Appl Phys B (2009) 96: 247–250
DOI 10.1007/s00340-009-3612-y

Applied Physics B
Lasers and Optics

RAPID COMMUNICATION

A novel ultra-broadband transient spectrometer with microsecond measurement range based on a supercontinuum fiber laser

C. Schriever · I. Pugliesi · E. Riedle

Received: 30 April 2009 / Published online: 18 June 2009

Abstract We show that the combination of a free-running 24 kHz supercontinuum fiber laser with a kHz femtosecond laser renders a sensitive and easy to implement transient spectrometer. It can directly extend the observation range of a standard broadband femtosecond spectrometer from the usual limit of a few nanoseconds to 1 millisecond and with the additional use of a chopper to seconds. The transmission signal from all supercontinuum pulses is recorded and assigned to the proper delay time by data post-processing. To demonstrate the performance of the device, the relaxation dynamics of Nd:YAG is measured.

PACS 42.65.-k · 42.55.Tv · 42.62.Fi · 78.47.jc

1 Introduction

Transient pump-probe spectroscopy is a very versatile tool for the investigation of photoinitiated dynamics in physical, chemical and biological systems [1], and in particular solar cells and novel functional materials [2–4]. Two major approaches are commonly used to achieve time resolution. Femtosecond spectroscopy derives pump and probe pulse from a single femtosecond laser source. Using (time) integral detection the time resolution is given by the length of pump and probe pulse. By varying the relative optical path length, dynamics on the time scale from a few femtoseconds to nanoseconds can be investigated. In flash photolysis spectroscopy, pump and probe are generated from separate light sources, usually a nanosecond pump laser and an ultra-broadband xenon lamp [3, 5]. The time resolution is typically achieved by using a detector with a fast electronic response time. Thereby the dynamics on time scales from a few nanoseconds up to milliseconds can be accessed.

Xenon lamps offer an unsurpassed spectral coverage from the deep UV to the MIR, but being a classical light source, tight focusing and short pulse generation are problematic. It is therefore often desirable to replace flashlamps with pulsed laser-like light sources. The advent of supercontinuum generation in photonic crystal fibers in recent years has led to the development of commercially available high repetition rate lasers that generate intense nanosecond whitelight pulses from 350 to beyond 2000 nm [6, 7].

While in femtosecond pump-probe spectroscopy ultrashort time resolution can be easily achieved, the power of flash photolysis is the ultrabroad spectral coverage due to the spectrum of the xenon lamps. Here we present a novel approach that combines the advantages of both methods. We use a femtosecond pump pulse that can be easily tuned to the absorption of the investigated system by noncollinear optical parametric amplification (NOPA) [8]. Pulses from a commercial supercontinuum fiber laser with pulse lengths of ∼1 ns are employed as probe. This setup is capable of measuring the transient dynamics from nanoseconds to seconds, with minimal thermal load on the sample. In contrast to earlier attempts, where a 400 ps pulsed diode laser was used as probe [9], the supercontinuum probe pulse allows us to record transient spectra from 450 to 2000 nm (presently limited by the photodetector). As proof of the capability of the setup we performed test measurements on the relaxation lifetime of Nd:YAG.

C. Schriever · I. Pugliesi · E. Riedle (✉)
Lehrstuhl für BioMolekulare Optik,
Ludwig-Maximilians-Universität München, Oettingenstrasse 67,
80538 München, Germany
e-mail: eberhard.riedle@physik.uni-muenchen.de
Fax: +49-89-21809202

