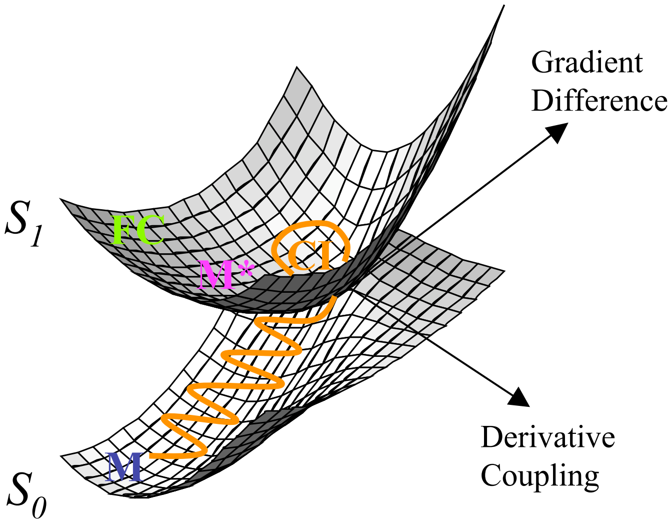
    - DHA/VHF photochromism
    - Photoactivation of the Photoactive Yellow Protein (PYP)

Degradation through a peaked intersection



- Peaked intersection: crossing point is lowest energy point on excited state.
- Several channels arising on ground state from the crossing.
- Even if quantum yields of photoproducts A and B are small, over many photocycles the reactant will degrade.
- Conclusion: accessible peaked intersection is bad for photostability.

Photostability through a sloped intersection



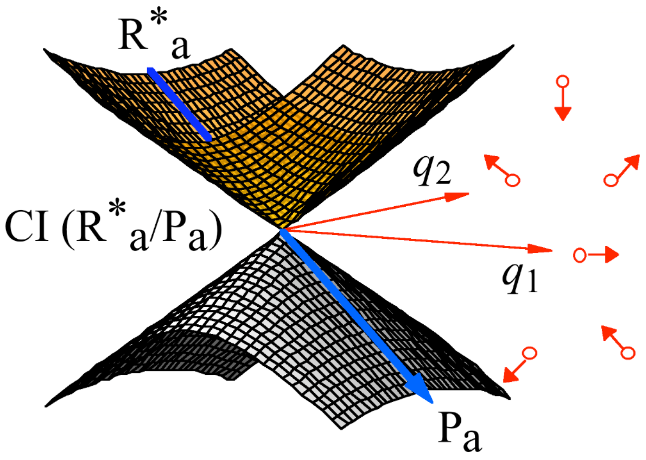
- Sloped intersection: lower energy excited state minimum than crossing point.
- Only one relaxation channel on ground state leading back to reactant.
- Vibrationally “hot” reactant M can be regenerated on an ultrafast timescale if the energy gap between M* and the CI is small.
- Model case for photostability.

3 essentials coordinates to understand non-adiabatic processes:

- non-adiabatic coupling vector: q_1
- gradient difference vector: q_2
- reaction path: Rx

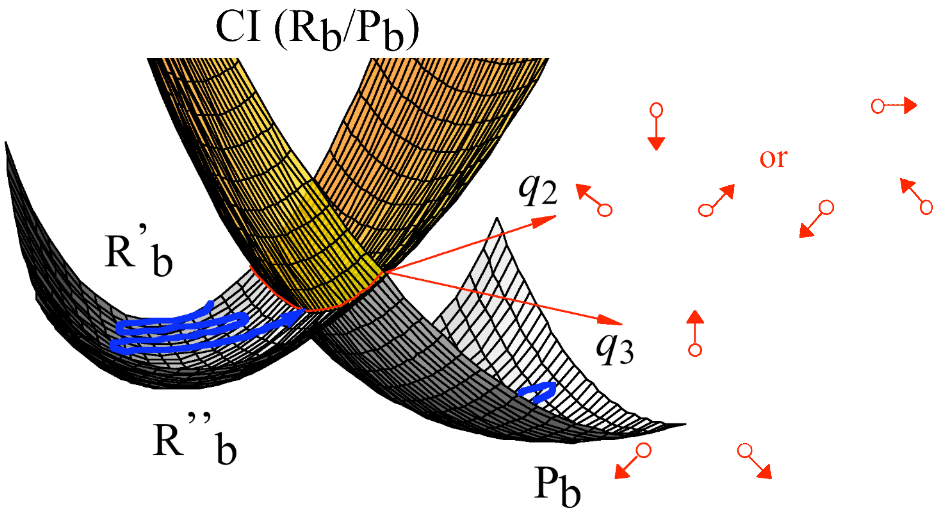
} branching space characterising the crossing

