



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 pumpprobe configuration in order to perturb the on-going pumpinduced 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 groundto-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 frequencynarrowed (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 polarization compensator 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)



Principle of multi-pulse time-resolved transient absorption spectroscopy

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HARPIA optical layout for multi-pulse experiments







Outline drawings of HARPIA system with extensions



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