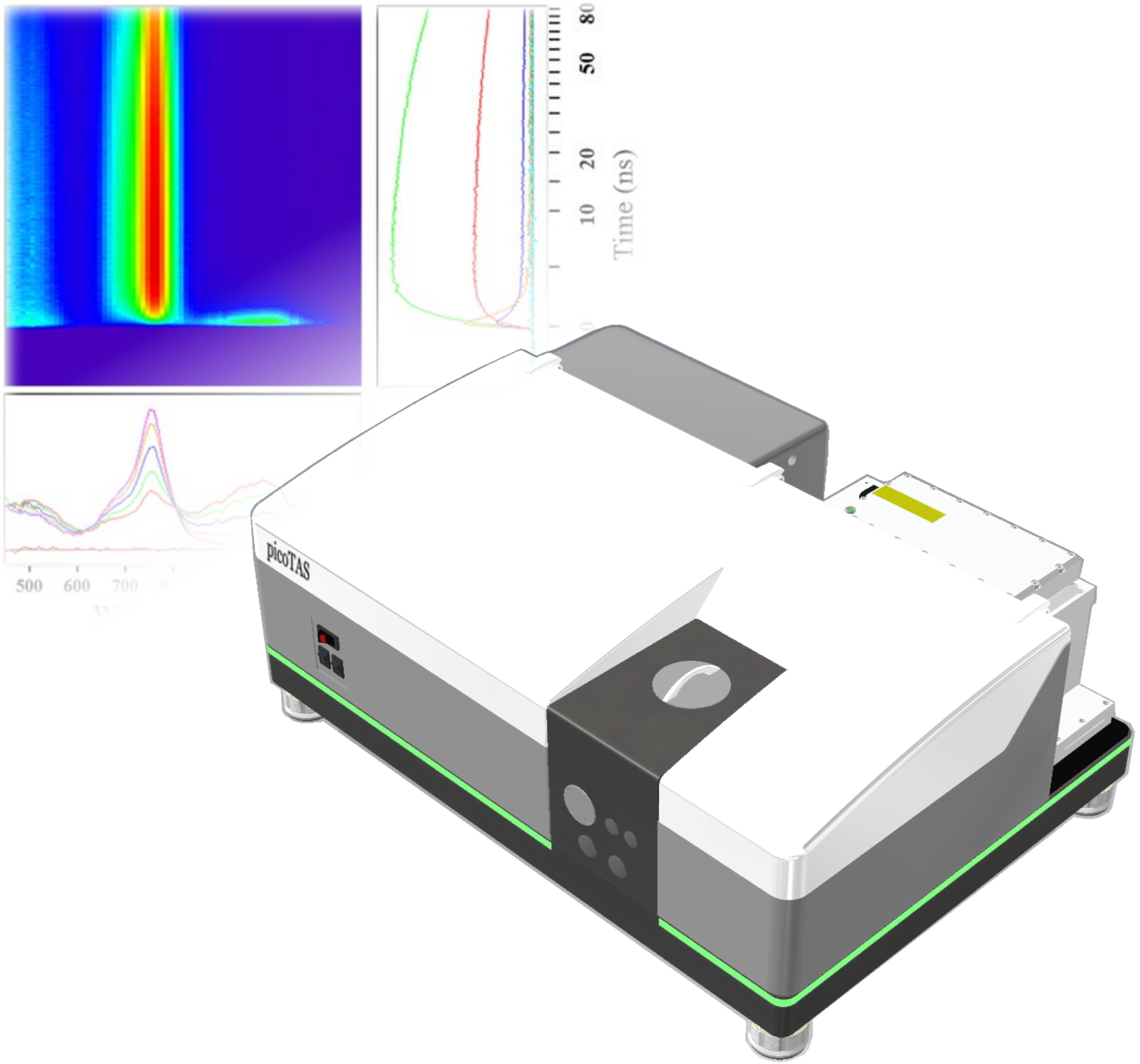
Picosecond Transient Absorption Spectroscopy System

picoTAS



Unisoku has been developing this product in cooperation with Nihon University, Osaka University and Meijo University in the framework of the Japan Science and Technology Agency's "Development of Systems and Technologies for Advanced Measurement and Analysis (JST-SENTAN)" program.

UNISOKU Co., Ltd
2-4-3 Kasugano, Hirakata, Osaka 573-0131, Japan
TEL: +81-72-858-6456 / FAX: +81-72-859-5655

Catalog No.
UBPT 2018-05A

picoTAS

Can Easily Measure Short-Lived Intermediates.

