

Figure 1: A conical intersection plotted in the 2-dimensional branching space that is spanned by the gradient difference vector (g) and the derivative coupling vector (g). Motion away from the intersection in the $g-h$ plane lifts the degeneracy between the two electronic states S_1 and S_0 . The dotted line shows a path of a nuclear trajectory passing from one electronic state (S_1) to another (S_0) through the intersection funnel.

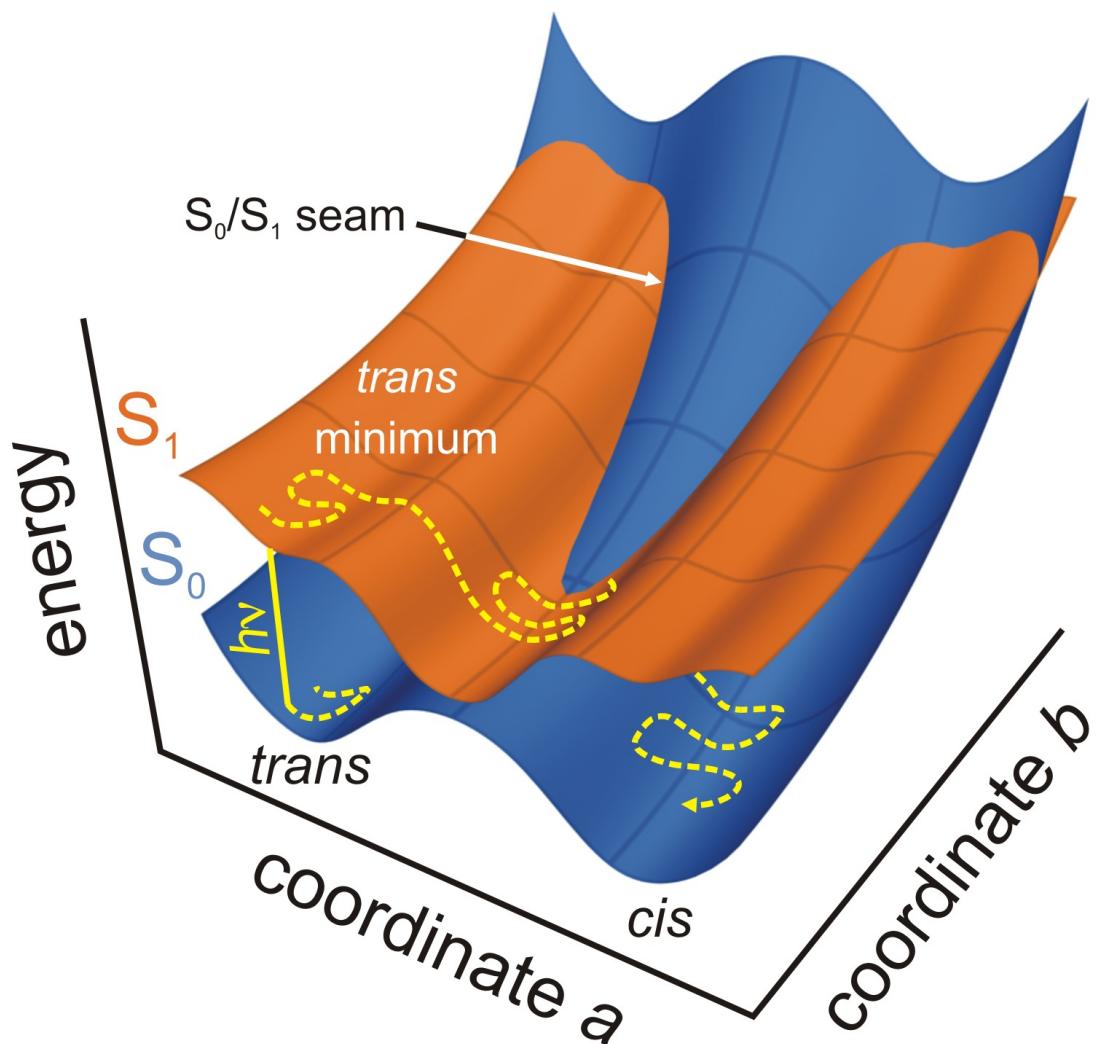


Figure 2: Schematic overview of a photochemical reaction pathway (dashed line). After photon absorption, evolution takes place on the excited state potential energy surface (red) until the system hits the S_1/S_0 intersection seam. At the intersection, a radiationless transition to the ground state occurs (blue). After the decay, the system continues evolving in the ground state.

