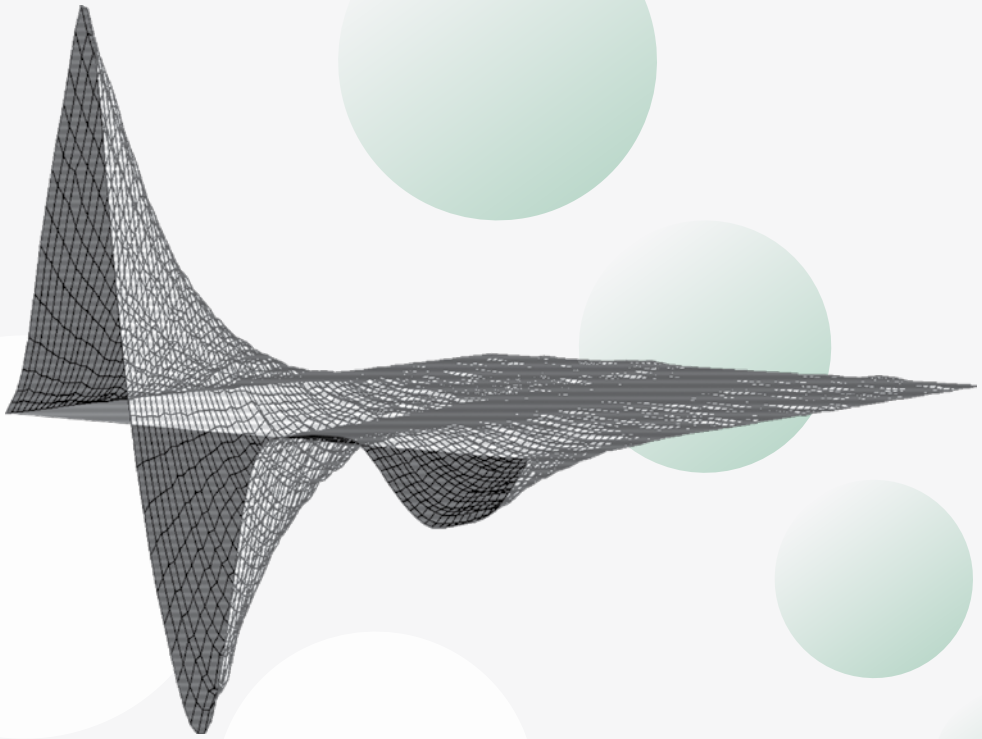
LP920

Laser Flash Photolysis Spectrometer

EDINBURGH PHOTONICS

A Division of Edinburgh Instruments



Pride in Precision

Laser Flash Photolysis Spectrometer

LP920

Edinburgh Photonics is proud to present the LP920 laser flash photolysis spectrometer. The modular design concept combines maximum flexibility with astonishing ease of use. As a fully computer controlled turn-key system, the LP920 sets the standard for technical performance in laser flash photolysis both for fundamental research and for routine laboratory applications.

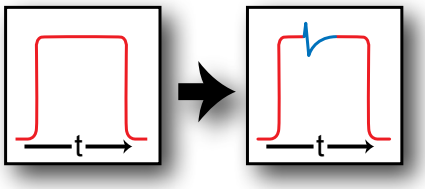
Laser Flash Photolysis is a technique for studying transient chemical and biological species generated by the short intense light pulse from a nanosecond pulsed laser source (pump pulse). This intense light pulse creates short lived photo-excited intermediates such as excited states, radicals and ions. All these intermediates are generated in concentrations large enough for chemical and physical interaction to occur and for direct observation of the associated temporally changing absorption characteristics.

These absorption changes are recorded using a spectrally continuous xenon lamp (probe source) forming the background in a single beam absorption spectrometer. The probe source is operated in a pulsed mode to enhance the photon flux for measurements in short time ranges. Transient absorption features can be measured with temporal resolutions from nanoseconds to milliseconds in pulsed mode, and milliseconds to seconds in continuous mode.

Laser flash photolysis is applicable to liquid, gaseous, and solid samples. Liquids are usually measured in a cuvette with the pump beam and the probe beam overlapping orthogonally (transverse excitation). In gaseous samples the concentration of the participating molecules is much lower and a co-linear setup between the pump and probe beam is preferred to improve the signal to noise ratio. Film samples, powders and non transparent bulk samples are generally studied in a diffuse reflectance setup.

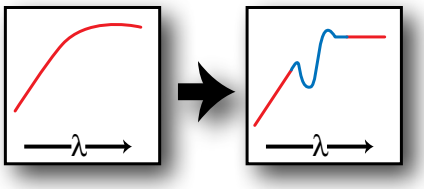
There are two modes of operation of the laser flash photolysis spectrometer : Kinetic mode and Spectral mode.

Kinetic Data Acquisition



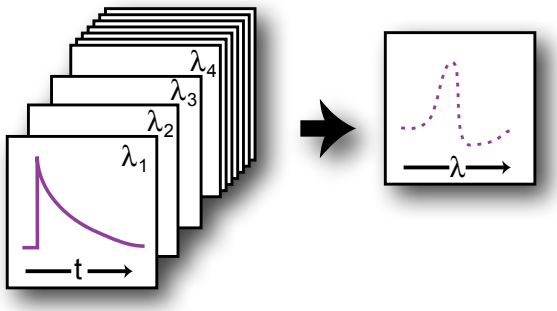
Kinetic Mode:- where transient absorption, generated by the intense laser pulse, is recorded at a single analysis wavelength as a function of time using photodetector and digital storage oscilloscope. This mode provides very accurate measurement of transient kinetics since a complete time resolved measurement of the transients is made in a single flash experiment. Lifetimes from nanoseconds to seconds can be measured over a wavelength range from 200 nm to 2500 nm (depending on the detector).

Spectral Data Acquisition



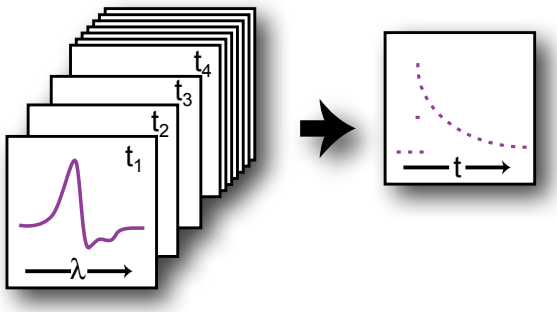
Spectral Mode:- where complete transient absorption spectra are measured at a specific time after excitation using a time-gated array detector. Spectral mode measurements provide the full picture of the transient spectral features by exposing the sample to only a few laser shots. This is especially useful when studying biological samples, which can easily undergo photo-degradation under high levels of light. Time resolutions down to 3ns can be achieved with a spectral coverage from 200nm to 930nm.

Spectral Slicing



Time Resolved Absorption Spectra can be generated in kinetic mode laser flash experiments by automatic scanning through a pre-defined spectral range and subsequent data slicing. This technique requires many laser shots, in particular when high spectral resolution is required.

Kinetic Slicing



Spectrally Resolved Absorption Kinetics can be extracted from spectral mode measurements by automatically stepping the gate delay through a pre-defined time range. Subsequent data slicing reveals the details of the transient absorption kinetics.

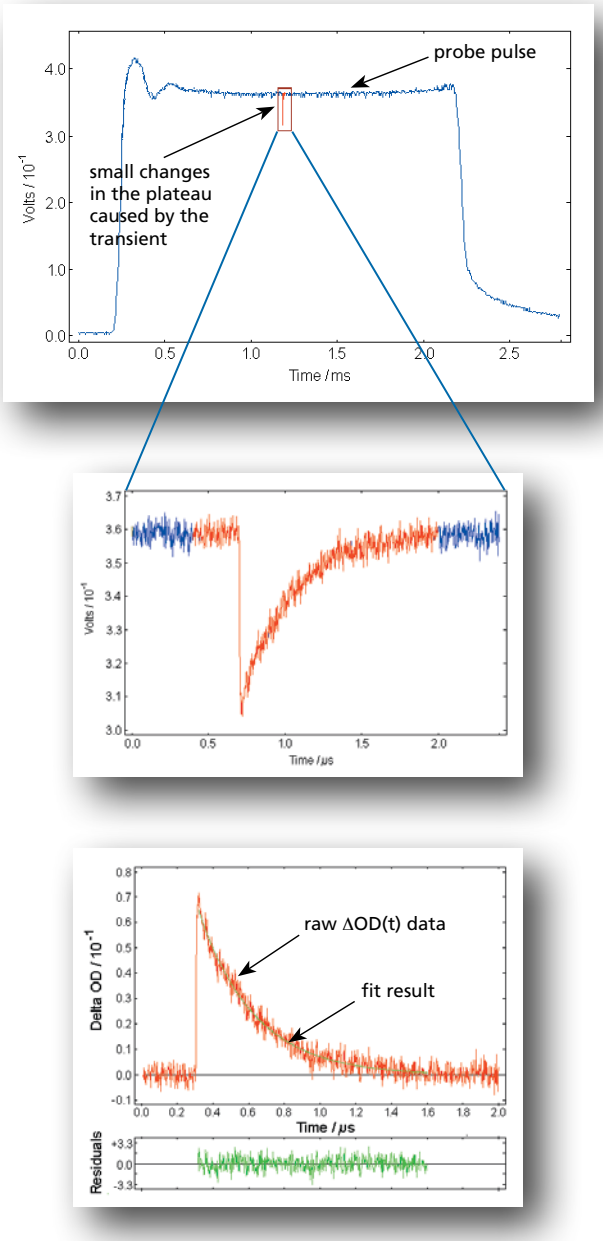
LP920-K - Kinetic Mode Laser Fl

The LP920 Laser Flash Photolysis Spectrometer uses the same basic optical-electrical setup for operation in both the Kinetic and the Spectral Mode, i.e. laser excitation source, probe source, sample compartment (including optics, attenuators, laser shutter and probe shutter), monochromator / spectrograph, and control electronics. The difference between the two modes is the detector and the data acquisition electronics.