Features

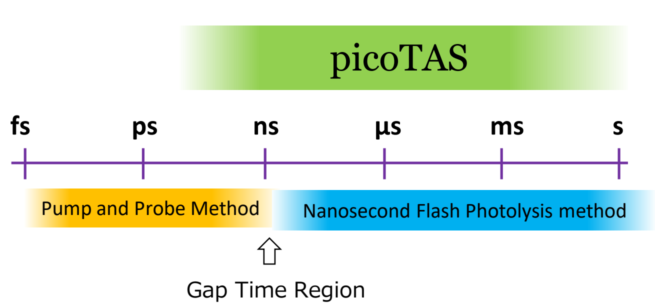
- **Completely Covers Gap Time Region (1 ns ~ 20 ns)**
- **Measures Wide Time Range from 100 ps to s**
- **Broadband Wavelength Coverage from VIS to NIR**
- **Removes Fluorescence Signal**
- **Asynchronous Operation**
- **Compact Size / No Optical Bench Required (-ns model)**

What is Transient Absorption Spectroscopy (TAS) ?

- Fast Time Resolved Absorption Measurement
- Detects and Identifies Short-Lived Intermediates
- Both Non-Luminescent and Luminescent Intermediates are detectable
- Explores and Analyzes Multi-step Complex Processes

Transient Absorption Spectroscopy (TAS) is a method of first time-resolved absorption measurement. A pulsed light (pump light) induces reactions of a target sample, then subsequent processes are observed by absorption change of probe light.
It is known that fluorescence lifetime measurement is also a time resolved method, but information obtained is limited to a fluorescent process at the first stage of the reaction (excited singlet state). On the other hand, information about non-fluorescent processes in a wide time region (short-lived radical species, charge transfer states, etc.) can be obtained by TAS, so we can explore and analyze multi-step complex processes.

What is the Difference between picoTAS and Conventional Techniques?

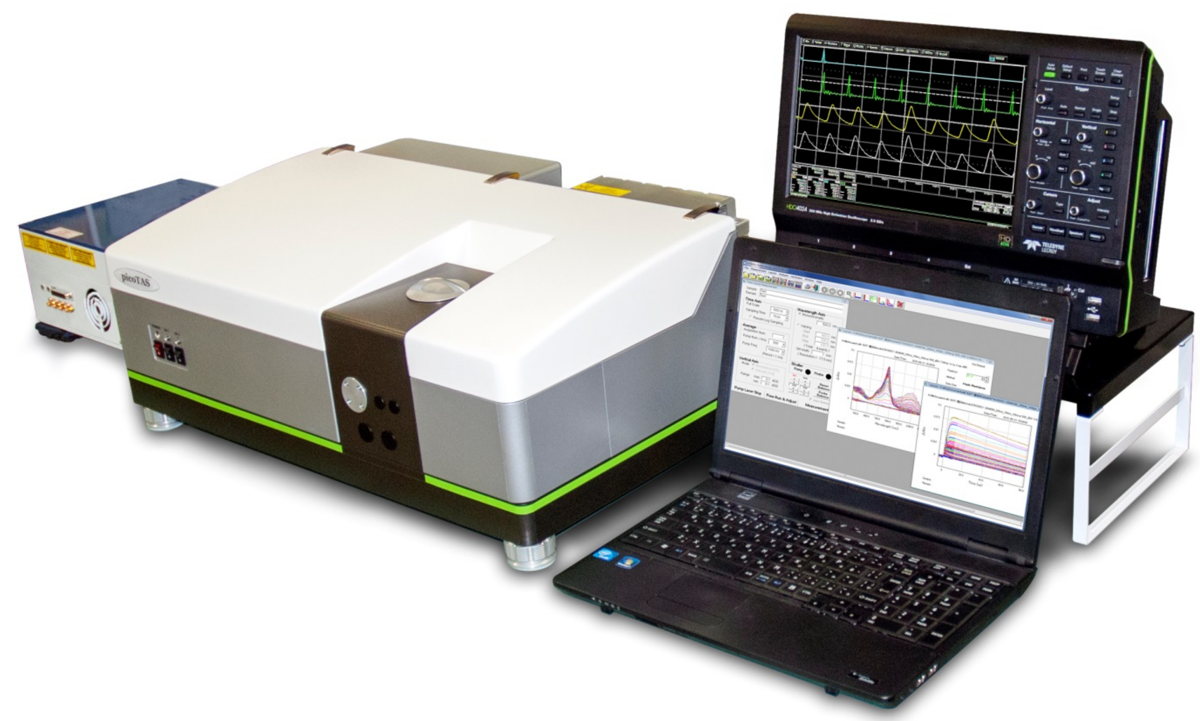


There are mainly two conventional transient absorption (TA) techniques, Pump & Probe method and Nanosecond Flash Photolysis method. However these methods have difficulty in measuring the time region from 1 to 20 nanoseconds in which many important phenomena exist.

picoTAS can measure wide time range including this "Gap Time Region" (1-20 nanoseconds) where conventional methods have hardly observed. In addition, picoTAS has a capability of eliminating the influence of fluorescence, therefore, not only non-fluorescent but also fluorescent intermediates can be detected and identified correctly which have never been observed so far.

In most of light induced phenomena, intermediates (transient species) play important roles to determine reaction efficiency and final products, and single reaction cycle often involves multiple intermediates which are observed in different time and wavelength regions.

picoTAS can observe light absorption of these intermediates in wide range of time and wavelength. Therefore, **picoTAS** can contribute to various researches of rapid reactions and development of high-performance materials and devices.



