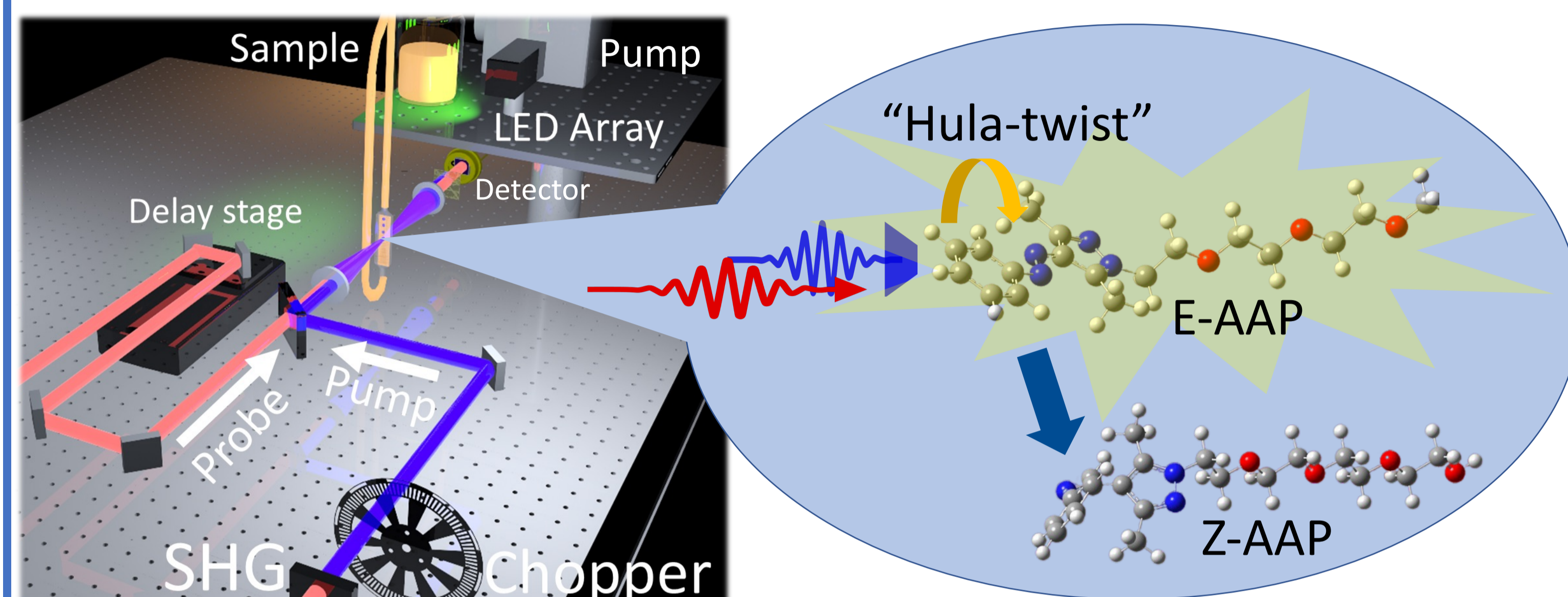


Motivation

Light responsive molecules such as photoswitches are subject to great interest because they allow for precise external control of chemical properties. The switching property originates from two inversely affected absorption cross sections between Z(cis) and E(trans) isomers. In contrast to conventional Azobenzene (AB) photoswitches, AAPs replace one of the benzyl rings with a less bulky five-membered ring (pyrazole). The addition of two methyl groups at the pyrazole then optimizes the Z-configuration which significantly improves back switching (Z→E) performance [1]. Furthermore, AAPs have good resistance against photobleaching in presence of the antioxidant GSH, found in most cells [2]. These amazing properties make AAPs a photoswitch of choice in biological applications. The multitude of changes in respect to sterical hinderance therefore opens the question if the established ultrafast switching dynamics of azobenzene can be transferred to arylazopyrazoles.

