Improved experimental technique for determining double hydrogen *transfer rates in porphycenes with the use of transient absorption anisotropy*

Piotr Ciąćka*, Piotr Fita* and Czesław Radzewicz*†

*Institute of Experimental Physics, University of Warsaw, Ul. Hoża 69, 00-681 Warsaw, Poland
†Institute of Physical Chemistry, Polish Academy of Sciences, Ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

introduction

The use of transient absorption anisotropy decay for determining double hydrogen transfer rates in porphycene and its derivatives has been recently proposed and successfully applied in our laboratory [1, 2] Contrary to stationary and time resolved emission anisotropy, the technique allows determination of ground state reaction rates. However, to take full advantage of the technique, there was a need for more sensitive and more robust instrumentation. Experimental setup and detection scheme presented here greatly decrease the influence of short term intensity instabilities. It allows us to obtain good results with small number of scans, which saves time and in turn minimizes occurrence of error caused by long term instabilities.
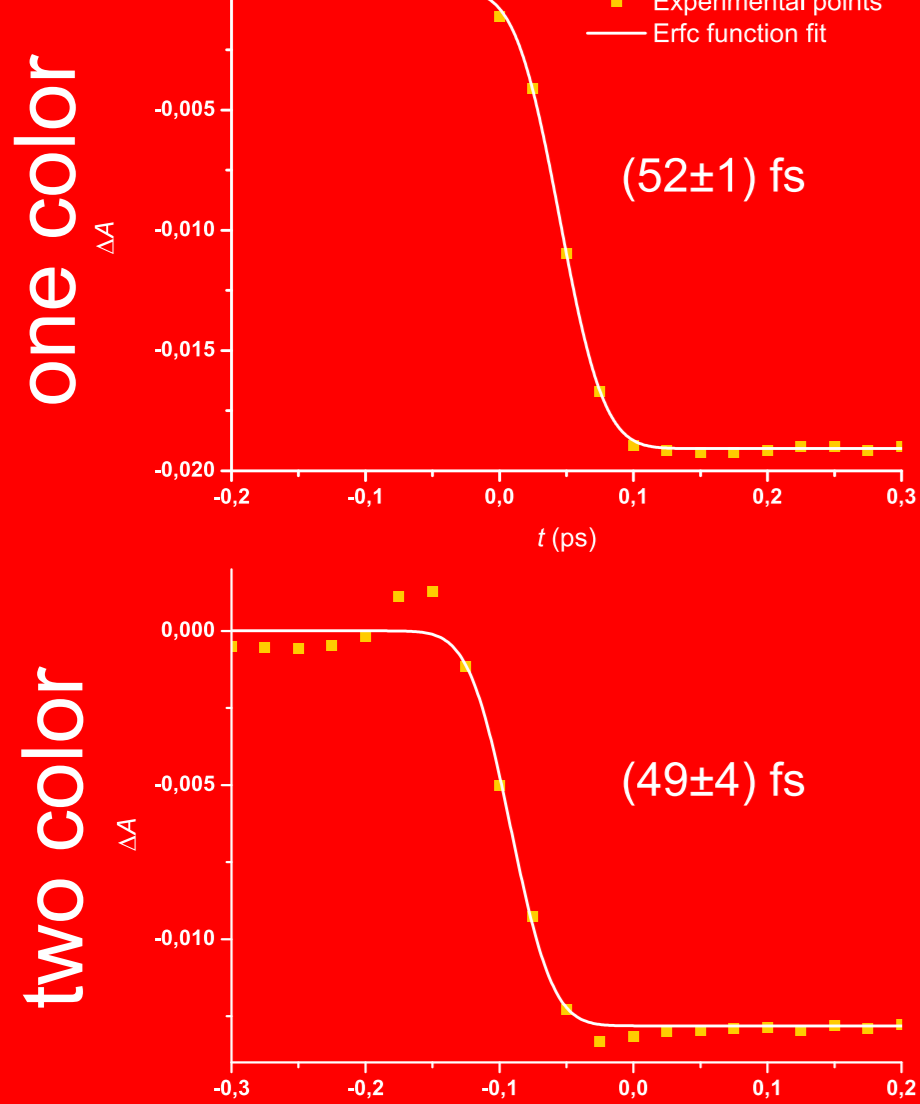
linearity