Wide Applications

Target Areas

- Fluorochrome-Labeled DNA
- Photochromism
- Optical Switching
- Quantum-Dot
- Artificial Photosynthesis
- Photocatalyst
- Organic Solar Cell, etc

Target Phenomena

- Excited Singlet State
- Triplet State
- Electron Transfer
- Charge Separation
- Radical Formation
- Excimer Formation
- Energy Transfer, etc.

Target Samples

- Fullerene
- Porphyrin
- Photoreactive Organic Molecule
- Various Metal Complex
- Titanium Dioxide
- Organic EL Device
- Carbon Nanotube, etc.

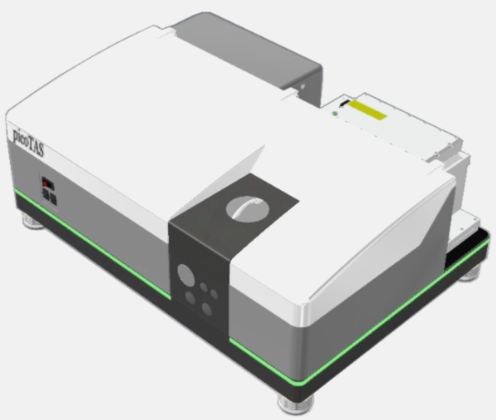
Target Fields

- Photochemistry
- Photophysics
- Photobiology
- Nanoscience
- Materials Chemistry
- Energy Science
- Environmental Science, etc.

picoTAS System Configuration

picoTAS Optical Unit

(Monochrometers, Optics, Sample Chamber, Detectors)

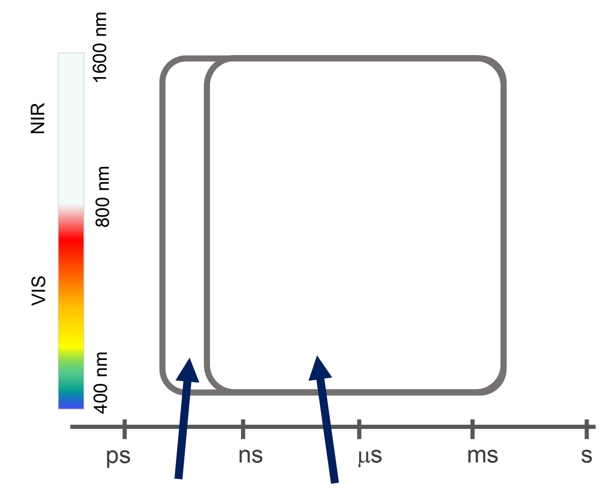


- 410 – 1600 nm
  optical design minimizing chromatic aberration
- Double Beam Optical System
  corrects light intensity fluctuation
- 2 mm Solution Cell Holder
- Thin Film Holder
- Oblique Incidence Excitation
  high excitation efficiency for thin samples
- Automatic shutter (pump, probe)
- Probe Light Auto-Balancing Mechanism

PC

Dedicated Oscilloscope

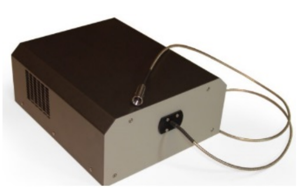
Models – Coverage of Time and Wavelength



-ps (picosecond) model

-ns (subnanosecond) model

Photonic Crystal Fiber



Probe Light Source

High-Repetition-Rate Super Continuum Light Source
50-100 ps, 20 MHz, 410-1600 nm

Pump Light Source

-ns model : Pulse Width 350 ps, 1 kHz

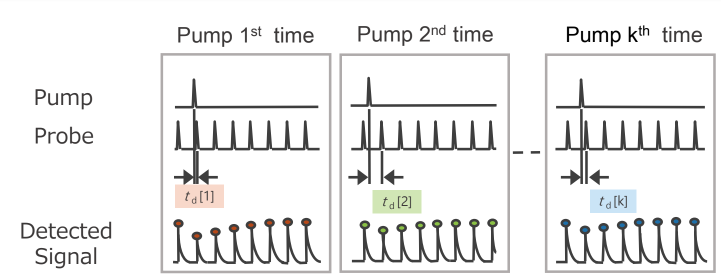
OR

-ps model : Pulse Width 25 ps, 1 kHz

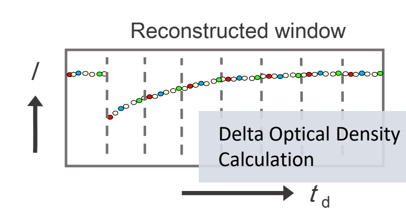
Pump Light and Probe Light of picoTAS are Asynchronous

Principle: Randomly Interleaved Pulse Train (RIPT) Method

In the RIPT method, signal waveforms of both pump light and probe light are recorded by high-speed detectors on each pump light irradiation. The delay time of a probe pulse just after the pump pulse is calculated from these waveforms. Each light intensity of probe light pulse that is transmitted through a sample is recorded by using a detector with amplifier, and the intensity is plotted based on the delay time. When pump light irradiation is repeated, the delay time differs every time because pump light and probe light are asynchronous. In this way, the plot generates a continuous curve after many-time pump light irradiation. By executing delta optical density calculation, transient absorption curve is reconstructed.

