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Femtosecond laser studies of excited state intramolecular proton transfer in an ultraviolet-filter molecule

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Abstract

Following excitation by a femtosecond laser pulse at 346 nm, phenol,2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl] in *n*-heptane relaxes towards its ground state in a four-step mechanism. By excited state intramolecular proton transfer (50 fs) the enol S_1 state produces the keto S_1' state responsible for a small gain spectrum above 600 nm. The latter relaxes to its keto ground state S_0' (130 fs) and the keto \rightarrow enol back proton transfer (500 fs) yields the vibrationally hot enol ground state, the cooling of which is a relatively slow process ($\gg 2$ ps). We present kinetics and detailed transient absorption and gain spectra between 380 and 720 nm. © 2000 Published by Elsevier Science B.V.

1. Introduction

Photoinduced excited state intramolecular proton transfer (ESIPT) is an elementary chemical reaction frequently occurring on ultrafast timescales in the condensed phase (for a recent overview, see Ref. [1]). Ever since the early work of Heller and Blattmann [2,3], 2-(2'-hydroxyphenyl)benzotriazole derivatives are among the most widely used commercially available ultraviolet (UV)-photostabilizers. Their stability to UV irradiation was attributed early to ESIPT [4]. 2-(2'-hydroxy-5-methylphenyl)benzotriazole (commercial name TIN or TINUVIN P; see Fig. 1) is archetypal of this family and has been

studied by numerous experimental (steady state and time-resolved absorption and emission spectroscopy, X-ray diffraction, NMR, ...) and computational techniques and in many media (in solution as well as in the solid state or included in polymers or glass matrices, at room and low temperatures) [5–32]. The relaxation mechanism of the photoexcited molecule, as initially described by Otterstedt [4], first involves ESIPT from the enol to keto form in their S_1 states, then relaxation to the ground state of the keto form, which is followed by back transfer of the proton causing a return to the ground state of the enol form (see Fig. 2). Although the lifetimes of the various excited states of TIN (100, 150 and 600 fs) were measured a few years ago [31], very scarce spectral features are described in the literature for the excited states of molecules of this family [32].

In this Letter, we present detailed time-resolved transient absorption/gain spectra between 380 and

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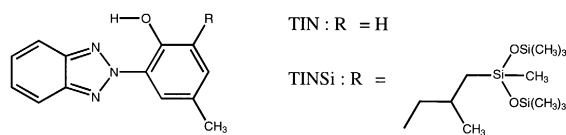


Fig. 1. Formula of TIN and TINSi.

720 nm, obtained for pump–probe delay times less than 3 ps for phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl] (TINSi; see Fig. 1) in solution in *n*-heptane, following excitation at 346 nm in resonance with the S_0 – S_1 absorption transition. TINSi follows a relaxation scheme similar to that previously described for TIN and we analyze the kinetics at various wavelengths to show the contributions of the different transients.

2. Experimental

Femtosecond pump pulses (25 μ J energy) are generated at 346 nm by frequency-mixing, in a 100- μ m-thick BBO crystal, the outputs of a Ti:Sapphire laser system at 800 nm and of a dye amplifier at 610 nm. The Ti:Sapphire system consists of a mode-locked oscillator and regenerative and multipass amplifiers working at a repetition rate of 20 Hz, out of which we extract 1 mJ pulses (60 fs FWHM). Part of the 800 nm pulse is used to produce a continuum of light in a water cell before spectral dispersion and selection prior to amplification in a four-stage dye amplification system. A small part of the 800 nm pulse is focussed in a 100- μ m-thick CaF_2 plate to produce a continuum between 350 and 800 nm. The white-light pulses are separated into two beams so as to have a probe and a reference going through the sample, and the transmitted light is dispersed and detected by a CCD camera. The signal is recorded on a PC and averaged over 2500 pump pulses per delay timestep. The pump–probe intercorrelation (120 fs FWHM) is measured by monitoring the photobleaching of Rhodamine 6G in methanol in the 500–515 nm domain (where the excited species absorption and gain are minimal and do not complicate the signal). The group velocity dispersion (GVD)

correction for the zero time delay versus wavelength was realized by a method described in Ref. [33].

TINSi (L'Oréal, batch DG004) was dissolved (4 mM) in spectroscopic grade *n*-heptane (Merck, UVASOL). The solution is pumped through a flow cell (sample thickness, 250 μ m) and we checked the steady-state absorption spectrum before and after every experiment to verify that no photodegradation had taken place.

