*Philosophical Magazine*,
Vol. 87, Nos. 3–5, 21 January–11 February 2007, 731–740

Taylor & Francis
Taylor & Francis Group



# A real-time acquisition system for pump–probe spectroscopy

P. BARTOLINI*†‡, R. ERAMO†‡§, A. TASCHIN†‡, M. DE PAS† and R. TORRE†‡§

†European Lab. for Non-Linear Spectroscopy (LENS), Università di Firenze, Via N. Carrara 1, I-50019 Sesto Fiorentino, Firenze, Italy
‡INFM-CRS-Soft Matter (CNR), c/o Università la Sapienza, Piaz. A. Moro 2, I-00185, Roma, Italy
§Dipartimento di Fisica, Università di Firenze, Via Sansone 1, I-50019 Sesto Fiorentino, Firenze, Italy

(*Received 12 May 2006; in final form 23 June 2006*)

An innovative acquisition system for time-resolved spectroscopy is presented. It is based on the real-time acquisition of the experimental signal during the rapid scan of an optical delay line and enables data acquisition with high absolute time resolution (1 femtosecond), high scanning velocity (2.5 cm/s) and long time delay (several nanoseconds). We report precise interferometric tests of the acquisition system, focusing on technical features of the optical delay line. We check this data acquisition technique by performing ultra-fast time-resolved experiments with laser sources of high and low repetition rates.

## 1. Introduction

The implementation of time-resolved pump–probe experiments always faces the problem of the proper acquisition system. This includes an optical delay and an electronic acquisition chain, i.e. the optical detector, the integration/filtering apparatus and the data acquisition (DAQ) board. A typical tricky aspect is the control and communication between these devices.

The step-by-step acquisition method is often utilized in ultra-fast pump–probe experiments [1]. In this method the delay line moves one step and stops, and during the stops the signal is acquired. Typically 50% of the acquisition time is spent in communicating with the translation stage, losing many valid signal measurements. Nevertheless this acquisition procedure permits very good results with low repetition-rate laser systems [2].

Alternatively a real-time acquisition procedure can be employed. Two different methods exist to achieve this purpose: one is again to use a mechanical delay line which moves continuously [3–6] and the other one is to employ an asynchronous optical sampling technique (ASOPS [7]). The ASOPS technique allow us to scan over a nanosecond time delay at a kilohertz scanning rate, but with a time resolution of

*Corresponding author. Email: bart@lens.unifi.it

*Philosophical Magazine*
ISSN 1478–6435 print/ISSN 1478–6443 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/14786430600953780

a few hundred femtoseconds. In the first method, as stated before, the delay line moves continuously while the signal is simultaneously acquired and the line position is generally recovered using its velocity. Indeed this system decreases the acquisition time substantially, while improving the signal statistics and, depending on the translation line used, enables the employment of rapid-scan acquisition. Nevertheless it presents several drawbacks. The main drawback concerns the measurement of the delay line position, which usually relies on the hypothesis of constant and uniform scan velocity.

In this work we introduce a versatile acquisition system that enables rapid-scan with accurate measurement of the delay line position. We show that this technique is suitable for experiments performed with laser sources of high/low repetition rate. The presented data show that this acquisition method represents a convincing technique for ultra-fast pump–probe time-resolved experiments.

## 2. Optical set-up and acquisition system

In figure 1 we show the optical set-up and the schematic diagram of the detection assembly, enabling real-time rapid-scan acquisition in pump–probe experiments. A laser pulse, produced by a laser system not shown in the figure, is split by BS1 in the pump and probe beams. The probe beam is optically delayed by a precision hollow corner cube mounted on a 305 mm, computer controlled, precision translation stage (Micos, LS-180).

The optical delay is the key device in order to get real-time rapid-scan acquisition. Our translation stage is characterized by a flattness/straightness error $\sim \pm 1\,\mu$m

