Transient Absorption Spectroscopy

Pump, probe, delay, and the signals they reveal: a companion to the talk

1. The idea

Transient absorption (TA) spectroscopy, also called pump–probe spectroscopy, watches how the absorption of a sample changes after it has been excited by light. A short, strong pulse (the pump) prepares excited states. A second, weak pulse (the probe) arrives a controlled time later and measures what the sample now absorbs. Repeating the measurement at many delays turns a series of snapshots into a movie of the excited-state dynamics.

The time resolution comes from the pulse width, typically about 100 fs, because the delay is set by the path length of light rather than by electronics. This is why TA can follow processes that no detector could resolve directly.

2. The experiment

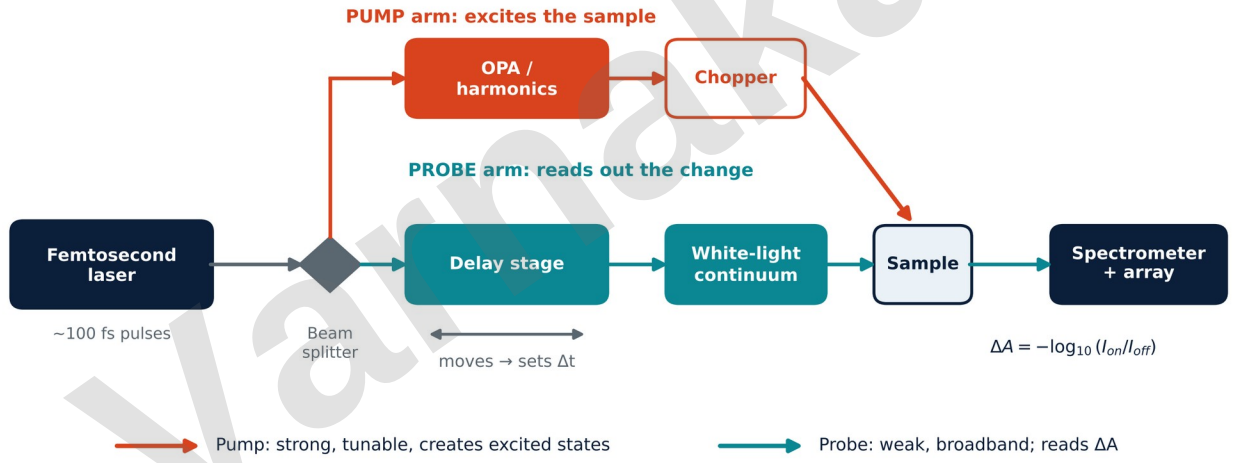


Figure 1. Schematic of a pump–probe experiment. The pump arm excites the sample; the delayed probe arm reads out the change.

A femtosecond laser is split into two beams. The pump beam passes through an optical parametric amplifier (OPA) or a harmonic generator so that its wavelength can be matched to an absorption band of the sample, and a chopper blocks every other pulse. The probe beam travels through a motorized delay stage and then through a crystal that converts it into a white-light continuum. After passing through the sample, the probe is dispersed onto an array detector.

2.1 Role of the pump

- Strong and tunable; its wavelength is chosen so that the sample absorbs it.
- Creates the excited states: excitons, free carriers, radicals or other species.

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- Its fluence (energy per area) sets how many excitations are formed, and should usually stay in the linear regime.

2.2 Role of the probe

- Weak, so that it measures the sample without creating excitations of its own.
- Broadband (white light), so a whole spectrum is recorded at each delay.
- Delayed by Δt relative to the pump; the measurement is made with and without the pump.

