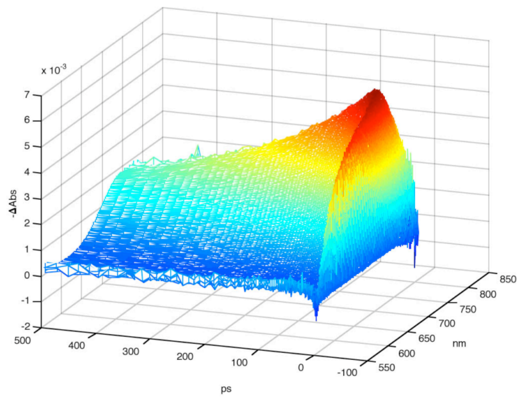
1 kHz detection system for femtosecond kinetics.

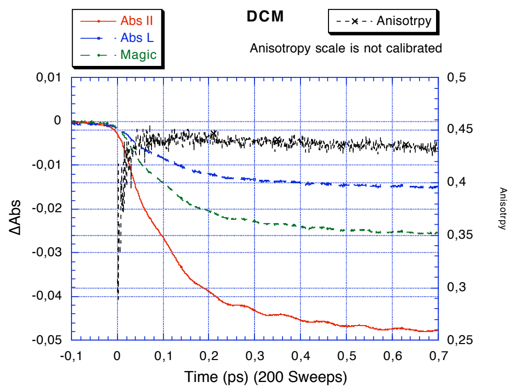
The system is based on photodiode detectors and a computer with powerful control and collection software sampling over 500 spectrum points per millisecond.

The hardware comprises
- Photodiode detectors
- Dual 512-diode array detector head
- Analog-to-digital converters
- Delay line controller
- Computer with software

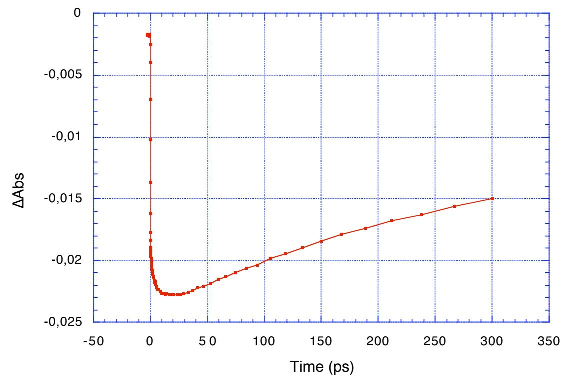
The software comprises routines for
- Assisting system alignment
- Control and data collection
- Diagnostics and data evaluation
- Performing the following experiments



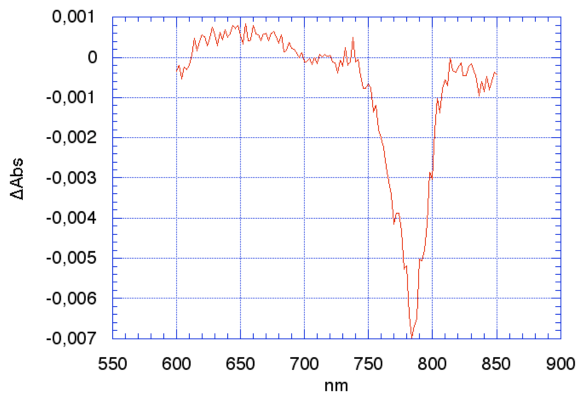
1) *Multiwavelength absorption kinetics: the diode array collects a whole spectrum for each laser shot.*



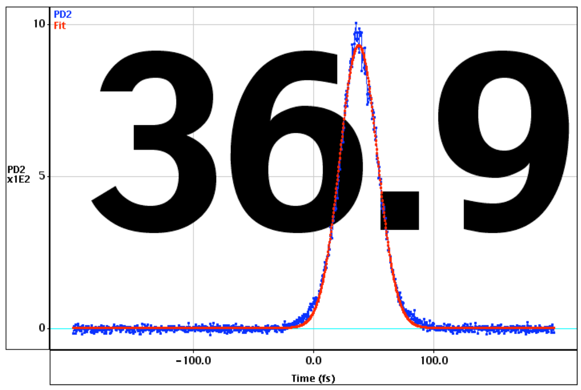
2) *Single wavelength anisotropy kinetics. Both parallel and perpendicular polarisations are collected simultaneously.*