In Kinetic Mode a photomultiplier detector is used and the transients are acquired using a fast, high resolution oscilloscope.

The LP920-K has been designed to meet the stringent demands of high quality research. At the same time, it is a true turn key system, suitable for routine applications, with ease of operation guaranteed by comprehensive software and a user friendly interface.

Operational Example



The sample being investigated is exposed to an intense laser pump pulse, which creates the transient species, and the probe source, which forms the background for the time dependant absorption measurement.

For time scales in the microsecond and nanosecond range the required high background level of the probe light is created by the intense flash from the pulsed xenon lamp which – after some stabilisation period - reaches a sufficiently flat plateau. This plateau level represents the pre-photolysis background level of the transmitted light through the sample. At a pre-set time after lamp triggering, when the pulse plateau is flat, the excitation laser is triggered creating the transient species under investigation. The absorption of the transient species is usually time dependent and produces a time dependent change in the transmission of the sample.

After recording the time dependent transmission of the sample, the optical density change is calculated using the level of the background light as 100% and the measurement baseline as 0%.

The change in optical density, ΔOD, can then be analysed using exponential least squares fitting algorithms, resulting in transient lifetimes or rate constants.

To protect the sample against unnecessary radiation exposure between measurements and as a means to control background measurements, high speed shutters are operated to control the probe and laser beam prior to entering the sample. For laser induced emission measurements the probe shutter remains permanently closed.

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Signal Detection and Data Acquisition

The LP920-K kinetic mode laser flash photolysis spectrometer is supplied with a standard red sensitive photomultiplier (PMT) which covers the spectral range from 200nm to 870nm. The detector housing also accommodates the high voltage power supply and the voltage divider circuit.

The photomultiplier detector system is designed to achieve a high dynamic range with exceptional current linearity. This is an essential requirement in measuring small signals on a large signal background. The voltage divider and power supply are configured to support this high linearity current mode by operating in a five stage dynode configuration.

The PMT detector contains two outputs within the same unit. The fast output has a rise-time of <3ns and is suitable for transients up to ca 1ms. The slow output has a selectable range of output rise times and is recommended for timescales >1ms, due to its improved signal to noise ratio. The rise times vary for ca 10µs to 10ms with corresponding relative gains, varying from 1 to 1000.

For transient absorption and emission measurements in the near infra-red spectral region, InGaAs detectors (up to 2550nm) are available as options.

The output signal from the detector is directly recorded by a digital storage oscilloscope (Tektronix) with a minimum specification of 100MHz bandwidth, 1.25GS/s sampling rate. Higher bandwidth and digitising rates are available as options. Instrument setup and data acquisition are fully computer controlled. The user does not need to be familiar with detailed operation modes of oscilloscopes.

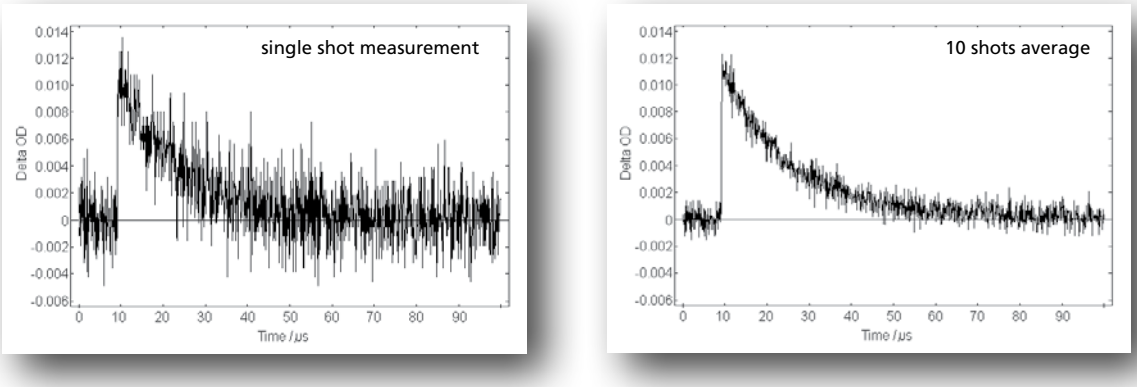
The bandwidth of the oscilloscope, together with the excitation laser pulse width and the detector response time, contribute to overall instrumental response function of the system. Hence, a significant increase in performance of only one of these parameters is of little benefit.

Detection Limit

The detection limit given by the RMS noise for single shot measurements is ΔOD=0.002 (fast detector) and ΔOD=0.0005 (slow detector option).

Data averaging is common in transient measurements in order to improve the measurement's signal-to-noise ratio. For transient absorption measurements this improves the detection limit by decreasing the minimum ΔOD that can be resolved.

Detection improvement is made in proportion to the number of pulses used in the measurement, e.g. 100 pulses improves the signal-to-noise ratio by ten times and hence the detection limit improves to ΔOD=0.0002 (fast detector) and ΔOD=0.00005 (slow detector).



Demonstration of the detection limit and of the Signal-to-Noise improvement by signal averaging using the fast detector version
Sample: Erythrosin B in water
Measurement Conditions: λ_{pump}=532nm, E_{pump}=1mJ, pulsed probe source, λ_{probe}=580nm

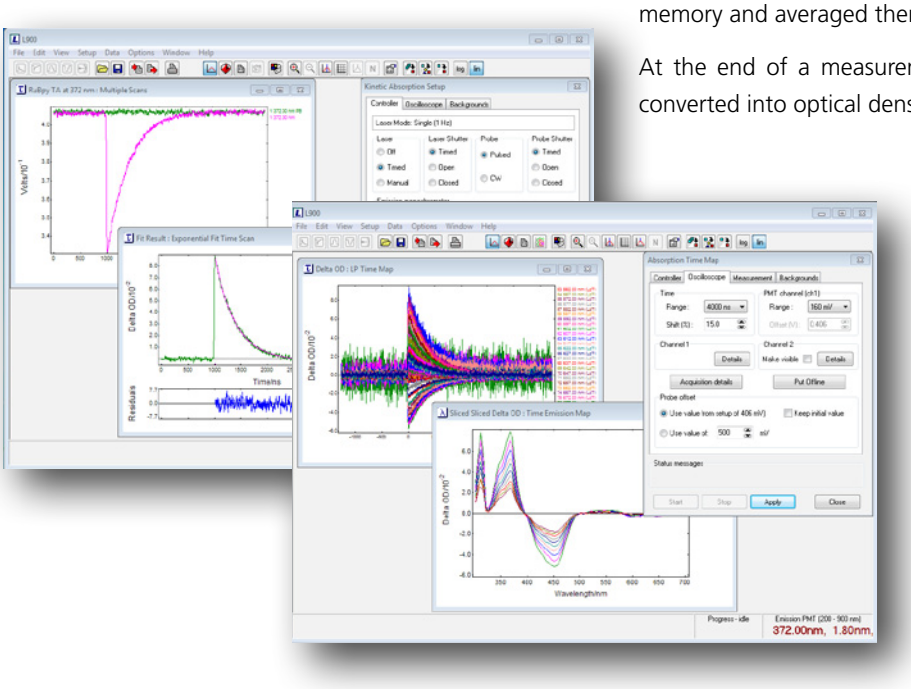
Software

The LP920-K spectrometer system is fully computer controlled by means of the comprehensive L900 software package.

A variety of different measurements and correction methods are available. For example, if the probe shutter is programmed to be closed during the measurement then normal time resolved emission measurements can be made. If a measurement sequence is made with alternate switching between probe shutter open and probe shutter closed then the result is a measurement of transient absorption which is corrected for emission.

The LP920-K data acquisition dialogue boxes allow the direct import of data captured with the digital storage oscilloscope. Data averaging can be made either within the oscilloscope in order to make effective use of high repetition rate sources, or the data can be transferred to the computer memory and averaged there.

At the end of a measurement sequence, the raw data is converted into optical density data.



The L900 software package offers a comprehensive library of data analysis routines, including 1- to 4-exponential and reconvolution fits, analysis of growth and decay kinetics.

