Transient Absorption Spectroscopy

Watching excited states live: pump, probe, delay, and the signals they reveal

P Pump

p Probe

Δt Delay

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What transient absorption tells you

1

Who is excited?

Which states or species form after light absorption

2

How fast do they change?

Lifetimes, cooling, transfer, trapping, recombination

3

Where does the energy go?

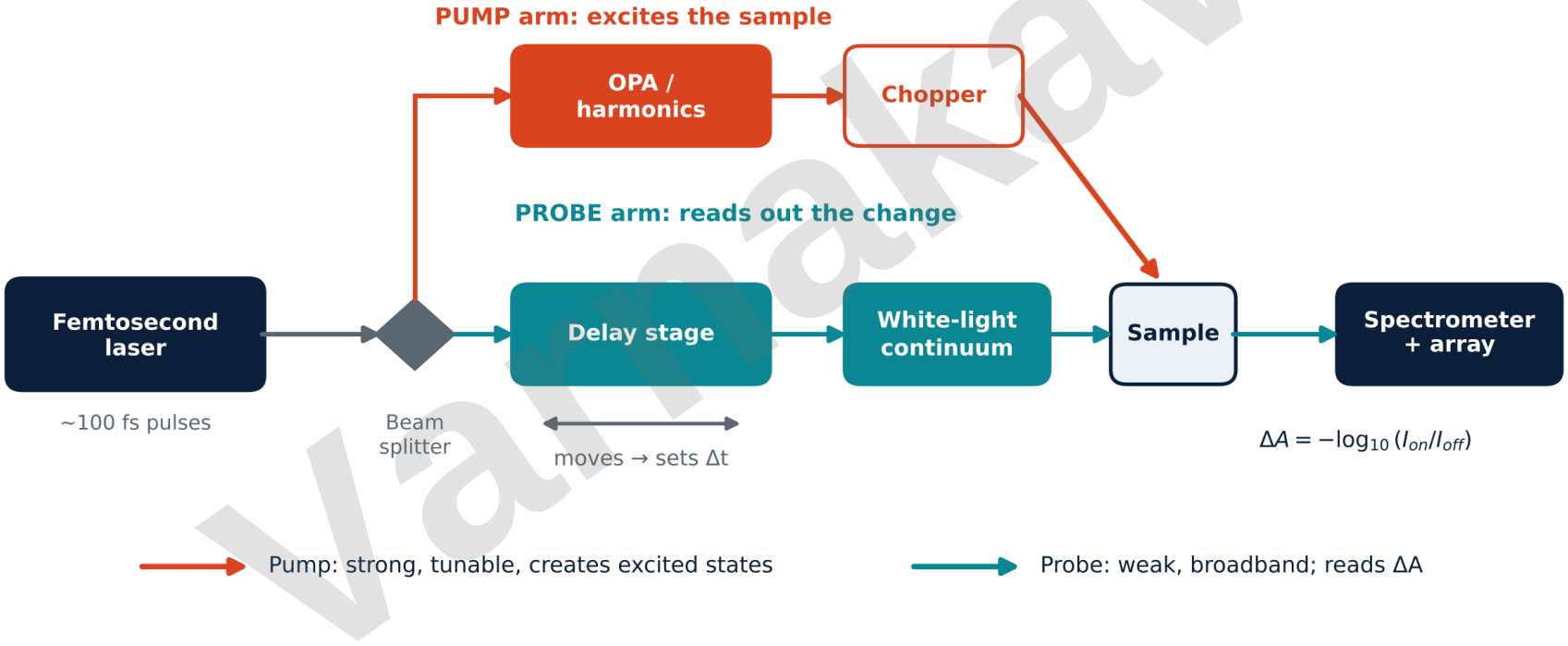
Competing pathways and their branching

~100 fs

time resolution is set by the laser pulse width, not by the detector

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The experiment in one picture



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One laser, split into two beams: a strong pump and a weak, delayed probe.