3) *Single wavelength absorption kinetics.*



4) *Chirp corrected time resolved absorption spectra.*



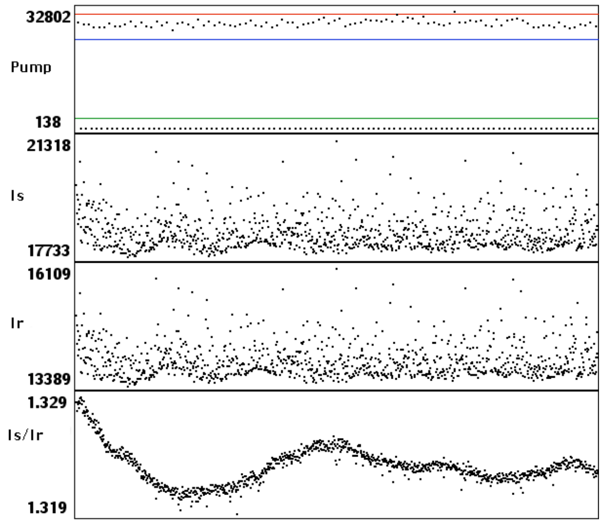
5) *Auto and cross correlation with pulse width measurements updated once per second.*

Great efforts have been made to minimise noise levels by correcting for probe light and pump pulse fluctuations and to develop efficient averaging procedures: After averaging 1000 times (2s) Δabs noise levels of $2 \cdot 10^{-6}$ and $2 \cdot 10^{-5}$ (per channel) have been obtained for single- and multi-wavelength measurements, respectively.

Correction of probe light noise in absorption measurements

For a double beam set-up, the Δabsorption is: (Δabs) = log((Ios/Ior)/(Is/Ir), where Is,Ir and Ios,Ior are the light intensities (I) of the sample (s) and reference (r) beams in absence (o) and presence of the pump pulse, respectively. By measuring Ir, the pulse-to-pulse fluctuations of the probe light intensity (Is) can be corrected for. This is important because these fluctuations are in the range of 1 to 10%. The measurements of Ios and Ior, without the pump pulse, makes it possible to zero the Δabs. The most convenient way would be to measure Ios/Ior once and use it for all the subsequent Is/Ir measurements. However, even if Is and Ir follow each other very well, their ratio is not constant, but fluctuates with time (see fig 6).

These fluctuations in Is/Ir occur on many time scales and also at lower frequencies than what is shown in figure 6. They are caused by instabilities in the laser and to some extent in the detection electronics. As can be seen in figure 6, the Is/Ir ratios are more similar when adjacent laser pulses are compared, but vary considerably over larger time intervals. This implies that Ios/Ior can not be determined once and for all, but has to be determined once for every Is/Ir pair. To accomplish this, the pump beam is chopped in order to block every second pulse. The collection computer then processes the data in Ios/Ior and Is/Ir pairs measured directly after each other. This puts high demands on the readout system of the diode array, since its collected data must be completely read out and processed between subsequent laser shots.



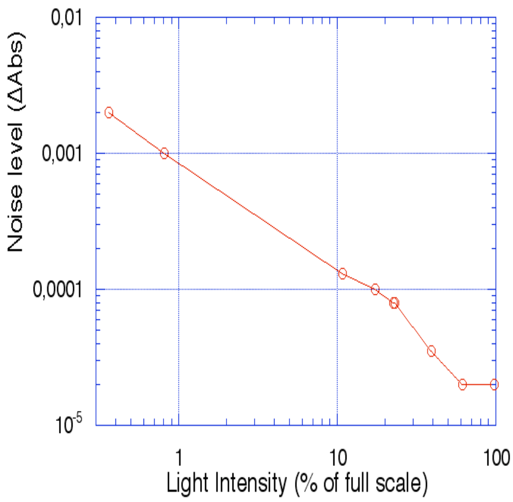
6) *The intensities of 1000 consecutive laser pulses (200 in case of the pump, so that the chopping is clearly seen). The coloured lines are gate levels*