Experimental Setup & Principal



Steps in Transient Absorption of Photoswitches:

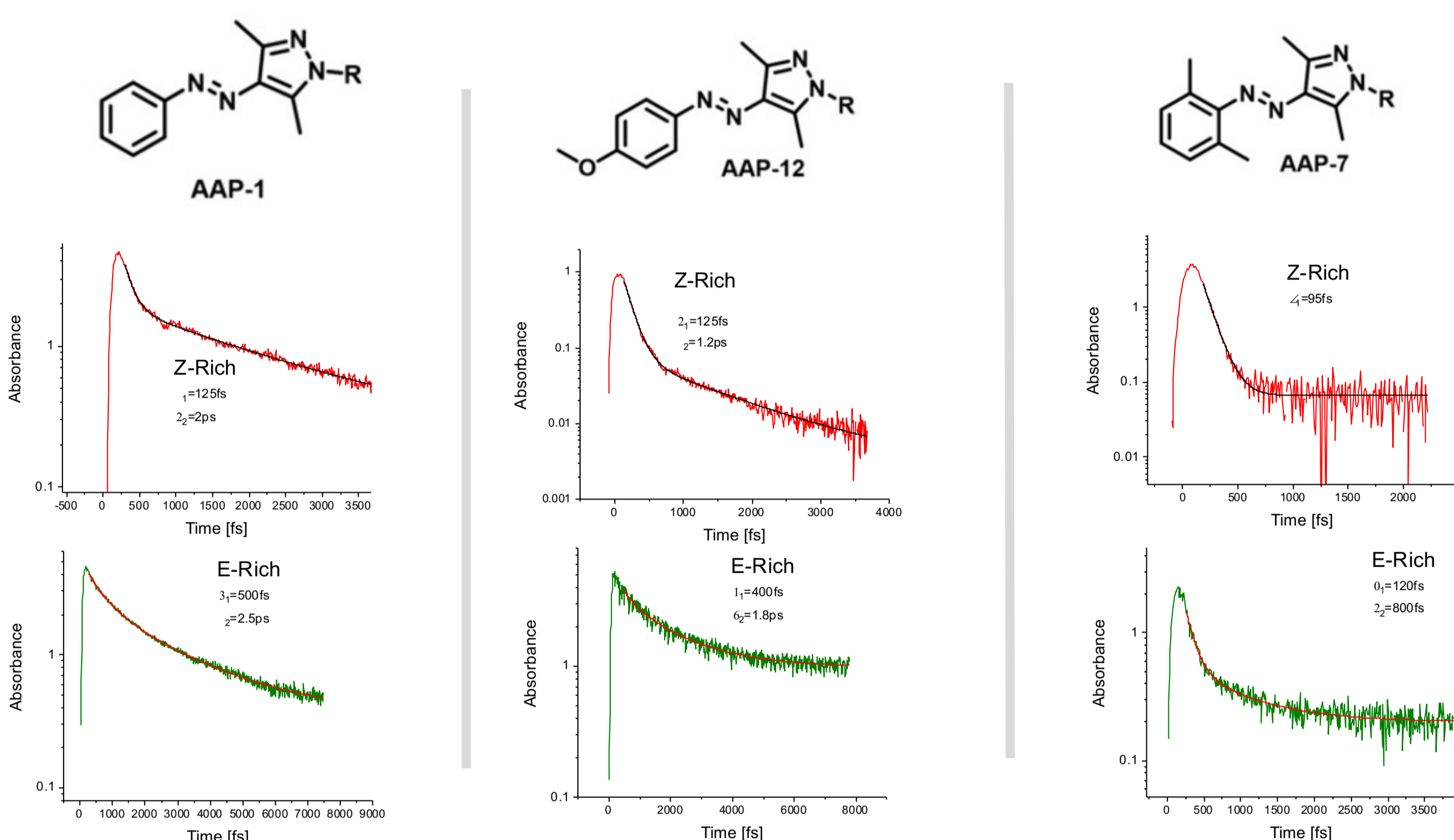
- 1.) Isomeration is initiated by absorption from a blue pulse (pump). At this instant molecular geometry remains identical, however intramolecular forces are modified which twist the molecule.
- 2.) During the process, the photoswitches can be further excited by red light (probe) to an even higher state. The decay in absorption is correlated with recovery to the ground state

Transient Absorption Kinetic Curves (Probe 640-670nm)