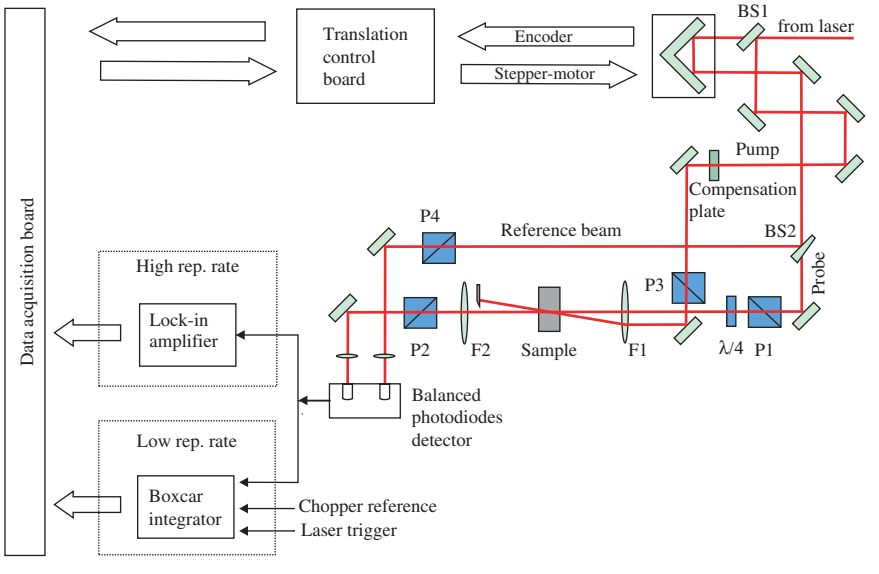


Figure 1. The optical set-up and acquisition systems realized and proposed in the present work. The high repetition-rate scheme and the low repetition-rate configurations are shown.

and by a pitch/yaw error $\sim \pm 30\,\mu$ rad on the full length. A linear encoder, with 100 nm resolution, measures the translation stage position. The maximum scan velocity is 2.5 cm/s (e.g. a scan of $10^{-10}$ s of the optical delay requires an acquisition time of about 0.6 s). During the scan the encoder board gives the absolute position in real-time, which is converted by the DAQ board (1 MS/s acquisition board from National Instruments, with 16 bit-resolution analog inputs and 32-bit, 80-MHz counters) and finally recorded in the computer memory.

The optical part reported in figure 1 is the standard one for heterodyne-detected optical Kerr-effect (HD-OKE) experiments [1]. Probe and pump beams are focused inside the sample by a plano-convex lens F1. The probe beam is then recollimated by a plano-convex lens F2 before being analyzed by the Glan–Taylor polarizer P2; for the measurements reported here the two lenses have 30 cm focal length. The pump beam is transmitted through a half-wave plate followed by a Glan–Taylor polarizer P3, giving a linear polarization at 45° with respect to the polarization of the probe beam. The probe beam is transmitted through the couple P1 and P2 of crossed Glan–Taylor polarizers providing an extinction ratio around $10^{-7}$. The quarter-wave plate allows for minimization of residual static birefringence due to the lenses and the sample cell windows. From this zero condition a small rotation of the quarter-wave plate creates the $\pm\pi/2$ local oscillator fields at the detector of the heterodyne measurement. The pump–probe measurement is given by the difference between two measurements made at two opposite rotations of the quarter-wave plate, starting from the zero condition.

Finally the optical signal is detected by a balanced photodiode. This photo-receiver consists of two well-matched photodiodes and an RF amplifier that generates an output voltage proportional to the difference between the photocurrents in the two photodiodes. Common-mode noise that is present on both the reference and signal beams (such as laser intensity noise) is cancelled out and thus does not appear as part of the signal.

In our acquisition technique the delay line moves, up and down, in a continuous mode. During the scan, the DAQ board receives the delay line position from the encoder board and the integrated-filtered signal measured by the balance photo-diode. The signals and positions are finally acquired and stored by the computer, which matches them to build the final signal decay. The single or averaged signal decay are available in the recorded files.

This acquisition system is suitable for high and low repetition-rate laser sources. The delay line and the optical set-up are valid for both sources; conversely, the photodiode and the integration electronics need to be adapted.

In our high repetition-rate measurements, performed with a pulsed Ti:sapphire laser oscillator with 73 MHz repetition rate, we utilized a lock-in amplifier and a fast balanced photodiode. The balanced photodiode (New Focus, Model 1607) is characterized by a bandwidth of 40 KHz–600 MHz, a 350 V/W peak conversion gain, and a $40\,\text{pW}/\sqrt{\text{Hz}}$ noise equivalent power. The high-frequency lock-in amplifier is homemade, based on a high-frequency mixer (AD831) mounted on a PC 104 standard board. The lock-in integration time constant is around 0.5 ms, and the lock-in reference is given by a fast photodiode monitoring the oscillator output.