/ determining range of pump energies to which absorption change is linearly proportional
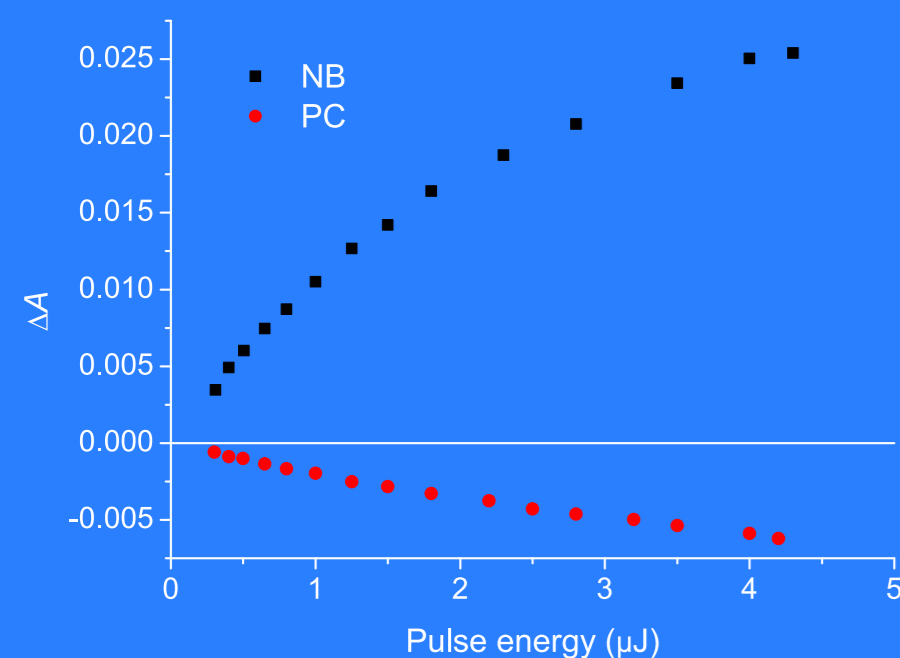
Influence of pump pulse energy on absorption change for Nile Blue (NB) and porphycene (PC). Probe pulse was ca. 20 times weaker than the pump.

temporal resolution
/ retrieved from rise time of ground state bleach

one color

(52±1) fs

two color

(49±4) fs

a word on noise sources

Typical relative intensity fluctuations of NOPAs were 1.3% rms as measured with a pulse energy meter. Propagating this value to obtain final noise of absorption change for n = 1000 and T = 30 s yielded $1.5 \cdot 10^{-5}$. Stability measurement performed using the setup's photodiodes and aquisition card that did take pump instabilities and electronic noise into account yielded final absorption change noise of $2.0 \cdot 10^{-5}$. Both results agree very well with directly measured value. Main contributors of measurement noise are light sources (NOPAs).
To determine sensitivity attainable with almost noisless light sources we have connected battery DC signals of the same amplitudes as peak photodiode voltage in a typical measurement. Resulting change of absorption noise read $8 \cdot 10^{-7}$. Therefore, sensitivity gain from using quieter light sources could be as much as two orders of magnitude.

tautomerization & anisotropy
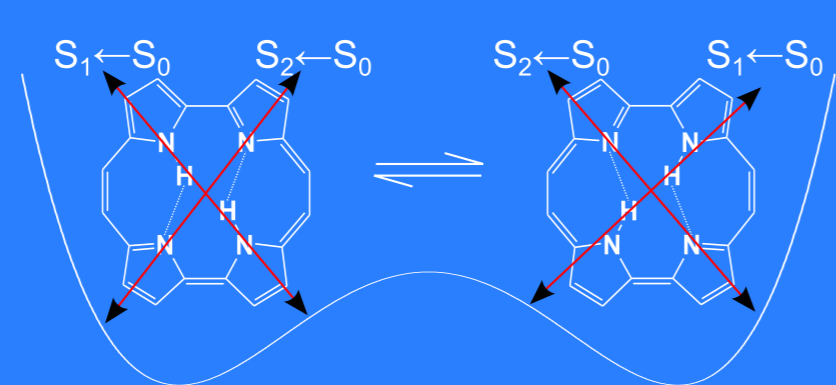
Tautomerization of porphycenes. Note the location of hydrogen atoms on opposite pyrole rings. Arrows indicate dipole moment directions for relevant transitions.