The effects of pump pulse fluctuation on Δabs noise

The pump pulse fluctuates with the same pattern as Is and, on a longer time scale, it can look similar to Is/Ir in figure 6. This is not fully obvious in figure 6 because the pump beam is chopped and the detector readings for the blocked pulses are also plotted. If the Δabs signal is large relative to the probe noise, the pump pulse fluctuation is the major noise source. Under certain circumstances, this noise can be corrected for by scaling each Δabs measurement with the corresponding pump pulse intensity. In the case that pump pulse energy fluctuation is the major type of pump noise, improvements in signal-to-noise up to a factor of 5 have been attained. If the pump pulse varies due to beam movements and intensity profile fluctuation, it can not be corrected for in this way. On the other hand, if the Δabs signal is small relative to the probe noise, pump pulse intensity corrections do not improve the signal-to-noise ratio.

Improvement of signal-to-noise by averaging

Usually a single Δabs measurement does not give sufficiently good data. Therefore, the measurement is repeated many times and averaged. This improves the signal-to-noise ratio proportional to the square root of the number of measurements. It also means that, if the signal-to-noise ratio of a single Δabs measurement can be improved by a factor of 10, the needed instrumentation time to measure a kinetic trace can be reduced by a factor of 100. Two procedures for averaging have been implemented: the "scan" and the "sweep" mode. In the scan mode the delay line moves to the first time point and a given number of Δabs measurements are performed. By repeating this procedure for all the time points a complete scan of the kinetic trace is collected. This scan procedure is then repeated until an appropriate signal-to-noise ratio is obtained. In the sweep mode, the delay line moves over the whole time window of interest at constant speed. The Δabs measurements are performed at successive time points, collecting a complete kinetic trace in each sweep. The sweep is then repeated for averaging purpose. A sweep is also collected when the delay line is moving backward. In the sweep mode, the pump pulse fluctuations are generally averaged out better than in the scan mode (cf figs 10-12).



7) *Noise level for the diode array versus probe light intensity after averaging 1000 times.*

With the CPA-2001/OPA (Clark-MXR Inc) laser set-up at Chemical Physics, Lund University, we have achieved noise levels of better than $2 \cdot 10^{-6}$ Δabs (one standard deviation) after averaging 1000 times (2000 laser pulses or 2 seconds, single wavelength measurements without pump pulse and empty sample holder). This noise level has been difficult to maintain in real measurements, using normal cuvettes, which scatter light more than high quality optics, but noise levels of a factor of 4 higher are readily achieved. With the diode array detector, using spectrally broadened probe pulses (OPO amplified continuum, ~100 nJ per pulse, see fig 9), a noise level of $2 \cdot 10^{-5}$ per channel was obtained for the part of the array (~200 diodes, ~100 nm) with the highest light intensity (see fig 7). If continuum is used as probe light the light intensity is significantly lower and the noise increases correspondingly. Likewise, at high continuum light levels the uncertainties in the polarisation give rise to increasing noise levels. With white light, generated at 800 nm, noise levels better than $2 \cdot 10^{-3}$ per channel over the entire array, covering from 480 to 750 nm, have been obtained.

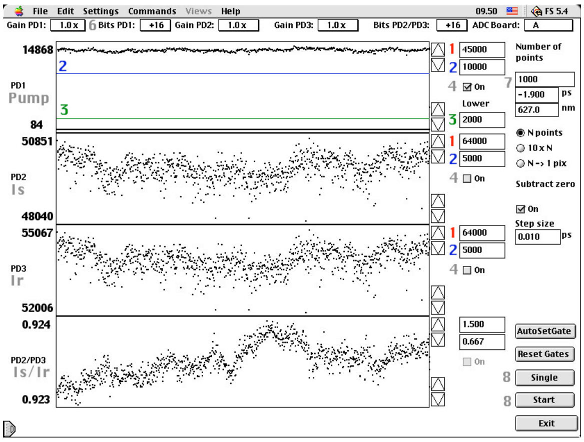
Options for time step lengths between measuring points

In the scan mode, consecutive time intervals can be defined and assigned time steps of constant length. Optionally, logarithmically increasing time steps can be assigned to the last interval. In the sweep mode, the step size is determined by the length of the time interval and the number of equally spaced points.