In the low repetition-rate measurements with laser pulses at 1 KHz, produced by an amplified Ti:sapphire laser system, the slowest balanced detector is used

(New Focus, Model 2107, with DC-10 MHz bandwidth, a peak conversion gain from $3.1\times10^2$ to $9.2\times10^6$ V/W and a 0.8 pW/$\sqrt{\text{Hz}}$ noise equivalent power). The integration is performed by a boxcar (Stanford, Mod. SR250) used in a synchronized scheme: a chopper, modulating the probe beam, is synchronized to the half-frequency of laser repetition rate at 500 Hz, and the detected background, acquired by the DAQ board, can be actively subtracted from signals.

## 3. Optical delay line test

To test the delay line a simple interferometric measurement with an He–Ne laser source was performed. The delay line controls the position of a mirror in one arm of a Michelson interferometer. Fitting the Michelson fringe signal by a sinusoidal function, a very precise measurement of the corner cube displacement can be made and compared with the encoder reading.

The difference between the mirror positions obtained by the Michelson fringes and by the encoder reading during a scan is shown in figure 2. This difference is a periodic function of the displacement, with a period given by the periodicity of the encoder optical track (40 μm). The encoder control board keeps this error below 200 nm using an interpolation unit. In the experimental set-up this error corresponds to an absolute maximum delay uncertainty of ±200 nm (corresponding to an optical delay of ~1.3 fs in the single-pass configuration).

In figure 3 we display the mirror position, extracted by the Michelson fringes, versus the acquisition time. The data show clearly that the velocity is not really constant during the scan, oscillating and fluctuating around the mean value with an amplitude of about 20%. The fluctuations produce an uncertainty when the position must be recovered from the velocity. This problem is negligible for short

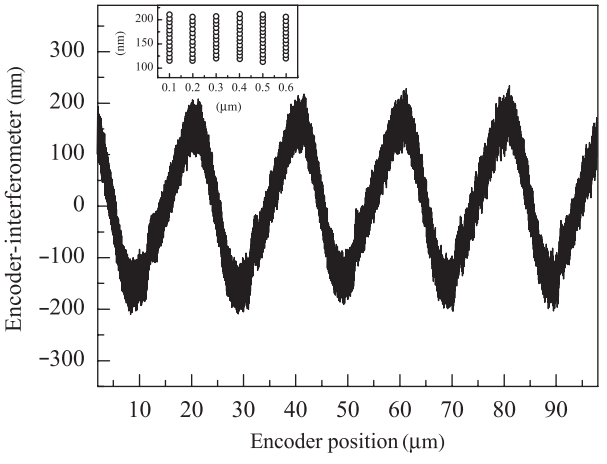


Figure 2. Difference between the mirror positions obtained by the Michelson fringe and by the encoder reading. The inset is a close up of the curve, showing the 100 nm resolution of the linear encoder.

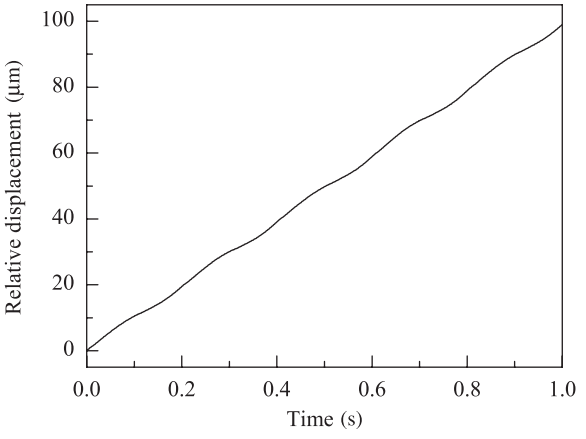


Figure 3. Position versus acquisition time. The averaged velocity is 0.1 mm/s.

scans and it can be partially reduced, averaging scans in the same direction. Nevertheless it prevents a proper averaging of the multiple scans when a high time resolution is required, as was recognized in the work of Feldstein *et al.* [4]. We would like to point out that our real-time acquisition of the encoder reading is not affected by these limitations and the scan average can be performed without introducing extra position uncertainty. So we avoid all the calibration or linearization procedures and no blurring due to scan-to-scan jitters affects the measurements.

## 4. Results

Using the presented real-time rapid-scan acquisition systems we performed three non-linear spectroscopic measurements. Two of them utilized laser pulses at high repetition rate (73 MHz), while the third one is made at low repetition rate (1 KHz).