Tautomerization products are chemically identical. However, intramolecular movement of hydrogen atoms can influence polarization of probing light by changing directions of transition moments.
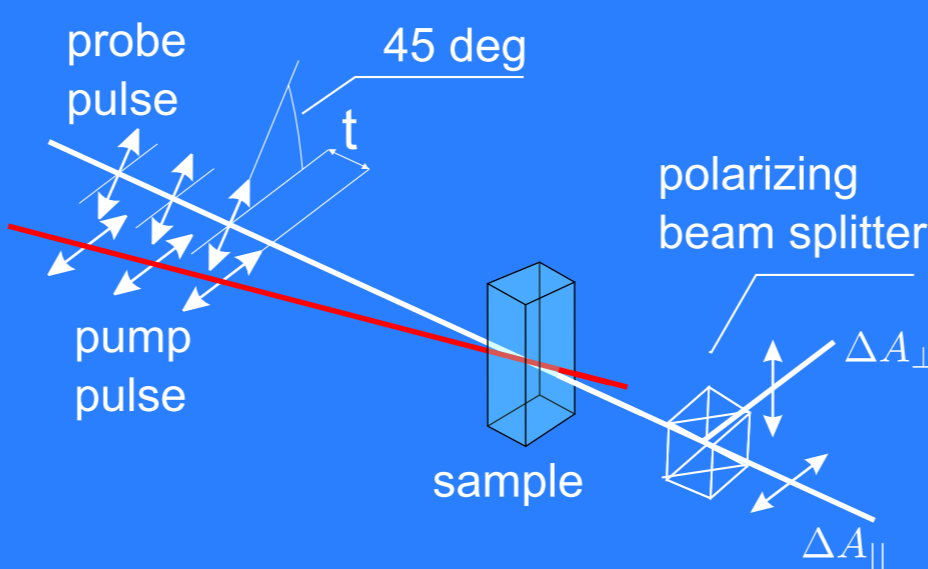
Shown on a scheme above, transient absorption anisotropy is a polarization-sensitive variant of pump-probe technique. It allows us to monitor time evolution of transient dipole orientation.

Measured quantity: anisotropy r

$$ r = \frac{\Delta A_{\parallel} - \Delta A_{\perp}}{\Delta A_{\parallel} + 2\Delta A_{\perp}} $$

Under appropriate conditions, rise/decay times of anisotropy reflect kinetics of double hydrogen transfer.
For instance, for one color experiment (pump & probe at 630 nm) we have:

$$ r(t) = a[(r_0^0 - r_\infty^0)e^{-2(k_0-k)t} + r_\infty^0] + (1-a)[(r_0^1 - r_\infty^1)e^{-2k_1 t} + r_\infty^1] $$

It is possible to retrieve both ground (k_0) and excited state (k_1) tautomerization rate in a single experiment.