Pump and probe: two different jobs

P

PUMP

Starts the clock

- Strong, tunable wavelength
- Absorbed by the sample
- Creates excited states (excitons, carriers, radicals)
- Fluence sets how many excitations form

p

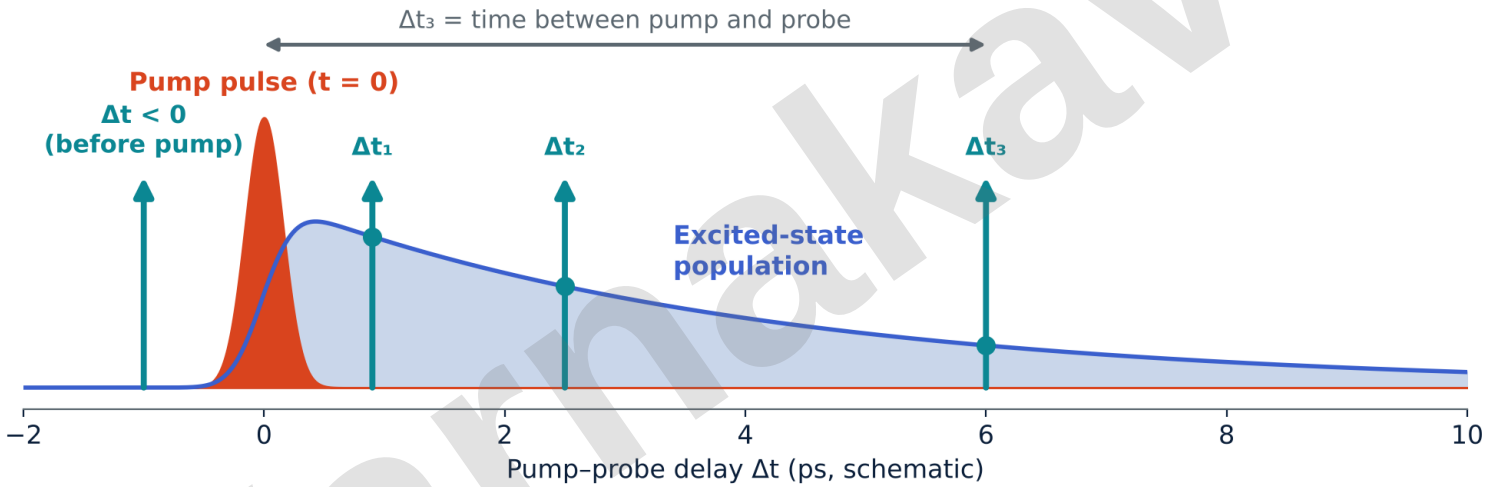
PROBE

Reads the change

- Weak: should not perturb the sample
- Broadband white light, many wavelengths at once
- Arrives after a controlled delay Δt
- Detected with and without pump

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The delay Δt: a movie, one frame at a time



Δt = 0: pump and probe overlap in time

Δt < 0: probe arrives first, giving the unperturbed reference

Delay stage: a mirror on a rail; 1 µm of travel ≈ 6.7 fs (light path doubles)

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What we actually measure: ΔA

ΔA(λ, Δt) = A(pump on) − A(pump off)

$$= -\log_{10}(I_on / I_off)$$

The chopper alternates pump on and off, so each wavelength and delay gives one difference spectrum.

ΔA < 0 — **Less absorption**

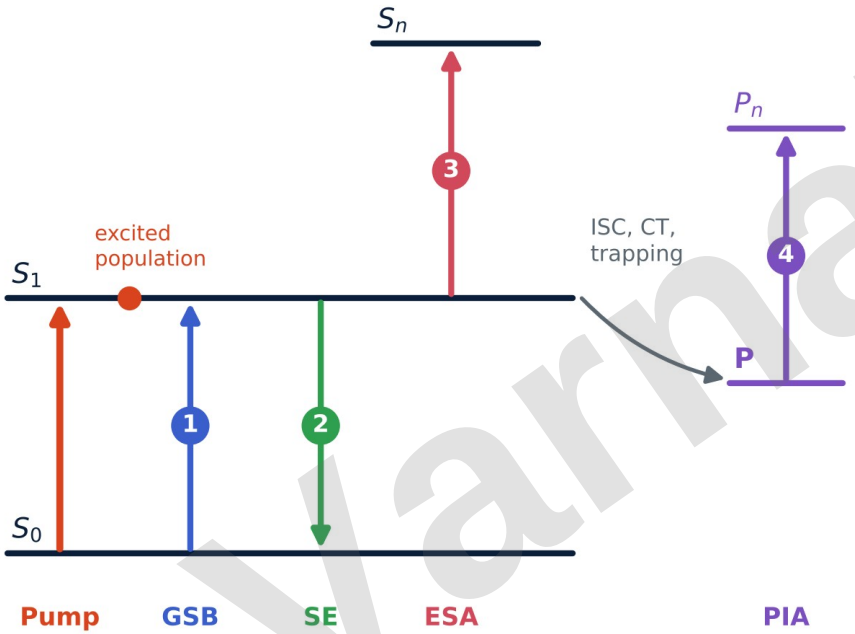
Ground-state bleach, stimulated emission

