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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 μ s 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	$< 1.4 \times$ 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 69

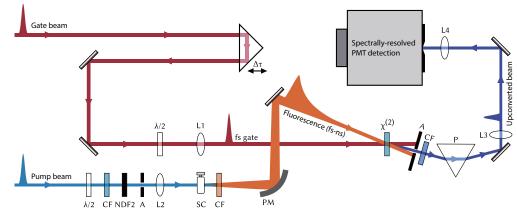
¹⁾ See www.becker-hickl.de for specifications.

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.

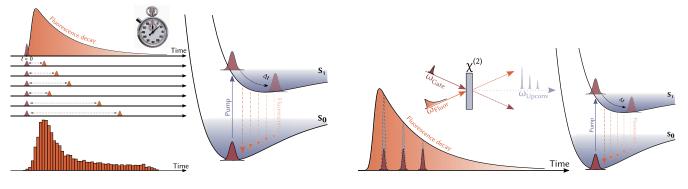
³¹ Estimated by fitting the kinetic trace measured in Rhodamine 6G solution at 580 nm with multiple exponentials, subtracting the fit from the data and taking the ratio between the STD of residuals and the 0.5 × maximum signal value. Laser repetition rate 250 kHz. Not applicable to all samples and configurations. 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.

Principle of time-resolved fluorescence upconversion



HARPIA optical layout for fluorescence upconversion experiments



Principle of time-correlated single photon counting (TCSPC)

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