

Ultrafast Dynamics of a Bistable Intramolecular Proton Transfer Switch

Julia Bahrenburg,¹ Michał F. Rode,² Andrzej L. Sobolewski,² and Friedrich Temps¹

¹Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Olshausenstr. 40, D-24098 Kiel, Germany

²Institute of Physics, Polish Academy of Science, al. Lotników 32/46, 02-668 Warsaw, Poland

bahrenburg@phc.uni-kiel.de

Abstract: The stepwise formation of the proton transfer product of a bistable molecular switch was unambiguously revealed by femtosecond fluorescence and absorption spectroscopy. The interpretation was supported by ab initio excited-state calculations.

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1. Introduction

Excited-state intramolecular proton transfer (ESIPT) reactions belong to the fastest chemical reactions known [1]. Moreover, many molecules showing proton transfer after UV excitation exhibit record photostabilities. ESIPT molecules thus offer huge advantages in numerous fields, e.g. as photostabilizers in sunscreens for protection against solar UV light [2] or for the development of novel photochromic molecular switches [3].

Here, we report on the stepwise ultrafast formation of the proton transfer product of the bistable ESIPT switch N-(3-pyridinyl)-2-pyridinecarboxamide (NPPCA, Fig. 1) by femtosecond fluorescence and absorption spectroscopy. The

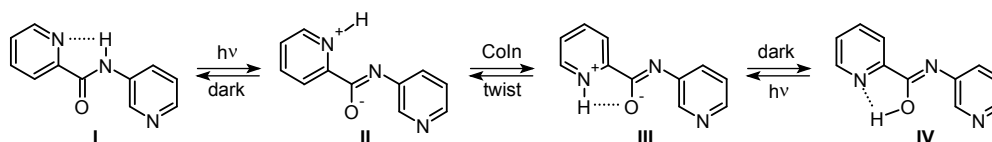


Fig. 1. Molecular structures and reaction scheme of the ESIPT switch NPPCA after UV excitation.

experimental results are complemented by ab initio excited-state calculations at the MP2/cc-pVDZ, CC2/cc-pVDZ and ADC(2)/cc-pVDZ levels of theory.

2. Results and Discussion

Measured fluorescence–time profiles, the two–dimensional (2D) transient absorption map and the transient absorption–time profiles at selected wavelengths after excitation of NPPCA in acetonitrile at $\lambda = 264$ nm are given in Figs. 2 a–e. The analysis of the fluorescence decay curves yielded lifetimes of $\tau_{fl,1} < 200$ fs as upper limit and $\tau_{fl,2} = 500 \pm 100$ fs mainly at longer emission wavelengths. The transient absorption map exhibits stimulated emission at $\lambda = 320 - 350$ nm and $450 - 550$ nm with lifetimes $\tau_1 = 100 \pm 10$ fs and $\tau_2 = 500 \pm 10$ fs, respectively, which correlate well with the fluorescence times. Additionally, we observe pronounced excited-state absorption (ESA) bands around $\lambda \approx 340, 470$ and 730 nm which feature a main decay time of $\tau_3 = 20 \pm 1$ ps next to the ultrashort τ_1 and τ_2 components.

The experimental data determined by a global analysis were assigned to sequential dynamical transformations of the photo-induced molecules as illustrated in Fig. 2f. Accordingly, the ≈ 100 fs component is the lifetime of the initially excited Franck-Condon state of the keto isomer I. The applied electronic excitation induces the subsequent ultrafast proton transfer to the excited enol tautomer II. The observed 500 fs fluorescence lifetime has to be attributed to the barrierless transition of the enol II to the electronic ground state through the CoIn encountered at a twisted configuration of the pyridine moiety. The ESIPT from I to II should thus be completed in < 500 fs. The main decay time of 20 ps seen in the absorption experiment must belong to states II and III in the electronic ground state and the proton transfer to the final product IV. As can be seen from the data in Fig. 2 b and c, this 20 ps decay contribution features a 500 fs rise time precisely as expected by the observed 500 fs electronic deactivation time of the excited state.