ΔA > 0 — **More absorption**

Excited-state and product absorption

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Four signals, one energy-level picture



1 Ground-state bleach (GSB)

Pump depletes S_0, so the probe is absorbed less: $\Delta A < 0$ (mirrors the absorption band)

2 Stimulated emission (SE)

Probe stimulates $S_1 \rightarrow S_0$ emission: extra light, $\Delta A < 0$ (mirrors red-shifted fluorescence)

3 Excited-state absorption (ESA)

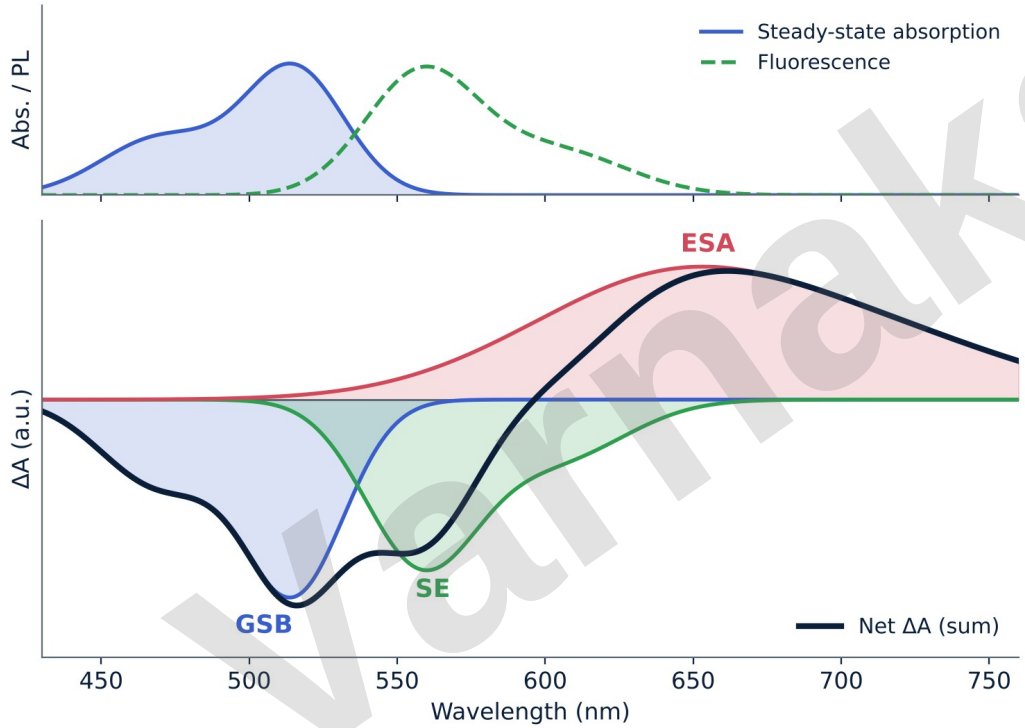
Probe lifts $S_1 \rightarrow S_n$: extra absorption, $\Delta A > 0$ (no steady-state counterpart)

4 Product / photoinduced absorption

New species (triplet, charge-separated, trapped carrier) absorb: $\Delta A > 0$, rising as they form

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Signals overlap: net ΔA is their sum