2 cases:



① Rx in the branching space:

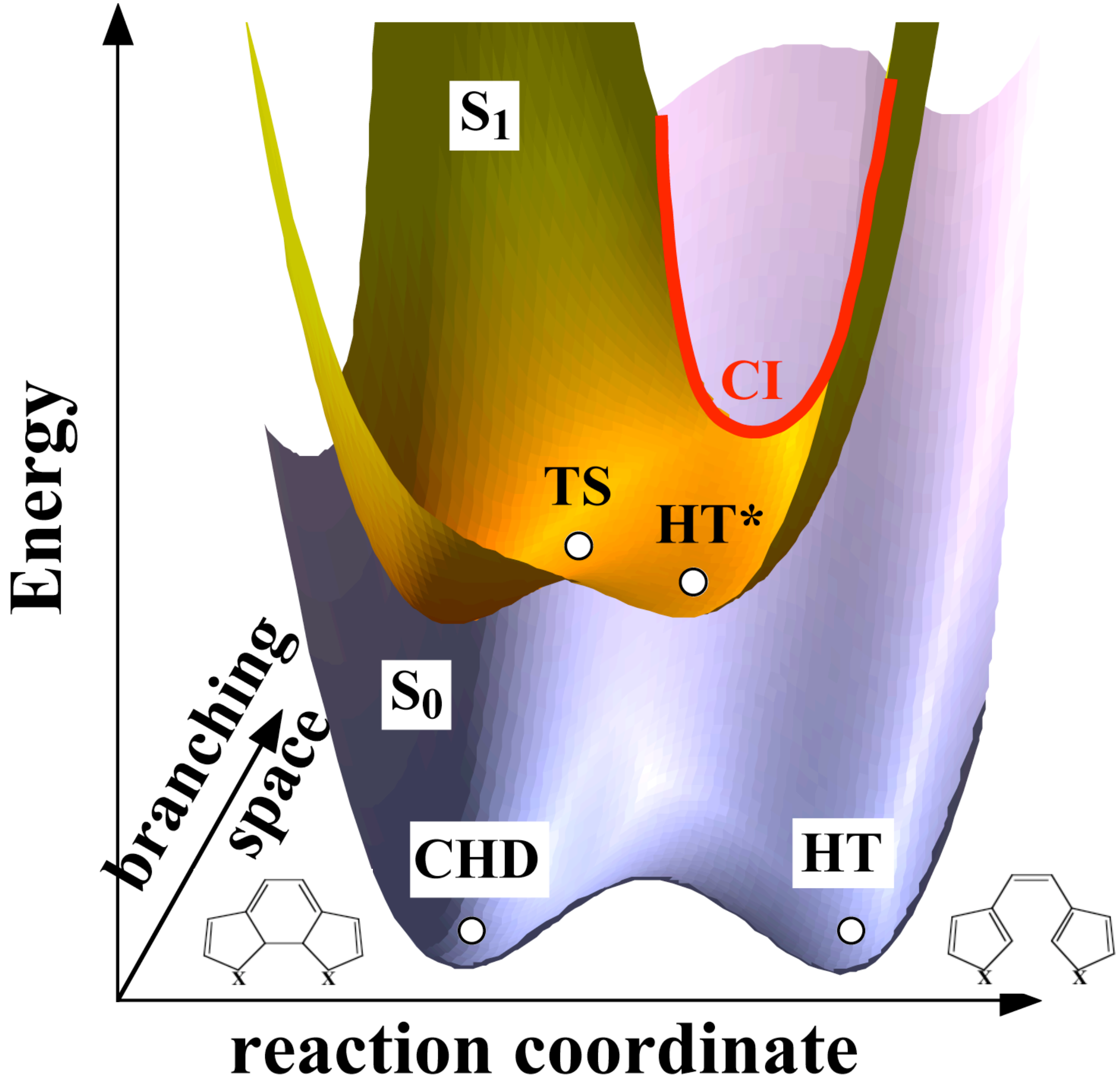
- Crossing appears as a double-cone.
- System relaxes in the upper cone and decays near the tip of the cone (hourglass-like funnel).
- Expect the system to decay near the lowest energy crossing point.