Software Functionality

The main challenge for the L900 software and the LP920 spectrometer controller is the correct time sequencing of the individual spectrometer components, i.e. pump laser, probe lamp, spectrograph, pump and probe port shutters along with the digital storage oscilloscope. This task has been accomplished with the LP920 spectrometer. While maintaining maximum flexibility in measurement modes the user has complete control.

Measurement Modes

- Measurement setup
- Single kinetic measurement
  - Transient absorption
  - Laser Induced emission
- Multiple kinetic measurements
  - Transient absorption
  - Laser Induced emission
- Time Resolved Absorption Spectra (TRAS)
- Time Resolved Emission Spectra (TRES)
- Stopflow mode for use with optional stopped flow accessory

Control Features

- Wavelength / slit control
- Grating selection
- Pump laser flashlamp trigger
- Pump laser Q-switch trigger
- Probe source pulse current
- Pump and probe shutters
- Oscilloscope trigger
- Oscilloscope time base
- Oscilloscope voltage scale
- Signal offset
- Time shift / delay
- Optional temperature controlled sample holder
- Optional cryostat mounting
- Stopflow synchronisation

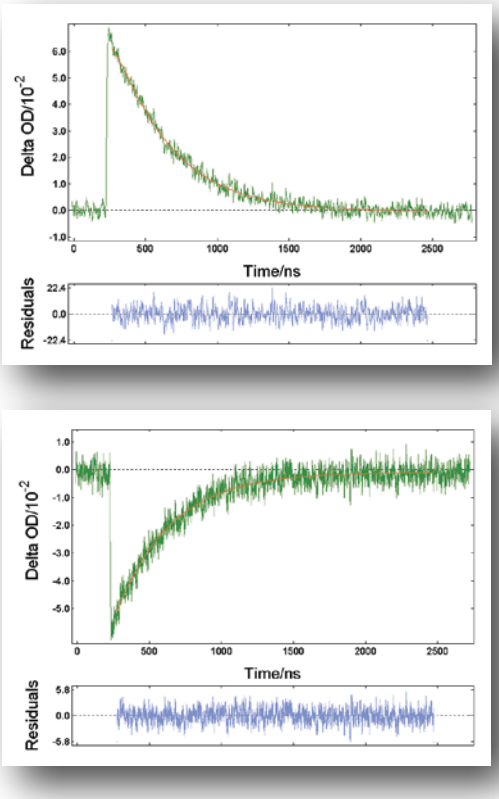
Data Manipulation and Display

- ΔOD calculation (automatic and manual)
- Arithmetic (+, -, x, /, append)
- Scaling
- Normalise
- Baseline subtraction
- Smoothing
- Data slicing – TRAS
- Data slicing – TRES
- Full data reconvolution using non-linear least square fitting routine
- 2D, 3D, Contour plotting and text

Transient Absorption and Photobleaching

In transient absorption, the presence of the transient species can cause the sample to have either increased or decreased levels of absorption relative to the absorption of the ground state species (positive ΔOD and negative ΔOD respectively). While an increased absorption is associated with triplet-triplet or singlet-singlet transitions, a reduction in the measured optical density is associated with either ground state depletion or sample emission.

Generally these effects can be separated spectrally, or by means of their lifetimes. In some special cases (such as with the ruthenium bipyridine complex) separation by lifetimes is not possible.

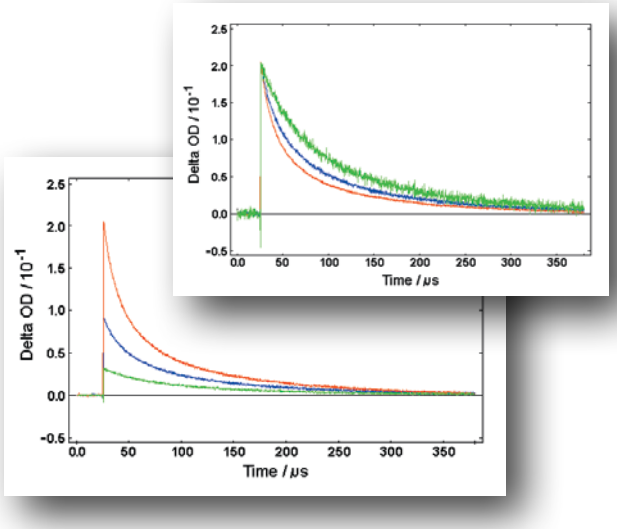


Sample: Ruthenium bipyridine in water
Measurement Conditions: λ_{pump}=355nm, E_{pump}=10mJ, pulsed probe source, λ_{probe}=365nm (top picture), λ_{probe}=450nm (bottom picture), 1 shot
Top picture: transient absorption at 365nm
Bottom picture: ground state depletion at 450nm

Triplet-Triplet Annihilation

Annihilation of excited states can take place if too many excited states are generated (due to high sample concentration or excessive pump energies) whose lifetimes are long compared to the diffusion times of the molecules. In this case diffusion controlled collisions become possible resulting in the de-activation of both molecules.

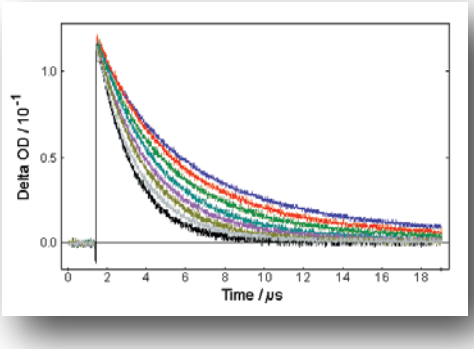
This example clearly shows the effect of laser energy on the transient dynamics. Annihilation is a non-exponential process but can be fitted with a series of exponential with the long lifetime representing the "true" excited state lifetime for the generated species.



Sample: Anthracene in cyclohexane (10^{-4}M), partially degassed
Measurement Conditions: λ_{pump}=355nm, 3 different laser excitation pulse energies: E_{pump}=50mJ (red), E_{pump}= 10mJ (blue), E_{pump}=1mJ (green).
Main figure: measured optical density data
Inset figure: same data but scaled to the same peak height. The green curve represents a single exponential decay with a lifetime of τ = 118µs

Oxygen quenching of transient absorption decays

The triplet states of organic molecules are often quenched by oxygen present in the solvent. Transient absorption measurements clearly reveal the sensitivity towards oxygen. The measurement example below shows the effect of different oxygen concentrations on the transient decay times, from 0% (blue curve) to 20% oxygen (black curve).

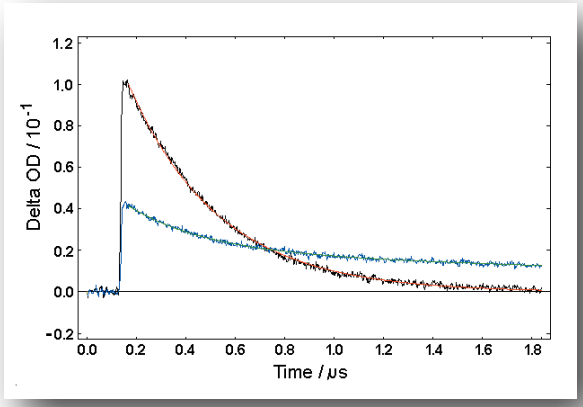


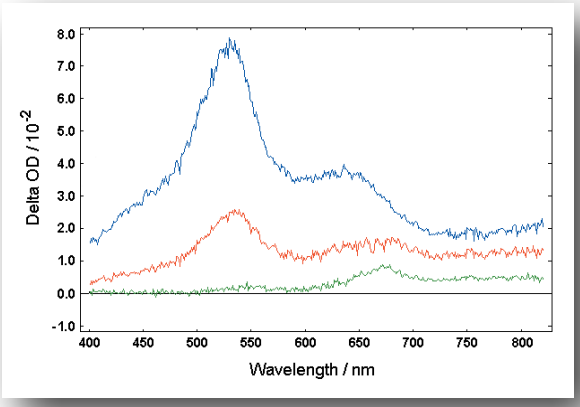
Sample: Erythrosin B in water
Measurement Conditions: λ_{pump}=532nm, E_{pump}=10mJ, pulsed probe source, λ_{probe}=580nm, 10 shots average

Spectrally dependent transient kinetics

Time resolved transient absorption spectra can provide substantially more information than kinetic measurements alone. The measurement of benzophenone in benzene shows two distinct absorption bands with the main band centre wavelength at 540nm and a second band above 600nm.

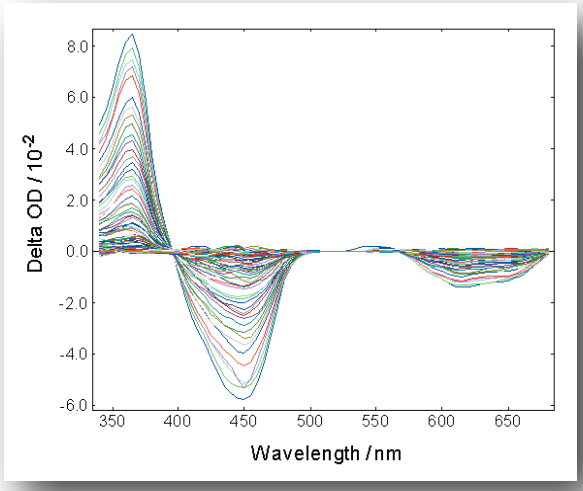
The spectra for three different time intervals reveal that the long wavelength band shifts towards the near infrared spectral range with time. Blue curve: 0 – 200ns, red curve: 600 – 800ns, green curve: 1.2µs – 1.4µs after laser excitation.