AAP-1: Standard AAP, no benzyl substituents. PSS>90%

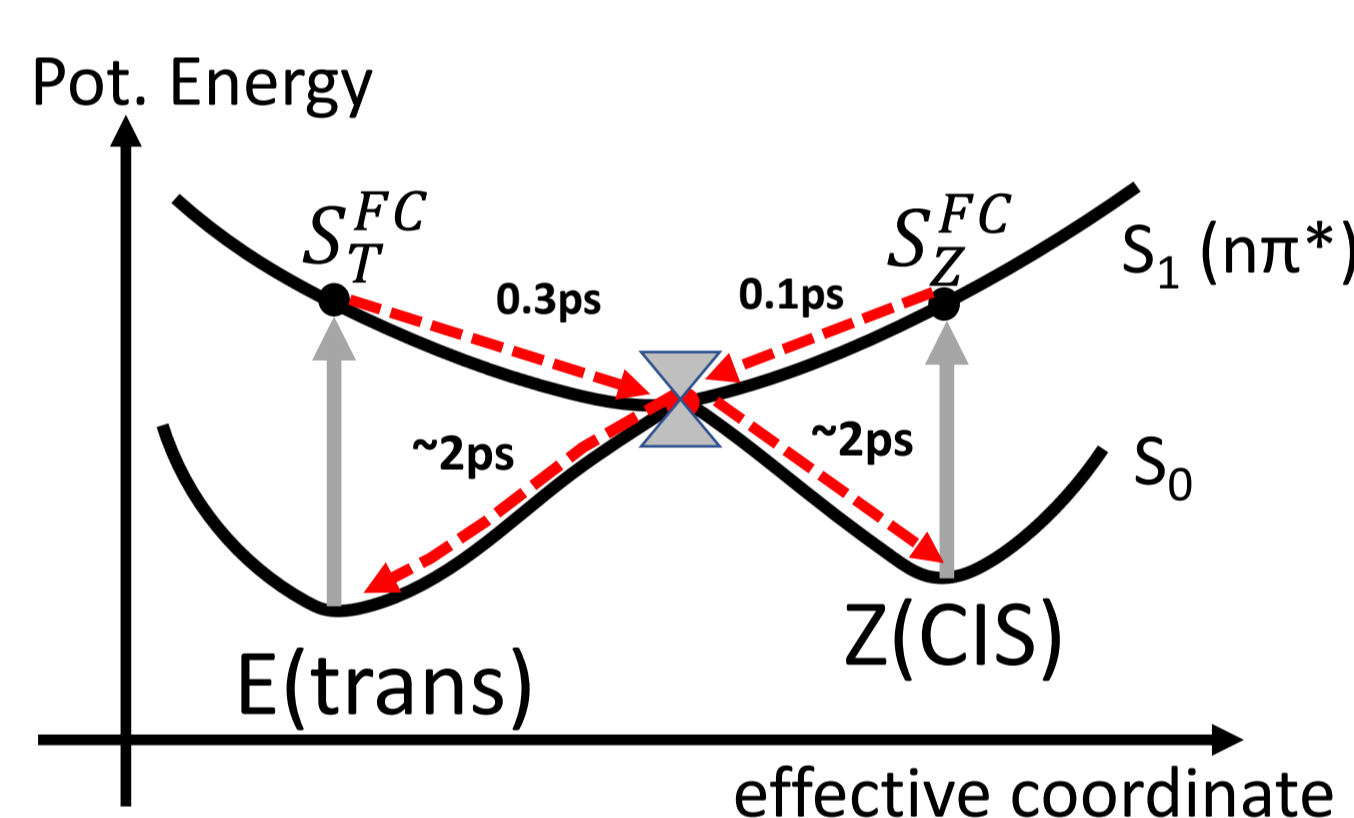
AAP-12 Purest photochemistry: PSS>98% of either E/trans or Z/cis

AAP-7 Extreme sterical hinderance: Has multi-year long lifetime for thermal isomerization. PSS>70%

