Competing ultrafast photo-induced ring closure and *E-Z* isomerization of a photochromic furylfulgide

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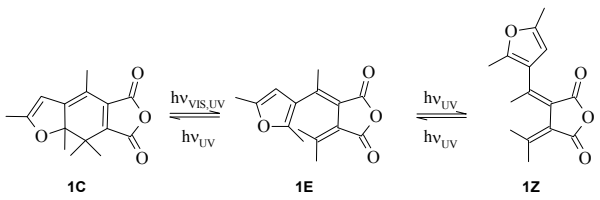
Introduction

- Fulgides and their derivates are thermally irreversible photochromic switches with high application potential, e.g., for optical memory devices or optical switches [1].



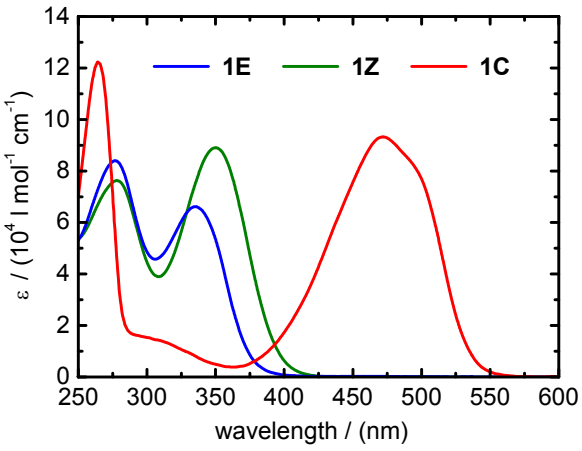
*Photoisomerization reactions of the photochromic furylfulgide 1-[1-(2,5-Dimethyl-3-furyl)-ethylidene]-2-(isopropylidene)-succinic anhydride (**1**)*

- The photochromism rests on the electrocyclic reactions, but the *E-Z* isomerization becomes an important competing side reaction for applications, where multiple switching cycles are required.
- The furylfulgide **1** offers unique opportunities to study the competition of the *E-C* and *E-Z* isomerizations because their quantum yields at λ = 365 nm are comparable [2]:

$$\Phi_{EC,365} = 0.18 - 0.20,\ \Phi_{EC,365} = 0.12 - 0.13$$

- Time-resolved studies so far have not taken the *E-C*/*E-Z* branching into account. Femto- to picosecond time scales were found for the ring opening/closure of fulgides and the related fulgimides [3] and the *Z-E* photoisomerization [4].
- We have used femtosecond time-resolved spectroscopy to investigate the molecular isomerization dynamics of photoexcited **1E** in detail.
- Our results are of relevance for understanding competition of ultrafast reactions of large molecules and influencing them by coherent control techniques. This should enable the design of optimized functional systems.

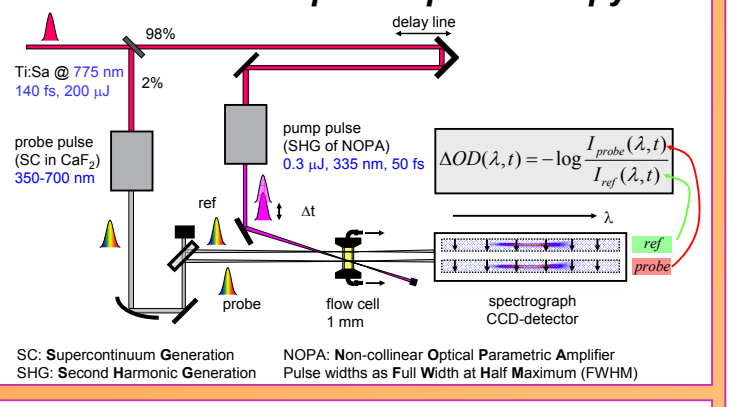
Stationary UV/VIS Absorption Spectra



*Stationary UV/VIS absorption spectra of **1C**, **1E** and **1Z** in n-hexane*

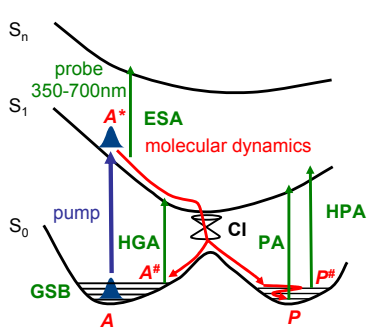
- The open isomers **1Z** and **1E** only absorb in the UV, with maxima of their first bands at λ_{max} = 335 and 350 nm.
- The closed isomer **1C** absorbs strongly in the visible with a maximum at λ_{max} = 470 nm.