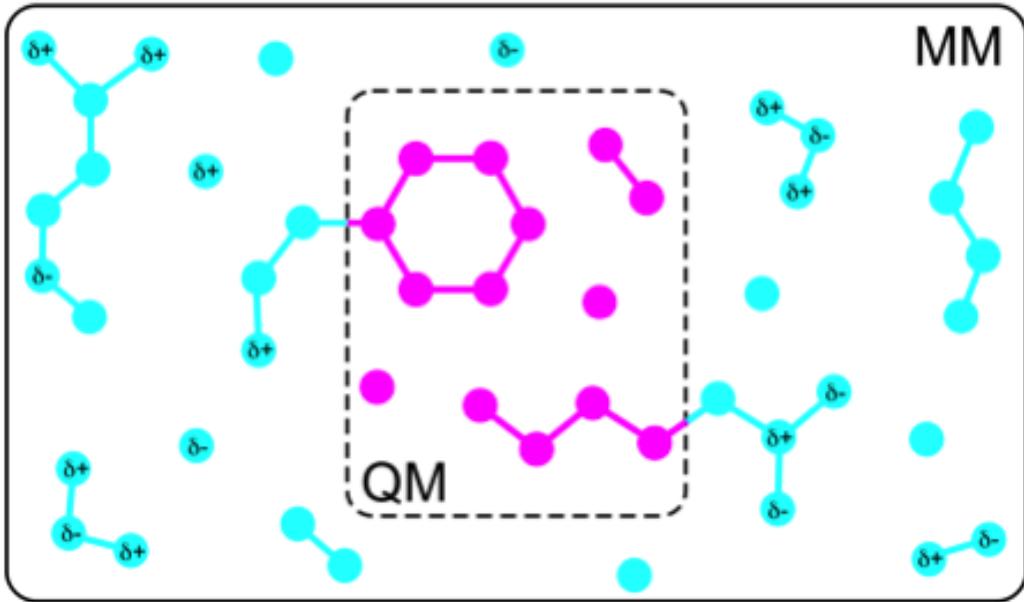


Figure 3: Illustration of the QM/MM concept. A small region, in which a chemical reaction occurs and therefore cannot be described with a force field, is treated at a sufficiently high level of QM theory. The remainder of the system is modelled at the MM level.

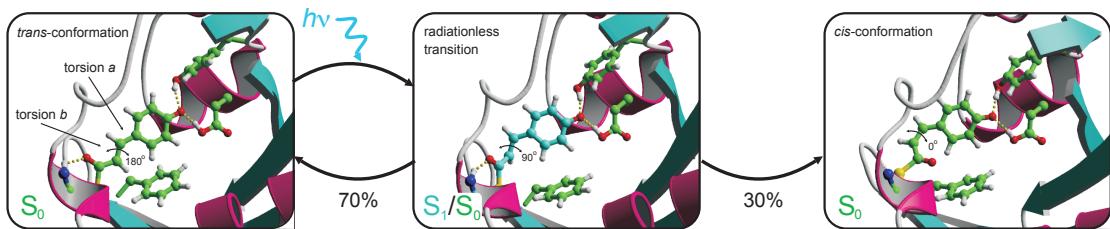


Figure 4: Snapshots from excited-state trajectories of wild-type PYP, showing the chromophore (pca) in the active site pocket. The first snapshot is at the excitation. The second shows the configuration at the radiationless transition from S_1 to S_0 . The third snapshot shows the photoproduct, in which the carbonyl oxygen of the thioester linkage has flipped and is no longer hydrogen bonded to the backbone of Cys69.

