

# Transient Absorption Anisotropy to Study Photocatalytic Reactions

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For design of novel catalysts, understanding mechanical details of reaction pathways in photocatalytic systems is crucial. As mechanistically relevant processes such as vibrational relaxation and internal conversion processes occur on femtosecond (fs) timescales, we use ultrafast spectroscopic techniques such as transient absorption (TA) to gain new insights.<sup>1</sup> Here, we describe how we upgrade a TA experiment to allow for a detailed study of pre-association between substrate and catalyst in a photocatalytic reaction.

We describe a TA setup with an optical pump and near-infrared (NIR) supercontinuum for probing. By detecting in the NIR region the ground-state bleach and stimulated emission are not observable, leaving excited-state absorption from *e.g.*, long-lived and photocatalytically active triplet states.<sup>2</sup>

Furthermore, we plan to study the time-dependent anisotropy of photocatalytic systems for further mechanistic insights about *e.g.*, the molecular volume as an indicator for pre-association. Hence, we want to extend the setup's capability to single-shot transient absorption anisotropy by incorporating a Wollaston prism, splitting the 45° polarized probe beam into parallel and perpendicular contributions, which can be detected separately and simultaneously. This can minimize errors during the acquisition time and increase the signal-to-noise ratio compared to the sequential approach.<sup>3</sup>

The combination of transient absorption anisotropy and computational methods will provide structural information, as it will prove or disprove the existence of photocatalyst-substrate pre-complexes. Hence, these results can give valuable insights into the underlying reaction mechanism from a new perspective, advancing the photocatalyst design and optimization process.

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