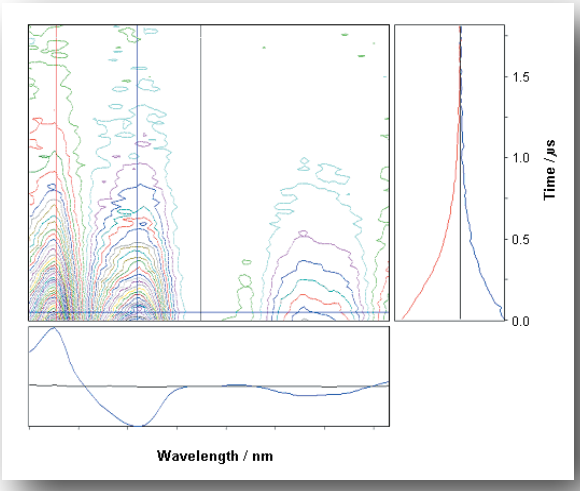




Sample: Benzophenone in benzene (10^{-4}M)
Measurement Conditions: λ_{pump}=355nm, E_{pump}=40mJ, single shot measurements, step increment 1nm.
Fit Results: at 540nm: τ = 340ns; at 660nm: τ_1= 340ns (ϕ_1 = 5%); τ_2 = 4.8µs (ϕ_2 = 95%)

Kinetic and spectral data sets can be viewed and manipulated in various ways using the L900 spectrometer software. 2D and 3D graphics are available as well as contour plot options. Data slicing converts a set of spectral data into a set of kinetic data and vice versa.

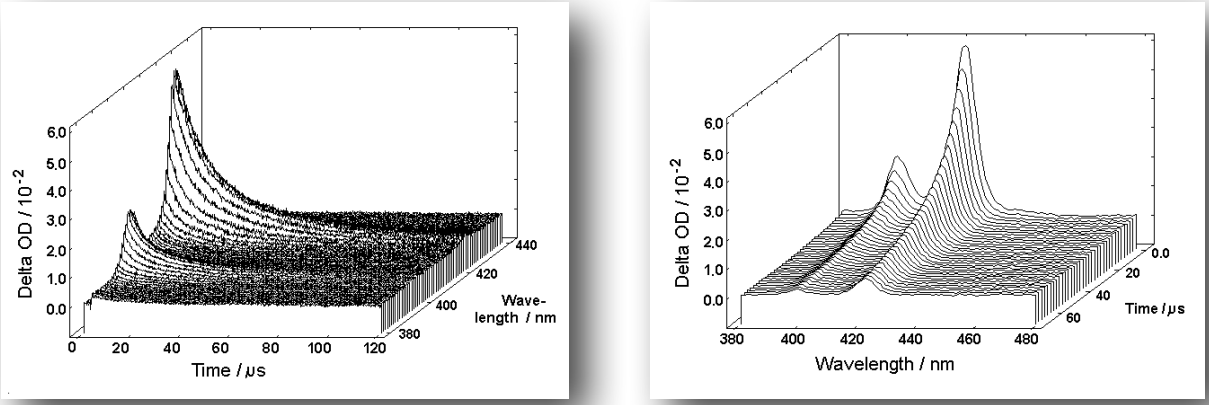




Sample: Ruthenium bipyridine in water
Measurement Conditions: λ_{pump}=355nm, E_{pump}=10mJ, pulsed probe source, automatic scanning from 340nm to 670nm in steps of 1nm, spectral resolution 0.5nm, 5 shots per decay profile.
left: data after spectral slicing, **right:** contour plot of the same data with the cross hair extracting more detailed spectral and kinetic information

The computer controlled operation of the LP920-K Laser Flash Photolysis Spectrometer enables the user to generate Time Resolved Absorption Spectra in a two-fold process: Firstly, a series of transient absorption measurements over a pre-defined range of probe wavelengths is recorded, and, secondly, this data is sliced at desired time windows and delays from the laser pulse excitation.

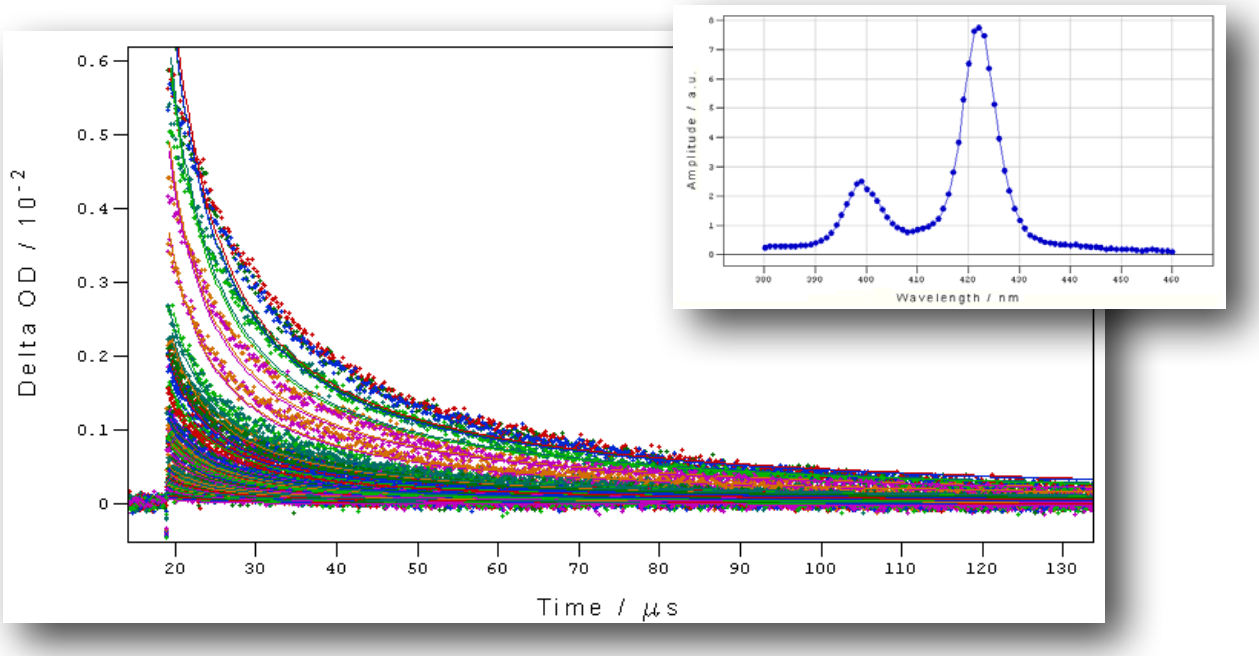
By automatically scanning through the spectral range the probe background level can change. The changing background level does not have an effect on the value of the optical density, but it has an effect on the noise of the individual measurements. The LP920-K has the software option to either automatically reset the probe background offset or to correct for this changing background level.



Sample: Anthracene in cyclohexane (10^{-4}M), partially degassed
Measurement Conditions: λ_{pump}=355nm, E_{pump}=20mJ, pulsed probe source, automatic scanning from 380nm to 480nm in steps of 1nm, spectral resolution 0.5nm, 10 shots per decay profile
left: raw data obtained in kinetic mode, **right:** data after spectral slicing

The spectrometer operating software can perform standard curve fitting of individual ΔOD(t) curves. The standard analysis is based on exponential decay models, taking into account the Gaussian statistics of the raw data.

For the advanced analysis of complex data sets an optional software package is available. The advanced analysis software offers batch and global fitting of multiple ΔOD(t) curves and can also test the measurements for second order decay kinetic models



Raw data and fitted curves of the set of 80 time resolved measurements of the above anthracene example.
Data were analysed with FLASH software using Global Analysis of a second order kinetic decay model, globally linking the rate constant. The result of the fit is a global second order rate constant of 1.8×10^3 $(M\ \mu s)^{-1}$ and a wavelength dependence of the amplitude as shown in the insert.

LP920-K - Technical Specifications

System

Optical Configuration	Single beam absorption spectrometer for monitoring transient kinetics generated by laser excitation, transverse excitation
Options	Co-linear excitation, diffuse reflectance

Sensitivity

Minimum ΔOD	0.002	(single shot, fast detector option)
	0.0005	(single shot, slow detector option)

Time Resolution

Instrument Response (FWHM)	7ns	(100MHz acquisition bandwidth, fast detector option) *
	10µs	(slow detector option)
	100ns	(InGaAs detector option)

* Lasers with pulse width of more than 6ns will result in a broadened instrument response.