### 4.1. *High repetition-rate measurements*

The high repetition-rate laser source is a Kerr-lens mode-locked Ti:sapphire laser (FemtoRose 10MDC, by R&D Ultrafast Laser) pumped by the second harmonic of a laser-diode-pumped Nd:$YVO_4$ laser (Millennia V, by Spectra-Physics). The pulse width is ~20 fs. The residual chirp present in the laser beam can be compensated by a pair of fused silica prisms followed by a set of chirped mirrors in order to optimize the pulse width on the sample. In fact all the optical elements (including wave plates, lenses, sample cell and polarizing cubes) produce a group velocity dispersion effect in the laser pulse and pump and probe pulses gain a different group delay dispersion (GDD), since they follow different optical paths. In order to compensate the different GDD we inserted a suitable quartz plate into the pump.

We performed an interferometric autocorrelation and a second-harmonic interferometric autocorrelation of these laser pulses, using the acquisition systems previously described. The optical set-up is the standard one for these measurements [8]

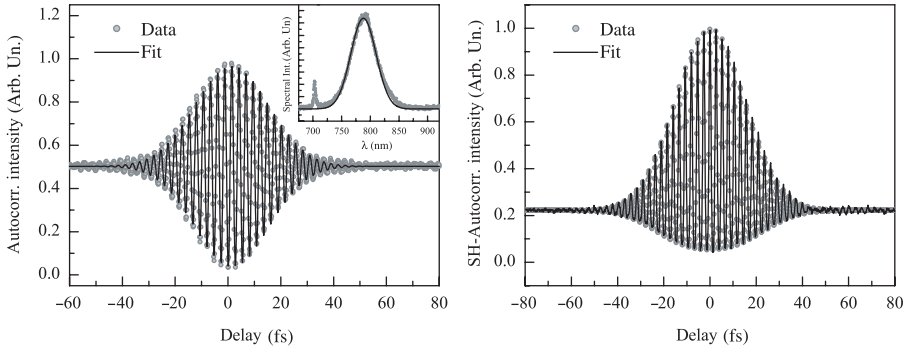


Figure 4. Left graph: Interferometric autocorrelation signal and frequency spectrum (inset) of the laser pulse. Right graph: Second-harmonic interferometric autocorrelation signal.

(not reported in figure 1). The time-resolved signal of these measurements presents complicated fine time structure characterized by the interferometric oscillations of the fundamental laser frequency. To resolve it, the time scale steps must be smaller then the minimum encoder step. This can be obtained by extrapolating the time scale from the scan velocity. As we discussed, this procedure is accurate enough to detect interference fringes when the measurements is performed by a single scan of the delay line. In figure 4 we report the data obtained in the autocorrelation test using a single rapid scan with a delay line velocity of 0.1 mm/s. In the left graph we report the interferometric autocorrelation signal together with the frequency spectrum of the laser pulse measured by a monochromator. The spectrum is well reproduced by a Gaussian profile centred at 790 nm with a FWHM of 52 nm giving a transform-limit pulse width of 17 fs ($\Delta t = 0.44\lambda^2/c\Delta\lambda$). This result is in agreement with the FWHM of the pulse intensity profile (16.6 fs) extracted by the fit of the interferometric autocorrelation. The right graph shows a second-harmonic autocorrelation in the case of the best compression. The fitting analysis yields a temporal length of 23 fs with a linear GDD of $\sim 0\,\text{fs}^2$. This discrepancy is probably due to higher order chirping terms which are not considered in the fitting function.

As a second experiment, we performed an HD-OKE measurement on a standard molecular liquid, $CCl_4$, using the optical set-up reported in figure 1 and the high repetition-rate Ti:sapphire laser. The pump pulse energy is around 1 nJ, and the probe pulse energy is one order of magnitude below this value. In figures 5 and 6 the measured signals at room temperature are shown.

The datum shown in figure 5 is made by a single scan of 1000 points. We used a DAQ sampling rate of 10 Ksample/s and a scan velocity of 0.1 mm/s, therefore we had 10 samples for each encoder position (100 nm, 0.67 fs). Thus the curve reported in figure 5 is obtained by averaging the signal data which have the same encoder position. The full acquisition time is about 1 second.

The datum shown in figure 6 is made by averaging 200 longer scans, with the same characteristic previously mentioned. In inset (a) we report the statistics histogram, showing that each final data point has been obtained with an average of around 1600 signal measurements per encoder reading (Ksample/bin).