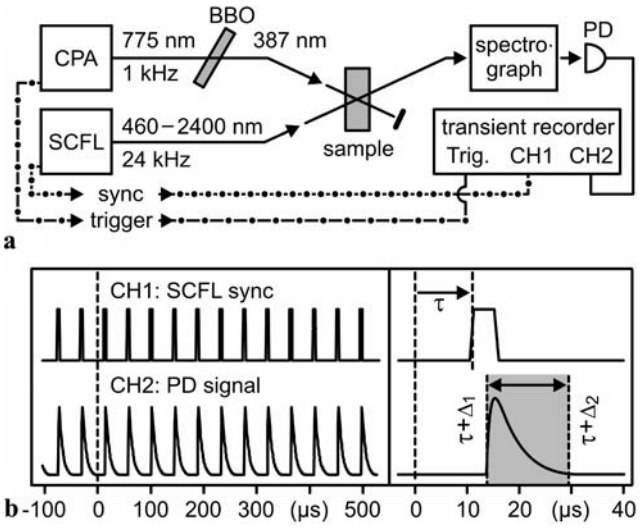

Fig. 1 (**a**) Schematics of the experimental setup. (**b**) The channel traces of the transient recorder analyzed to give the time delay between the CPA pump and the SCFL probe pulse (CH1) and to obtain the intensity of the transmitted probe light (CH2)

2 Experimental setup and data acquisition

A Ti:sapphire amplifier system (CPA-2001, Clark-MXR; 150 fs, 1 kHz, 775 nm) is frequency doubled in a β-barium borate (BBO) crystal cut for type I phase matching to generate intense ultraviolet excitation pulses (387 nm). A supercontinuum fiber laser (SuperK Compact; Koheras GmbH; SCFL) running at 24 kHz is used to generate extremely broad probe pulses from 450–2500 nm. The continuum is focused into the sample with an adjustable fiber collimator down to a beam diameter of 300 µm. The excitation pulses are spatially overlapped with the probe pulses at the sample. A lens with a focal length of $f = 200$ mm is employed to achieve a beam diameter slightly larger than the one of the probe. The transmitted probe light is dispersed in a grating monochromator (spectral width ∼5 nm) and the pulse energy is measured with an integrating photodiode module (PDI-400-UV; Becker&Hickel GmbH) which produces an electrical output signal with a decay constant of ∼5 µs. The SCFL delivers an energy of 4 µJ across the whole spectrum; the visible part amounts to ∼0.7 µJ; for the measurements presented here a Schott KG1 filter was used to block the NIR part and the visible part was suitably attenuated with a gray graduated filter placed in front of the sample to generate light intensities that do not saturate the photodetector (Fig. 1a).

Due to the differing repetition rates of the CPA and the SCFL each excitation pulse is followed by about 24 probe pulses. Since the probe pulses are low in energy and do not affect the photodynamics of the sample, not just the first, but all 24 pulses can be used to probe the excitation induced dynamics. The SCFL used in this investigation cannot be triggered externally and therefore runs asynchronously to the CPA. However, a TTL synchronization pulse (sync) is available that is produced synchronously to the light pulse. Therefore a data acquisition method that determines the time delay between pump and probe pulses is needed for the recording of transient transmission traces. For this purpose a PC transient recorder running at 100 MSa/s (NI PCI-5122; National Instruments Corp.) is triggered by the laser trigger of the CPA. It records simultaneously both the photodiode signal and the sync output of the SCFL for 800 µs. By data post-processing, the rising edges of the SCFL sync are detected and a time delay with respect to the CPA trigger is assigned to each of them. The photodiode signal is integrated over a 15 µs time window for each pulse of the SCFL to render a measure for the transmitted probe pulse energies (Fig. 1b).

The maximum time delay for the transient transmission measurement is given by the repetition rate of the pump laser. To allow for data averaging, the time range is divided into time bins. All transmission measurements with time delays that fall into the same bin are averaged. Due to the asynchronous relation between the CPA and the SCFL the pulses populate the bins in an arbitrary order. This can be compared to a fast scan procedure of an optical delay line setup [10]. The single shot transmission measurements that are averaged in each time bin are thus not correlated, and averaging yields a true $1/\sqrt{N}$ noise reduction. The temporal width of the bins gives the time resolution of the measurement. To complete the transient measurement in a reasonable amount of time (5 min), this width cannot be chosen arbitrarily small as a certain number of probe pulses ($N \approx 2000$) are required to fall in each bin for sufficient noise reduction. A bin width of 0.5–1 µs proved reasonable.