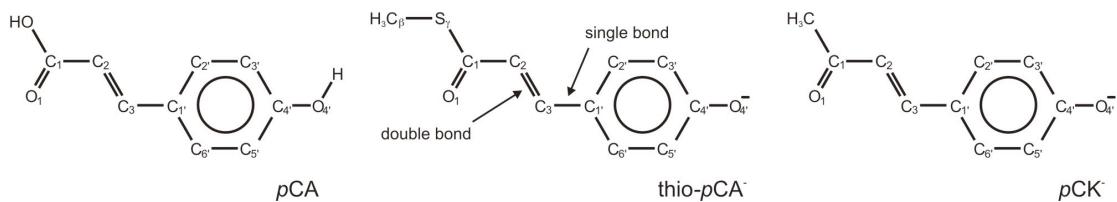
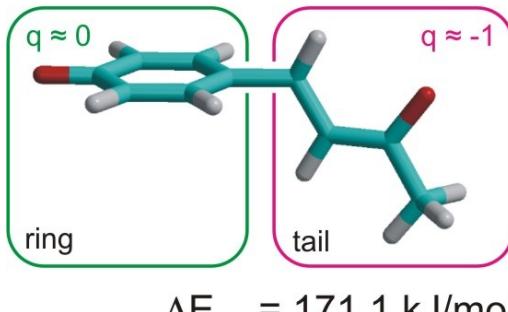


Figure 5: Schematic drawings of the *p*-coumaric chromophore and analogues used in our simulations.

a, single-bond twisted S_1 minimum



b, double-bond twisted S_1 minimum

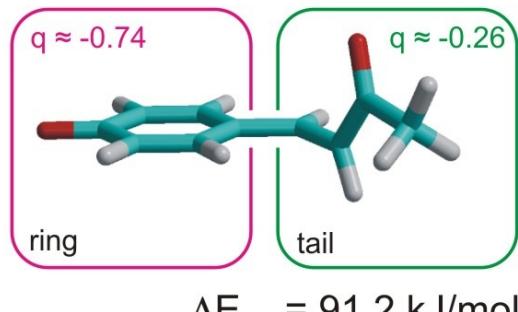


Figure 6: Excited-state minimum energy configurations of the pCK^- chromophore analogue. In both the single-bond twisted S_1 minimum (a) and the double-bond twisted S_1 minimum (b) there is a substantial energy gap between the ground and excited state. The distribution of the negative charge in these minima is opposite. The situation in the $thio-pCA^-$ is similar.

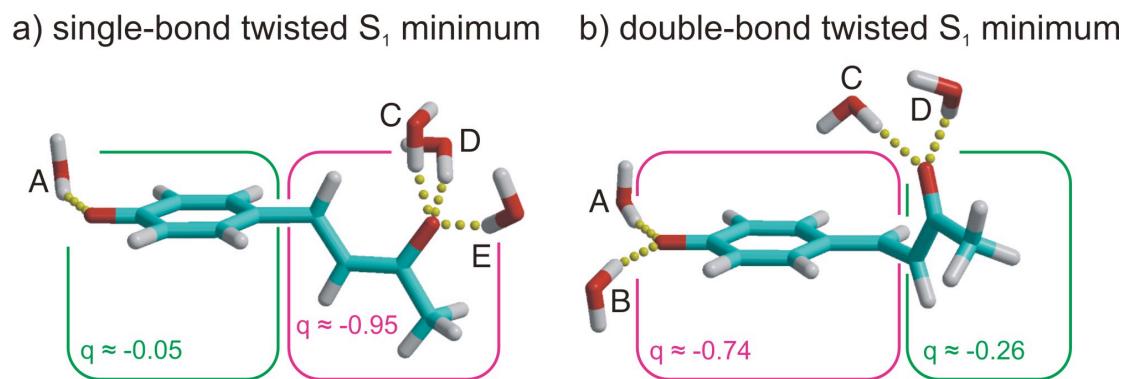


Figure 7: Excited-state minimum energy configurations of the $p\text{CK}^-$ chromophore analogue with five explicit water included.