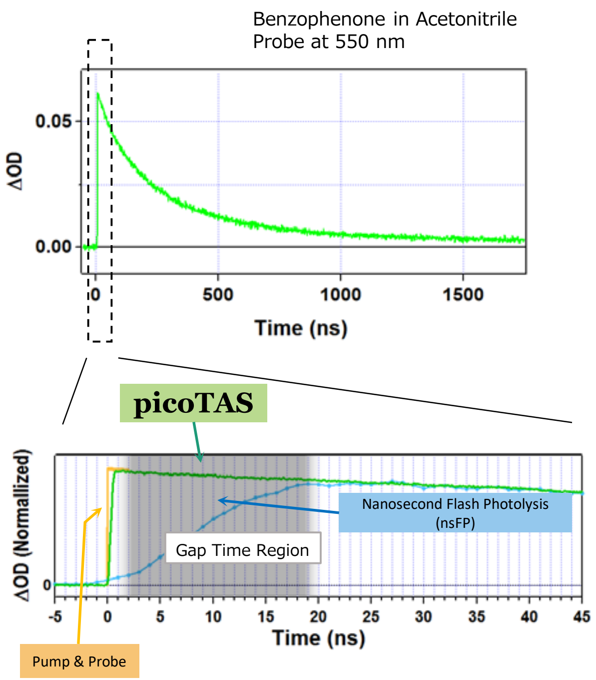


Optics Letters, 41, 1498 (2016)
Highlighted in Nat. Photon., 10 (2016), 285 and Science, 352 (2016), 669.



Completely Covers Gap Time Region (1 ns ~ 20 ns)

The conventional methods have difficulty in measuring from 1 to 20 nanoseconds, but **picoTAS** allows us to measure this "Gap Time Region" which has almost never been studied so far.

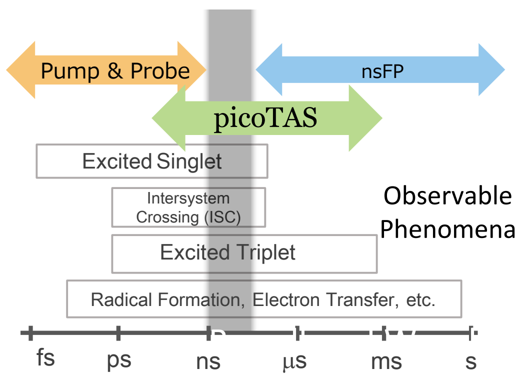


In the Gap Time region, there exists various states and processes inside and among molecules.

"Excited Singlet State"
the initial excited state of many photochemical reaction

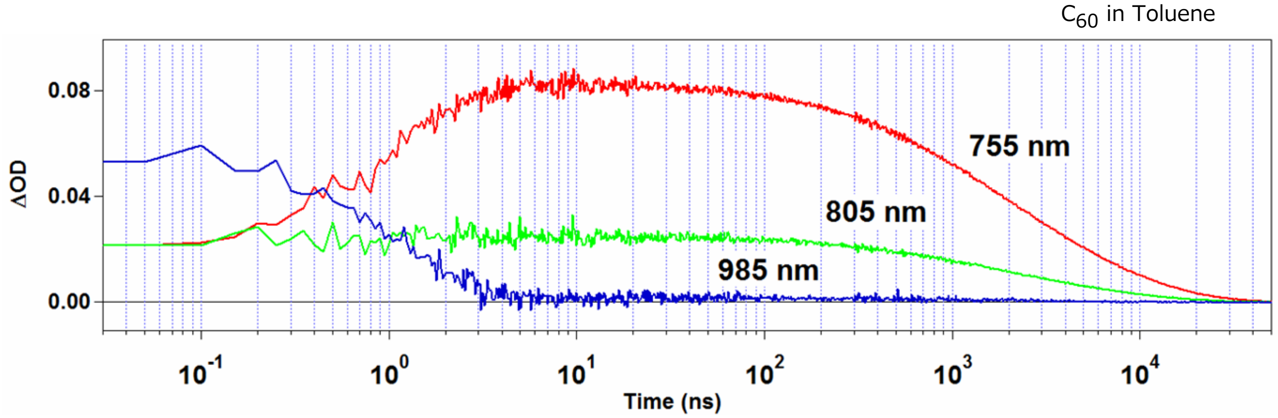
"Excited Triplet State"
the second excited state which plays a key role in determining the reaction products

"Radical Species"
highly reactive intermediate state



Measures Wide Time Range from 100 ps to ms

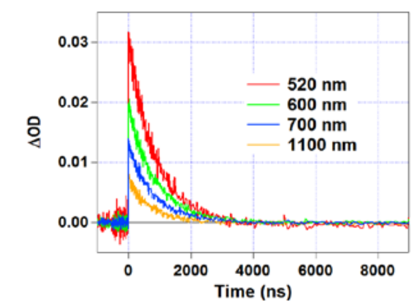
picoTAS can measure a wide time range. It covers more than 6 orders of magnitude from 100 picosecond to millisecond, from formation to full decay of intermediates.