experimental setup
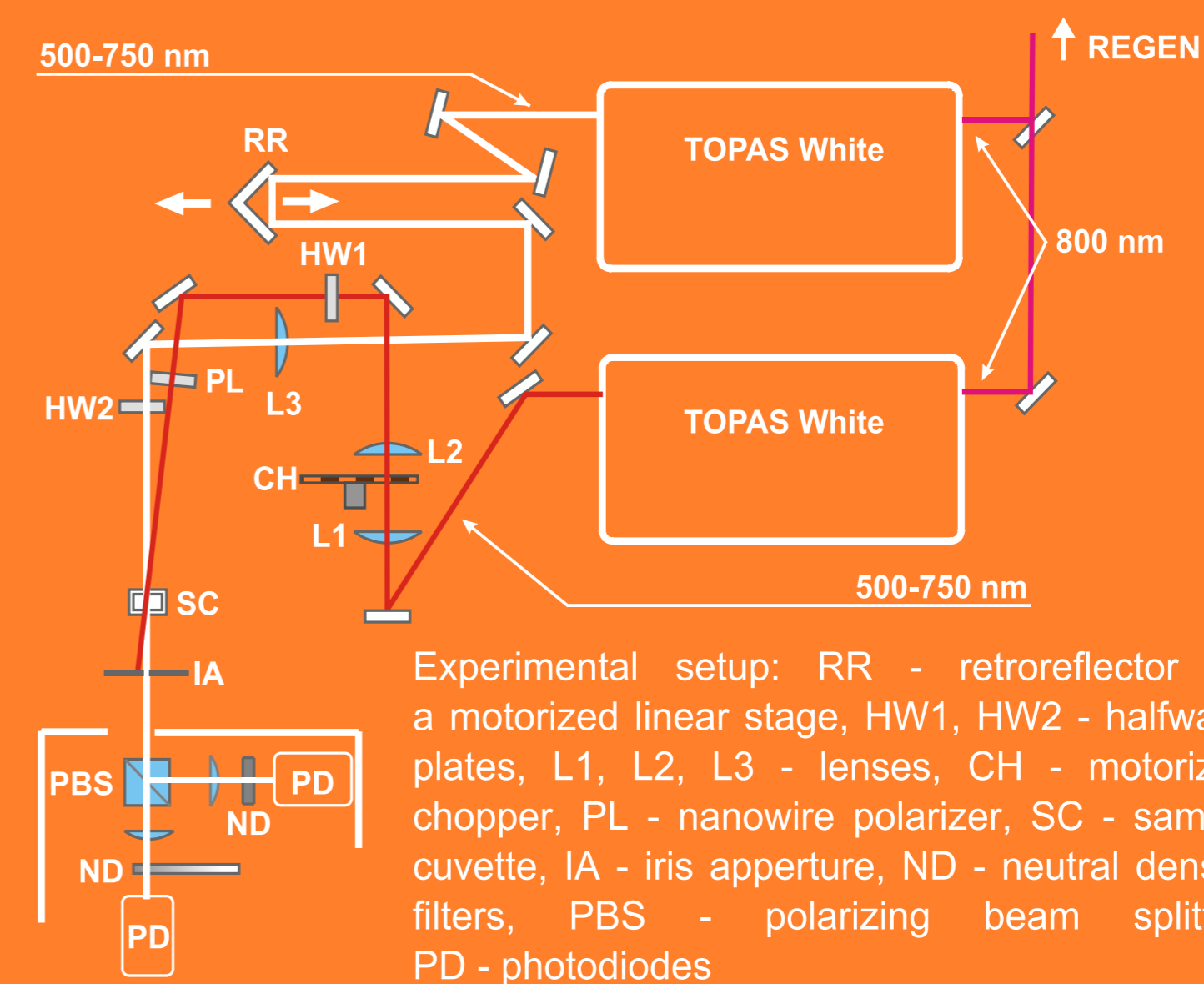
Experimental setup: RR - retroreflector on a motorized linear stage, HW1, HW2 - halfwave plates, L1, L2, L3 - lenses, CH - motorized chopper, PL - nanowire polarizer, SC - sample cuvette, IA - iris apperture, ND - neutral density filters, PBS - polarizing beam splitter, PD - photodiodes

Detection scheme uses two photodiodes with integrated amplifiers with response time of 30 µs. National Instruments NI-USB 6351 board is used to digitize the photodiodes signals by acquiring one sample per pulse after the arrival of trigger signal from the regenerative amplifier.

finding optimal workflow

/ testing data processing and averaging strategies
/ determining optimal number of pulses averaged and scans collected for fixed experiment time window