3. The delay Δt

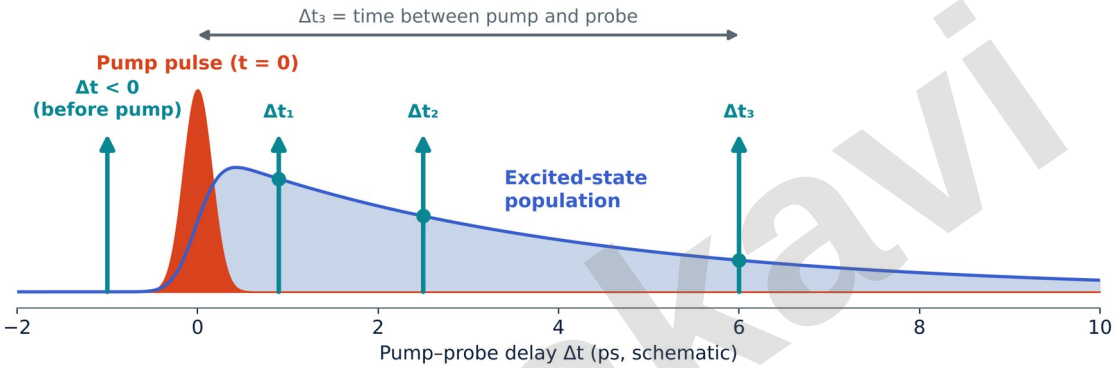


Figure 2. The probe samples the excited-state population at different delays after the pump pulse.

What the delay is. Δt is the time by which the probe arrives after the pump. At Δt = 0 the two pulses overlap. At Δt < 0 the probe arrives before the pump and records the unperturbed sample, which is a useful reference. At Δt > 0 the probe measures the sample as it evolves.

How it is set. The probe passes over a mirror on a motorized stage. Light travels about 0.3 µm per femtosecond and the path is traversed twice, so moving the mirror by 1 µm changes the delay by about 6.7 fs. A stage of 30 cm gives roughly 2 ns of delay. Longer delays (ns to µs) need electronic delay between two synchronized lasers.

4. What is measured

The quantity recorded is the pump-induced change in absorbance:

$$\Delta A(\lambda, \Delta t) = A(\text{pump on}) - A(\text{pump off}) = -\log_{10}(I_on \,/\, I_off)$$

A negative ΔA means the sample absorbs less light with the pump on; a positive ΔA means it absorbs more. (Some groups plot ΔT/T instead, which reverses the sign of the bleach.)

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5. The signals: bleach and the others

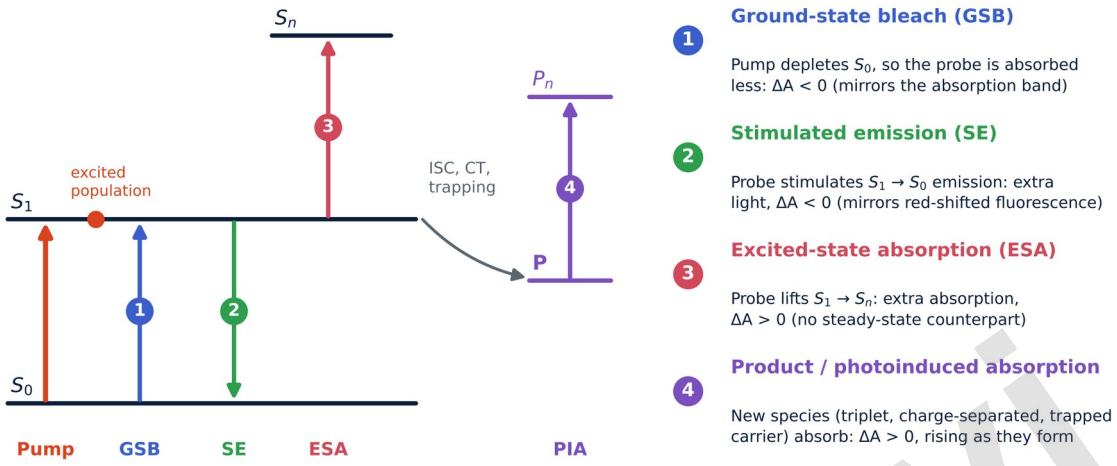


Figure 3. Energy-level picture of the four main TA signals.