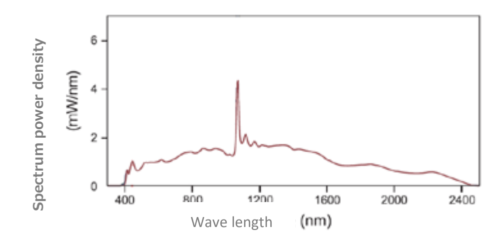


Broadband Wavelength Coverage from VIS to NIR

Recently, near-infrared measurements in transient absorption spectroscopy are highly demanded. As **picoTAS** uses a super-continuum light source for the probe light source, a broad wavelengths range from visible (> 410 nm) to near-infrared region (< 1600 nm) can be covered seamlessly.

Obtain Transient Absorption Temporal Profile at Every Wavelength

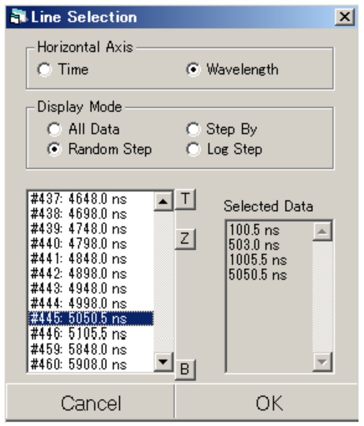




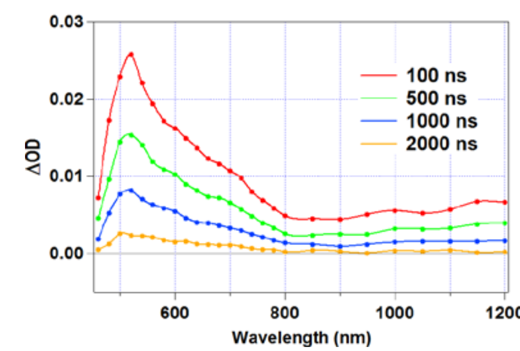
Spectrum power density

Super-continuum light source used as the probe light source in picoTAS emits light in a broad wavelength range from visible to near-infrared region. Though its light intensity has wavelength dependence, picoTAS can adjust the light intensity automatically which enters into detectors.

Select Time to Extract Transient Absorption Spectra



Display and Save the Spectra



$Ir(ppy)_3$ in THF

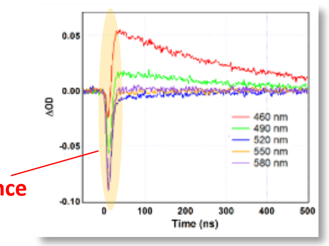
Future Prospect

By combination with picosecond probe light sources of infrared or X-ray region, studies of wider wavelength region (energy region) can be realized.

Removes Fluorescence Signal

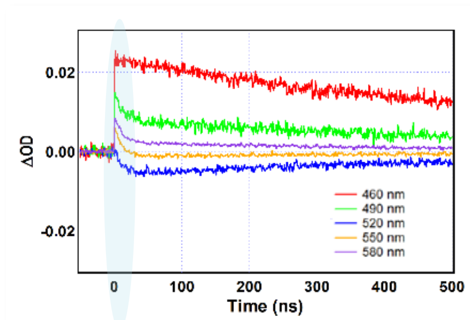
In conventional nanosecond flash photolysis measurements, luminescence from the sample often interferes with the signal. Since **picoTAS** has an ingenious way to remove luminescence signal, we can obtain accurate transient absorption (TA) signal of excited singlet and triplet, etc.