Laser Excitation Source **

Single Wavelength	Flashlamp pumped Q-switched Nd:YAG laser, operating at 1064nm, 532nm, 355nm or 266nm
Tuneable	Dye Laser, tunable range dependent on dye OPO, tunable between 210nm (with UV doubler) and 2500nm

** A fully tested laser system can be supplied by Edinburgh Instruments, or alternately supplied by the customer.

Probe Source

Type	Pulsed / steady state xenon arc lamp, 450W, ozone free
Pulsed Operation:	
Rep. Rate	10Hz to single shot
Pulse Current	0 – 200A
Pulse Duration	0.5 – 10ms
Current Pulse Ripple	≤ 0.2% over 5ms at 200A

Monochromator

Type	Czerny-Turner with Triple Grating Turret
Focal Length	300mm
Slits	<10µm to 10mm (continuously adjustable), motorised
Stray Light Rejection	$1:10^5$
Grating	Plane, ruled grating, 1800grooves/mm, 500nm blaze
Dispersion	1.8nm/mm
Options	A variety of gratings with 150–2400grooves/mm, optimised from UV to NIR
Mirror	Motorised to select detector

Detector

Type	Photomultiplier with 5 stage dynode chain for high current linearity
Spectral Range	200 – 870nm
Window Material	UV Glass
Detector Impedance	50Ω (amplified- fast detector, <3ns rise time), 1kΩ (slow detector, <100microsecond rise time)
Options	InGaAs detectors (900nm - 2550nm)

Data Acquisition

Oscilloscope	Fully remote controlled by operating software, or manually controlled when off-line
Bandwidth	100MHz***
Sampling Rate	1.25GS/s***
Interface	Ethernet

*** Higher specification oscilloscopes are available on request.

Software

Operating System	Windows ®
Data Manipulation	ΔOD calculation (with / without background correction), numerical fits by Marquardt-Levenberg algorithm, analysis of growth and decay kinetics, Time Resolved Absorption Spectra

Laser Pump Source

In Laser Flash Photolysis transient species are generated using a short pulse, high peak power laser, known as the pump pulse. Suitable lasers include fixed wavelength lasers, particularly Nd:YAG lasers (fundamental wavelength 1064nm) and their harmonics (at wavelengths 532nm, 355nm and 266nm), or tunable lasers, particularly optical parametric oscillators (OPOs). Other lasers sometimes used include nitrogen or excimer lasers and dye lasers.

The LP920 has been designed with the ultimate flexibility in mind. It can be supplied either as a turn-key, fully tested and performance guaranteed spectrometer, with integrated laser to suit individual need and budget, or as a system with comprehensive trigger and command pulses to control virtually any commercially available laser.

Edinburgh Instruments have experience of integrating lasers from a wide variety of manufacturers including Continuum (Minilite and Surelite I and II Nd:YAG lasers, broadband or narrow band OPOs), Quantel (Brilliant, Brilliant B and Brio Nd:YAG with optional Rainbow OPO), Opotek (Opolette and Vibrant OPOs), Solar (Nd:YAG and OPO systems), Spectra Physics (Quanta-Ray Pro, Lab and Indi). OPO's by Continuum and OPOTEK can have their wavelengths tuned from within the L900 software.

Generally, flashlamp pumped Nd:YAG lasers have pulse widths in the range 5-7ns. Pulse energies at the fundamental wavelength range typically from 50-1000mJ, dropping with each non-linear stage of harmonic generation to between 2 - 20mJ at 266nm.

When pumped by the third harmonic of the Nd:YAG laser at 355nm, OPOs provide broadly tunable output from both signal and idler bands spanning the range from 410nm – 2500nm. Additional frequency doubling can extend the wavelength tuneability to the UV down to 210nm. Type II OPOs are generally preferred as they do not suffer from a gap in tunability around the degenerate wavelength at 710nm although they characteristically have a slightly reduced pulse energy. With a pump pulse energy of 100mJ at 355nm OPOs have peak output energy of up to 35mJ at 450nm and several mJ over a wide tuning range. Edinburgh Instruments are happy to advise on the optimum laser for particular applications and budget.

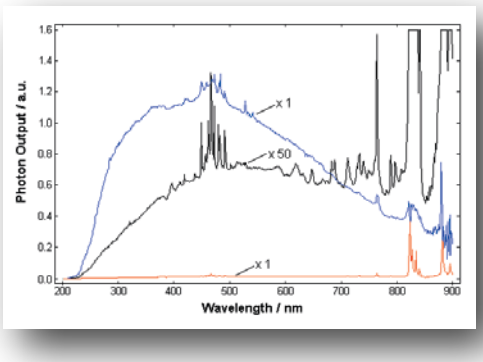
Probe Source

In a conventional absorption spectrophotometer, the time averaged absorption of a sample is measured from the light level being attenuated whilst passing through the sample. In flash photolysis the temporal change of the attenuated light following laser excitation is measured. As these changes often occur in the nanosecond time range, the available light level in the probe beam may be too low for an acceptable signal to noise ratio. In order to overcome this and to provide sufficient probe light levels, a pulsed probe source is used.

The best way of supplying a broad band, stable light pulse with a flat time profile is by using a xenon arc lamp operated by adding a "super current pulse" to the low current simmer supply. A pulsed xenon lamp exhibits a significant increase in the emitted photon flux during the period of the pulse, compared with the photon flux from the same lamp in steady state operation over the equivalent time period. During pulsed operation, the colour temperature of the arc is dramatically increased over its steady state equivalent and as a result, the emission profile is shifted towards the UV and the spectrum is less structured.

The xP920 pulsed xenon arc lamp system was specifically designed for laser flash photolysis measurements with particular emphasis on pulse flatness, reproducibility and minimum ripple.

For measurements in the millisecond and second range, an optional Halogen (continuous) probe source is offered. This provides greater stability than Xenon lamps over long timescales. Both probe sources can be accommodated simultaneously in the LP920 sample chamber.



Xenon arc lamp emission spectrum monitored over a 3ms period. Lamp in continuous operation (red curve – un-scaled; black curve – scaled) and in pulsed operation with a current pulse of 150A (blue curve). Spectra were measured using an ozone free xenon bulb and are corrected for the responsivity of the detection system.

LP920 - Laser Flash Ph

Monochromator / Spectrograph

The LP920 spectrometer has a three grating turret monochromator/spectrograph which gives maximum flexibility in wavelength coverage and spectral resolution, for both the UV-VIS and near IR spectral ranges.

The monochromator/spectrograph has a symmetric Czerny-Turner optical configuration with a focal length of 300 mm and a constant aperture of F/4.1.

For kinetic mode UV-VIS operation the system is fitted with a standard 1800 g/mm grating. It has a linear dispersion of 1.8 nm/mm, blazed at 500nm, and a wavelength coverage from 200nm to 900nm. For near IR operation the standard grating has 600g/mm, with a blaze wavelength of 1µm, covering the spectral range from 600nm to 2.7µm

For time-gated measurement applications in the spectral mode the standard grating has 150g/mm and is blazed at 500nm. It offers a spectral range of 540nm with the standard 25mm long detector array. Other grating options with wavelength coverage of 270nm and 135nm are available upon request.

A combination of up to three different gratings can be fitted to the grating turret. The selection of the grating type and the requested spectral position is made by a micro-stepping drive controlled from the system software. This gives unparalleled accuracy and reproducibility in the spectral performance of the system.

A unique feature of the monochromator is the computer controlled beam steering mirror at the exit port, allowing rapid selection of detectors (e.g. photomultiplier and InGaAs detector or single element and array detector) without the need for mechanical or optical adjustment.