To obtain the transient transmission change, in typical femtosecond pump-probe experiments for each time delay between pump and probe the intensity of the probe pulse behind the sample is recorded alternating with the pump pulse applied and blocked. In this experiment all measurements are performed with the pump pulse on. The transmission change is obtained by dividing the signal trace by the averaged value before zero time delay. Due to the statistical distribution of the time delays this referencing is virtually equivalent to the alternating measurement.

In our setup we use single channel detection to record time traces at different wavelengths. The spectral selection is achieved through a motorized monochromator. Transient spectra can be reconstructed from time traces by choosing a suitably narrow wavelength step.

3 Experimental results

To assess the suitability of the SCFL as probe laser in transient spectroscopy, we characterized the pulse-to-pulse en-

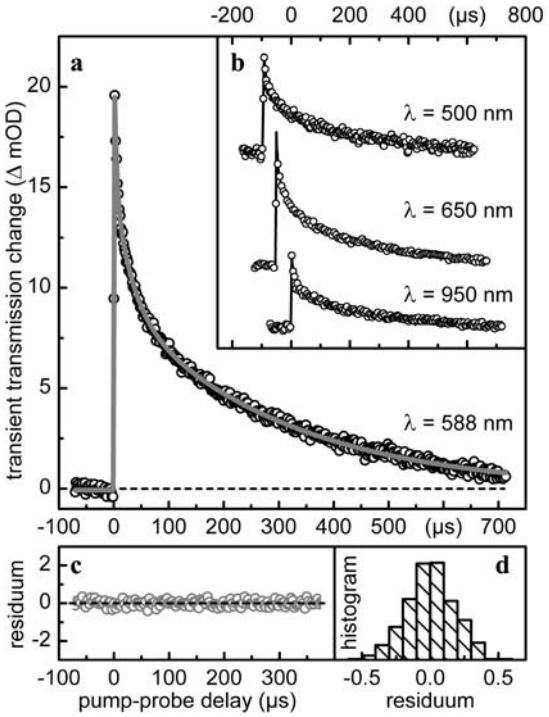

Fig. 2 Time traces of the Nd:YAG crystal recorded at (**a**) 588 nm and (**b**) other selected probe wavelengths. In (**c**) the residuum between the experimental and fitted curve in (**a**) is displayed. The statistical distribution of the residuum is shown in (**d**)

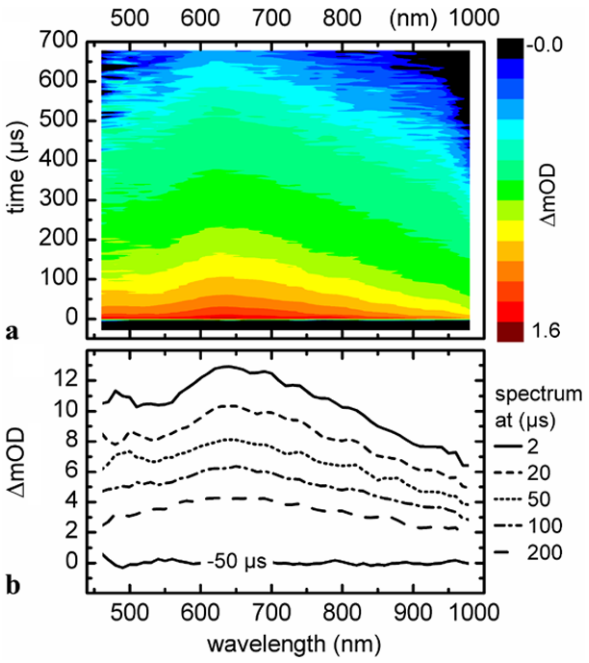

Fig. 3 (**a**) Transient spectrum reconstructed from 56 time traces in the spectral range from 450 to 1000 nm. (**b**) Single spectra for selected time delays

ergy integrated over the complete visible part of the output and for narrow wavelength bands. The resulting energy stability over 1000 successive pulses is 0.9% (rms) for the integral measurement and 1.1% (rms) in a 25 nm spectral band centered around 600 nm. We find a similar value in other spectral bands located in the visible. Normalizing the pulse energy of the spectral bands with the total visible energy, however, does not improve the signal to noise ratio.