Signal	Sign	Origin	Spectral signature
Ground-state bleach (GSB)	ΔA < 0	The pump removes molecules from S_0, so fewer are available to absorb the probe.	Mirrors the steady-state absorption band
Stimulated emission (SE)	ΔA < 0	The probe stimulates $S_1 \rightarrow S_0$ emission, adding photons to the probe beam.	Mirrors the fluorescence, shifted to longer wavelength
Excited-state absorption (ESA)	ΔA > 0	The excited state absorbs the probe and moves to a higher state ($S_1 \rightarrow S_n$).	Broad, no counterpart in the steady-state spectrum
Product / photoinduced absorption (PIA)	ΔA > 0	A new species (triplet, charge-separated state, trapped carrier) absorbs.	Rises as the species forms

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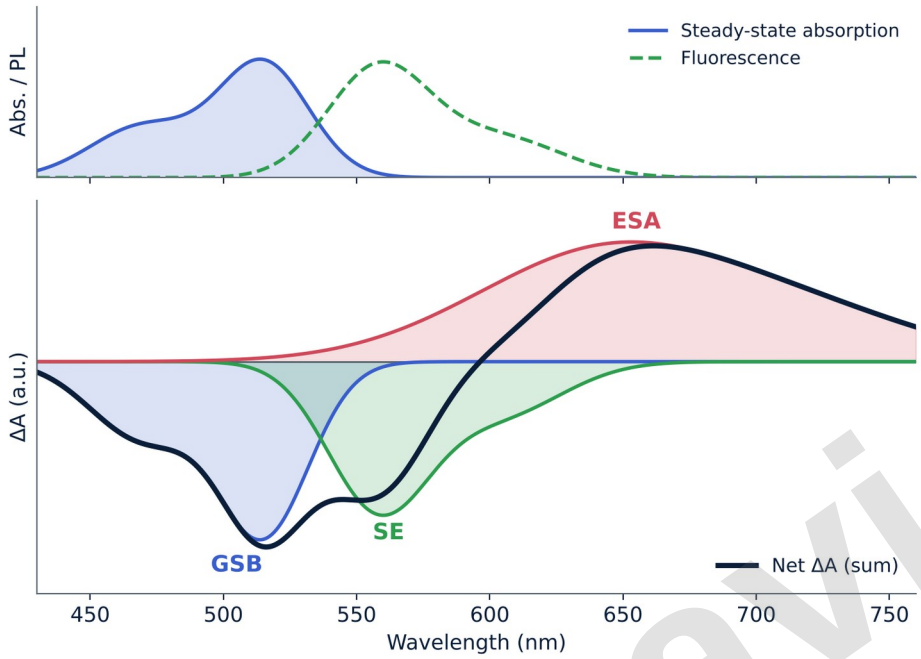


Figure 4. A measured transient spectrum is the sum of overlapping signals. Compare it with the steady-state absorption and photoluminescence spectra.

Because the signals overlap, a net spectrum can hide one of them. Measuring the steady-state absorption and photoluminescence first tells you where the bleach and stimulated emission should appear; what remains is excited-state or product absorption.