Conventional nanosecond Flash Photolysis

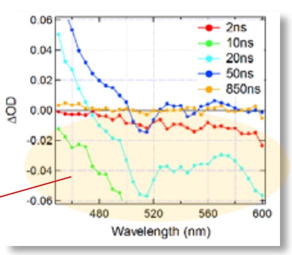


TA signals covered by fluorescence

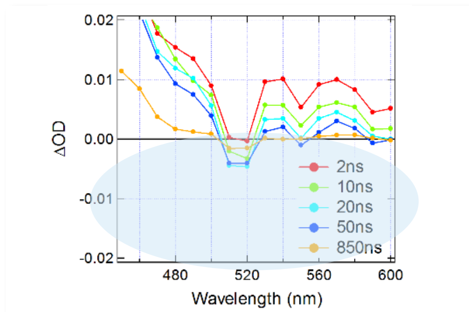
picoTAS



Accurate TA signals without fluorescence



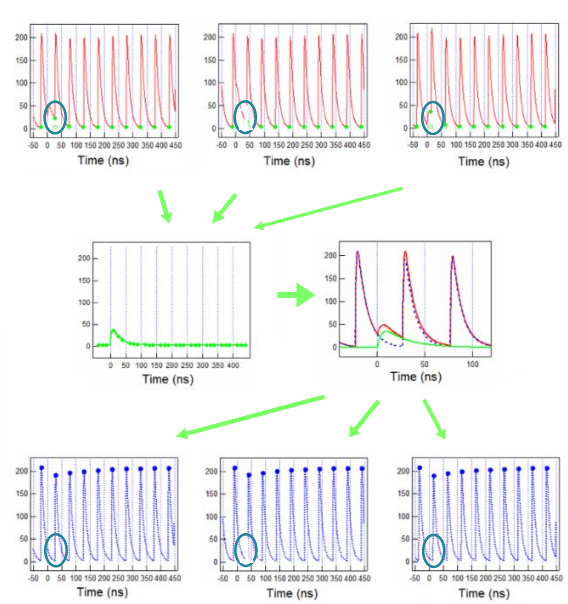
TA spectrum covered by fluorescence



Accurate TA spectra without fluorescence

Luminescence Signal Removal in picoTAS

In the RIPT method used in picoTAS, by picking up the signal intensity just before the rise of each probe pulse signal and repeating this procedure for a series of pulse train data set, a baseline curve including luminescence such as fluorescence and phosphorescence can be reconstructed. By subtracting the baseline curve from individual probe pulse train data, and then picking up probe light intensity, pure TA signals, where emission signals are removed, can be obtained.

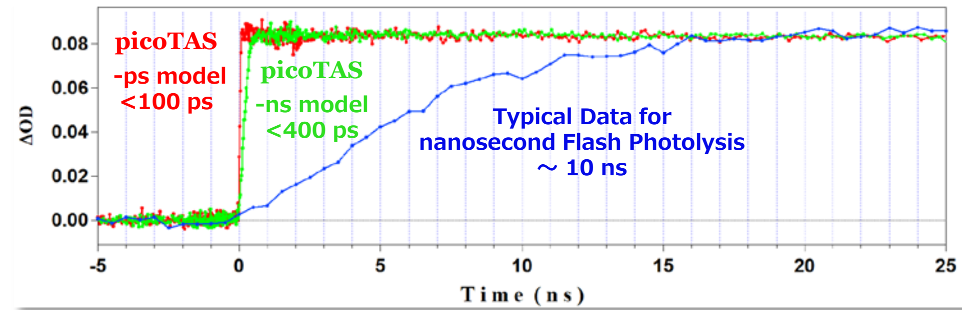


Data Example

picoTAS

Comparison of Time Resolution (10-90% Rise Time)

picoTAS has 100 times higher time resolution than conventional nanosecond flash photolysis systems. The time resolution (<100 ps for -ps model, <400 ps for -ns model) is comparable to TCSPC fluorescence lifetime measurements, so **picoTAS** can be widely applied to many reactions including non-luminescent samples.

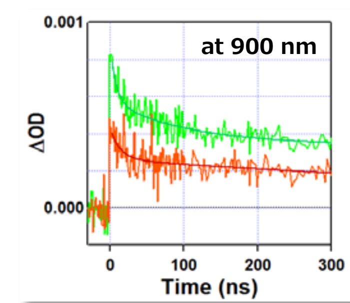


Observation of the fast (<10 ps) ISC of palladium porphyrin

Figure Courtesy of Dr. T. Suenobu, Osaka Univ.

High Sensitive Transient Absorption Measurement of Photocatalyst

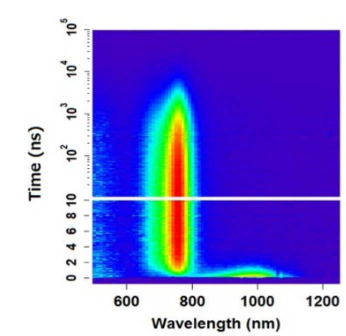
To elucidate the photoreaction mechanism of titanium dioxide which shows remarkable behavior as a photocatalytic material, it is known that the pump light intensity must be reduced and detection of very small TA signals is required. In this measurement, **picoTAS** catches less than 1 mOD changes (equivalent to 0.025% transmittance change) in nanoseconds time region.

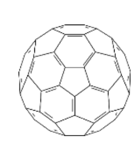


Samples Courtesy of Prof. R. Katoh, Nihon Univ.