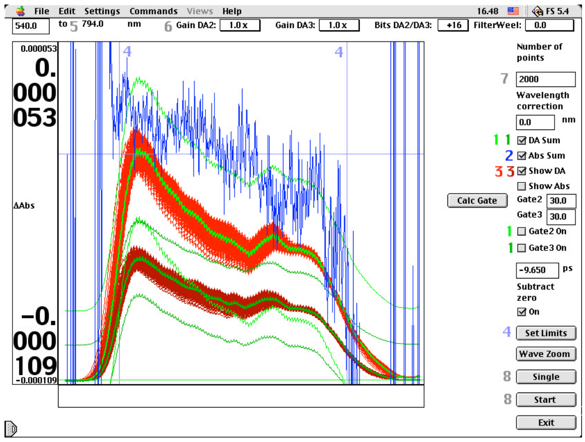
Diagnostic modes

Diagnostics are run at constant delay time, usually with the pump pulse arriving after the probe pulse. Their purpose is to check the performance of the system on shot-to-shot bases, and to adjust amplifier gain, gate levels and other characteristics. Four types of diagnostics have been implemented:

PD2 vs PD3 (Is vs Ir)	to monitor linearity between sample and reference channels.
PDs vs time	to monitor signal levels (I) from the photodiodes (PD). Fig 8.
ΔAbs vs time	to monitor the distribution of individual Δabs measurements.
DiodeArray	to monitor the signal levels and Δabs of the diode array. Fig 9.



8) *PDs vs time diagnostics. 1: Upper gate level; 2: Lower gate level; 3: Chopped pump gate level; 4: Gate on/off; 6: Digitizer options; 7: Number of collected points; 8: Collect single or repetitive.*



9) *Diode array diagnostics 1: Averaged intensity & gate levels; 2: Averaged absorption; 3: All 2000 individual intensities; 4: Limits for scaling of ΔAbs; 5: Wavelength range; 6,7,8: See fig 8*

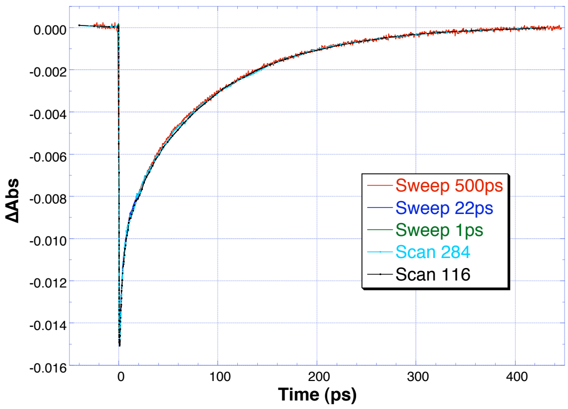
Experimental routines used as diagnostics modes

To minimise the probe noise in single wavelength absorption experiments, the measurement is run without pump pulse and the probe beams are adjusted to hit the photodiode detectors in an optimal way. The noise level of consecutively measured points can then be optimised. The overlap between pump and probe beams can be optimised in a similar manner with the pump beam at positive delay times. To facilitate these diagnostics, the delay line movements can be turned off. To characterise and optimise pulse widths, auto- and cross-correlation experiments can be used. In sweep mode, auto-correlation traces can be measured, fit to a gaussian, and displayed together with the pulse width once per second (see fig 5).