To test the new broadband spectrometer, we carried out transient measurements on a 1% Nd doped YAG crystal. Complete time traces with qualitative good signal to noise ratio are obtained in an acquisition time of merely 5 min by averaging 2000 pulses per time bin (cf. Fig. 2a and 2b). To assess the signal to noise ratio quantitatively, we fitted a model function to the data, which consists of a multiexponential decay and a step function at time zero, and we analyzed the residuum. Another possible method that could be used for this purpose is a long range adjacent averaging. For the time trace at 588 nm (Fig 2a) the standard deviation is 1.7×10^{-4} OD. For a typical signal of 2×10^{-2} OD this renders a very good signal to noise ratio of ∼85. For the probe wavelengths at 500, 650, 950 nm we find standard deviations of 7.4×10^{-4}, 2.1×10^{-4}, 2.4×10^{-4} OD, respectively. These values can be further improved by longer acquisition times. The Gaussian distribution of the residuum clearly proves that the applied averaging method really eliminates any correlation that could be intrinsic to the laser noise (Fig. 2d).

Time traces at 56 equally spaced wavelengths in the VIS and NIR spectral range from 450 to 1000 nm have been measured to reconstruct the time evolution of the transient spectrum of Nd:YAG (Fig. 3). By fitting the time traces, we obtain three time constants of $\tau_1 = 4.65$ μs, $\tau_2 = 31.5$ μs and $\tau_3 = 290$ μs. The transient spectra obtained show a broad unstructured excited state absorption (ESA) across the whole spectral range. Transient measurements carried out recently [11] show that the ESA of Nd:YAG has sharp bands when the excitation is tuned to a transition of the Nd^{3+} ion. At 387 nm (the pump wavelength) there is no sharp absorption band but rather a broad absorption background [12]. The unstructured ESA is most probably due to the excitation of a color center which contributes to the dynamics with the first two time constants. The last and longest time constant is comparable to the 230 μs relaxation dynamics of Nd^{3+} given in the literature [13].

4 Conclusion and outlook

We have described a novel setup for the measurement of transient transmission signals based on a femtosecond excitation source and an ultra-broadband supercontinuum fiber laser as probe. With just a few optical components added to a standard femtosecond pump-probe setup, the two asynchronously operating laser sources can directly be employed for

the recording of the dynamics on time scales ranging from nanoseconds to microseconds. If the kHz repetition rate of the pump laser is reduced by a simple mechanical chopper, this range can even be extended to seconds. Acquisition times of merely five minutes yielded time traces with a signal to noise ratio of ∼85. The measurement of submicrosecond dynamics, however, is still somewhat time-consuming with the present free-running SCFL. The time scale has to be subdivided into bins significantly smaller than the dynamics. Due to the asynchronous operating mode the number of probe pulses that statistically fall into these bins is small and leads to a long recording time.

With triggered SCFLs based on microchip lasers now becoming commercially available, the pump-probe delay can be scanned electronically. Alternatively, existing triggerable nanosecond lasers can be coupled to improved microstructured fibers. In this way classical Q-switch Nd:YAG lasers [14, 15] readily available in many laboratories and compact DFB laser diodes amplified in further diode stages [16] can be used. This will significantly reduce the acquisition times for sub-microsecond dynamics. As the pulse length of the SCFL is ∼1 ns, a time resolution down to single nanoseconds should be possible. This corresponds well to the end of the scanning range of mechanical delay lines.