Acquisition time T was divided into m segments (corresponding to delay line scans), during every one of which N pulse intensity values were collected. Two collections, N/2 values each (pump blocked/unblocked), were averaged and processed yielding m values of absorption change. Those m values were subsequently averaged. One then obtains (for pulse repetition rate f):

$$ T = \frac{m \cdot N}{f} $$
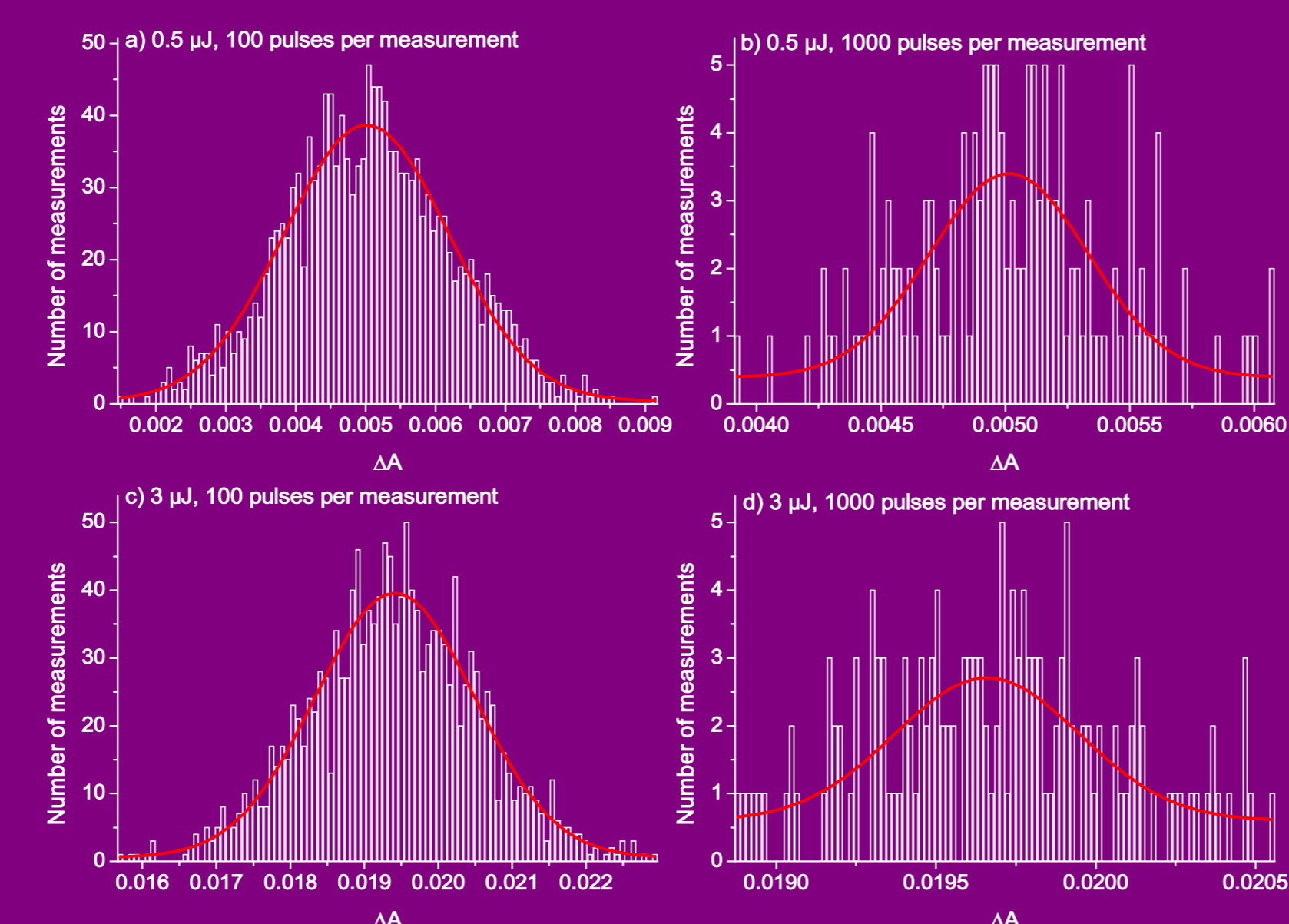
Distributions of absorption change values registered for fixed T = 30 s at several pump pulse energies and different number N of averaged pulses.
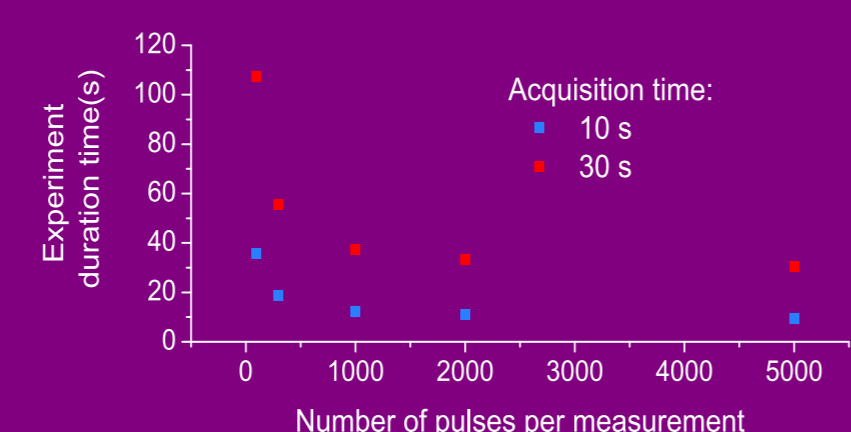