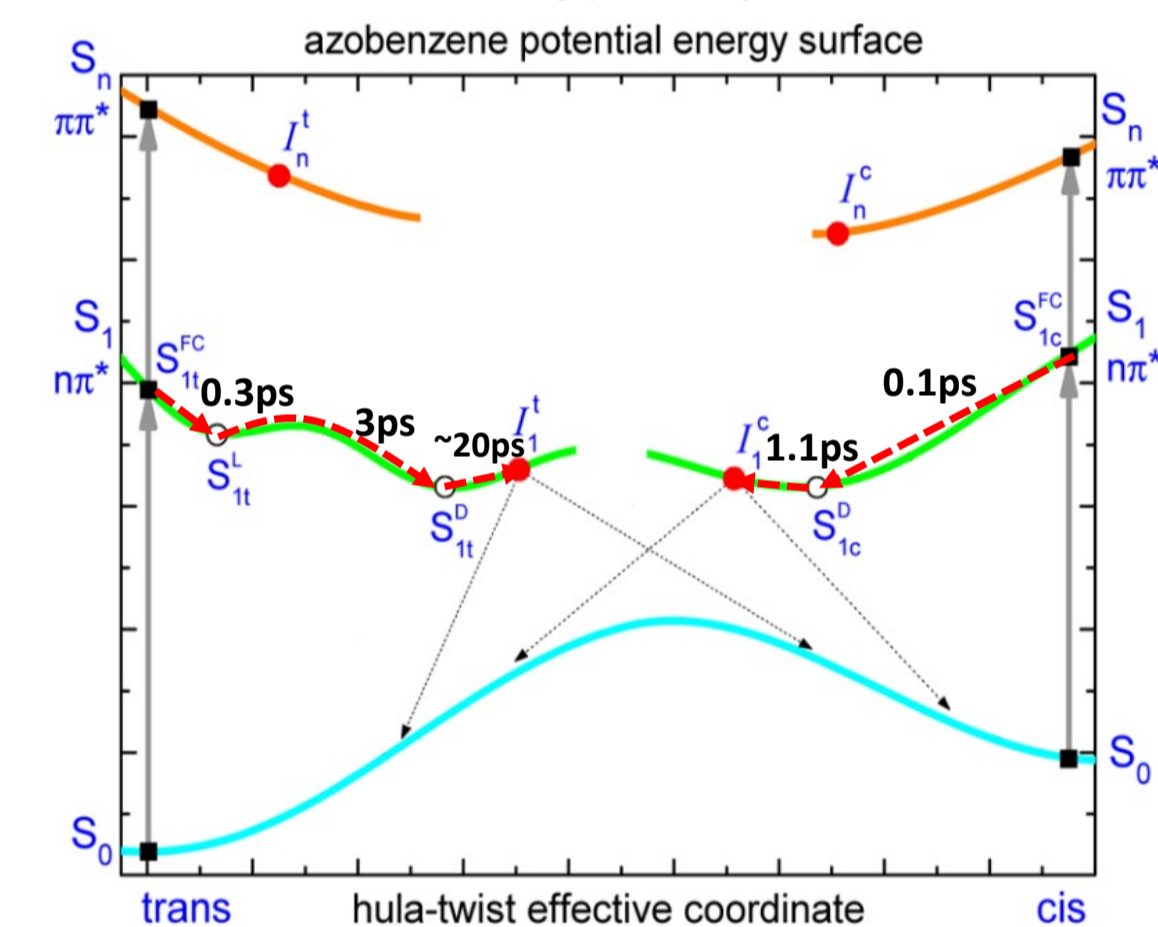


Isomeration Mechanism

Conventional potential surface diagram of AB



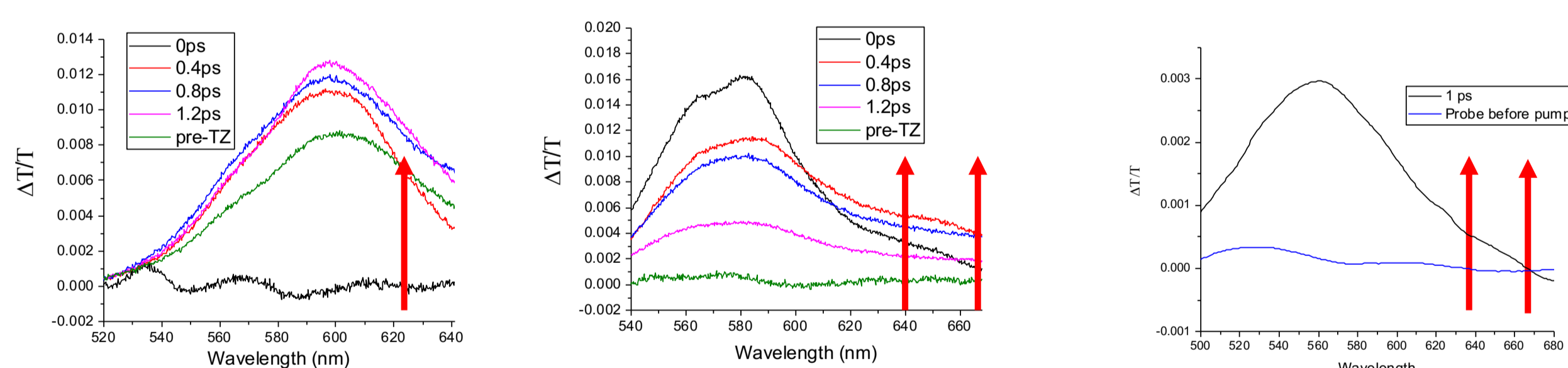
Potential Energy Diagram of AB [3]



Conventional isomeration model of AB. The excited state surface towards conical intersection is barrierless. Such surfaces have been suggested for AAPs. The second time constant is a result of product absorption changes.

