HARPIA

new

Extended Spectroscopic Systems

Capabilities of HARPIA-TA spectrometer can be further expanded by HARPIA-TF and HARPIA-TB extensions. Fundamentally, the all-integrated HARPIA system can be viewed as a miniaturized lab facilitating all the most popular time-resolved spectroscopy experiments in a single package. The all-inclusive HARPIA system can provide an extensive comprehension of the intricate photophysical and photochemical properties of the investigated samples.

Switching between different experimental realizations is fully automated and requires very little user interference. The optical layout of HARPIA system is refined to offer both an incredibly small footprint (see the dimensions below) and an easy and intuitive user experience. Despite its small size, HARPIA is easily customizable and can be tailored for specific measurement needs. All the experiments that the HARPIA system provides are managed by a new and improved user application with experiment guiding wizards, measurement presets, and development kit for custom applications.

HARPIA setup unifies multiple time-resolved spectroscopy capabilities, including:

- Femtosecond transient absorption
- Femtosecond transient reflection
- Femtosecond multi-pulse transient absorption/reflection measurements
- Femtosecond fluorescence upconversion
- Hundred picoseconds-to-microsecond time-correlated single photon counting (TCSPC)
- Automated measurements of intensity dependence of transient absorption and time-resolved fluorescence signal
- Possibility to perform time resolved femtosecond stimulated Raman scattering (FSRS) experiments

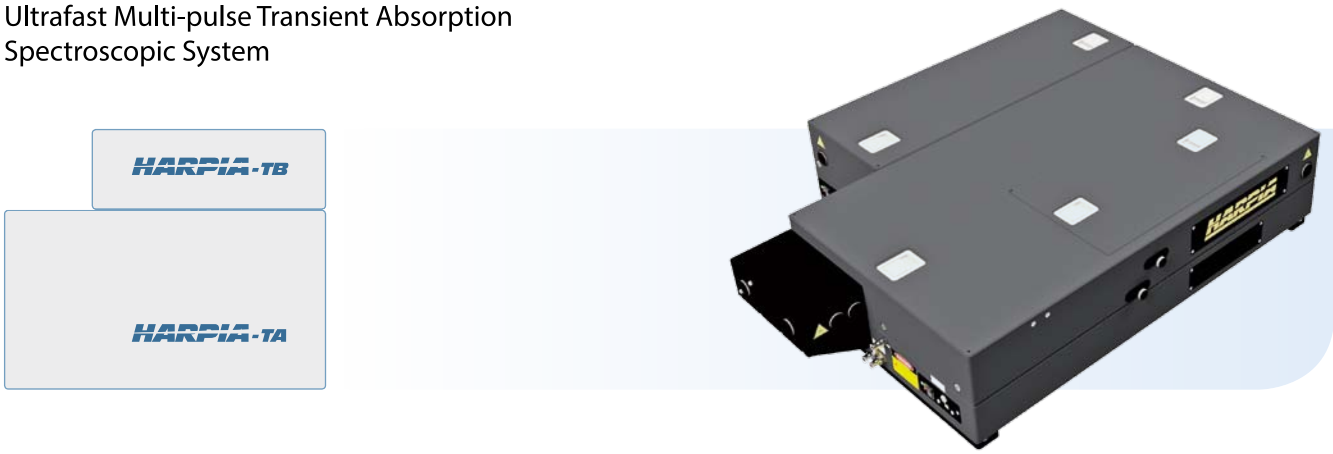
Available HARPIA configurations

HARPIA

Ultrafast Transient Absorption, TCSPC and Fluorescence Upconversion Spectroscopic System

HARPIA

Ultrafast Multi-pulse Transient Absorption Spectroscopic System



HARPIA

Ultrafast Multi-pulse Transient Absorption, TCSCP and Fluorescence Upconversion Spectroscopic System

HARPIA-TA

new

Ultrafast Transient Absorption Spectrometer

APPLICATION FIELDS

- Photochemistry
- Photobiology
- Photophysics
- Material science
- Semiconductor physics
- Time-resolved spectroscopy

The popular transient absorption spectrometer HARPIA has been reimagined and redesigned to meet the needs and standards of today's scientific world. The new improved HARPIA offers a sleek and compact design and together with intuitive user experience and easy day-to-day maintenance. Adhering to the standards raised by the OPRHEUS line of devices, the entire spectroscopic system is now contained in a single monolithic aluminum casing that inherently ensures excellent optical stability and minimal optical path for the interacting beams. In contrast to its predecessor, the dimensions of the device are greatly reduced. The area was reduced roughly by 2.6×, whereas volume was reduced by nearly 4×. The new HARPIA can be easily integrated with both PHAROS / ORPHEUS and Ti:Sa / TOPAS laser systems. Just like its precursor, it features market leading characteristics such as 10^{-5} resolvable signals along with other unique properties such as the ability to work at high repetition rates (up to 1 MHz) when used with PHAROS/ORPHEUS system. High repetition rate allows measuring transient absorption dynamics while exciting the samples with extremely low pulse energies (thereby avoiding exciton annihilation effects in energy transferring systems or nonlinear carrier recombination in semiconductor/nanoparticle samples).

