



## Novel detection scheme for application in pump–repump–probe spectroscopy

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### ARTICLE INFO

#### Article history:

Received 9 September 2009  
Received in revised form 28 October 2009  
Accepted 28 October 2009

#### Keywords:

Pump–repump spectroscopy  
Indolylfulgide  
Detection setup  
Photochemistry  
Ultrafast

### ABSTRACT

A novel detection scheme for pump–repump–probe spectroscopy is presented, where the use of modulation and referencing allows to record the efficiency of a photochemical reaction as a function of the pump–repump delay in a single measurement. This new technique is applied to investigate the ring-opening reaction of an indolylfulgide after pre-excitation. Here the reaction efficiency doubles, when the excitation pulse is very close to the pre-excitation pulse, and the improvement of the efficiency decays with increasing pump–repump delay on the time scale of about 5 ps.

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### 1. Introduction

In numerous investigations the pump–probe scheme has been used to record the dynamic properties of the investigated system. In the last 25 years femtosecond pump–probe spectroscopy has evolved as one of the most important techniques to investigate ultrafast processes in biology, chemistry and physics [1]. Ti:Sa-based laser systems play a key role in the generation of the pulses required for these investigations [2,3]. The development of different frequency conversion mechanisms (like second harmonic generation (SHG), white light continuum generation (WL), optic parametric processes) has made accessible a broad frequency range. In pump–probe spectroscopy a laser pulse excites the sample and thereby changes its optical properties. Afterwards another, often less intense, laser pulse records the transmission of the sample as a function of the time-delay between the two pulses. These transmission changes contain the information on the dynamics of the system under investigation. In more advanced experiments pump–dump or pump–repump schemes [4–9] were used to investigate special properties of reacting systems.

In a recent study we investigated the ring-opening reaction (initiated by the excitation pulse) of a trifluorinated indolylfulgide after a preceding ring-closure reaction (initiated by the pre-excitation pulse) [9]. It was shown that reaction dynamics and quantum efficiency of the ring-opening reaction strongly depend on the de-

lay time  $\Delta t_1$  between pre-excitation and excitation pulse. In this experiment it was difficult to record the dynamics of the small quantum yield with sufficient precision. Therefore we developed a new experimental scheme, where the change in quantum efficiency as a function of pump–repump delay  $\Delta t_1$  can be measured directly.

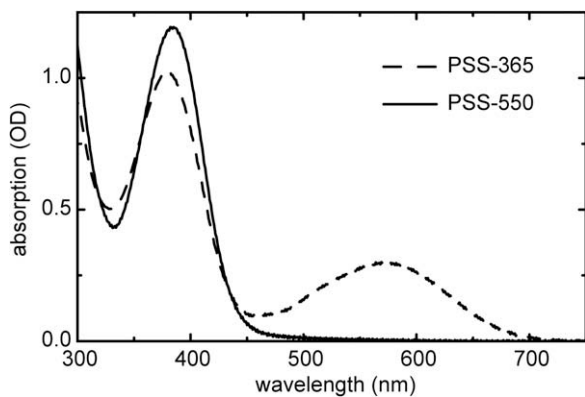
### 2. Experimental

#### 2.1. The laser system

The home-built Ti:Sapphire laser system working at 800 nm with repetition rate of 1 kHz has been described in detail in reference [10]. It provides a fundamental laser pulse that is split into several parts. For the probe and reference pulses a white light continuum (WL) is generated in a 3 mm thick sapphire plate. The excitation pulse at 630 nm (duration 35 fs) with 45 nJ pulse energy is produced in a noncollinear optical parametric amplifier (NOPA) [11,12] and afterwards compressed in a quartz prism compressor. Second harmonic generation (SHG) of the fundamental laser pulse in a 0.5 mm thin  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> crystal provides the pre-excitation pulse. Its energy at the sample position was adjusted to about 1  $\mu$ J. To avoid destruction of the sample the pulses were stretched in a 250 mm fused silica glass block. In a reference measurement on the laser dye Oxazine 1 [13], the pulse duration (FWHM) was determined to 1050 fs and the zero point of the delay time  $\Delta t_2 = 0$  was determined (see Section 3.3). Reference (*p*-polarisation), pre-excitation (*s*-polarisation), excitation (*p*-polarisation)

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**Fig. 1.** Steady-state absorption spectra for PSS-365 (mainly C-form, broken line) and PSS-550 (mainly E-form, solid line) of indolyfulgide in the solvent 1,4-dioxane.

and probe pulse (*p*-polarisation) are spatially overlapped in the sample.

The sample concentration was adjusted to an optical transmission of about 10% at 400 nm. It was kept in a fused silica flow cuvette with optical pathlength of 200  $\mu\text{m}$  (Hellma). The excited volume of the sample was exchanged by a peristaltic pump from shot to shot and the sample reservoir was illuminated continuously to preserve the defined concentration of the open *E*-isomer. Two identical multi-channel detection setups each consisting of a monochromator, 42 diode array and ADC were used [14] to record the spectra of the probe and the reference pulse.