② Rx ⊥ to the branching space:

- Crossing appears as a seam of intersection.
- Vibrational motion orthogonal to the reaction path and included in the branching space takes the system to the seam where it can decay.
- Expect non-radiative decay to take place over a large section of the seam.

Delicate interplay between the Rx coordinate and the intersection seam

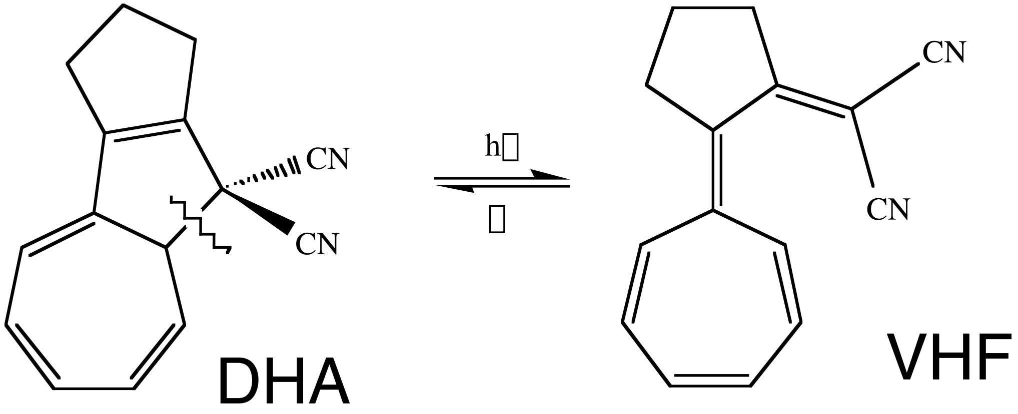


Diarylethenes photochromism

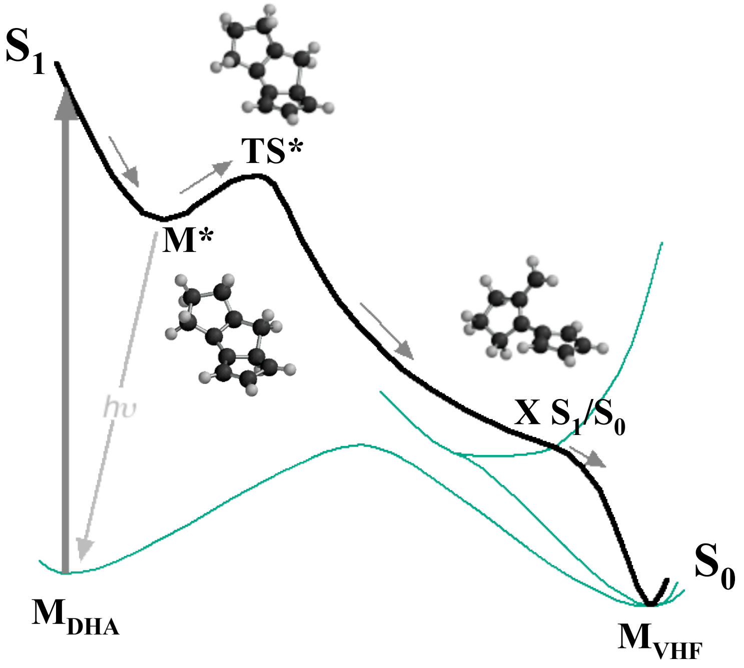
- Reaction path orthogonal to the branching space
- Mechanism controlled by motion orthogonal to the Rx
- Competition between adiabatic reaction, radiationless decay, and emission