A number of probe configurations and detection options are available starting with simple and cost effective photodiodes for single wavelength detection and ending with spectrally-resolved broadband detection combined with white light continuum probing. Data acquisition and measurement control are now integrated within the device itself and offer such improved detection capabilities as:

- Single (sample-only) or multiple (sample and reference) integrated spectral detectors;
- Simple integration of any user-preferred external spectrograph;
- Beam monitoring and self-recalibration capabilities (both along the optical path of the pump/probe beams and at the sample plane) and an option for automated beam readjustment;
- Straightforward switching between transient absorption or transient reflection measurements;
- Capability to combine both transient absorption and Z-scan experiments on the same device;

Moreover, different delay line options can be selected to cover delay windows from 2 ns to 8 ns and HARPIA may house either standard linear leadscrew (20 mm/s) or fast ball-screw (300 mm/s) optical delay stages.

A number of optomechanical peripherals are now compactly enclosed in the HARPIA casing, including:

- An optical chopper that can either phase-lock itself to any multiple of the frequency of the laser system or operate in a free-running internally-referenced regime (standard);
- Motorized and calibrated Berek's polarization compensator that can automatically adjust the polarization of the pump beam (optional);
- Motorized transversely translatable supercontinuum generator (applicable for safe and stable supercontinuum generation in materials such as CaF_2 or MgF_2; optional);
- Automated sample raster scanner that translates the sample in the focal plane of the pump and probe beams, thus avoiding local sample overexposure (optional).

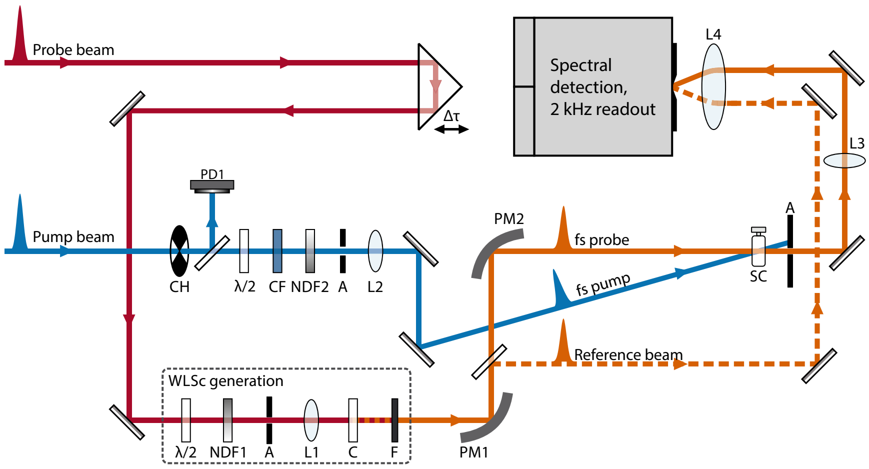
Moreover, the new HARPIA is designed to be compatible with any user-favored cryostat and/or peristaltic pump system (see mounting sheme). Capabilities of the new HARPIA can be further extended by introducing a third beam to the sample plane, thus allowing the user to perform multi-pulse transient absorption measurements.

In addition to experiment automation software, HARPIA includes data analysis package CarpetView for inspecting the acquired data and performing global and target analysis, probe dispersion compensation, exponential fitting etc. The software package features an intuitive and user friendly interface; it is delivered with a data analysis tutorial that offers seamless transition from the raw data to publication quality graphs and model based parameter estimation. All the software runs under MS Windows and it is easy to use. Even a novice will become an analysis expert in a matter of days!

SPECIFICATIONS

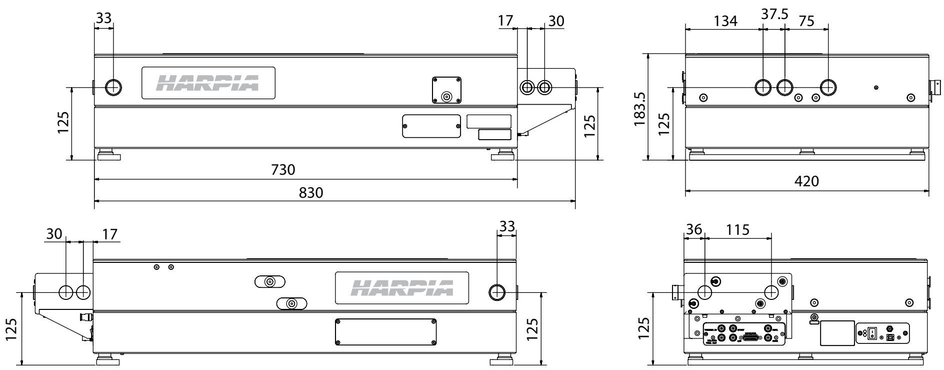
Probe wavelength range, supported by the optics	240 – 2600 nm
Probe wavelength range, white light supercontinuum generator, pumped by 1030 nm	350 – 750 nm, 480 – 1100 nm
Probe wavelength range, white light supercontinuum generator, pumped by 800 nm	350 – 1100 nm
Probe wavelength range of the detectors	200 nm – 1100 nm, 700 nm – 1800 nm, 1.2 µm – 2.6 µm
Spectral range of the spectral devices	180 nm – 24 µm, achievable with interchangeable gratings
Delay range	4 ns, 6 ns, 8 ns
Delay resolution	4.17 fs, 6.25 fs, 8.33 fs
Laser repetition rate	1 – 1000 kHz (digitizer frequency <2 kHz)
Time resolution	< 1.4 x the pump or probe pulse duration (whichever is longer)
Physical dimensions L×W×H	730 × 420 × 160 mm [1]