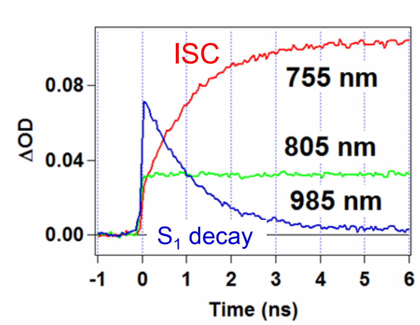
Fullerene (τ_{ISC} ≃ 1 ns)

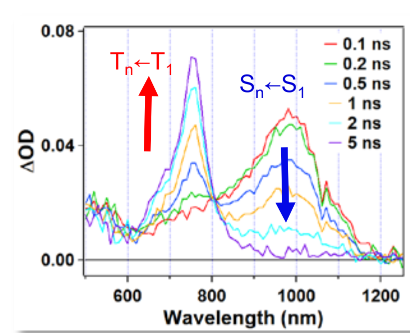
Fullerene is an promising material for electron acceptors of organic thin-film solar cell and its time constant of intersystem crossing (ISC) is known ~1 ns, so it is difficult to measure TA of this attractive reagent by both pump & probe and nanosecond flash photolysis methods. With the use of **picoTAS**, the spectra of the excited singlet, ISC and triplet state can be clearly observed from visible to infrared wavelength region. Also, a complete decay curve of the triplet with lifetime of microseconds can be observed.