Fs-Transient Absorption Spectroscopy



SC: **S**upercontinuum **G**eneration
SHG: **S**econd **H**armonic **G**eneration
NOPA: **N**on-collinear **O**ptical **P**arametric **A**mplifier
Pulse widths as **F**ull **W**idth at **H**alf **M**aximum (FWHM)

Transient Absorption Signal Contributions

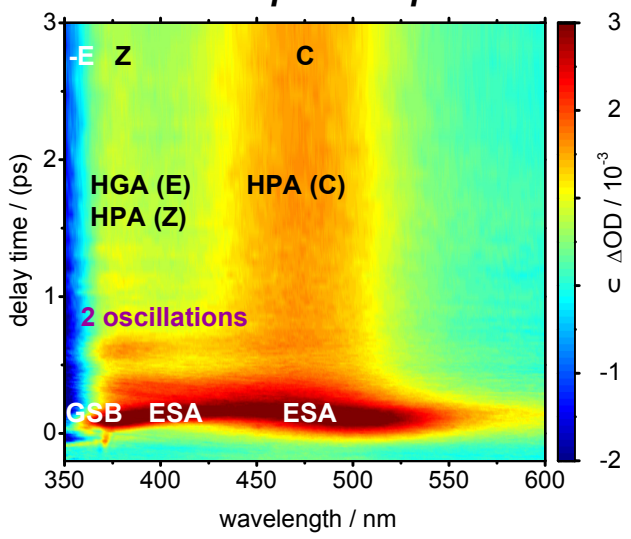


Conical **I**ntersection
Ground **S**tate **B**leach
Excited **S**tate **A**bsorption
Hot **P**roduct **A**bsorption
Product **A**bsorption
Hot **G**round State **A**bsorption

Kinetic scheme:

$$A \xrightarrow{+h\nu} A^* \xrightarrow{\tau_{ESA1},\tau_{ESA2}} A^{\#},P^{\#} \xrightarrow{\tau_{HGA},\tau_{HPA}} A,P$$

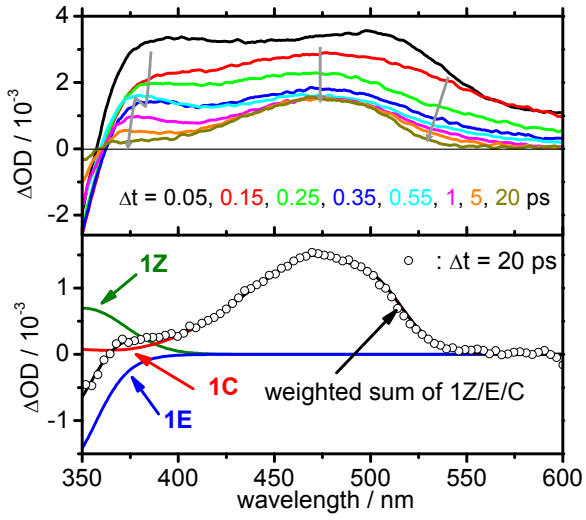
2D Transient Absorption Map



*Transient Absorption ΔOD(λ,t) following 335 nm excitation of **1E** for probe wavelengths from 350 nm to 600 nm and delay times –0.2 ps ≤ Δt ≤ 3.0 ps.*

- GSB / SE: negative ΔOD at $\lambda_{probe} \leq$ 365 nm.
- ESA : immediate rise of positive ΔOD at $\lambda_{probe} \geq$ 365 nm, decays in < 0.5 ps (time scale of excited-state dynamics).
- Oscillations at $\lambda_{probe} \leq$ 450 nm decay on same time scale.