M. Boggio-Pasqua et al., *J. Phys. Chem. A* 107, **2003**, 11139.

Dihydroazulene (DHA) / Vinylheptafulvene (VHF) Photochromism



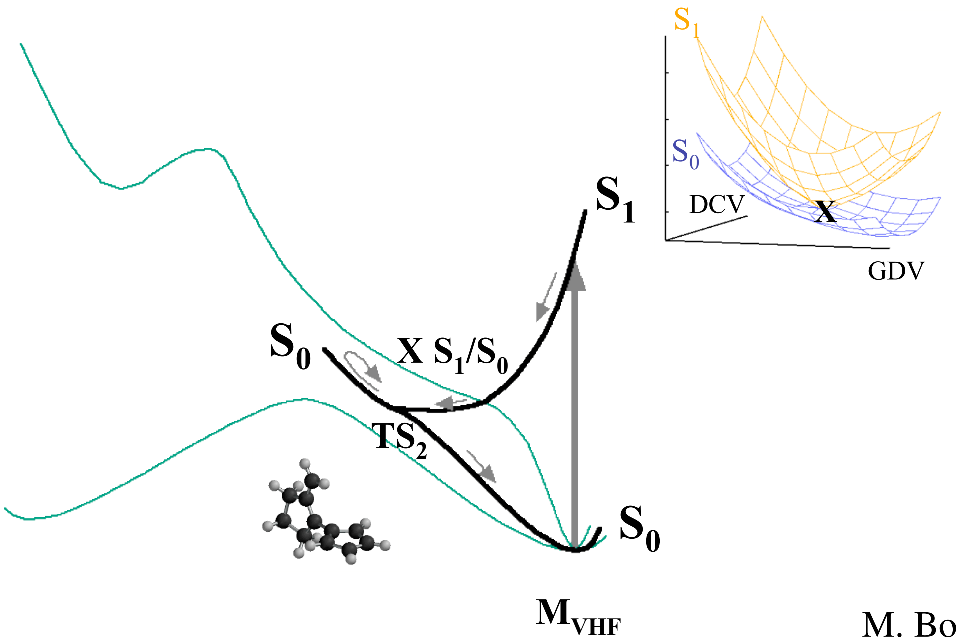
- fluorescence from DHA
- no fluorescence from VHF
- DHA -> VHF: photochemical reaction
- VHF -> DHA: thermal backward reaction
- $\Phi_{\text{DHA->VHF}} \approx 1$ at room temperature!!!



The S$_1$ DHA → VHF pathway

- Minimum **M*** accounts for fluorescence from DHA.
- Transition state **TS*** accounts for competition between photochemical ring-opening reaction and fluorescence.
- Conical intersection **X** accounts for ultrafast non-radiative decay.

The S$_1$ VHF → VHF pathway



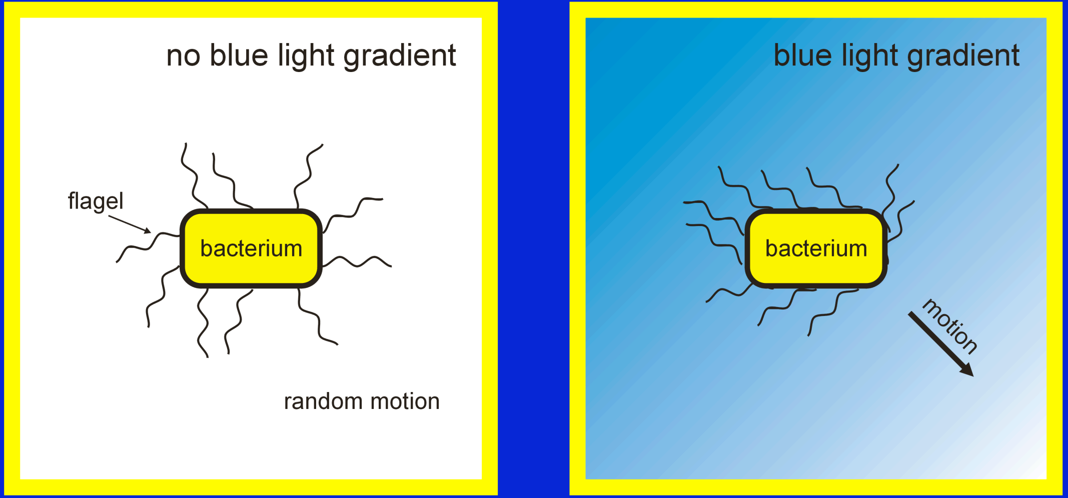
- Crossing **X** is lowest energy point on S$_1$ surface.
- No excited state minimum on VHF side: accounts for lack of fluorescence from VHF.
- No relaxation pathway leading back to DHA on S$_0$ after decay at crossing **X**: accounts for one-way photochromism.