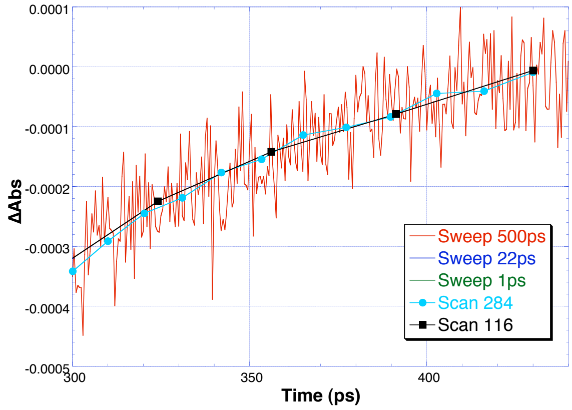
Experiments

Single wavelength absorption kinetics, averaging by scan and sweep modes.

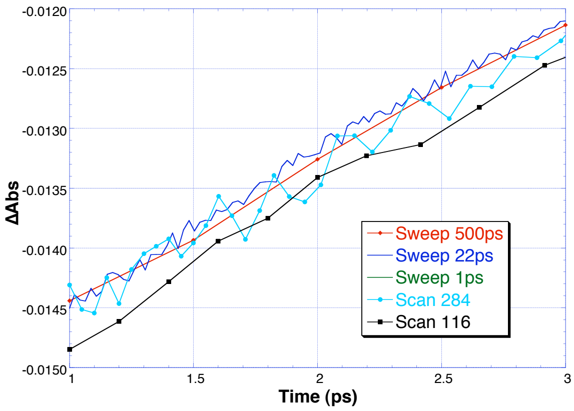
To evaluate the efficiency of noise reduction in the scan and sweep modes, three sets of experiments were performed, each using the same amount of instrumentation time (~ 24 minutes). Two sets of scans with different numbers of time points, and one set of three sweeps containing 1000 time points each with different time steps (1fs, 22fs and 500fs) were performed. In the figures 10 to 12, the backward sweeps are omitted for clarity. Thus, the displayed sweeps represent half the data collection times compared to the scans. When the traces were fit to retrieve rate constants and uncertainties, all the sweeps where used. Errors are estimated using F-statistic. The rate constant for which the uncertainty is sought is varied in fixed steps around the optimum value and the other parameters are fitted at each step. When the sum of squared deviations have increased by a factor of $1 + M/(N-M) \cdot F(M,N-M,1-P)$ the error limit is reached. (M; number of parameters, N; number of data points, P; probability level (in this case 68.25% or one standard division))



10) *Superimposed sweep and scan traces.*



11) *Excerpt of the region with low signal levels.*



12) *Excerpt of the region with high signal levels.*

From the two excerpts of the kinetic traces, the effects of probe and pump noise in scan and sweep experiments are shown. In regions with low signal amplitude (fig 11) probe noise is dominant, and the sweep trace appears to be much noisier. In regions with high signal levels (fig 12), pump noise is dominates, and the sweep traces are less noisy despite significantly less averaging per point. ☐

Result from the fits of the rate constants for the kinetic traces of figure 10 – 12.

Type of experim-ent	*Number of time points used*	*Measure ments / point*	*Number of repeats*	*Total measure ments*	*k1 (1/ps)*	*Uncert ainty 1 ±%*	*k2 (1/ps)*	*Uncert ainty 2 ±%*	*k3 (1/ps)*	*Uncert ainty 3 ±%*
Scan	116	300	12	3600	0.309	13.3	0.0348	89.8	0.00975	36.7
Scan	284	500	4	2000	0.327	13.2	0.0445	52.0	0.00977	13.6
Sweep	5652	1	100	100	0.314	3.6	0.0365	16.1	0.00962	3.9

When the uncertainties of the fitted rate constants are examined, the importance of the increased number of time points and efficient reduction of pump pulse noise becomes obvious. In the sweep mode, the uncertainties are reduced by a factor of 3 to 4 compared to the scan mode.

