

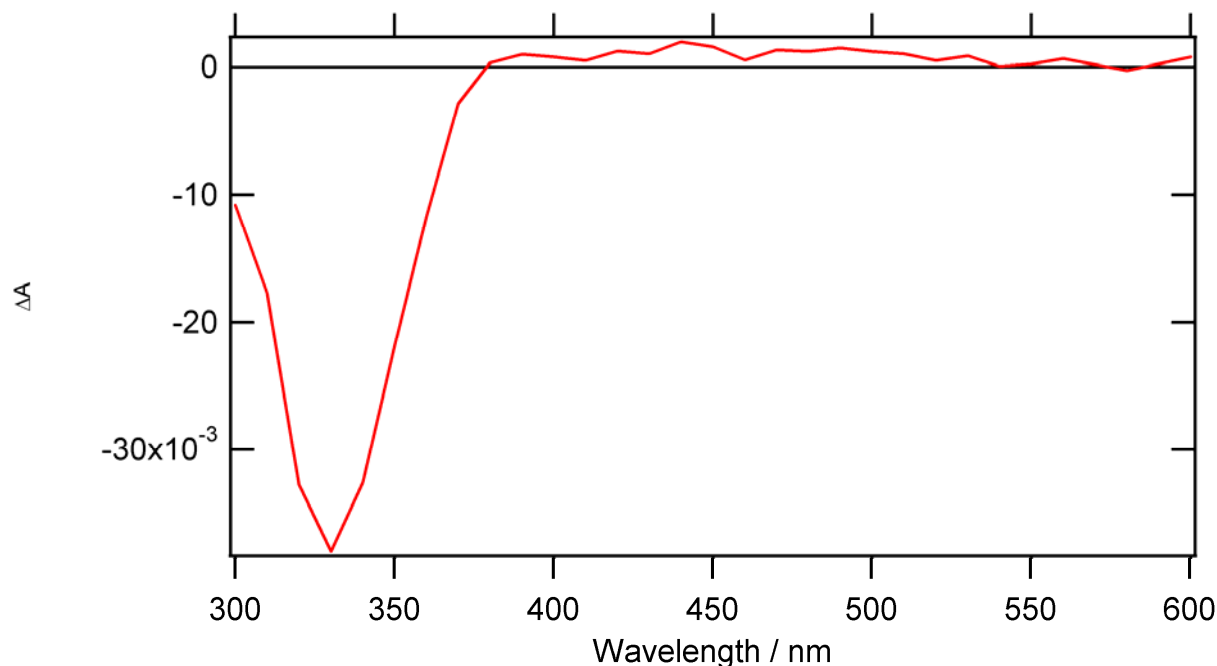
Supplementary Information

Investigation of ultrafast photoinduced processes for salicylidene aniline in solution and gas phase: toward a general photo-dynamical scheme.

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1) Spectrum of the twisted-enol for SAOMe:

Figure 1: Nanosecond transient spectrum at 20 μ s time delay for SAOMe in acetonitrile after 266 nm excitation.