Compared to optical parametric oscillators, pulsed laser diodes [9] or CaF_2 supercontinua [17], a major advantage of a SCFL is that without changes to the setup a probe range from 450–2500 nm can be accessed. With new SCFLs entering the market right now, even the range down to 350 nm should be covered. Due to this ultrabroad spectral range and the high spectral brightness, the single channel detection employed here can easily be extended to a multichannel recording of transient spectra using a fast photodiode array or CCD line scan camera as detector.

The compactness of the setup and its easy handling renders it an ideal completion to a state-of-the-art femtosecond laboratory permitting the measurement of whole reaction cycles with the same excitation source. The SCFL probe minimizes the stress to the sample and prevents any significant photochemistry induced by the probe light.

Acknowledgements We thank Andreas Böck for valuable help in the early stages of the experiment and Koheras GmbH (Sascha Häuser) for the generous loan of the SuperK-Compact supercontinuum fiber laser. We appreciate stimulating discussions with Thomas Bein and are grateful for advise on the YAG dynamics by Günter Huber. The work was supported by the DFG-Cluster of Excellence: Munich-Centre for Advanced Photonics, by the Austrian Science Fund within the Special Research Program F16 (Advanced Light Sources) and by the SFB 749 (Dynamics and Intermediates of Molecular Transformations). I.P. gratefully acknowledges financial support from the Alexander von Humboldt Stiftung.

References

1. G. Cerullo, C. Manzoni, L. Lüer, D. Polli, Photochem. Photobiol. Sci. **6**, 135 (2007)
2. B.V. Bergeron, G.J. Meyer, J. Phys. Chem. B **107**, 245 (2003)
3. Y. Tachibana, J.E. Moser, M. Grätzel, D.R. Klug, J.R. Durrant, J. Phys. Chem. **100**, 20056 (1996)
4. T. Kato, N. Mizoshita, K. Kishimoto, Angew. Chem. Int. Ed. **45**, 38 (2006)
5. T. Danger, K. Petermann, G. Huber, Appl. Phys. A **57**, 309 (1993)
6. P.-A. Champert, V. Couderc, P. Leproux, S. Février, V. Tombelaine, L. Labonté, P. Roy, C. Froehly, P. Nérin, Opt. Express **12**, 4366 (2004)
7. J.M. Dudley, G. Genty, S. Coen, Rev. Mod. Phys. **78**, 1135 (2006)
8. E. Riedle, M. Beutter, S. Lochbrunner, J. Piel, S. Schenkl, S. Spörlein, W. Zinth, Appl. Phys. B **71**, 457 (2000)
9. U. Schmidhammer, S. Roth, E. Riedle, A.A. Tishkov, H. Mayr, Rev. Sci. Instrum. **76**, 093111 (2005)
10. J.A. Moon, Rev. Sci. Instrum. **64**, 1775 (1993)
11. S. Küch, L. Fornasiero, E. Mix, G. Huber, Appl. Phys. B **67**, 151 (1998)
12. D. Findlay, D.W. Goodwin, Adv. Quantum Electron. **1**, 77 (1970)
13. S. Singh, R.G. Smith, L.G. Van Uitert, Phys. Rev. B **10**, 2566 (1974)
14. G.E. Town, T. Funaba, T. Ryan, K. Lyytikainen, Appl. Phys. B **77**, 235 (2003)
15. J. Cascante-Vindas, A. Diez, J.L. Cruz, M.V. Andrés, E. Silvestre, J.J. Miret, A. Ortigosa-Blanch, Opt. Commun. **281**, 433 (2008)
16. M. Kumar, C. Xia, X. Ma, V.V. Alexander, M.N. Islam, F.L. Terry Jr., C.C. Aleksoff, A. Klooster, D. Davidson, Opt. Express **16**, 6194 (2008)
17. P. Tzankov, I. Buchvarov, T. Fiebig, Opt. Commun. **203**, 107 (2002)