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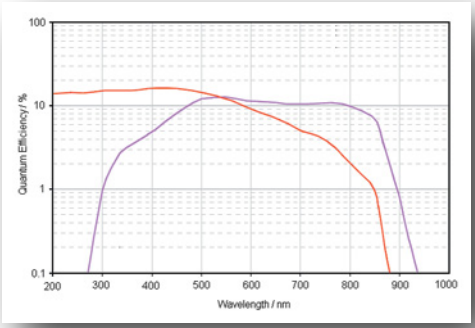
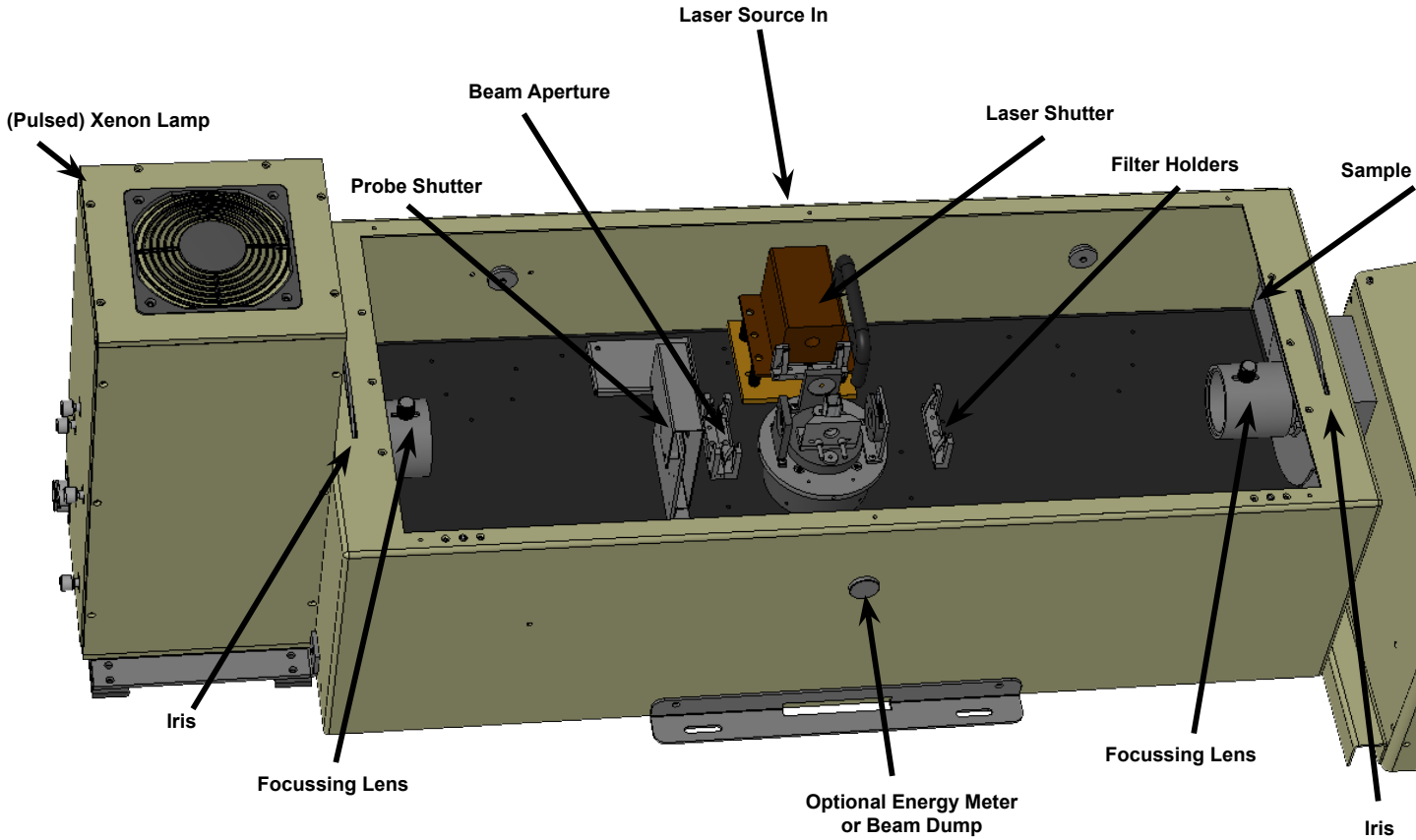
Detectors

The LP920 in its kinetic mode is supplied, as standard, with a red sensitive photomultiplier which covers the spectral range from 200nm to 870nm.

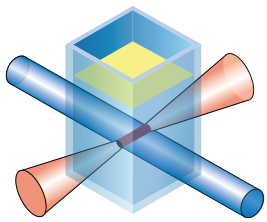
For transient absorption and emission measurements in the near infra-red region, InGaAs photodiodes can be used with coverage up to 2550nm. When infrared photodiodes are used as detectors the temporal resolution will be limited.

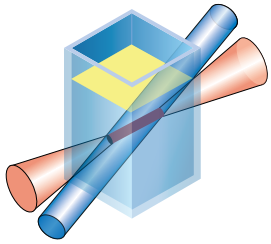
In the spectral mode of operation, the LP920 can be supplied with alternative models, either with standard UV-VIS coverage, or with enhanced NIR sensitivity.

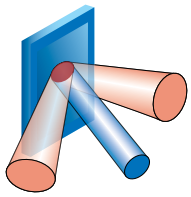




Sample Chamber and Beam Geometry





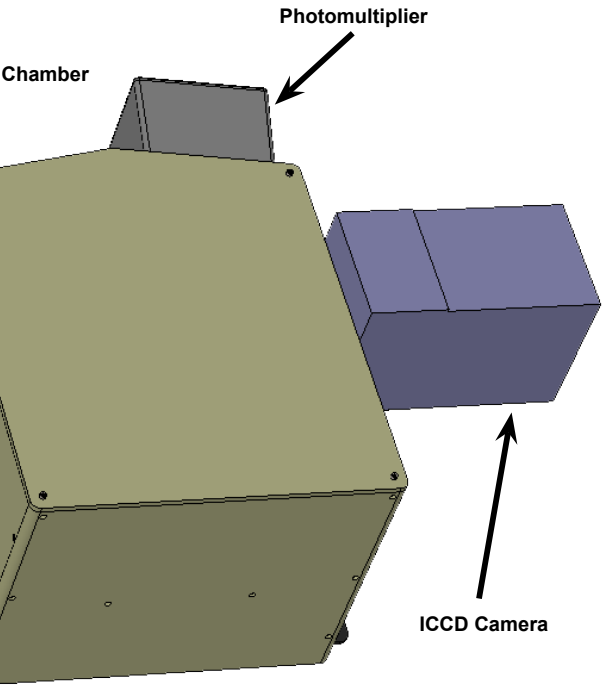


The sample chamber contains imaging optics, two irises for attenuating the probe beam in front and after the sample, two fast shutters to control the laser and the probe beams before entering the sample, and filter holders.

The beam geometry and the overlap of excitation and probe beams at the sample position are critical in laser flash photolysis. In the standard LP920 system, with a liquid sample, the laser beam intersects the sample perpendicular to the probe beam. This is often referred to as cross-beam or perpendicular geometry.

The probe beam from the xenon light source is focused to provide an ideal overlap with the excitation spot from the laser. The high parallelism of the probe beam ensures high signal collection and minimisation of fluorescent light affecting the absorption measurement.

To achieve the optimal overlap of the pump and probe beams the pump laser beam is adjustable in both horizontal and vertical directions.



Accessories

Laser safety goggles

Available to protect the user against radiation in the range 1064nm, 532nm, 355nm and 266nm.

Laser energy meters

Available for monitoring over the spectral range 250nm – 3.0µm.

Stopped flow accessory

A rapid kinetic accessory for manual multi-mixing capabilities is available to allow stopped flow analysis. It comprises a sample handling unit fitted with three 1.0ml drive syringes, 600mm long umbilical, manual or software controlled drive, and 12.5mm square mixing/observation cuvette.

Temperature control systems

Oxford Instruments liquid nitrogen or helium cryostats with ITC controllers are used when low temperature measurements are required. The cryostat is provided with an adapter to fit into the standard sample chamber, which is controlled by the L900 software. A temperature controlled cuvette holder with range of -10°C to +105°C (extended versions available), and ±0.02°C precision, is also available.

Co-linear beam accessory

Accessory comprising laser beam steering optics, laser beam dump; sample holder is required to be specified by the customer.

Diffuse reflectance accessory

Accessory comprising beam folding optics for the probe beam and a front face sample holder for bulk, powder, or film samples.

LP920-S - Technical Specifications

System

Optical Configuration	Single beam absorption spectrometer for monitoring transient kinetics generated by laser excitation, transverse excitation
Options	Co-linear excitation, diffuse reflectance

Sensitivity

Minimum ΔOD	0.0005 (single shot)

Time Resolution

Instrument Response (FWHM)	7ns *

* Lasers with pulse width of more than 6ns will result in a broadened instrument response.

Laser Excitation Source **

Single Wavelength	Flashlamp pumped Q-switched Nd:YAG laser, operating at 1064nm, 532nm, 355nm or 266nm
Tuneable	Dye Laser, tunable range dependent on dye OPO, tunable between 210nm (with UV doubler) and 2500nm

** A fully tested laser system can be supplied by Edinburgh Instruments, or alternately supplied by the customer.

Probe Source

Type	Pulsed / steady state xenon arc lamp, 450W, ozone free
Pulsed Operation:	
Rep. Rate	10Hz to single shot
Pulse Current	0 – 200A
Pulse Duration	0.5 – 10ms
Current Pulse Ripple	≤ 0.2 % over 5ms at 200A

Monochromator / Spectrograph

Type	Czerny-Turner with Triple Grating Turret
Focal Length	300mm
Slits	<10µm to 10mm (continuously adjustable), motorised
Grating	Plane, ruled grating, 150grooves/mm, 500nm blaze, 540nm coverage
Dispersion	21.6nm/mm
Spectral Coverage	540nm (active horizontal ICCD dimension: 25mm)
Spectral Resolution	0.56nm (spectral coverage / 960 pixels)
Options	Gratings with 300grooves/mm for 270nm coverage and 0.28nm resolution
Mirror	Motorised to select detector

Detector

Type	Image intensified CCD camera
Spectral Range	200 – 850nm
Min. Optical Gate Width	7ns (FWHM)
Active Pixels	960 x 256
Active Area	25mm x 6.7mm
Cooling	-10°C (-25°C with additional water circulation)
Option	3ns min. optical gate width 300-930mm spectral range

Data Acquisition

ICCD	Fully remote controlled by operating software
Fast Vertical Binning	16 bit data resolution
Image	24 bit data resolution

Software

Operating System	Windows ®
Data Manipulation	ΔOD calculation, mathematical, smoothing, automatica kinetic spectra acquistion, transformation into kinetics by data slicing, 2D, 3D graphics, contour plotting

LP920-S - Spectral Mode Laser F

The generation of spectra in kinetic mode by successive measurements at different wavelengths requires many excitation flashes. This can sometimes be problematic because of sample photodegradation and instability. This is true in particular when highly spectrally resolved results (with small wavelength steps) are anticipated.