2) Ultrafast time-resolved experiments for SAOH after 390 nm excitation

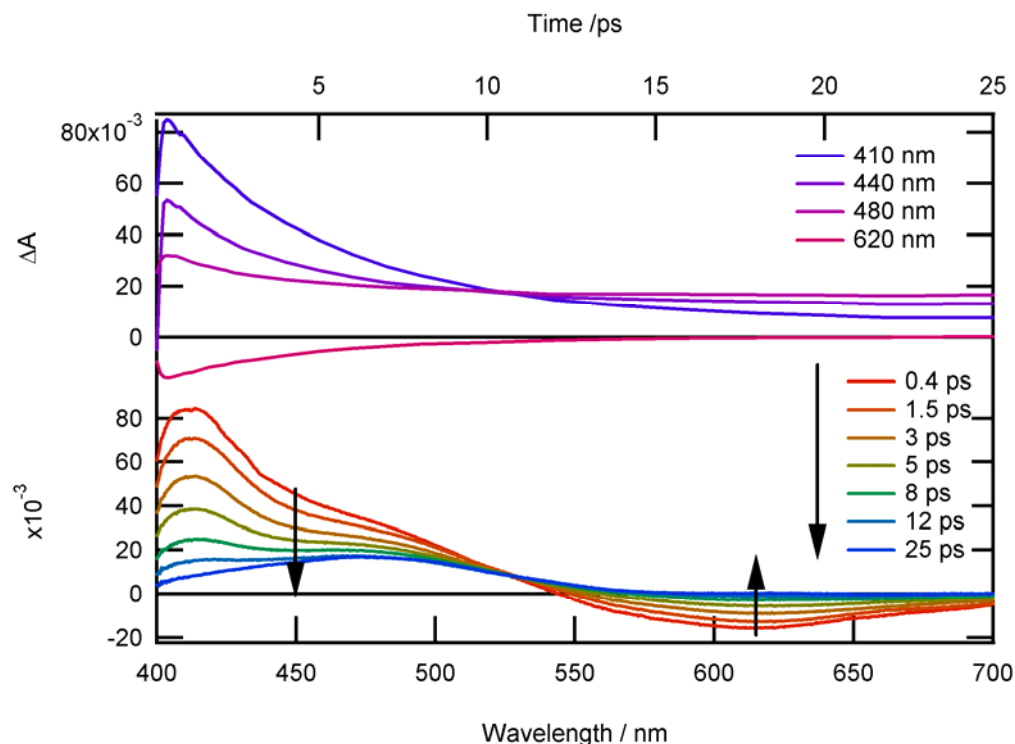
Figure 2 shows the transient absorption spectra of SAOH measured in acetonitrile following excitation at 390 nm for time delays in the 0 to 25 ps range. Strong artifacts and nonlinear transient absorption signals from the pure solvent are observed in the broad absorption band covering the 400-550 nm range during the first few hundreds of fs (not shown). After 400 fs two main bands are observed, their respective intensity decreasing with time: a positive absorption band covering the 400 – 540 nm domain, which has one maximum around 410 nm and a shoulder around 490 nm, and a weak negative band in the 540 – 750 nm domain. After complete decay of these two bands contributing to the initial spectrum (25 ps), a complete change of the spectral features is observed leading to a single, very broad, positive absorption band in the 400 – 600 nm range which remains nearly constant until 5 ns.

Taking into account the fact that it is notably truncated by the presence of the partly overlapping transient absorption band on its high energy side, the position of the short-time negative band satisfactorily corresponds to that of the steady-state emission related to cis-keto* fluorescent species. This band is thus assigned to the stimulated emission of the cis-keto* species formed after the ESIPT reaction. The decay of stimulated emission can be well fitted with one exponential decay components of 5 ps.

Regarding the positive absorption band, a second component (< 2 ps) is needed to fit the absorption kinetics in addition to the identical component also characterizing the stimulated emission decay. Therefore the positive absorption band was considered to be the signature of the fluorescent S₁ cis-keto* species and an additional species. Indeed, this shorter component is usually assigned to the relaxation of the species created just after the ESIPT, a hot cis-keto* which overlaps the cold cis-keto*. Experiments after 266 nm excitation (see the main manuscript) lead us to conclude that this second components can be also assigned to a twisted-enol and an unstable trans-enol.

We recently reported a method to extract the contribution of overlapping species in femtosecond spectroscopy based on MCR.¹ At short time scale, solvent contribution and instrumental response function can be considered in order to assess efficient deconvolution of the time-dependent concentration profiles extracted from MCR. In this way, a characteristic time of 45 ± 5 fs was recovered for the ESIPT. The existence of an intermediate species which relaxes in 250 ± 5 fs was also confirmed.² These conclusions are in agreement with previous results reporting for SAOH in solution 50 ± 10 fs and 430 ± 40 fs for ESIPT and hot cis-keto* relaxation, respectively.³ Finally the broad positive absorption band in the 400 – 600 nm range can be attributed to the trans-keto photo-product due to its similarity with the spectra of the final trans-keto photo-product measured at 355 nm excitation with the nanosecond transient absorption experiment. Moreover, due to the overlap between the absorption spectra of the cis-keto* species and the final trans-keto photoproduct, it is not possible to determine which of the cis-keto* isomers (hot cis-keto* or cold fluorescent cis-keto) is the precursor of the photo-product and to find its real time formation constant. Our recent results² led to the conclusion that the formation of the trans-keto photoproduct is observed from the long lived cold fluorescent cis-keto* within 5 ps, as suggested by Ziolek and Peon.^{3,4}

Fig.5 (Top) Kinetic traces of transient absorption at characteristic wavelengths and (bottom) transient absorption spectra of SAOH in acetonitrile obtained for different time delays after 390 nm excitation (3 mJ/cm²).



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