[1] *Without external spectrograph.*



HARPIA-TA optical layout

Cryostat mounting scheme



HARPIA-TA outline drawings

HARPIA-TF

new

Femtosecond Fluorescence Upconversion & TCSPC Extension

HARPIA-TF is a time-resolved fluorescence measurement extension to the HARPIA-TA mainframe that combines two time-resolved fluorescence techniques. For the highest time resolution, fluorescence is measured using the time-resolved fluorescence upconversion technique, where the fluorescence light emitted from the sample is sum-frequency mixed in a nonlinear crystal with a femtosecond gating pulse from the laser. The time resolution is then limited by the duration of the gate pulse and is in the range of 250 fs. For fluorescence decay times exceeding 150 ps, the instrument can be used in time-correlated single-photon counting (TCSPC) mode that allows for measuring high-accuracy kinetic traces in the 200 ps – 2 µs temporal domain. HARPIA-TF extension is designed around the industry leading Becker&Hickl® time-correlated single-photon counting system, with different detector options available.

The combination of two time-resolved fluorescence techniques enables recording the full decay of fluorescence kinetics at each wavelength; with full data available, spectral calibration of the intensity of kinetic traces taken at different wavelengths is possible, where the integral of time-resolved data is matched to a steady-state fluorescence spectrum.

High repetition rates of PHAROS laser system allows for measuring fluorescence dynamics while exciting the samples with extremely low pulse energies (thereby avoiding exciton annihilation effects in energy transferring systems, or nonlinear carrier recombination in semiconductor/nanoparticle samples). Preset or custom delay times, number of averages per transient spectrum, automated upconversion signal search and optimization and other options are available at a click of the mouse.

FEATURES

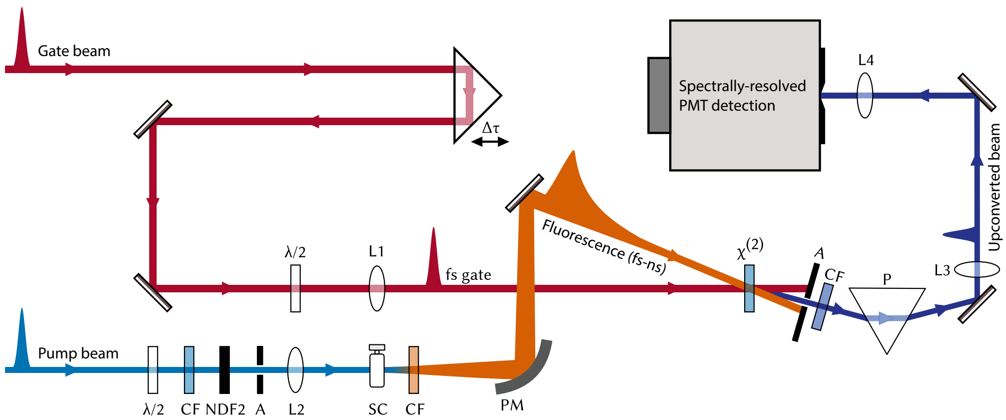
- An unique first of its kind all-encompassing time-resolved spectroscopic system
- A small and compact design
- Straightforward operation and easy day-to-day maintenance
- Can be installed as an add-on to HARPIA-TA mainframe or it can be acquired as a standalone time-resolved fluorescence measurement system
- Easy switching between different spectroscopic measurement modes
- Compatible with PHAROS series lasers running at 50 – 1000 kHz
- Integrates industry-leading Becker&Hickl® time-correlated single-photon counter
- Automated spectral scanning and upconversion crystal/prism tuning – collect spectra or kinetic traces without major system adjustments
- Measure fluorescence dynamics from hundreds of femtoseconds to 2 microseconds in a single instrument
- Full control over the following parameters of pump beam:
  - Polarization (automated Berek variable waveplate in the pump beam);
  - Intensity (continuously variable neutral density filters in both beams with automated versions available);
  - Delay (gate/probe light is delayed in the optical delay line);
  - Wavelength (fluorescence is detected after the monochromator)
- Standard Andor Kymera 193i USB dual output monochromator. When combined with HARPIA-TA mainframe, a single monochromator can be used for both time-resolved absorption and fluorescence measurements with no detector swapping necessary. Other monochromator options are possible, such as double subtractive monochromator to ensure higher TCSPC time resolution, if necessary
- Standard 4 ns delay line with electronics and full software integration. Optional extension of probe times up to 8 ns is possible. Delay line is fully integrated in to HARPIA-TA mainframe housing
- Data analysis software for inspecting the acquired data and performing global and target analysis, dispersion compensation, exponential fitting etc. Includes user-friendly interfaces, runs under MS Windows and is supplied with a manual describing how to get started with target analysis of your data