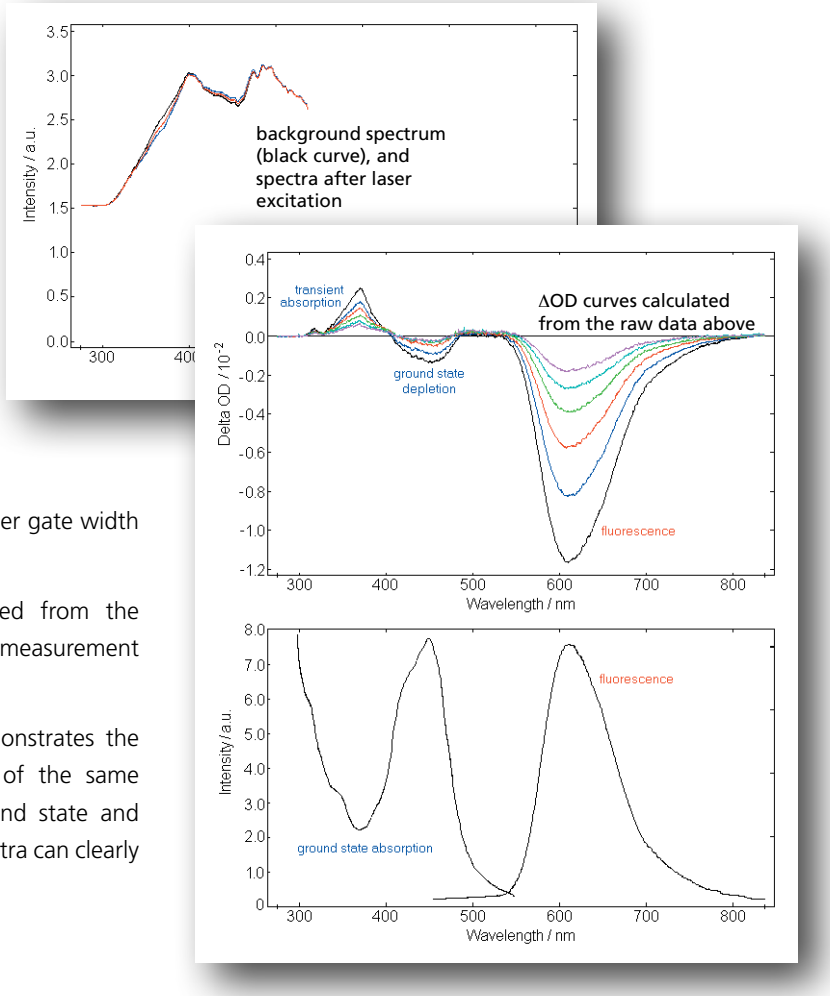
An efficient method to overcome these issues is to use the LP920-S – the spectral mode version of the LP920 laser flash photolysis spectrometer.

The LP920-S has an array detector fitted to the spectrograph exit port to measure a full range of wavelengths simultaneously. By means of a swing mirror and a slit at the second exit port, a kinetic detector can still be fitted to the spectrometer.

The array detector is a CCD camera with an integrated gated image intensifier (ICCD). The device exhibits a high sensitivity and allows time resolved spectra to be measured in a window as narrow as 3ns.

Operational Example

The continuous spectral output of the xenon lamp forms the background light level for time gated spectra. The spectral characteristics of this background light is determined by many factors, such as the xenon lamp output, monochromator efficiency, ICCD spectral responsivity and sample ground state absorption characteristics.



After laser excitation the continuous background will be modified according to the transient features of the sample, depending on image intensifier gate width and delay.

The optical density change is calculated from the differences between background and measurement after sample excitation.

For comparison, the bottom figure demonstrates the ground state absorption and emission of the same Ru(bpy) sample. The effect of the ground state and excited state phenomena on the ΔOD spectra can clearly be seen.

lash Photolysis Spectrometer

Signal Detection and Data Acquisition

The LP920-S uses an externally triggerable, gated ICCD camera optimised for spectroscopy applications (e.g. Andor's iStar, Princeton Instruments' PI-MAX). The ICCD detector has the high sensitivity of a photomultiplier as well as nanosecond time resolution. It combines a highest quality scientific grade CCD array detector with image intensifier, gating and delay circuits, and CCD cooling fully integrated into one compact detector.

The CCD multi-channel detector has a characteristic high dynamic range and an ultra-low readout noise.

The gain of the image intensifier is user adjusted so the sensitivity of the detector can be set to the best level for the measurement. At low gain the sensitivity is comparable to that of a normal CCD detector. When operated at high gain the ICCD detector can detect single photons.

The ICCD camera is a software-controlled devicce with its hardware / software interface located in the spectrometer control computer. This permits all image intensifiers parameters, CCD parameters, and data transfer operations to be fully controlled by the L900 spectrometer software.

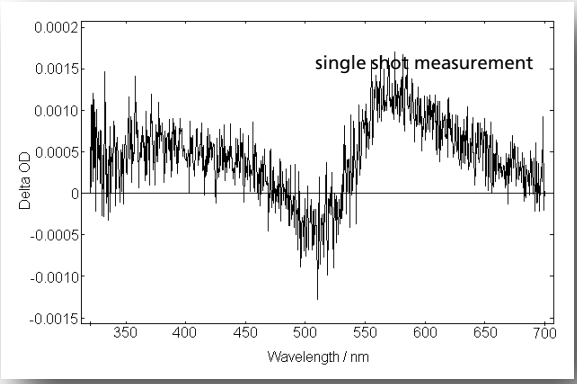
Andor iSTAR

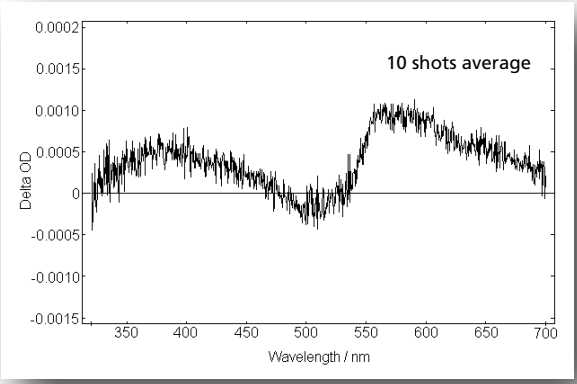
Detection Limit

The information from the CCD detector can be read with a rate of 1µs/pixel for fast results or with read-out rates of up to 32µs/pixel for the lowest possible readout noise. In addition, the controller PC card allows cooling of the CD down to -25°C (with additional water circulation) for further noise reduction and minimal baseline drift when measurements are made over extended periods.

The LP920-S can operate the ICCD in either fast vertical binning mode, where the information contained in the 256 vertical pixels are accumulated on the CCD before being transferred to the computer, or in image mode, where all pixels are read individually and the information of the vertical columns is averaged in the computer memory. For laser flash photolysis experiments the latter mode is desired as it improves the dynamic range, at the cost of a slower experimental repetition rate.

The detection limit of the ICCD array detector is ΔOD= 0.0005 for a single shot measurement. It can be further enhanced by signal averaging.





Demonstration of the detection limit and of the Signal-to-Noise improvement by signal averaging
Sample: Erythrosin B in Water
Measurement Conditions: λ_{pump}=532nm, E_{pump}=1mJ, pulsed probe source, 10µs gate width, 1µs gate delay

Software

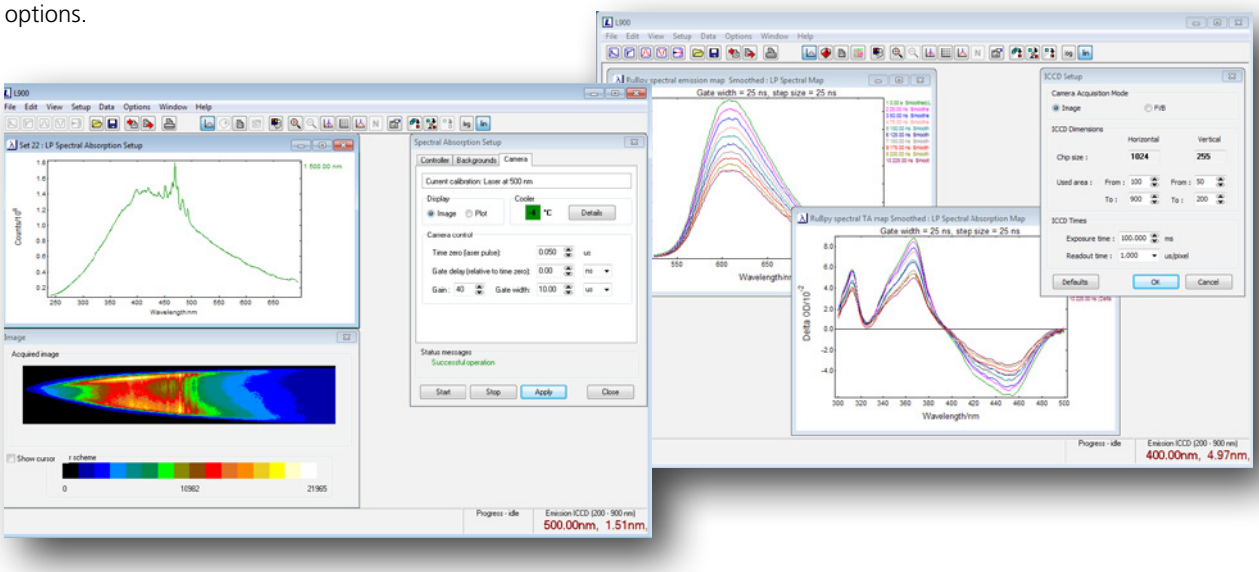
The L900 software package controls the LP920-S spectral mode operation as well as the LP920-K kinetic mode operation. This ensures full compatibility between the two modes as well as a user friendly software environment for systems able to operate in either mode.