6. Kinetics and the full data set

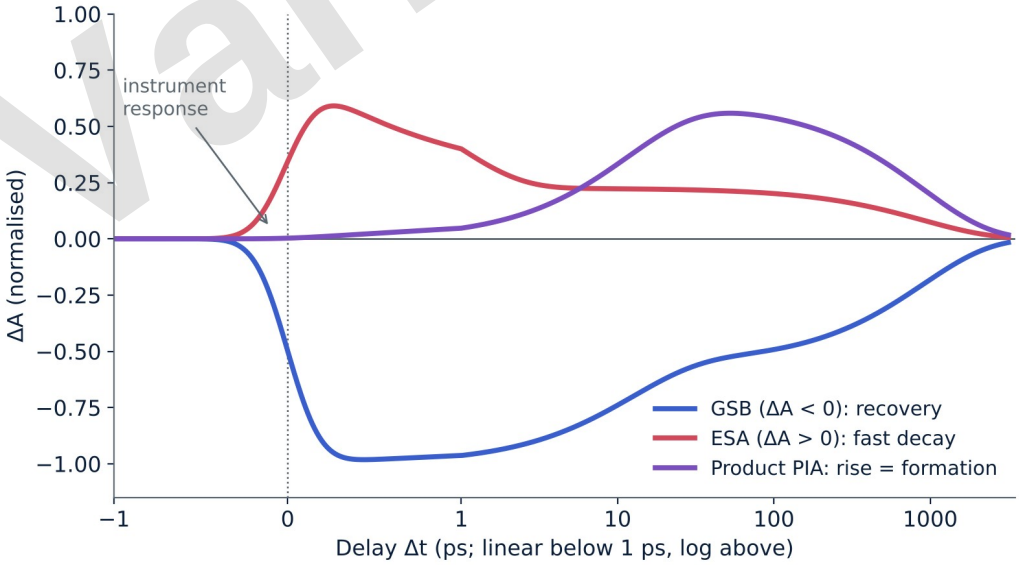


Figure 5. Kinetic traces at three wavelengths (linear time axis below 1 ps, logarithmic above).

- **Bleach recovery** tracks how fast the ground state refills.

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- **ESA decay** tracks loss of the excited state.
- **PIA rise** shows when a new species forms.
- Matching rates in different spectral regions suggest the same species.

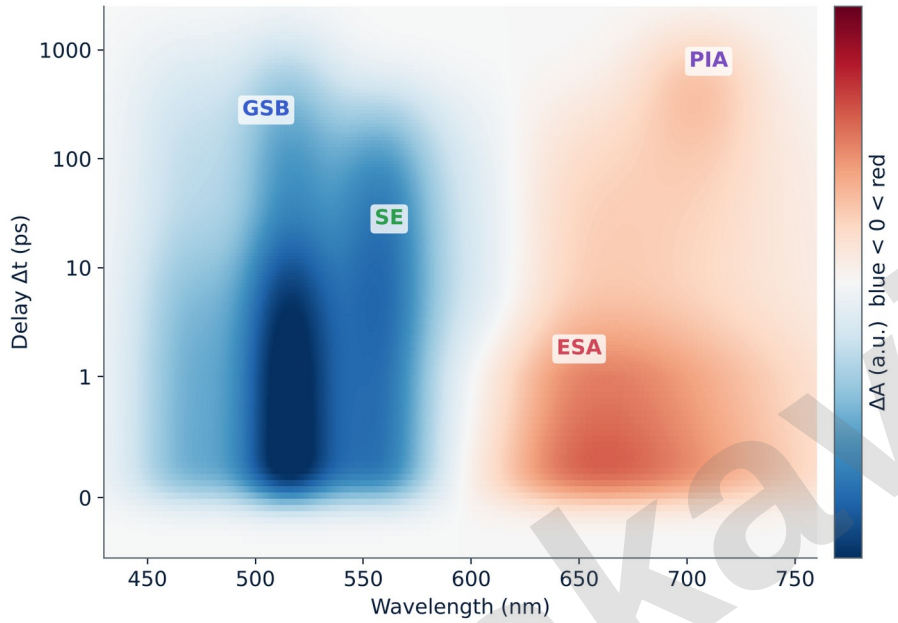


Figure 6. The full data set ΔA(λ, Δt). A row is a spectrum at one delay; a column is a kinetic trace at one wavelength.

Global analysis fits all wavelengths and delays together with a sum of exponentials, giving lifetimes and the spectrum associated with each component (decay-associated or evolution-associated spectra).