SPECIFICATIONS

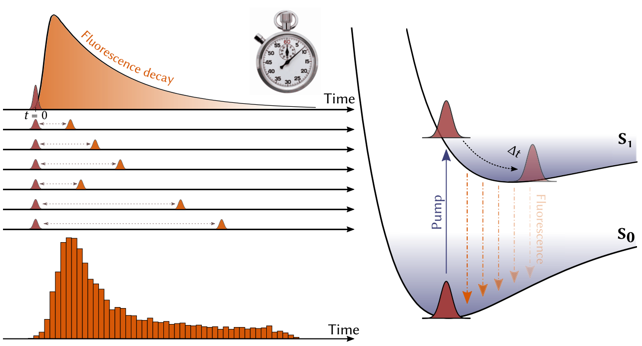
TCSPC mode	
TCSPC module	Becker&Hickl SPC 130, fully integrated into the software [1]
Detector control	Becker&Hickl DCC 100
Photomultiplier	Becker&Hickl PMC 100 1 standard
Wavelength range	300 – 820 nm
Intrinsic time resolution	<200 ps
Time resolution with monochromator	<1.2 ns [2]
Signal-to-noise	< 100 : 1, assuming 5 s accumulation time per trace [3]

Upconversion mode	
Wavelength range	300 – 1600 nm [4]
Wavelength resolution	Limited by the bandwidth of gating pulse, typically around 100 cm^{-1}
Delay range	4 ns, 6 ns, 8 ns
Delay resolution	4.17 fs, 6.25 fs, 8.33 fs
Time resolution	< 1.4 × the pump or probe pulse duration (whichever is longer), 420 fs with standard PHAROS laser [5]
Signal-to-noise	100 : 1.5, assuming 0.5 s accumulation time per point [6]

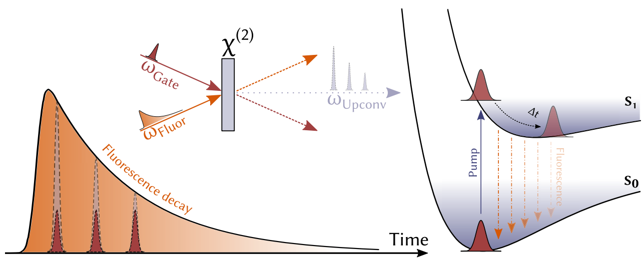
1) See www.becker-hickl.de for specifications.
2) Estimated as the FWHM of the upconverted white-light supercontinuum generated in the sample or the derivative of the rise of the upconversion signal.
3) Estimated by fitting the kinetic trace measured in Rhodamine 6G solution at 580 nm with multiple exponentials, subtracting the fit from the data and taking the ratio between the STD of residuals and the 0.5 × maximum signal value. Laser repetition rate 250 kHz. Not applicable to all samples and configurations.
4) Depending on the gating source, may be achievable with different nonlinear crystals.
5) Estimated as the FWHM of the upconverted white-light supercontinuum generated in the sample or the derivative of the rise of the upconversion signal.
6) Estimated as standard deviation of 100 points at 50 ps measured in Rhodamine 6G dye at 360 nm upconverted wavelength with PHAROS laser running at 150 kHz repetition rate. Not applicable to all samples and configurations.



HARPIA optical layout for fluorescence upconversion experiments



Principle of time-correlated single photon counting (TCSPC)



Principle of time-resolved fluorescence upconversion

HARPIA-TB

Third Beam Delivery Extension

new

When standard spectroscopic techniques are not enough to unravel the intricate ultrafast dynamics of photoactive systems, multi-pulse time-resolved spectroscopic techniques can be utilized to shed additional insight. HARPIA-TB is a third beam delivery unit for the HARPIA-TA mainframe system that adds an additional dimension to typical time resolved absorption measurements. A temporally delayed auxiliary (third) laser pulse, as depicted below, can be applied to a typical pump-probe configuration in order to perturb the on-going pump-induced photodynamics.

An auxiliary pulse resonant to a stimulated emission transition band can deliberately depopulate the excited state species and thereby revert the excited system back to the ground state potential energy surface. This type of experiment is usually referred ad pump-dump-probe (PDP).

When the wavelength of the third pulse corresponds to an induced absorption resonance, the pulse is thus able to elevate the system to a higher excited state (that may or may not be detectable in the standard photoevolution) or return it to an earlier evolutionary transient. This type of measurement is typically referred as pump-repump-probe (PrPP).