Alternative potential surfaces which can also explain the photodynamics in AB: The excited state molecule encounters energy barriers before reaching crossing points S1→S0.

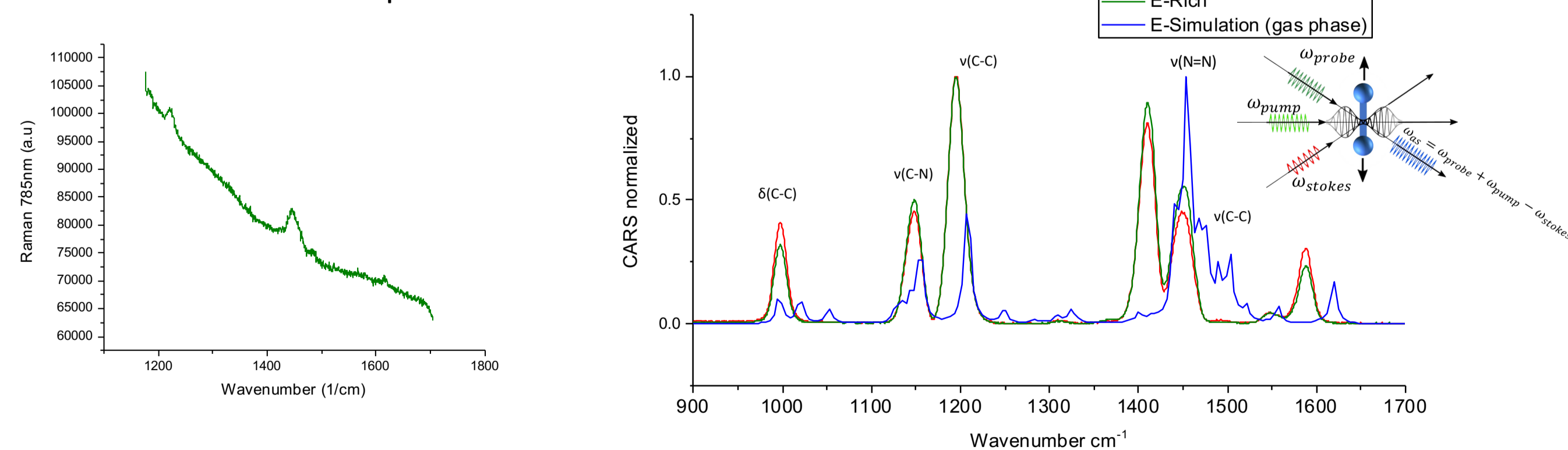
Transient Absorption Spectra of AAP



Raman Scattering of AAP using CARS

AAP-1 Raman $\lambda_{pu}=785\text{nm}$

AAP-1 CARS



Fluorescence strongly interferes in AAP Raman bands. By employing three-color coherent anti-stokes raman scattering(CARS) contrast is improved greatly.

Almost all bands have a reduced cross section in the Z-isomer. There are unfortunately no clearly visible N=N bands which can differentiate Z and E isomers

Conclusion and Outlook

- Photoswitches with faster kinetics are generally associated with higher photostability and quantum efficiency [4]. AAPs show similar fast dynamics like ABs. AAP-7-TEG despite its comparatively poor PSS may be especially interesting for this reason.
- Excited state Raman spectroscopy may provide additional information into the structure of the excited state dynamics
- Ground state CARS spectroscopy is a poor tool in distinguishing the E and Z isomers for AAPs

Acknowledgements

Funding by German Research Foundation (DFG) within the Collaborative Research Center 1242 (project A04, project number 278162697)

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[2] Stricker, L., Böckmann, M., Kirse, T. M., Doltsinis, N. L., & Ravoo, B. J. (2018). *Chemistry - A European Journal*, 24(34), 8639–8647.

[3] Adapted with permission from Quick, M., Dobryakov, A. L., Gerecke, M., Richter, C., Berndt, F., Ioffe, I. N., Granovsky, A. A., Mahrowald, R., Ernstring, N. P., & Kovalenko, S. A. (2014). *J. Phys. Chem. B*, 118(29), 8756–8771.

[4] Renth, F., Siewertsen, R., & Temps, F. (2013). *Revs. in Phys. Chem.* (Vol. 32, Issue 1, pp. 1–38).