3. Results and discussion

Pump–probe measurements were performed over the probing spectral range extending from 380 to 720 nm. The pump wavelength is 346 nm (28 894 cm^{-1}), near the maximum of the ground state absorption band of lowest energy (see Fig. 3). Transient spectra were recorded for time delays between pump and probe extending over 3 ps by 30 fs steps.

First, in Fig. 3, we present transient spectra measured at various delay times as changes in absorbance

$$\Delta\text{OD} = \log \left[\frac{T_{\text{ref}}(\delta t)}{T_{\text{pr}}(\delta t)} \right] - \log \left[\frac{T_{\text{ref}}(\delta t < 0)}{T_{\text{pr}}(\delta t < 0)} \right],$$

where $T_{\text{ref}}/T_{\text{pr}}$ is the light intensity transmitted at reference/probing positions through the sample and

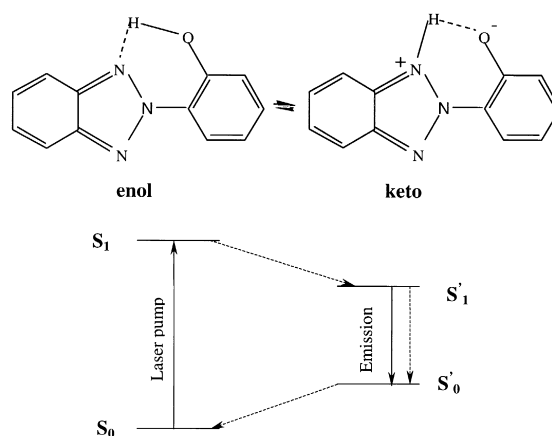


Fig. 2. Schematic excitation–relaxation cycle of TIN-like molecules in non-polar solvents.

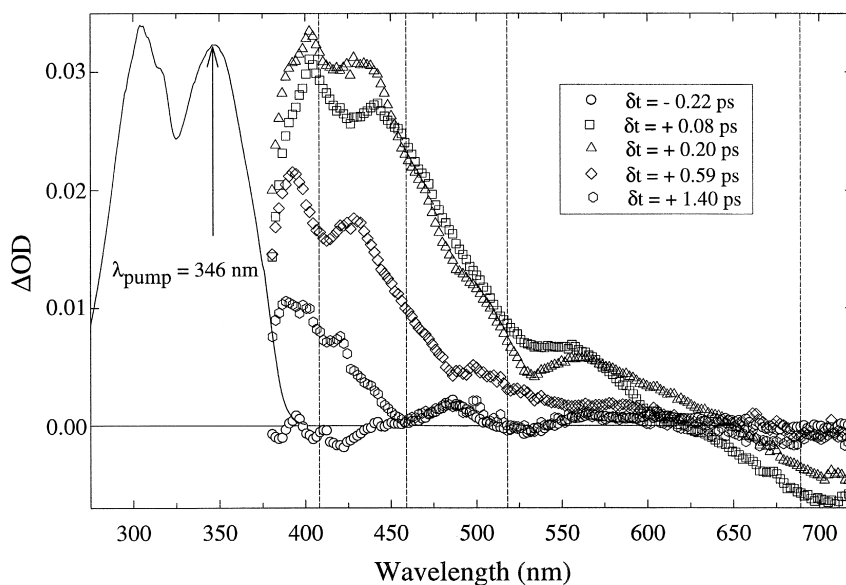


Fig. 3. Symbols: transient absorption and gain differential spectra of TINSi in *n*-heptane (4 mM) at various time delays δt between pump (346 nm) and probe (pump–probe inter-correlation FWHM 120 fs). Solid line: normalized steady-state absorption spectrum. Dashed lines: wavelengths of the kinetics shown in Fig. 4.

δt is the delay time between pump and probe, so that absorbance increases are positive and bleaching and gain are negative. All the data are corrected for group velocity dispersion. Each spectrum was obtained by averaging the transmitted intensities over 2500 laser pulses. We have CCD pixels every 0.6 nm, i.e. a slight spectral oversampling for the resolution of ca. 1 nm.

At early delay times ($\delta t = 80$ fs) where pump and probe overlap, we observe a strong absorption increase in the blue spectrum with two peaks at ca. 403 and 443 nm and a broad weaker band extending from 500 to 600 nm, as well as gain above 600 nm. This spectrum then changes over the next 500 fs as the double band below 450 nm narrows, increases in intensity ($\delta t = 200$ fs) and then decays ($\delta t = 590$ fs) as well as shifts to the blue (peaks at 392 and 427 nm at $\delta t = +0.59$ ps), while the gain band decays. Finally all the absorption bands disappear over the next 1.5–2 ps except for a small residual absorption (max. intensity about 10% of the original signal) confined to below 450 nm.