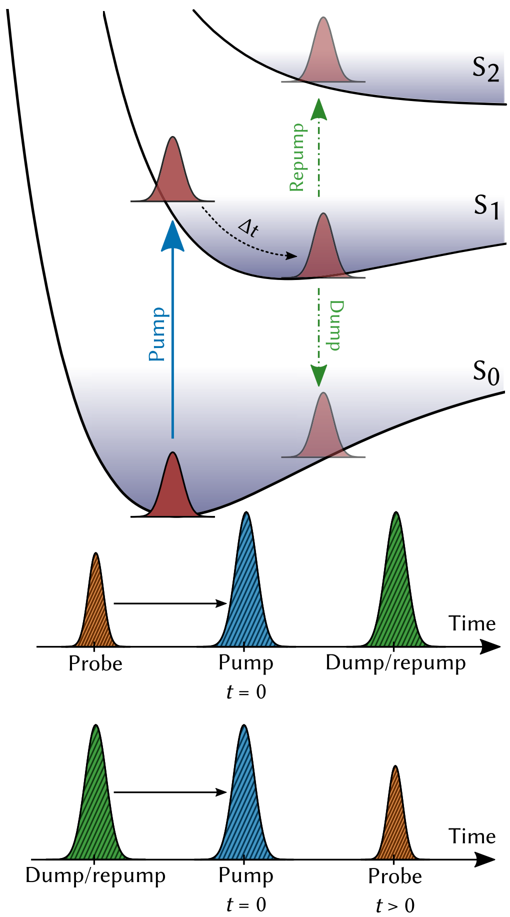
When the auxiliary pulse is resonant to an electronic ground-to-excited state transition, i.e., $S_0 \rightarrow S_n$, it makes it possible to either "replenish" the excited state population or to prepare a small portion of excited state population before the "main" pump pulse. This type of measurement is typically referred as prepump-pump-probe (pPPP).

Since both probe and the auxiliary pulse can be delayed in time in respect to one another, both kinetic trace and action trace experiments can be performed with a HARPIA-TB setup. In other words, we can obtain either the information on how a perturbation disturbs the standard photodynamic behavior of the investigated system (when the probe pulse is propagated in time), or we can monitor how the exact timing of perturbation influences the transient absorption spectrum at a fixed evolutionary phase system (when the auxiliary pulse is propagated in time).

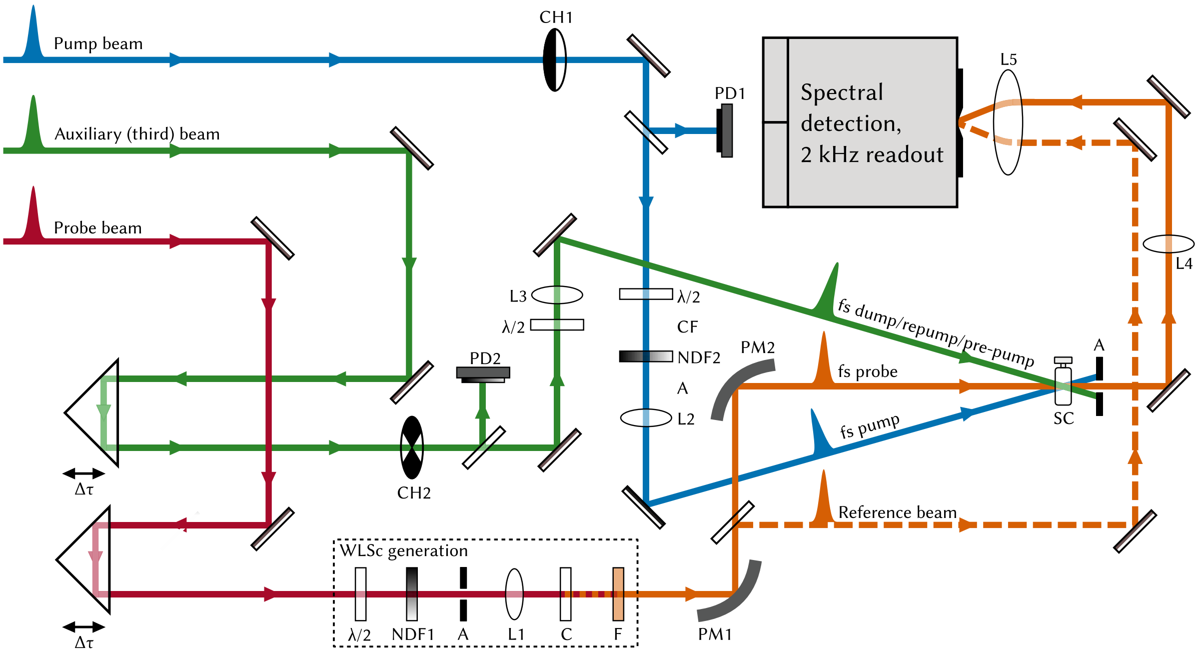
Moreover, HARPIA-TB can be utilized to deliver frequency-narrowed (i.e., picosecond) pulses, thus providing the capability to perform time-resolved femtosecond stimulated Raman scattering (FSRS) spectroscopic measurements.