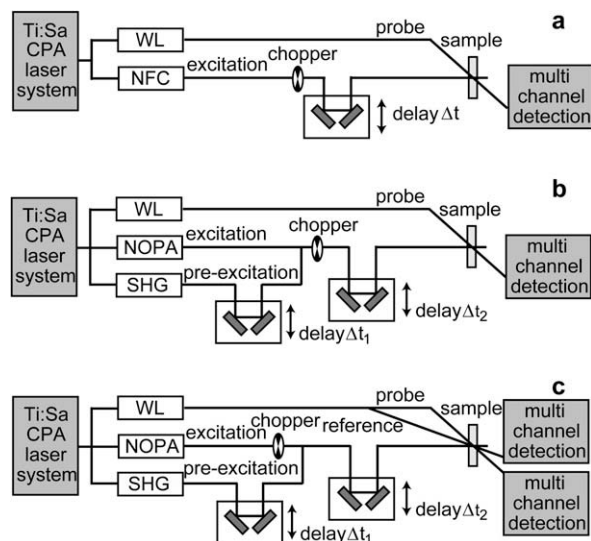
## 2.2. The sample

Details of the synthesis of the investigated indolyfulgide are published in [15]. These indolyfulgides can occur in three thermally stable isomers, the closed C-form and the open forms *E* (which is cyclisable) and *Z* (which is not cyclisable and can be neglected for the further observations) [16]. The indolyfulgide molecules were dissolved in 1,4-dioxane (Sigma Aldrich Chemie). The reaction efficiencies and reaction dynamics were determined as presented for similar indolyfulgides and indolyfulgimides in [10]. The ring-opening pump-probe experiment was performed on a sample in the photostationary state PSS-365 prepared by illuminating the sample around 365 nm with a Hg(Xe) lamp (Hamamatsu, 8251, 10 mW) using an optical filter UG1 (1 mm, Schott). In this PSS-365 state the sample mainly consists of closed C-isomers. The ring-closure reaction and the ring-opening after pre-excitation were studied on a sample in the PSS-550, where mainly *E*-form molecules and no C-form molecules exist. To obtain the PSS-550 the sample was first transferred to the PSS-365 and then illuminated by a cold light source (KL 1500 electronic, Schott) filtered with an optical long pass OG550 (3 mm, Schott).

Fig. 1 shows the absorption spectra of the indolyfulgide dissolved in 1,4-dioxane in the two photostationary states PSS-365 and PSS-550 measured in a spectrophotometer (Perkin-Elmer, Lambda 19). Only the C-isomer absorbs in the visible spectral range at  $\lambda > 550$  nm, so the ring-opening reaction is selectively accessible.

## 3. Novel experimental detection scheme and results

Fig. 2 shows three experimental setups for the different transient absorption experiments. The classical pump-probe design is depicted on the top (a). In (b) the build-up used in [9] for pump-repump-probing and in (c) the new setup presented in this publication are shown.



**Fig. 2.** Three different setups for time resolved spectroscopy. (a) Setup for standard pump-probe spectroscopy. (b) Setup for pump-repump-probe spectroscopy from reference [9]. Here for referencing two delay time ( $\Delta t_2$ ) traces at distinct  $\Delta t_1$  values have to be recorded, one with and one without the pre-excitation pulse. (c) Novel setup for pump-repump-probe spectroscopy with improved detection possibilities. Details see text.

### 3.1. Pump-probe

In a standard pump-probe experiment (Fig. 2a) an ultrafast laser pulse is split into two parts, the excitation and the probing pulse. Frequency conversion of the probe pulse occurs in a thin sapphire plate (white light continuum generation). The excitation pulse is converted to the required wavelength by non-linear frequency conversion (NFC): SHG to 400 nm for the ring-closure or NOPA to 630 nm for the ring-opening reaction. The time interval  $\Delta t$  between excitation and probe pulse can be regulated via a mechanical delay stage. Both pulses are overlapped in the sample and the transmission of the probe pulse is detected by a multi-channel detection setup. Two different techniques are used to improve the precision of the measurement of the excitation induced transmission change: (i) Chopping: every second excitation pulse is blocked by a chopper. The transmission change is directly determined from the data recorded for open and closed chopper position. (ii) Referencing: another possibility not shown in Fig. 2a (but used in the scheme of Fig. 2c), is to split the probe pulse into two parts: The actual probe pulse and the reference pulse, which passes the sample prior to excitation and probe pulse. The transmitted energy of reference and probe pulse is detected by two identical spectrometers and the change in transmission/absorption induced by the excitation pulse is calculated with high precision.

As an example the transient absorption data of ring-closure and ring-opening reaction of the indolyfulgide dissolved in 1,4-dioxane are depicted in Fig. 3. Fig. 3a shows the transient absorption of the indolyfulgide sample in PSS-550 (containing predominantly the open *E*-isomer) excited by the SHG of the laser fundamental at 400 nm and detected at the probe wavelength 630 nm. The data show around delay time  $\Delta t = 0$  an absorption feature, a coherent artifact [17]. Subsequently an absorption increase due to the absorption of the excited state is observed and the signal decays on the time scale of 200 fs until a positive offset remains for longer delay times. This offset indicates the absorption due to the newly formed C-form molecules. The data are in very good agreement with other experiments on the ring-closure reaction of related indolyfulgides and indolyfulgimides, where it was found that the ring-closure reaction is an ultrafast process on the sub-picosecond

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