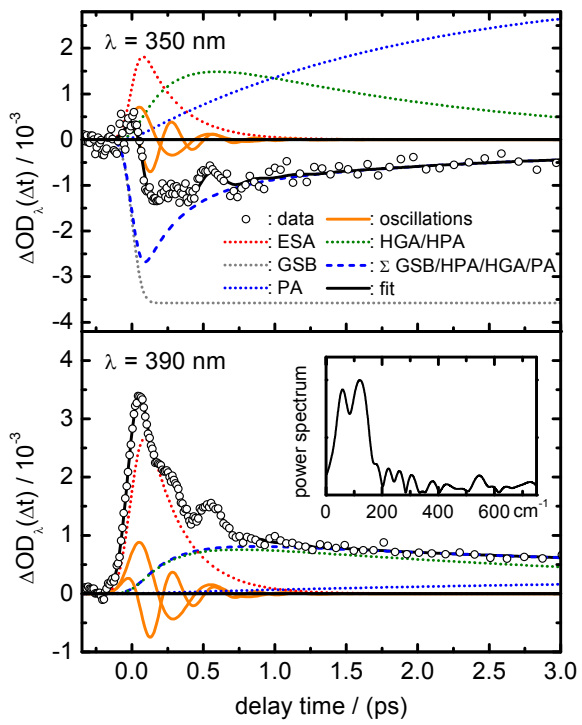
Transient Absorption Spectra



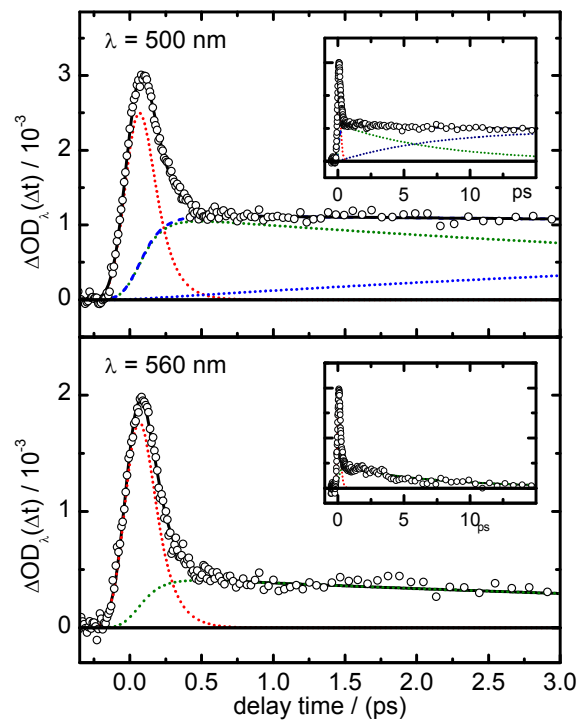
Transient spectra $\Delta OD_{\Delta t}(\lambda)$ at selected delay times 0.05 ≤ Δt ≤ 20ps.

- HPA (Z): at λ_{probe} < 450 nm appears within 0. 5 ps.
  HPA (C): at λ ≥ 450 nm appears within 0.25 ps.
- HGA: at λ_{probe} < 450 nm, fills in GSB on ps time scale.
- PA: virtually no change beyond Δt > 10 ps, final spectra: weighted sum of static spectra of all isomers.
- *E-C* / *E-Z* branching ratio is 2:1 (in agreement with [2]).

Transient Absorption Time profiles



Transient absorption time profiles $\Delta OD_\lambda(\Delta t)$ at λ_{probe} = 350 and 390 nm.



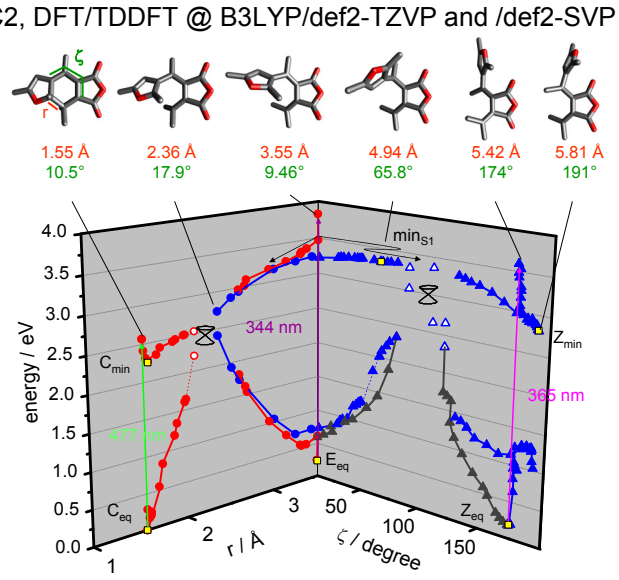
Transient absorption time profiles $\Delta OD_\lambda(\Delta t)$ at λ_{probe} = 500 and 560 nm.

λ / nm	τ_{ESA1} / ps	τ_{ESA2} / ps	τ_{HPA} / ps	ν_{osc} / cm^{-1}
350 – 450	0.25 (6)	–	4.0 (8)	64 (7) & 114 (6)
500 – 650	–	0.10 (10)	7.5 (10)	–

- Parameters from global fit with sequential kinetic scheme.
- τ_{ESA1} is related to the initial dynamics out of the Franck-Condon region, τ_{ESA2} is the *slowest* isomerization time scale
- The oscillations are interpreted as vibrational coherences.

Quantum Chemical Calculations

- CC2, DFT/TDDFT @ B3LYP/def2-TZVP and /def2-SVP



Excited-state geometry optimizations of equilibrium and geometry-optimized structures at constrained r / ζ values (B3LYP/def2-SVP)

- Excited-state minima: excitation of low-frequency modes.
- Narrowing of energetic gap indicates conical intersections (CI) that allow ultrafast deactivation/isomerization.
- CI_{E-C} and CI_{E-Z} accessible with zero/low energy barrier.

Conclusions

- The ultrafast decay of the ESA indicates that the photoisomerizations occur within only 0.1 – 0.25 ps.
- The ultrafast simultaneous appearance of the HPA shows that the *E-C* / *E-Z* branching happens on the excited state surface within this time.
- Possible interpretations of the ESA time constants are:
  1. Late branching: population of a dark intermediate state within 0.1 ps, subsequent isomerization and de-activation to the electronic ground states from there.
  2. Early branching in the Franck-Condon region: two separate excited-state pathways with different *sub*-ps time constants.
- Quantum yields are rationalized by observed dynamics.
- The results were supported by the TDDFT calculations
  1. Indications for easily accessible CI_{E-C} *and* CI_{E-Z} provide explanation for ultrafast time scale.
  2. Local excited-state minima with low frequency vibrational modes rationalize oscillations.

References

[1] Y. Yokoyama, *Chem. Rev.* **100**, 1717 (2000)
[2] E. Uhlmann *et al.*, *J. Photochem. Photobiol.* A **98**, 45 (1996)
[3] F. Renth *et al.*, *Chem. Phys. Lett.* **428**, 62 (2006)
[4] B. Heinz *et al.*, *J. Am. Chem. Soc.* **129**, 8577 (2007)