FEATURES

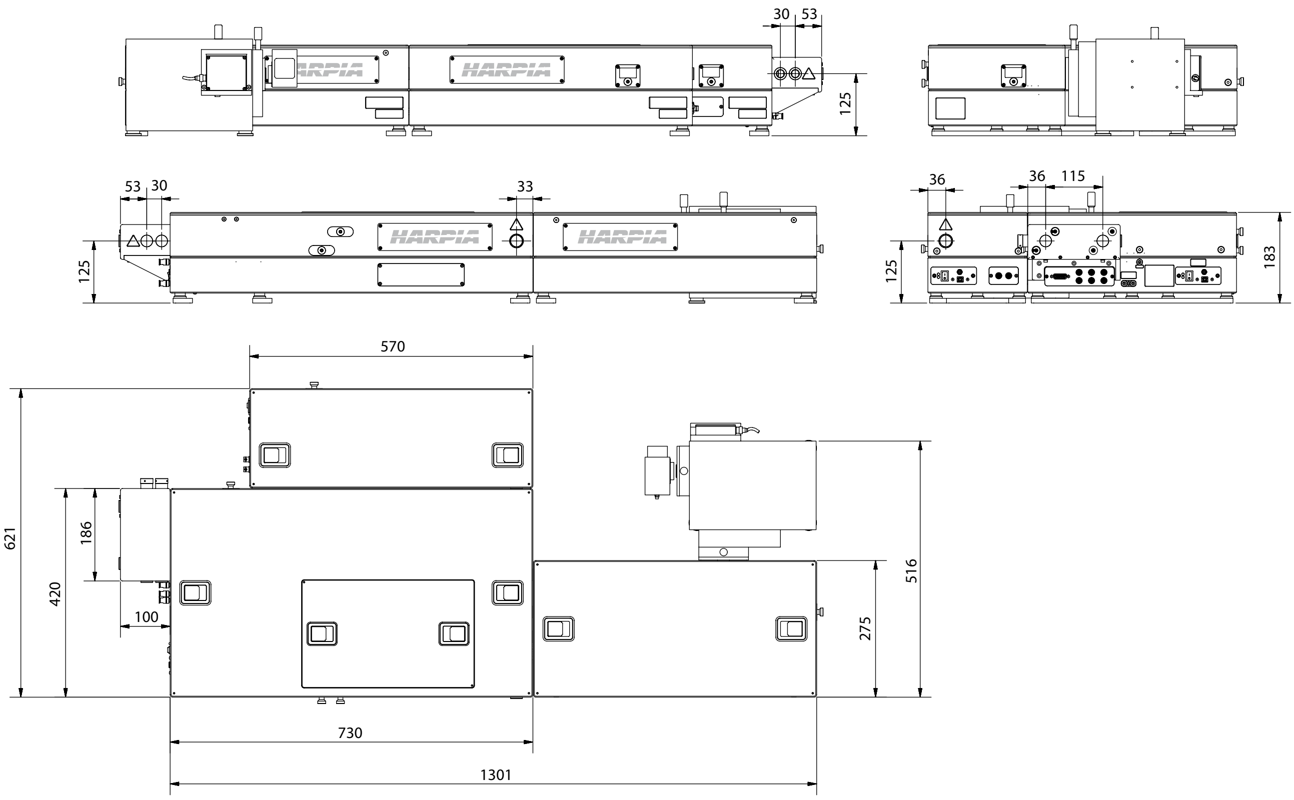
- Extends the capabilities of HARPIA-TA system
- Can be installed as an add-on to an already existing HARPIA-TA mainframe basis
- Provides an additional dimension to pump-probe measurements
- Provides additional insight to complex photodynamic systems
- Full control of the third beam:
  - Polarization (manual or automated Berek variable waveplate in the third beam path);
  - Intensity (continuously variable neutral density filters in the third beam path with automated version available);
  - Delay (the auxiliary laser pulse is delayed in an optical delay line with full delay ranging from 1.3 to 2.6 ns)
- Data analysis software for inspecting the acquired multi-pulse data and performing global and target analysis



Principle of multi-pulse time-resolved transient absorption spectroscopy



HARPIA optical layout for multi-pulse experiments



HARPIA drawings

CarpetView

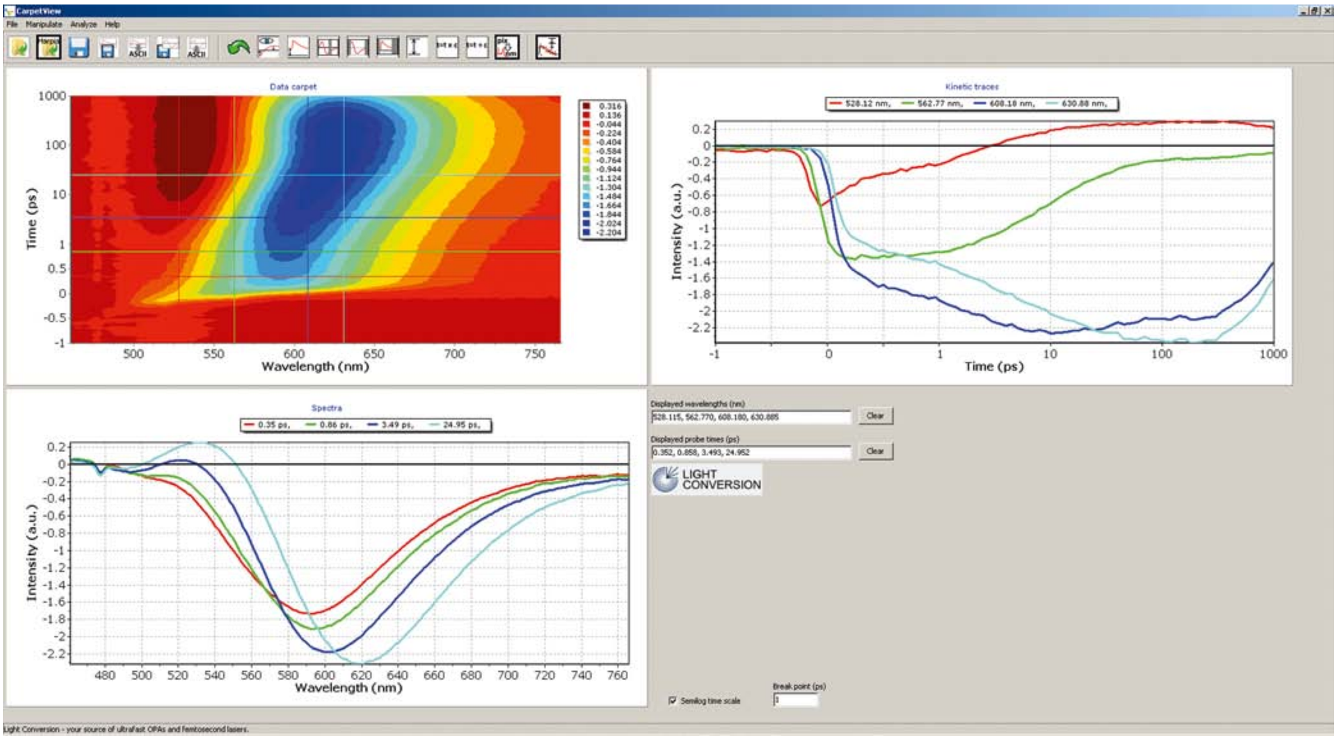
CarpetView is a software package dedicated for inspection, visualization and analysis of ultrafast spectroscopy data.

