Supporting Information

Predicting the Efficiency of Photoswitches Using Force Analysis

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Thermal effects

To capture thermal effects, ab initio Molecular Dynamics (AIMD) simulations in the excited state would need to be performed, which are, however, prohibitively expensive even for small molecules on the relevant time scales. Moreover, during these AIMD trajectories one would have to calculate the energy distribution for the potential and kinetic energy terms separately. For the kinetic energy, this is far from trivial when redundant internal modes are used as the coordinate system. Therefore, we limit our discussion to photochemical processes that arise from relaxation of the internal modes during the motion along the excited state PES.

Circumventing the calculation of the excited state Hessian

An alternative method to derive the energy a photoswitch can release into its environment is to calculate the gradient of the energy at the Franck-Condon point and multiply it with the displacement vector between the Franck-Condon point and the minimum of the excited state potential. This approach has the advantage that the expensive calculation of the Hessian in the excited state is avoided. However, in the case of a potential that can be approximated as harmonic, this approach yields an energy that is much too high, especially if $\Delta q$ is large. This is analogous to approximating a second order polynomial by a first order instead of a second order Taylor series. In the case of carbon monoxide, this approach overestimates the ab initio energy difference by a factor of 2.3. Hence, we refrain from this gradient based analysis and recommend using the excited state JEDI analysis for the cases in which the harmonic approximation is applicable. Nonetheless, the linear approach described here can be considered a first step for treating systems in which the excited state PES can be approximated as linear rather than as harmonic.

Details on the generation of the color-coded structures

For the generation of the color-coded structures shown in the manuscript we have used VMD 1.9.1. For each type of internal coordinate (bond length, bond angle and dihedral angle), the color red is assigned to the highest energy in this particular kind of mode, while green symbolizes zero energy. Depending on the energy in each redundant internal mode, a color in the range between green and red (with yellow as an intermediate) is determined and a specific covalent bond is colored accordingly. In the case of the bonds, this procedure is straightforward. The coloring of bond angles and dihedral angles, however, is challenging. We circumvented this problem by splitting the energy in a given bond angle and dihedral angle among the bonds involved in these modes. Subsequently, all contributions for a given bond were added up and the appropriate color was determined. Further details have been given previously.

References


Full references from the main paper