Top left: Total measurement time as function of number N of collected pulses for acquisition time T = 10 s and T = 30 s. True measurement time is longer than acquisition time T due to acquisition card initialization, processing of data and translating the delay line.
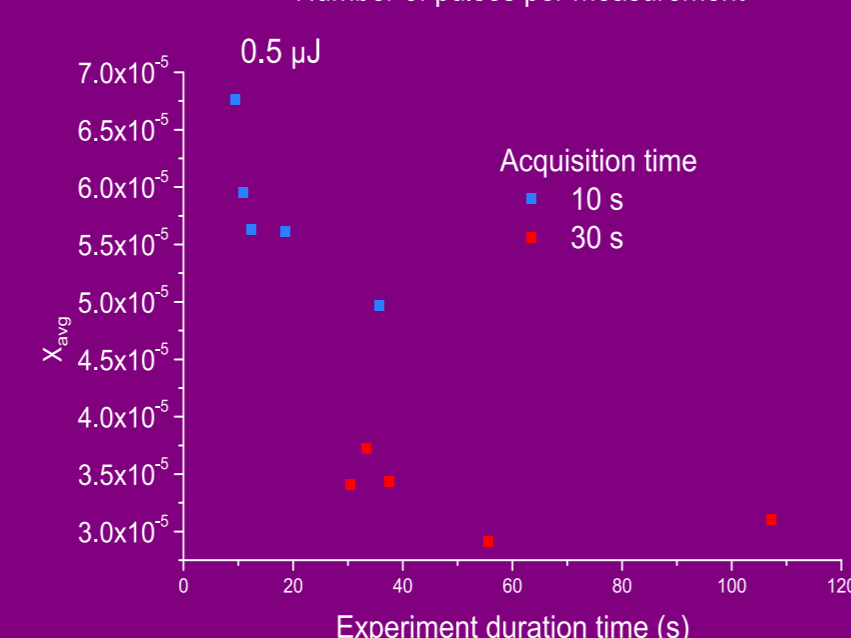
Middle and bottom left: Standard deviation of final absorption change value as a function of total time needed to obtain it for two values of T, for 0,5 and 3 µJ. Decreasing number N of averaged pulses didn't improve standard deviation significantly and made measurement time too long. Better results were achieved for higher N, therefore for considerably low number of scans, m.
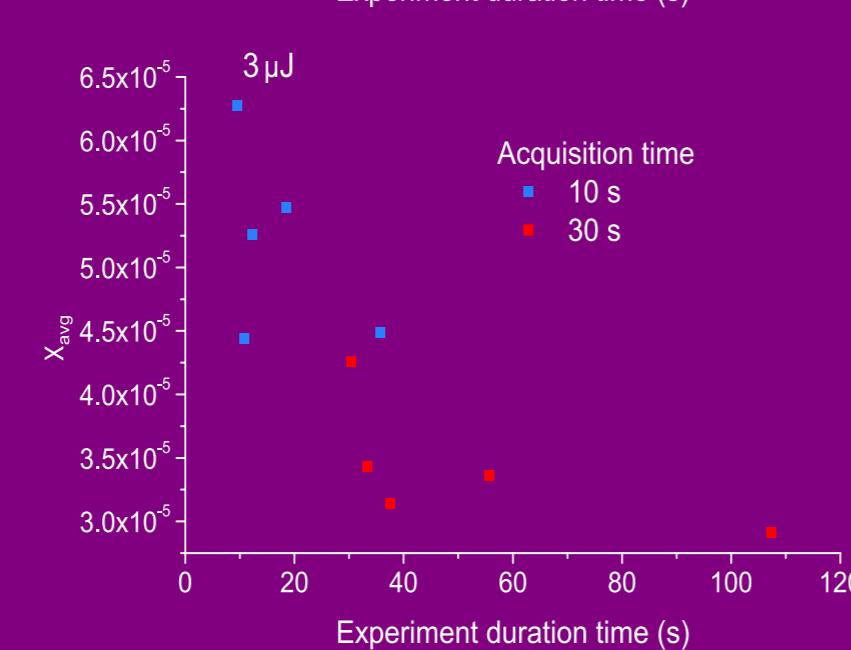
Maximum practical sensitivity (assuming 1 minute limit for measurement time and S/N ratio of 1):