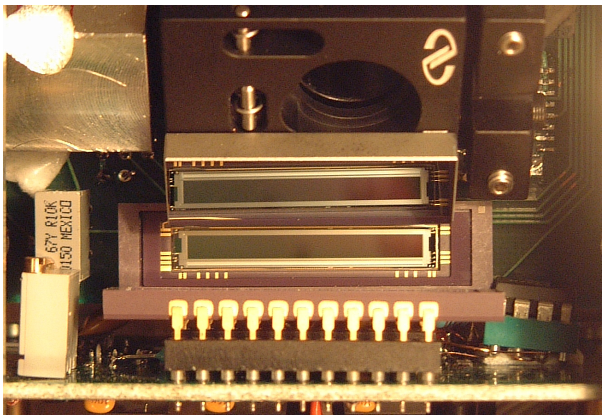
Chirp-corrected time resolved absorption spectra (fig 4).

Absorption spectra are collected one wavelength after another by changing monochromator or TOPAS position and simultaneously adjusting the delay line to correct for frequency chirp.

Single wavelength anisotropy kinetics.

Both parallel and perpendicular polarised absorption traces are collected simultaneously. The probe beam passes through the sample at 45° relative to the pump beam and is split into parallel and perpendicular beams afterwards. Alternatively, both parallel and perpendicular polarised probe beams are passed through the sample.

Multiwavelength absorption kinetics.

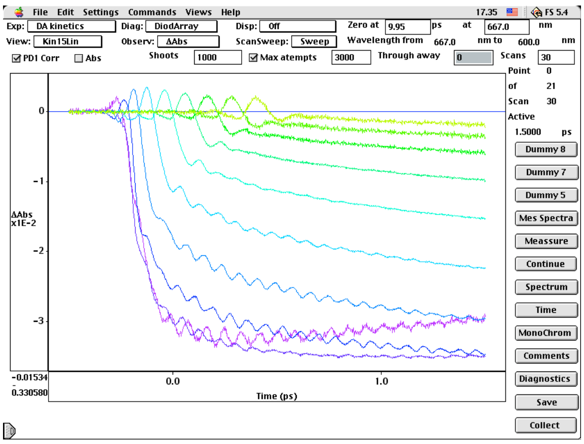


13) Diode array detection head for a small spectrograph.

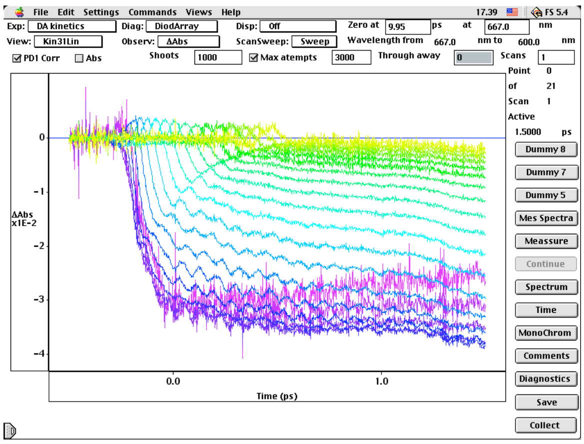
The real challenge for the detection system is multiwavelength absorption kinetics. Due to the fact that the signal displayed (Δabsorption) is not linearly proportional to the signal measured (%transmittance) and, owing to fluctuations in the Is/Ir ratio, it is necessary to read out collected data after every laser shot. This puts high demands on the readout circuit that must handle 1 (pump) + 512 (Is) + 512 (Ir) readouts per millisecond instead of just three in single wavelength experiments. The pump pulse intensity is also measured for gating and intensity scaling purposes. Usually, gating is only applied on the pump pulse, however, if the probe pulses are unusually unstable, gating can also be applied on the probe pulses.

The two diode arrays can be placed above each other at the output of the spectrograph. If a smaller spectrograph is used, for which the two output spectra can not be separated sufficiently, a mirror can be used to achieve a 5-mm separation between the two spectra (see fig 13).