Pump 355 nm, 25 ps
500 nm ~ 1250 nm
Minimum Bin 50 ps

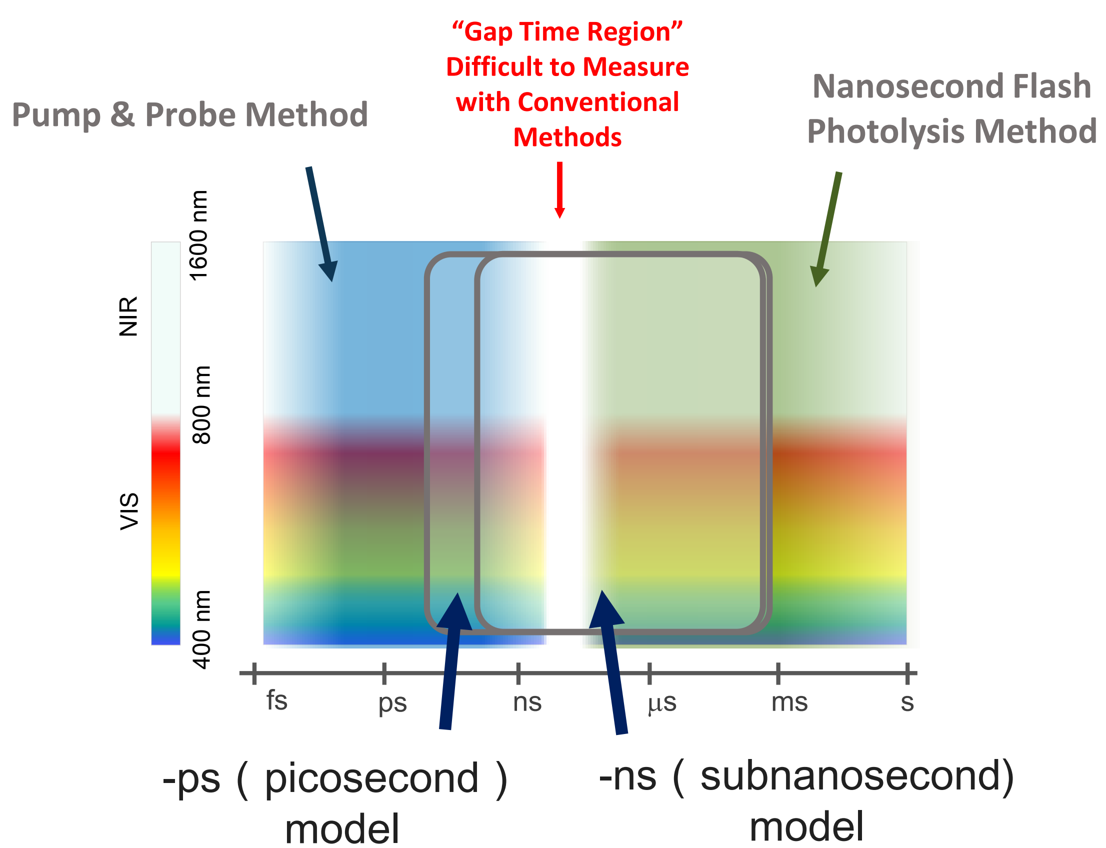




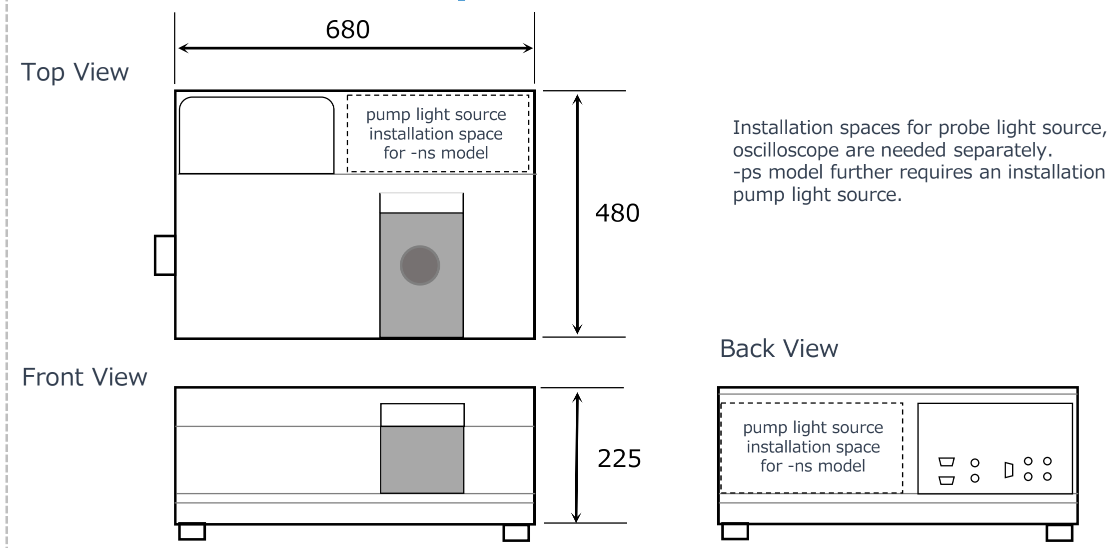
Specifications

Model		picoTAS-ns	picoTAS-ps
Method		RIPT method (Randomly Interleaved Pulse Train method)	
Time Resolution (10%-90% Rise Time)		<400 ps	<100 ps
Delay Time Resolution		10 ps, 20 ps, 50 ps, 100 ps, 200 ps, 500 ps, 1 ns, 2ns, 5 ns, 10 ns, 20 ns	
Time Window		100 ns ～ 2 ms	
Wavelength Range		410 ～ 1600 nm	
Automatic Control		Wavelength Scan, Light Intensity Adjustment, Shutter Control	
Sample Holder		Solution (Optical Path Length of 2mm) 、Thin Film	
Pump Light	Light Source	passive Q-SW Microchip Laser	picosecond Mode-Locked Laser
	Wavelength	532 nm and/or 355 nm	532 nm and/or 355 nm and/or 266 nm
	Pulse Width	<350 ps	<25 ps
	Pulse Energy	>20 μJ	>80 μJ
	Repetition Rate	100 - 1000Hz (variable)	1000 Hz
Probe Light	Light Source	Picosecond Supercontinuum Light Source	
	Pulse Width	<50-100 ps (dependent on wavelength)	
	Repetition Rate	20 MHz ± 5%	
PC & Software	OS	Windows 7/10	
	Function	Automatic Reconstruction of Transient Absorption Temporal Profile, Conversiont to Transient Absorption Spectra, Curve Fitting (Nonlinear Least Square method), Data Storage in Text Format	
Installation Environment		No Optical Bench Required	On Optical Bench

picoTAS Models (Coverage of Time and Wavelength)



Dimensions of Optical Unit



Installation spaces for probe light source, PC and oscilloscope are needed separately.
-ps model further requires an installation space for pump light source.

Options

Wavelength-Tunable Pump Light Source for -ps model

Excitation Wavelength Can be Varied.

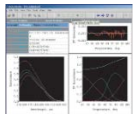
Type	Optical Parametric Generator (OPG)
Pump Laser	Picosecond mode-locked laser 1kHz, 355 nm, 0.3W
Wavelength Range	410-709 nm, 710-2300 nm
Pulse Energy	50μJ@450nm

CoolSpeK Low-Temperature Cell Holder (for 2mm cell)

Temperature Range from -80°C to +100°C

Temperature Range	-80℃ ～ Room Temperature (~100°C)
Temperature Control	Flow control of liquid nitrogen by an automatic valve
Functions	Low Dew Condensation by Heating of Optical Window, Stirrer
Liquid Nitrogen Reservoir	Stainless, 2L Duration of 2H at -80℃

Global Analysis Software



Spectrum Analysis of Multicomponent and Various Analysis Functions

Software	Globalworks - made by US Company OLIS
Analysis Feature	Singular Value Decomposition (SVD), Global Fitting
	Lifetime Calculation, Selection of Reaction Mechanism Model
OS	Windows XP/7

Customization

We will construct a customized system with existing pump source, probe source in your lab.

Recommended Specification for Pump Light Source	Repetition rate 1 kHz, Pulse width <500 ps, Output energy 20 μJ/pulse ※Please contact us for the source out of the specification above
Recommended Specification for Probe Light Source	① Supercontinuum light source with repetition-rate of 20 MHz ② Supercontinuum light source equipped with a pulse picker (Settable at 20 MHz.) ③ Picosecond laser diode with high output energy (100nJ/pulse)

Notes: System performance might be limited depending on the specifications of pump light source and/or probe light source.

■ Single Wavelength Measurement by Picosecond Diode Laser

Probe Light Source	Picosecond Diode Laser
Wevelength (nm)	450, 532, 1000, 1100, 1200, 1300, etc.
Pulse Width	Dependent on Light Source Selected 200 ps@532 nm, 50 ps@1000 nm, etc

■ Please feel free to contact us for the transient absorption system that can eliminate long-lived luminescence by making the most use of the RIPT method and a lower repetition-rate supercontinuum light source.