Then, in Fig. 4 is shown the kinetics of absorption and gain for four different probing wavelengths: 408, 459, 518 and 689 nm. The circles stand for the

experimental data, the solid lines represent the fits, and the dashed and dotted lines show the contributions to the kinetics of the various species. The fits were calculated from a rate equation model compris-

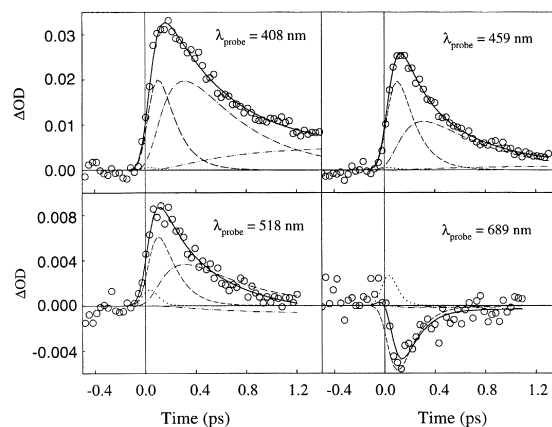


Fig. 4. Time-resolved kinetics of TINSi in *n*-heptane (4 mM) after excitation at $\lambda_{\text{pump}} = 346$ nm. Top left: $\lambda_{\text{probe}} = 408$ nm; top right: $\lambda_{\text{probe}} = 459$ nm; bottom left: $\lambda_{\text{probe}} = 518$ nm; bottom right: $\lambda_{\text{probe}} = 689$ nm. Experimental data (open circles), calculated fits (solid line); contributions to the fits of the enol-type S_1 (dotted line), keto-type S'_1 (dashed line), keto-type S'_0 (dash-dot line) and hot enol-type S_0 (dash-dot-dot line) states.

ing four electronic levels consecutively populated and assuming that the last species has a spectrum different from that of the initial ground state; they were optimized simultaneously for 100 wavelengths regularly spaced between 380 and 720 nm. First, the laser excitation leads to the formation of the enol S_1 which then decays with a time constant $\tau_1 = (50 \pm 20)$ fs; this state contributes to the kinetics essentially through a small absorption above 500 nm (Fig. 4, dotted line). It disappears by ESIPT and formation of the keto S'_1 state, which is responsible for the gain spectrum above 600 nm and the early absorption peaking at ca. 440 and 400 nm (Fig. 4, dashed line). The presence of this gain was expected from the small emission observed in steady-state fluorescence experiments in *n*-heptane (yield $\Phi = 10^{-6}$). In turn S'_1 relaxes with a lifetime $\tau_2 = (130 \pm 30)$ fs toward the keto ground state S'_0 , which absorbs more in the blue (Fig. 4, dash-dot line) than the S'_1 state and is responsible for the shift observed in the time-resolved spectra. Finally the S'_0 state relaxes toward the vibrationally hot enol ground state S_0 with a lifetime $\tau_3 = (500 \pm 50)$ fs. The thermalization of the ground state is a process which requires the observation of much longer delay times than those used in our experiment.

The model used is in effect the classical model proposed more than 20 years ago by Otterstedt [4] assuming that the relaxation of the molecule leads ultimately to the hot enol ground state. Considering the small contribution to the fit from the first excited state necessitated by the model, we tried to fit the experimental data with a model involving only three electronic levels (i.e. where such a contribution would be absent) but the results were never satisfactory. Both the time constants and the spectra are similar to those reported by Elsässer et al. for the TIN molecule [31,32] but for three small differences: (i) all the relaxation steps of TINSi seem to be a little quicker than those observed for TIN, (ii) two distinguishable absorption bands are observed in the 400–500 nm region for both the S'_1 and S'_0 keto-type states, and (iii) no absorption was observed above 600 nm after the disappearance of the gain signal. The last two points are probably the result of much better spectral resolution at the expense of a loss in the signal-to-noise ratio in comparison to the data presented by these authors.

4. Conclusion

The sub-picosecond proton transfer dynamics of a new hydroxyphenylbenzotriazole derivative, TINSi, has been studied by femtosecond pump–probe spectroscopy. Detailed time-resolved absorption/gain spectra have been presented in the 380–720 nm domain and the time evolution of the reaction products has been determined. The relaxation scheme of the molecule follows a classical pathway involving fast ESIPT and ground-state back proton transfer (50 and 500 fs, respectively).

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