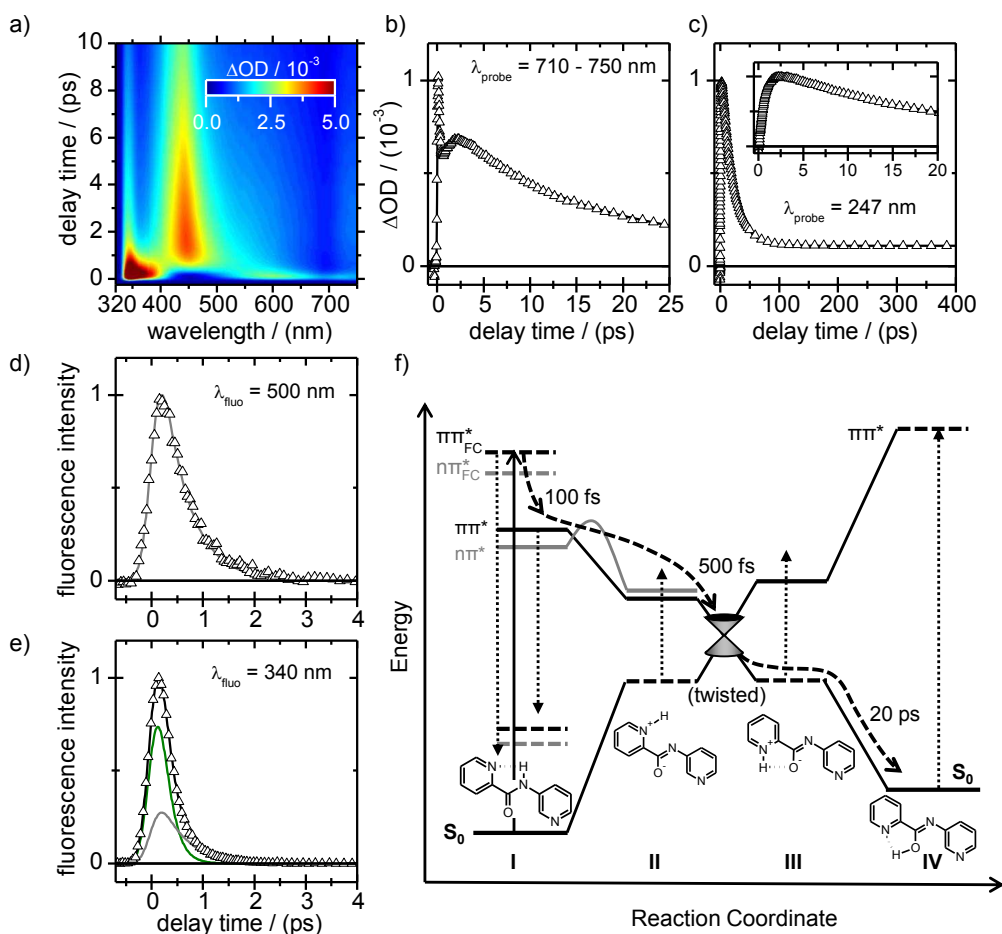


Fig. 2. a) 2D transient absorption map. b) Transient absorption–time profile at $\lambda_{\text{probe}} = 710 - 750$ nm. c) Transient absorption–time profile at $\lambda_{\text{probe}} = 247$ nm. d) Fluorescence–time profile at $\lambda_{\text{fl}} = 500$ nm. e) Fluorescence–time profile at $\lambda_{\text{fl}} = 340$ nm. f) Scheme of the photo-induced proton transfer in the investigate switch NPPCA obtained by combination of the experimental and computational [CC2 and ADC(2)] results. The assigned time scales belong to the distinctive reaction steps denoted by the dashed arrows. Dotted arrows indicate the observed transient emission and absorption bands.

Last but not least, the formation of **IV** is confirmed by the weak positive permanent absorption ($\tau \gg 1$ ns) in the time profile at $\lambda = 247$ nm.

In conclusion, our experimental and computational results clearly demonstrate the stepwise proton transfer reaction in the bistable photochromic ESIPT switch NPPCA. The ultrafast fluorescence decay within a time $\tau = 500$ fs, the delayed rise within $\tau \approx 500$ fs of the absorption at $\lambda > 700$ nm and the persistent (permanent) absorption at $\lambda = 247$ nm provide unambiguous evidence for the proposed ESIPT switching process.

References

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