The user can view pixel bitmaps of the CCD image to assess the quality of the image at the ICCD photocathode. This is particularly useful for setup and optimisation purposes prior to measurement sequences.

For standard measurements 2D images of the raw data and the resulting optical densities are the preferred plot options.

Comprehensive spectral calibration features are available, and automatic software subtraction of camera dark noise is provided.

A variety of different spectral measurement and correction options can be made. For example, with the probe shutter permanently closed normal time resolved emission spectra are taken. If a measurement sequence is made with a fixed gain and fixed gate width, but with incremental increase of the gate delay, a map of time resolved spectra is automatically generated. These can be sliced to produce kinetic decays at a given wavelength.



Software Functionality

While maintaining full flexibility for users who want to use the ICCD in specific setup modes (like restriction of image size, modification of data transfer rates, use of fast vertical binning mode), particular attention has been paid to make the software user friendly for scientists who have their minds focussed entirely on the sample and transient absorption results. It will take a newcomer only a few minutes to become familiar with the requirements for standard measurements in the spectral mode.

Measurement Modes

- Measurement setup
- Single spectral measurement
  - Transient absorption
  - Laser induced emission
- Multiple spectral measurements
  - Transient absorption
  - Laser induced emission
- Time gated absorption maps
- Time gated emission maps

Control Features

- Wavelength / slit control
- Grating selection
- Spectrograph port selection
- Pump laser flashlamp trigger
- Pump laser Q-switch trigger
- Probe source pulse current
- Pump and probe shutters
- ICCD gain
- ICCD gate delay
- ICCD gate width
- ICCD temperature
- Cryostat
- Temperature-controlled cuvette holder

Data Manipulation and Display

- ΔOD calculation (automatic and manual)
- Arithmetic (+, -, x, /, append)
- Scaling
- Normalise
- Baseline subtraction
- Smoothing
- Data slicing
- 2D, 3D, Contour plotting and text

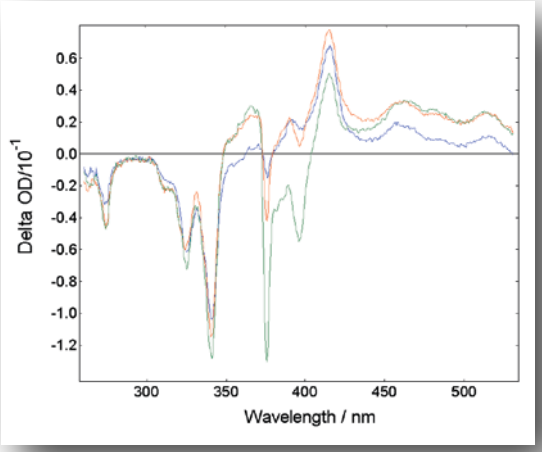
Time gated spectra in nanosecond time scale

Pyrene is characterised by distinct spectral bands when viewed time resolved in the nanosecond time scale. In a time span of 50ns after laser excitation spectral features of fluorescence, singlet-singlet absorption and triplet-triplet absorption become evident.

Green curve: 10ns after laser pulse. The spectrum shows the features of the ground state depletion (below 350nm), fluorescence (370nm-420nm) and the beginning of transient absorption bands (400nm-550nm).

Red curve: 30ns after laser pulse. At this time the fluorescence feature (370nm-420nm) is almost diminished, ground state depletion is slightly decreased, transient absorption at about 415nm is still rinsing, whereas transient absorption above 450nm is beginning to decrease.

Blue curve: 50ns after laser pulse. Ground state depletion is continuing to decrease, triplet-triplet absorption at 415nm is dominating, and the broad singlet-singlet absorption band continues to decrease.

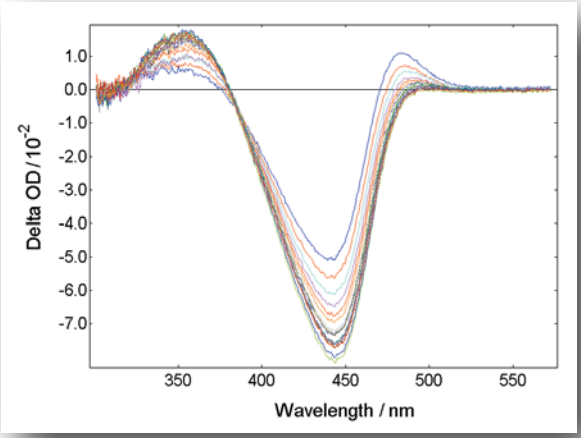


Sample: Pyrene in methanol (10^{-4}M)

Measurement Conditions: λ_{pump}=341nm, E_{pump}=5mJ, pulsed probe source, 10ns gate width, 5 shots average per curve.

Time gated spectra in microsecond time scale

The photocycle of the photoactive yellow protein shows kinetics throughout the nanosecond to millisecond time scale. In the microsecond time range, shown here, a transition from a red shifted to a blue shifted intermediate takes place.

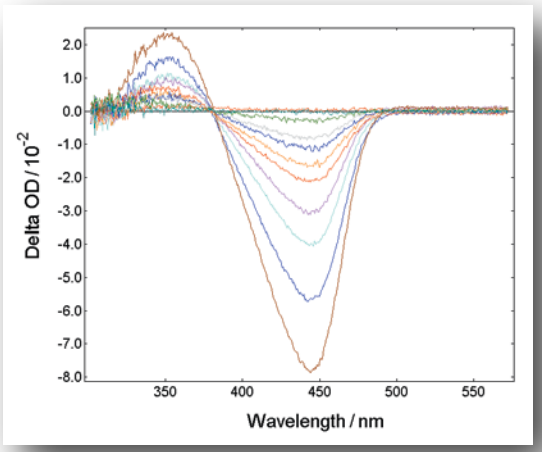


Sample: Photoactive Yellow Protein

Measurement Conditions: λ_{pump}=450nm, E_{pump}=10mJ, pulsed probe source, 50µs gate width, 5 shots average per curve, gated spectra from 50µs (violet curve) to 500µs (blue curve) after laser excitation in steps of 50µs

Time gated spectra in millisecond time scale

At the end of the photocycle of the photoactive yellow protein both transient absorption features and ground state depletion are decaying to zero, enabling the protein to undergo a new photocycle. this is shown with time gated spectra in the millisecond time scale.



Sample: Photoactive Yellow Protein

Measurement Conditions: λ_{pump}=450nm, E_{pump}=10mJ, continuous probe source, 50ms gate width, 5 shots average per curve, gated spectra from 50ms (brown curve) to 45ms (green curve) after laser excitation in steps of 50ms

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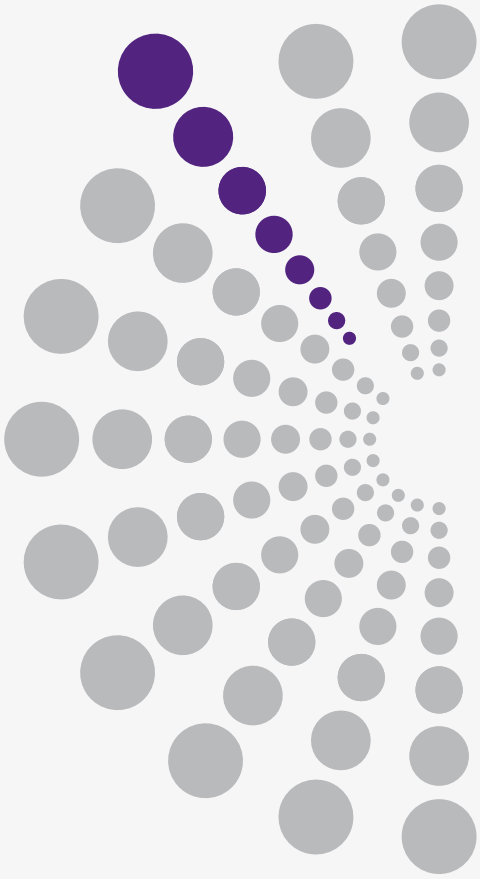

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