7. Semiconductors and nanocrystals

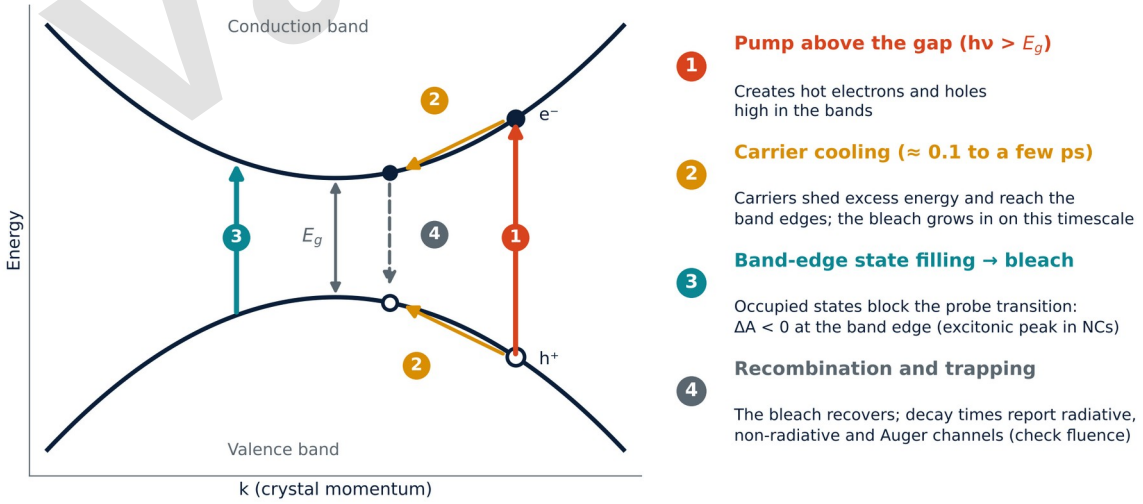


Figure 7. In a semiconductor, the pump creates hot carriers that cool to the band edge, where state filling produces the bleach.

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In semiconductors and nanocrystals (for example $CsPbBr_3$) the band-edge bleach is often proportional to the number of carriers, because occupied states block the probe transition. Keep the pump fluence low enough to avoid multi-carrier effects and Auger recombination unless these are the subject of the experiment.

8. Timescales and delay methods

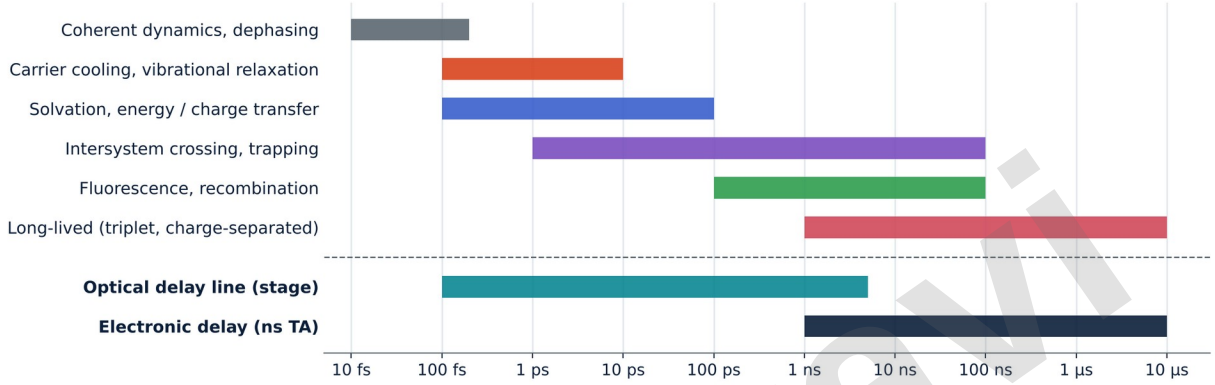


Figure 8. Typical timescales of photophysical processes and the delay methods that cover them.

An optical delay line covers femtoseconds to a few nanoseconds. Electronic delay extends TA to nanoseconds, microseconds and beyond, which is needed for triplets and charge-separated states.

9. Pitfalls worth checking

Issue	What to do
Pump fluence	Stay in the linear regime; avoid multi-exciton effects.
Photodamage	Stir or flow the sample and re-check its absorption after the measurement.
Coherent artifact	Signals near $\Delta t = 0$ from pump–probe overlap; do not fit them.
White-light chirp	Different wavelengths reach t_0 at different times; correct before fitting.
Solvent and cuvette	Measure the solvent and cuvette alone.
Polarization	Use the magic angle between pump and probe for population kinetics.

10. Summary

- The pump creates excited states at $\Delta t = 0$.
- The probe, delayed by Δt, measures the change in absorption.
- Negative ΔA: ground-state bleach and stimulated emission.
- Positive ΔA: excited-state and product absorption.

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