The program comes in two guises:

- ***Classical***, intended to be used with pump-probe and time-resolved fluorescence datasets,
- ***3D***, designed to be used with 2D electronic spectroscopy (2DES), and Fluorescence lifetime imaging (FLIM) datasets.

Visualization functions include:

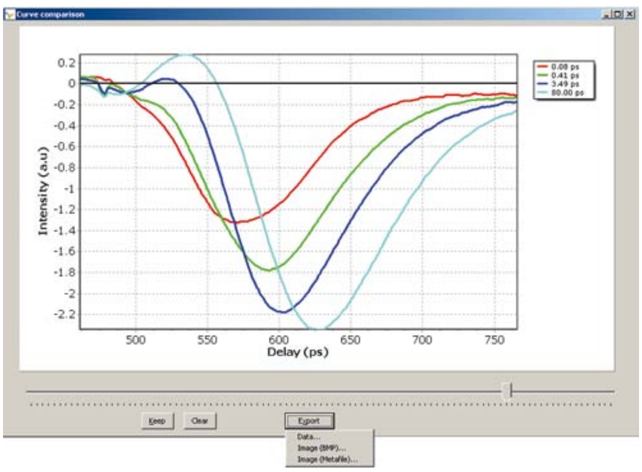
- Overview of your spectro-temporal transient absorption or fluorescence data as contour plot.
- Click-based selection of temporal and spectral slices.
- Comparison of several time-gated spectra or kinetic traces in a single graph.
- Export of produced graphs in bitmap or metafile formats.
- Export of the data of selected graphs in ASCII format.
- Linear and semi-logarithmic time axis in kinetic traces to aid visualizing spectral changes extending over many orders of magnitude in time.



Main window of *Classical* CarpetView displaying a pump-probe dataset

Besides viewing your data you can perform the trivial data manipulations, such as:

- Correct for the chirp in the probe light.
- Merge two datasets measured at different spectral windows.
- Limitation or removal of contaminated spectral or temporal region.
- Pre-time zero signal subtraction.
- Calibration of the spectrum using a reference absorption spectrum measured on your setup.
- Shift or rescale probe times.
- Change wavelength scales between wavenumbers, electron-volts and nanometers.
- Smooth spectra or traces to combat noise.