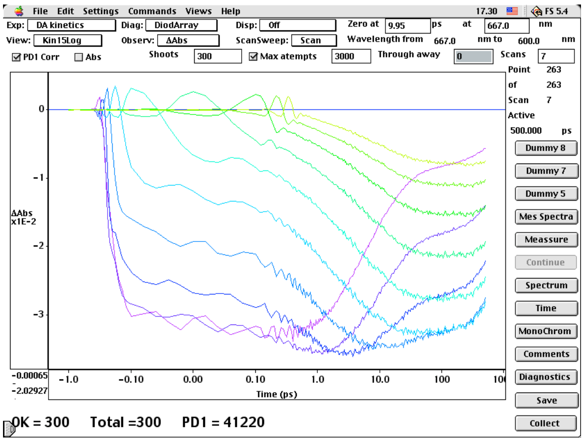
With the huge amount of data collected by the diode arrays, several display modes are needed to judge what's going on in both the time and wavelength domain (see figs below).



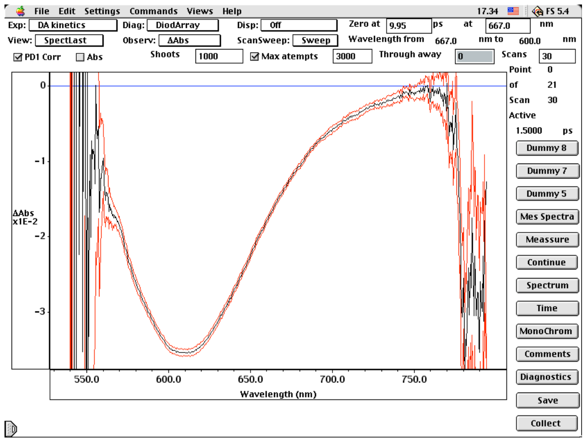
14) *Kinetic traces averaged from 30 sweeps, 150 seconds, including 30 back sweeps.*



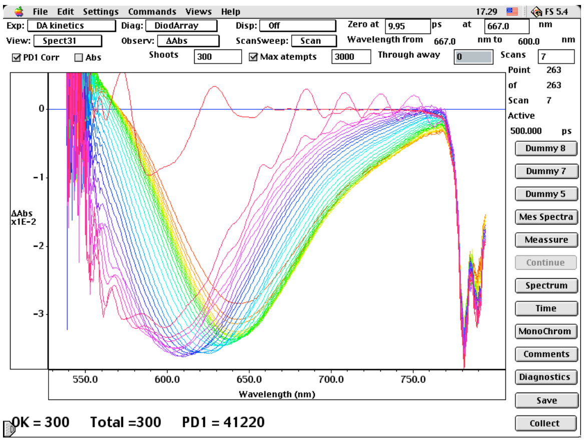
15) *Kinetic traces of a single sweep, 5 seconds accumulation time including the back sweep.*



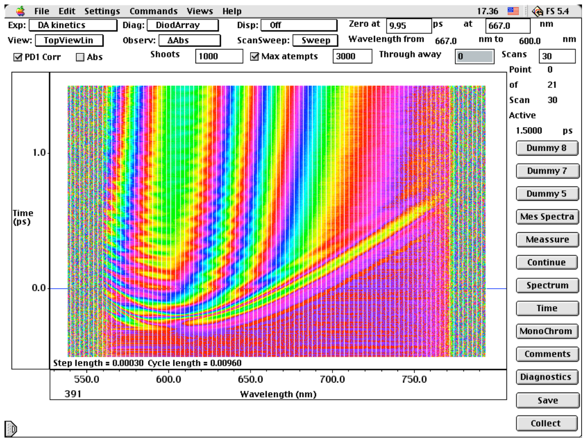
16) *Kinetic traces averaged form 7 scans in a log plot. 300 x 7 measurements per point.*