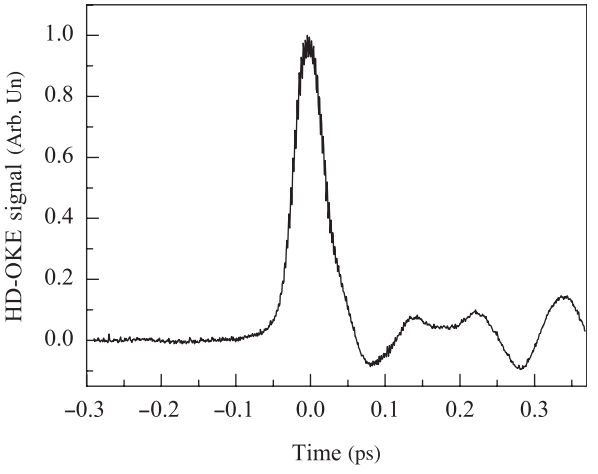


Figure 5. Single-scan HD-OKE signal from the $CCl_4$ signal at 300° K.

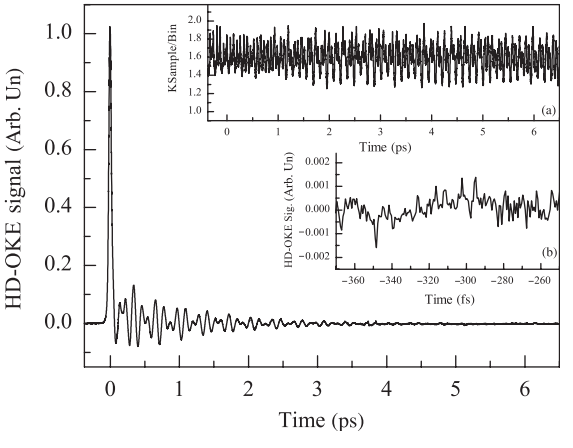


Figure 6. Averaged HD-OKE signal from the $CCl_4$ signal at 300° K.

The oscillating structure in the inset histogram, not washed out by the average, is due to the aforementioned velocity oscillations, and it amounts to ~15% of the average. In inset (b) a detail of the baseline shows a signal-to-noise ratio of around $10^3$.

### 4.2. *Low repetition-rate measurements*

The low repetition-rate laser source is an amplified Ti:sapphire laser system. The main oscillator has been previously described (FemtoRose 10MDC). The amplification is performed by a regenerative amplifier (Pulsar, by Amplitude Technologies) pumped

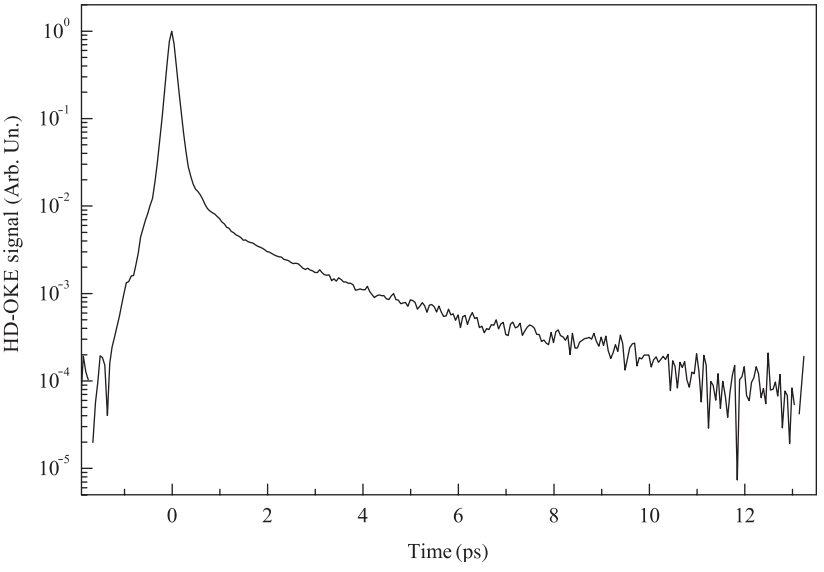


Figure 7. HD-OKE signal from supercooled water at 263° K.

by a *Q*-switched Nd:YLF laser (Evolution X, by Spectra Physics). The minimum pulse width is around 40 fs and has ~0.7 mJ of energy.