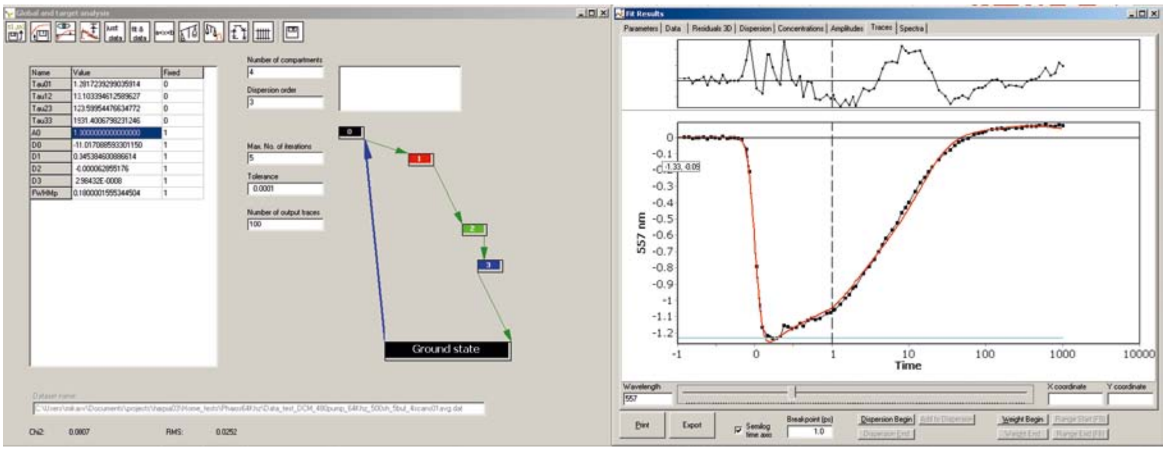


Spectra viewer window of CarpetView

GLOBAL AND TARGET ANALYSIS OF ULTRAFAST DATA

A powerful analysis tool provides the fitting functionality for your spectro-temporal data. The data is analyzed using user-defined compartmental models, where different compartments are interconnected using sets of linear differential equations. The fitting procedure also allows including the chirp of the probe light in the data performs deconvolution with a Gaussian instrument response function.

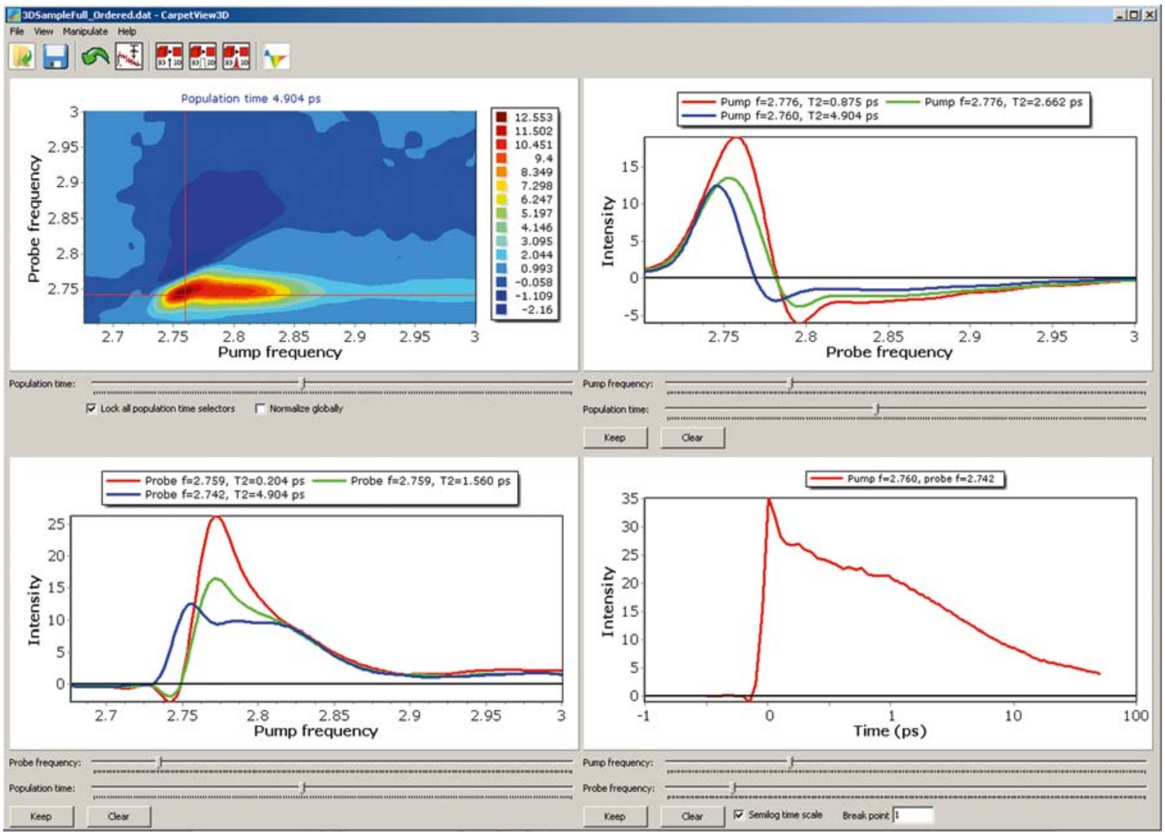
- Graphical construction of the model.
- Point-and-click based estimation of initial parameters of the dispersion curve.
- Advanced point weighting functions for physically sensible fitting.
- Comprehensive overview of the fitting results, including compartment populations, compartment-attributed spectra, fitting curves superimposed on the data and residuals.
- Report generation.
- Export of fitting data in ASCII format.
- Export of fitting graphs in metafile and bitmap formats.



Global and target analysis window of CarpetView

3D VERSION OF CARPETVIEW:

- Includes all the functionality of *Classical* version.
- Allows to visualize, inspect and manipulate data *cubes* obtained in 2DES or FLIM experiments.
- Performs global and target analysis either on the entire data cube, or its two-dimensional cuts.
- Performs trivial data manipulations:
  - Binning
  - Axis rescaling
  - Extraction of two-dimensional datasets from data cubes.



Main window of CarpetView-3D displaying a two-dimensional spectroscopy dataset

ULTRAFAST LASERS
OSCILLATORS
HARMONICS GENERATORS
OPTICAL PARAMETRIC AMPLIFIERS
TOPAS DEVICES
SPECTROMETERS
AUTOCORRELATORS