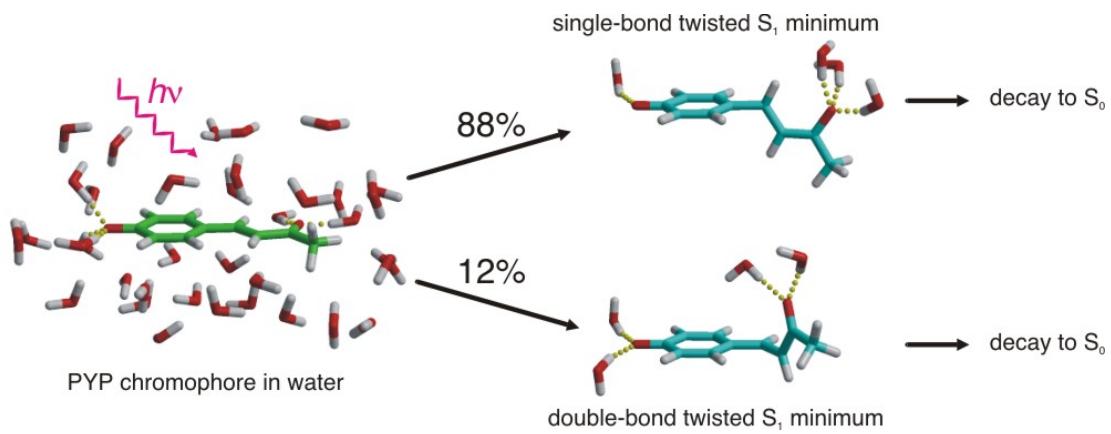


Figure 8: In water the chromophore undergoes both single and double bond isomerization. Excited state decay from these minima is very efficient due to stabilization of the chromophore's S_1 charge distribution by specific hydrogen bond interactions.

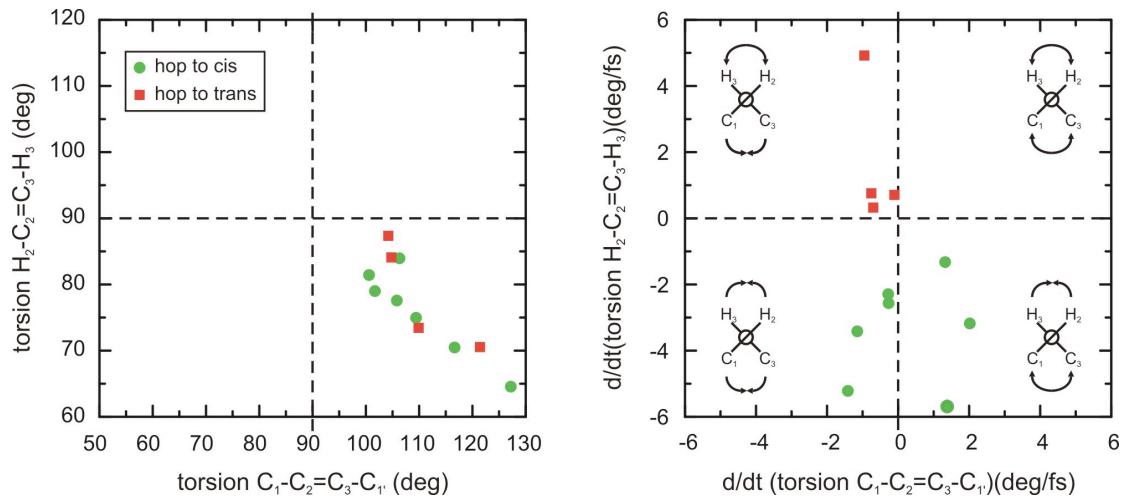


Figure 9: Values of torsion angles, and their time-derivatives.