We check the new acquisition scheme in the low repetition-rate experiments using as sample supercooled water. This is a particularly difficult sample and it requires quite a complex procedure to be properly investigated with step-by-step acquisition [2]. For the measurement reported in [2], the entire time scan was divided into three sections. A short laser pulse (60 fs) was used for a short time scan; for the intermediate time delay interval the laser pulse duration was stretched up to 120 fs; for the longer time we used stretched laser pulses of 500 fs duration. In this procedure the pulse energy was increased to keep the peak power roughly constant. The larger pulse had ~5 mJ pump energy. A measurement took about 24 hours.

With the new acquisition system we are able to measure the full decay in a single time scan without modifying the laser pulse width. The pump pulse has 0.2 mJ of energy and 75 fs of duration. We scan at 0.1 mm/s which yields about 1 signal point for each encoder reading. The delay line displacement is 3 mm, corresponding, in a single-pass configuration, to a 15 psec time delay and each scan has about $3 \times 10^4$ samples.

In figure 7 we report the HD-OKE signal of water supercooled to 263 K. This is the average of about 400 scans and the total acquisition time was almost 3 hours. The reported curve is obtained by performing an adjacent point average giving a datum with 400 points and a time step of 50 fs. The signal-to-noise ratio of this datum, normalized to the acquisition time, is worse by a factor of two compared to the one measured in [2]. We would like to remark that this is a preliminary result obtained without the expedients employed in the old experimental work. In particular we use

a pulse energy 20 times lower than the energy used in [2] for the long time scan acquisition.

## 5. Conclusions

We introduced an innovative acquisition system for pump–probe spectroscopy. This system enables real-time rapid-scan acquisition with accurate track of the position/time scale. With respect to the scheme proposed by Scherer *et al.*, our set-up improves the control of position in the delay line, thanks to the linear encoder. This device permits us to measure the optical delay in absolute scale with excellent precision. Thus, no calibration and linearization procedures are necessary. Furthermore it is a particularly adaptable system, which can be used with high or low repetition-rate laser sources. It allows scans with very accurate time scale as required to characterize the laser pulses, or less accurate multiple rapid-scan acquisitions, needed in spectroscopic investigation of relaxation processes.

In the near future we are planning to use this data-acquisition technique in optical Kerr-effect experiments performed with amplified laser pulses. In particular we plan to extend the structural relaxation measurements on supercooled water.

In our opinion this acquisition technique is also suitable for time-resolved pump–probe spectroscopy on samples in a non-equilibrium transient state. These experiments measure the proprieties of matter during the relaxation process towards the equilibrium state, requiring an experimental acquisition time faster then the decay time scales towards equilibrium. The data-acquisition speed turns out to be quite a severe limitation and only a few examples of such experimental investigations have been reported in the literature [9–11]. The real-time rapid-scan acquisition introduced here overcomes some of these constraints.

## Acknowledgments

The research has been performed at LENS. We would like to thank R. Righini for his support in the present research. This work was also supported by EC grant No. RII3-CT-2003-506350, by CRS-INFM-Soft Matter (CNR) and MIUR-COFIN-2005 grant N. 2005023141-003. We thank Riccardo Ballerini for indispensable mechanical support, and Mauro Giuntini for providing continuous assistance in the set-up of the electronics.

## References

[1] P. Bartolini, M. Ricci, R. Torre, *et al.*, J. Chem. Phys. **110** 8653 (1999).
[2] R. Torre, P. Bartolini and R. Righini, Nature **428** 296 (2004).
[3] G.C. Cho, W. Kütt and H. Kurz, Phys. Rev. Lett. **65** 764 (1990).
[4] M. Feldstein, P. Vöhringer and N. Scherer, J. Opt. Soc. Am. B **12** 1500 (1995).
[5] K. Winkler, J. Lindner, H. Bürsing, *et al.*, J. Chem. Phys. **113** 4674 (2000).
[6] K. Winkler, J. Lindner and P. Vöhringer, Phys. Chem. Chem. Phys. **4** 2144 (2002).
[7] A. Bartels, F. Hudert, C. Janke, *et al.*, Appl. Phys. Lett. **88** 041117 (2006).

[8] R. Trebino, *Frequency-Resolved Optical Gating: The Measurament of Ultra-Short Laser Pulses* (Kluwer, Boston, 2000), p. 84.
[9] S. Fujiyoshi, S. Takeuchi and T. Tahara, J. Phys. Chem. A **107** 494 (2003).
[10] J. Bredenbeck, J. Helbing, R. Behrendt, *et al*., J. Phys. Chem. B **107** 8654 (2003).
[11] A. Matsuda, K. Kondo and K.G. Nakamurab, J. Chem. Phys. **124** 54501 (2006).