

A comprehensive kinetic model for the excited-state dynamics of *all-trans* retinal and *all-trans* retinoic acid

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Derivatives of *all-trans* retinal, the aldehyde of vitamin A, play a key role in microbial rhodopsins initiating energy conversion and cellular signaling by subpicosecond photoinduced switching. Here we investigate the ultrafast excited-state dynamics of *all-trans* retinal and its carboxyl analogue *all-trans* retinoic acid in solvents of different polarity using UV-Vis pump - supercontinuum probe transient absorption spectroscopy in the 260-660 nm range.^[1] Photoexcitation of *all-trans* retinal at 400 nm populates the short-lived (*ca.* 60 fs) $^1B_u^+$ state with subsequent formation of the $^1A_g^-$ and $^1n\pi^*$ states on a subpicosecond time scale. $^1n\pi^*$ is the gateway state for formation of the long-lived T_1 triplet state and is energetically up-shifted in *all-trans* retinoic acid resulting in the shut-down of the triplet channel. The $^1A_g^-$ state exhibits considerable intramolecular charge transfer (ICT) character, as indicated by a characteristic stimulated emission band observed in polar solvents. Photoisomerization of $^1A_g^-$ /ICT leads to the formation of *cis* isomers with a quantum yield of $\leq 21\%$ in all solvents. We will present a detailed kinetic mechanism providing a unified picture of the complex excited-state dynamics of these seemingly simple terminally carbonyl-substituted polyene systems, with the aid of accurate absolute steady-state absorption spectra of the ground-state isomer species. Implications of our solution-phase results for the photoinduced dynamics of the *all-trans* retinal Schiff base of microbial rhodopsins will be discussed.

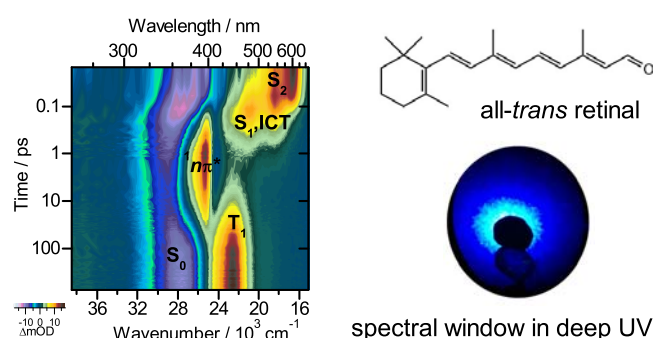


Figure 1. Contour plot of transient absorption data showing the formation of several transient species after photoexcitation of *all-trans* retinal in *n*-hexane at 400 nm and probing with a UV-Vis multifilament supercontinuum (bottom right).

Reference:

- [1] O. Flender, M. Scholz, K. Oum, T. Lenzer, *PCCP*, **2016**, 18, 14941