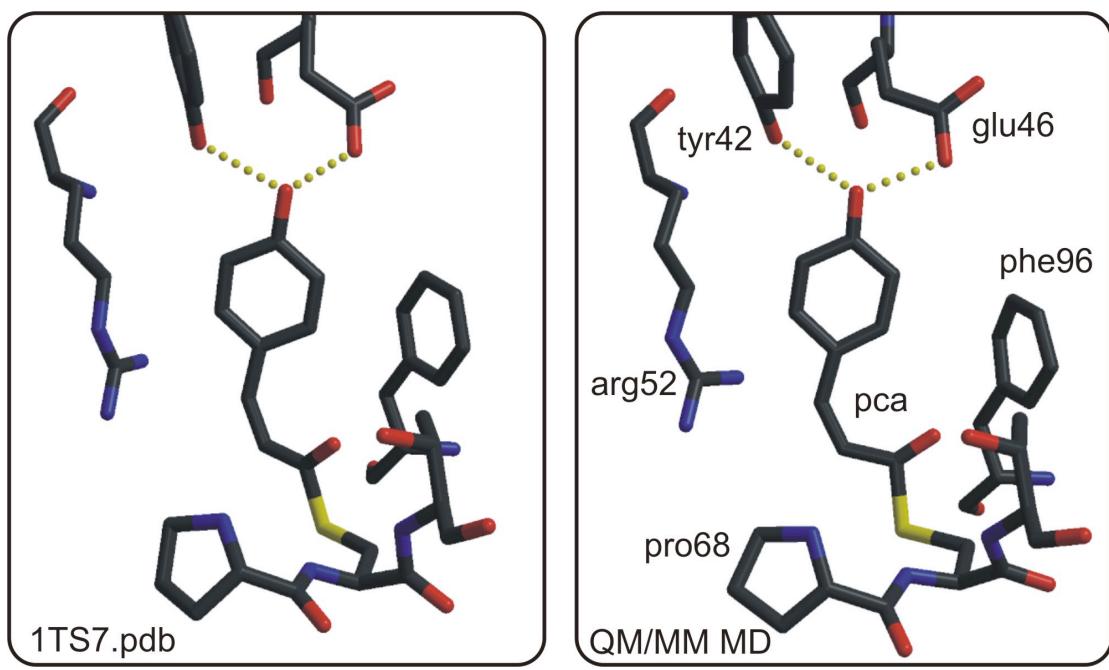


Figure 10: Comparison between time-resolved Laue structure (left) and simulated structure (right) of the pR_{CW} intermediate state. The structures were superimposed, using the C_α atoms for the least-squares fit.

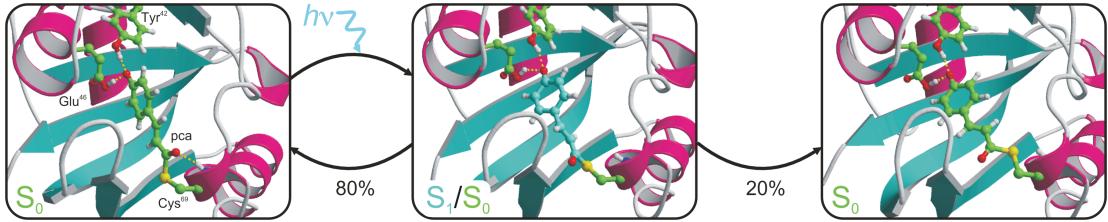


Figure 8: Snapshots from an excited-state trajectory of the Arg52Gln mutant of PYP, showing the chromophore (pca) in the active site pocket. The first snapshot is at the excitation. The second shows the configuration at the radiationless transition from S_1 to S_0 . The third snapshot shows the photoproduct. In the mutant isomerization takes place around the single-bond. Like in the wild-type protein, the carbonyl oxygen of the thioester linkage flips, causing the break of the hydrogen bond to the backbone of Cys69.

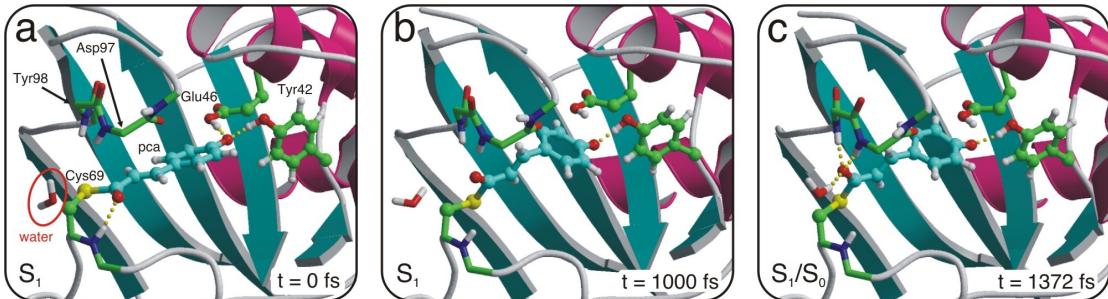


Figure 12: Snapshots from an excited-state trajectory of the Arg52Gln mutant of PYP, demonstrating that three hydrogen bonds to the carbonyl moiety are essential for S_1 decay at the single bond twisted minimum. The first snapshots is at the excitation to S_1 . The second snapshot shows the twisted configuration without hydrogen bonds to the carbonyl. The gap between S_1 and S_0 is far too high for decay at this configuration. However, as the third snapshot shows two backbone amino groups and a bulk water, that has moved into the chromophore pocket during the excited state dynamics, donate the three hydrogen bonds that are required for efficient decay from the S_1 minimum.