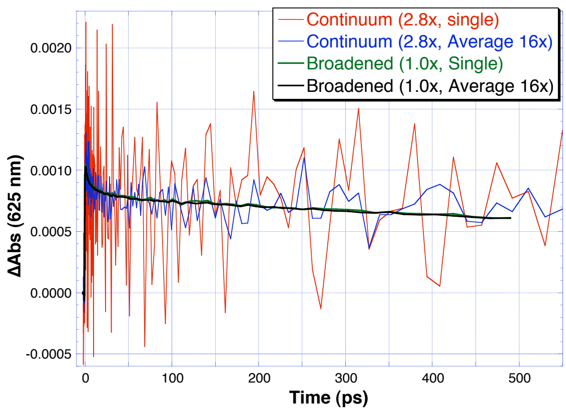
17) *Spectrum with error limits (99% in red).*



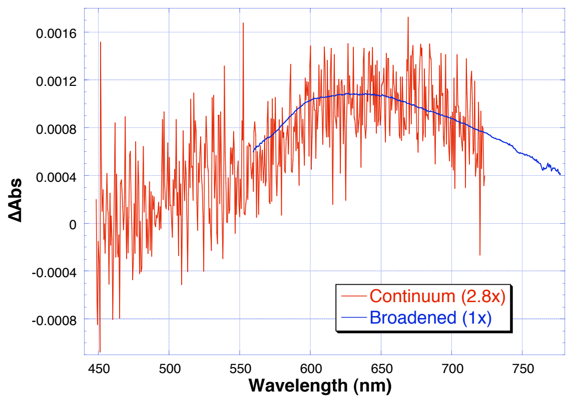
18) *31 spectra covering from negative time to 500 ps. Scan with logarithmic time steps.*



19) *Top view with colour coded amplitudes. One cycle through the spectrum represent 9.6 mAbs. Sweep data averaged 30 times.*



20) *Single diode channel traces for Trp exited at 295 nm. Average of 16 adjacent diode channels.*



21) *Time zero spectra of Trp from globally fitting the whole diode array trace.*

In order to compare the signal-to-noise ratio for the diode array obtained using continuum and spectrally broadened probe pulses, respectively, the signal of tryptophan in buffer excited at 295 nm is used as an example. The data acquisition times were ~4 hours for the continuum and 35 minutes for the spectrally broadened probe pulse measurements. As seen in figs 20 and 21 above, the more intense probe light of the spectrally broadened pulse results in much better signals.

Detection System

Hardware

Minimal set-up consisting of: 3 photodiode detectors, computer with digital IO card (and GPIB and serial ports), instrument case with power supply and circuit boards for digital IO, (stepping motor control) and analog-to-digital conversion for pump, probe and reference.

Extension for multiwavelength measurements: detector head with dual 512 diode (of which 511 are usable) arrays and analog-to-digital conversion board.

Extension for anisotropy kinetics: 2 extra photodiode detectors, an analog-to-digital conversion board for polarised probe and reference intensities.

Software

The data collection program has been developed over several years. It contains a number of methods for system alignment and diagnostics to optimise laser performance, noise and pump/probe overlap. Control and collection modes for a variety of experiments have been implemented, as well as efficient methods for noise reduction (averaging). During data collection, the progress of events can be monitored by a variety of display modes. (cf. text)

Associated hardware

Delay lines

Three types of delay lines have been implemented so far: One stepping motor driven (in principle any that can be controlled by a move pulse train and a direction signal), and two controlled by serial ports purchased from Aerotech, Inc and H2W Technologies. Other delay lines can be implemented on request.

Monochromator / spectrographs

Thus far, spectrographs from ACTON and SPEX (controlled by GPIB) and Oriel (controlled by a serial port) have been implemented with specific gratings optimised for the intended experiments. Others can be adapted on request.

Computer controlled wavelength tunable lasers

The software can control TOPAS tunable lasers (Light conversion Ltd) via a serial port in connection with collection of chirp corrected time resolved absorption spectra.

Repetition frequencies

The diode array has a maximum readout frequency of 1 kHz. If only single wavelength kinetics is used, the detection system can be run at frequencies as fast as 5 kHz.

Contact for further information:
Torbjörn Pascher
Stora Råbybyaväg 24
S224 78 Lund
Sweden
Telephon: +46 46 134155
Fax: +46 46 134155
Mobil: +46 702 696861