M. Boggio-Pasqua et al., *J. Am. Chem. Soc.* 124, **2002**, 1456.

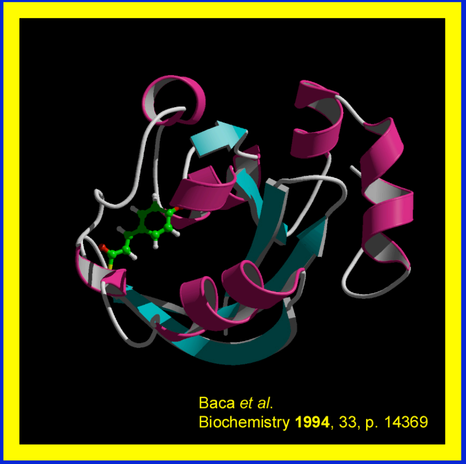
Photoactive Yellow Protein

Groningen: Gerrit Groenhof, Alan E. Mark et al;
Imperial/KCL Mathieu Bouxin-Cademartory, Michael Robb
Sienna: Massimo Olivucci

- negative photo-tactic response to blue light:

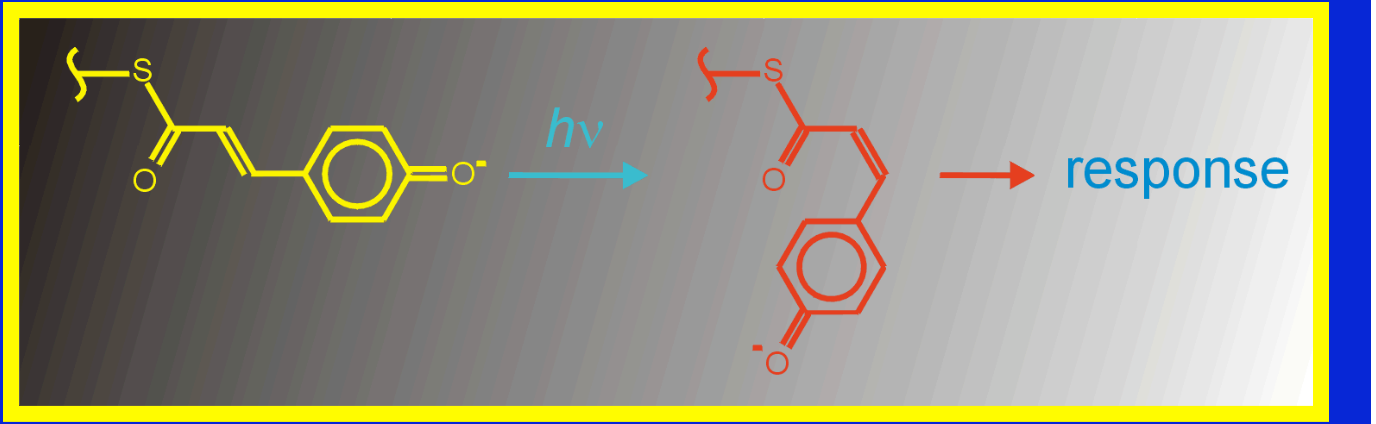


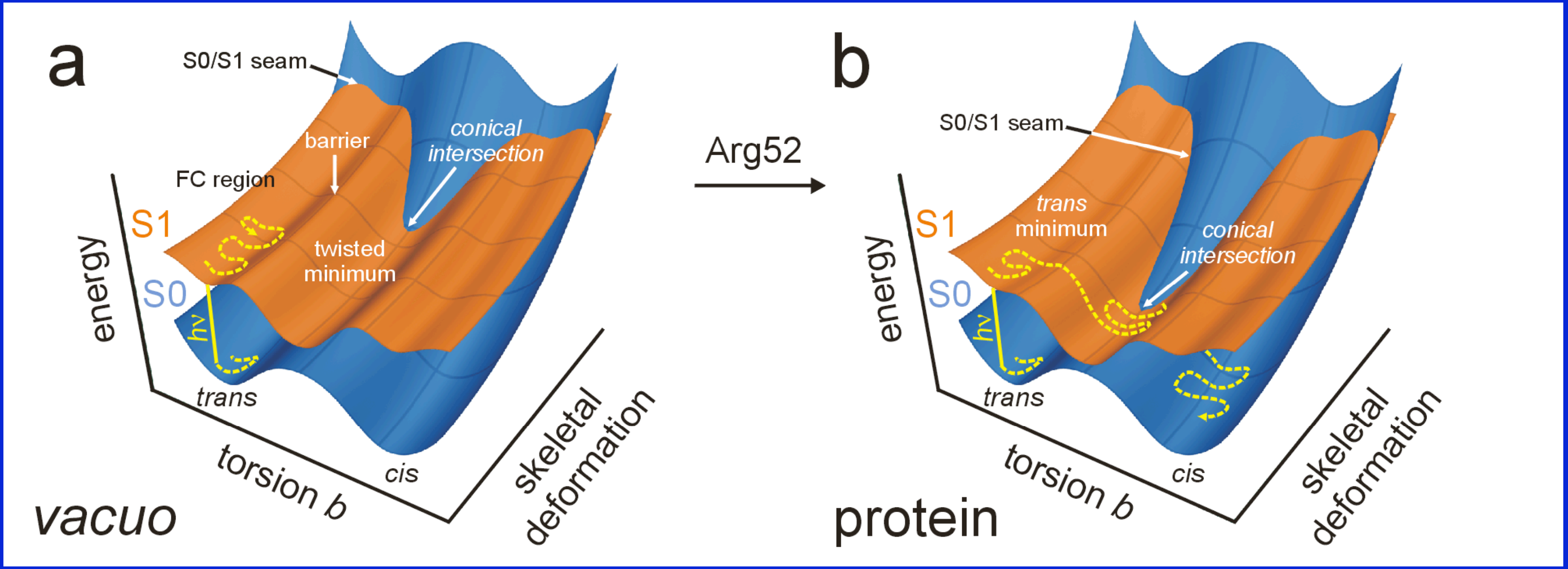
PYP protein:



Baca *et al.*
Biochemistry **1994**, 33, p. 14369

Trans-to-cis photoisomerization of the chromophore:





torsion *b* = *trans*-to-*cis* isomerization coordinate, skeletal deformation = stretching of the bonds

- **In vacuo, the S_1 barrier to photoisomerization is too high and the system is trapped in a *trans* minimum on S_1 before decaying back by fluorescence.**
- **In the protein, the S_1 barrier decreases and the system can relax to a global twisted minimum on S_1 before reaching the conical intersection and decaying to S_0.**
- **Non-radiative decay occurs along the crossing seam depending on vibration orthogonal to torsion *b* (torsion *b* is orthogonal to branching space).**
- **The electrostatic field of the protein stabilizes the excited state of the twisted chromophore moving the seam closer to the twisted S_1 minimum.**
- **Proton transfer becomes favorable in the *cis* isomer and induces the unfolding of the protein.**

G. Groenhof et al., *J. Am. Chem. Soc.* 126, **2004**, 4228.

Conceptual basis of Mechanistic Photochemistry

- Radiationless decay via conical intersections.

- CI topography (peaked *vs.* sloped) controls photophysical *vs.* photochemical outcome (DHA/VHF).

- Surface topology (eg. barrier separating FC region from CI?) controls competition between radiative and non-radiative processes (diarylethenes).

- Reaction path direction *vs.* funnel coordinates can control product formation (diarylethenes, PYP).