$$ \Delta A = 3 \cdot 10^{-5} $$

High sensitivity results from chosen averaging scheme and relatively high pulse repetition rate of 5 kHz. Pulse energy fluctuations are suppressed due to time passed between detecting pumped and not pumped absorption being only 200 µs.

conclusions

We have built an improved transient absorption anisotropy setup, characterized its linear response range and time resolution and found optimal working parameters. Sensitivity was characterized and its limits discussed. Low noise in transient absorption and anisotropy even in presence of moderate pulse intensity instabilities allowed us to obtain high quality results on tautomerization rates in porphycene and its derivatives. Independent pump and probe tuning and excellent sensitivity make the setup a flexible tool for investigating absorption anisotropy in wide range of light absorbing compounds.

[1] Fita, P.; Urbańska, N.; Radzewicz, C.; Waluk, J. Chemistry – A European Journal 2009, 15, 4851–4856.
[2] Fita, P.; Garbacz, P.; Nejbauer, M.; Radzewicz, C.; Waluk, J. Chemistry – A European Journal 2011, 17, 3672–3678.

results

/ contrary to [1], no assumption on fast $S_2 \rightarrow S_1$ relaxation needed
/ compared with values for [1] where applicable
/ note excellent signal to noise ratio

porphycene
values from [1] in yellow
$k_0 = (6.6\pm0.2)\times10^{11}$
$k_0 = (5.8\pm0.3)\times10^{11}$
$k_1 = (11.4\pm0.5)\times10^{10}$
$k_1 = (7.4\pm0.9)\times10^{10}$

2,3,6,7,12,13,16,17- octaethylpoprhycene
$k_0 = (7.28\pm0.14)\times10^{9}$
$\approx k_0 10^{10}$
$k_1 = (6.2\pm0.5)\times10^{8}$
$k_1 \leq 10^{9}$

9,10,19,20-tetrapropylporphycene
$k_0 \approx 10^{13}$
$k_0 \approx 10^{13}$
$k_1 = (2.49\pm0.07)\times10^{12}$
$k_1 = (1.9\pm0.2)\times10^{12}$

2,7,12,17-tetra-tert-butylporphycene
$k_0 = (13.5\pm0.4)\times10^{11}$
$k_0 = (13.7\pm0.8)\times10^{11}$
$k_1 = (3.32\pm0.09)\times10^{11}$
$k_1 = (2.0\pm0.1)\times10^{11}$

9,10,19,20-tetramethylporphycene
$k_0 \approx 10^{13}$
$k_0 = 10^{13}$
$k_1 = (2.12\pm0.08)\times10^{12}$
$k_1 = (1.9\pm0.2)\times10^{12}$

2,7,12,17-tetra-(methoxyethyl)porphycene
$k_0 = (9.1\pm0.2)\times10^{11}$
$k_1 = (2.16\pm0.05)\times10^{11}$