GSB mirrors the steady-state absorption band

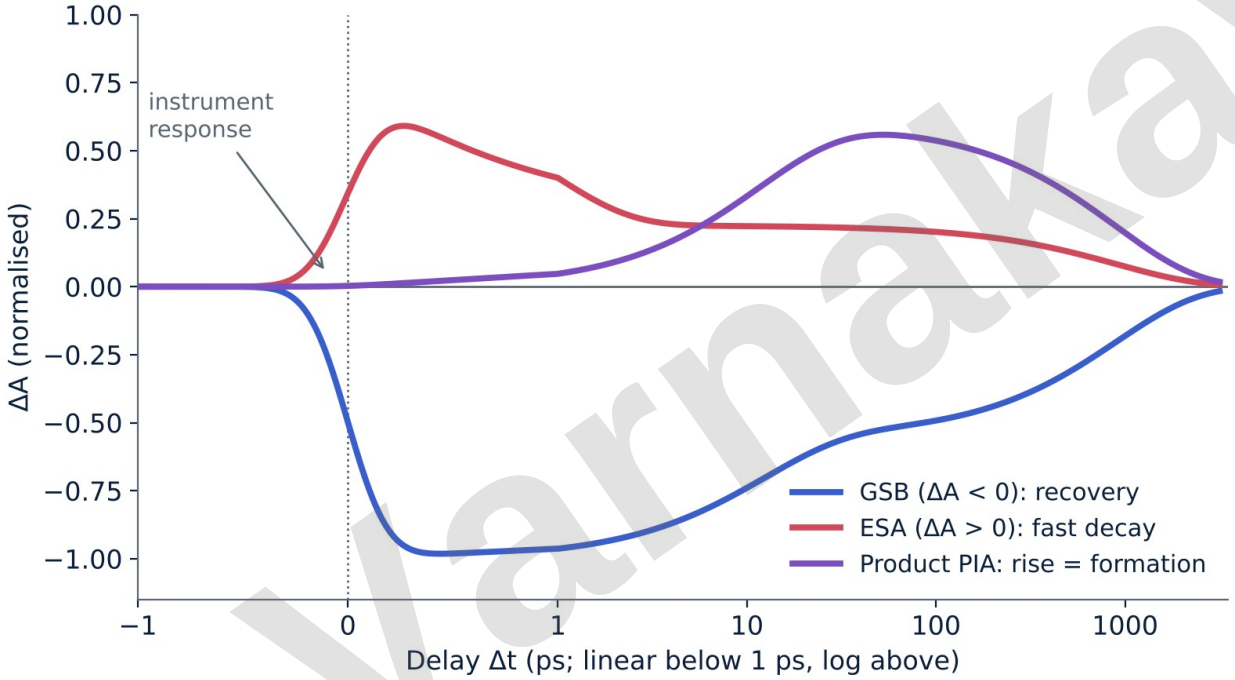
SE mirrors fluorescence, shifted to longer wavelength

ESA broad, positive, no steady-state counterpart

Overlap can hide or distort one signal, so compare with the absorption and PL spectra

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Kinetics: slice at one wavelength



GSB recovery tracks how fast the ground state refills

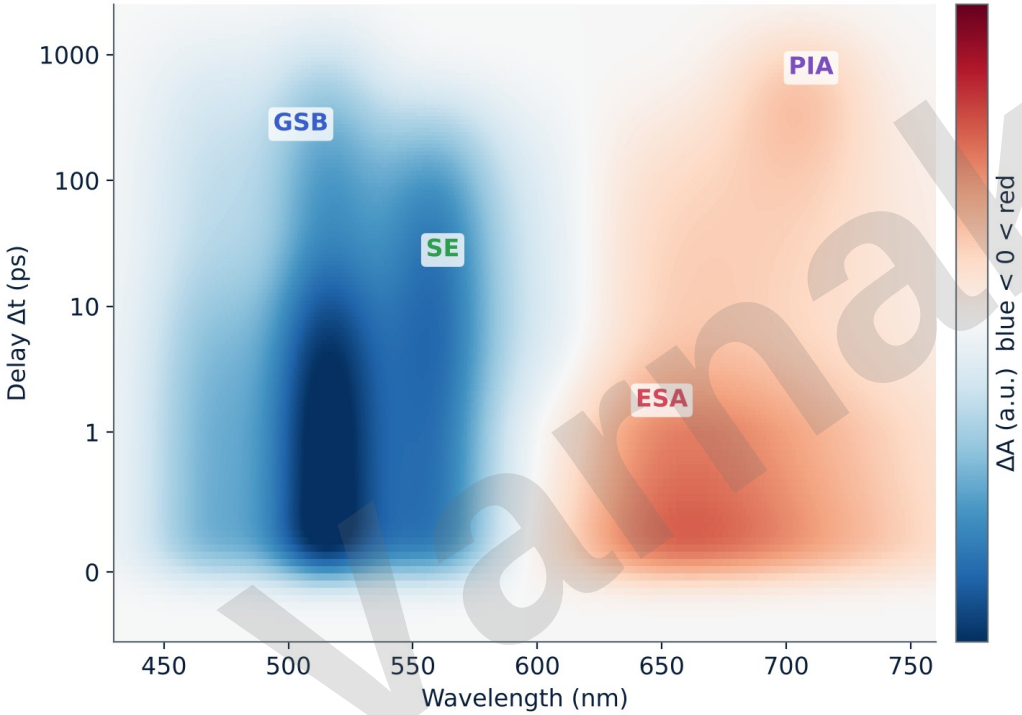
ESA decay tracks loss of the excited state

PIA rise shows when a new species forms

Matching rates across bands suggest one species

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The full dataset: ΔA(λ, Δt) map



Row: spectrum at one delay

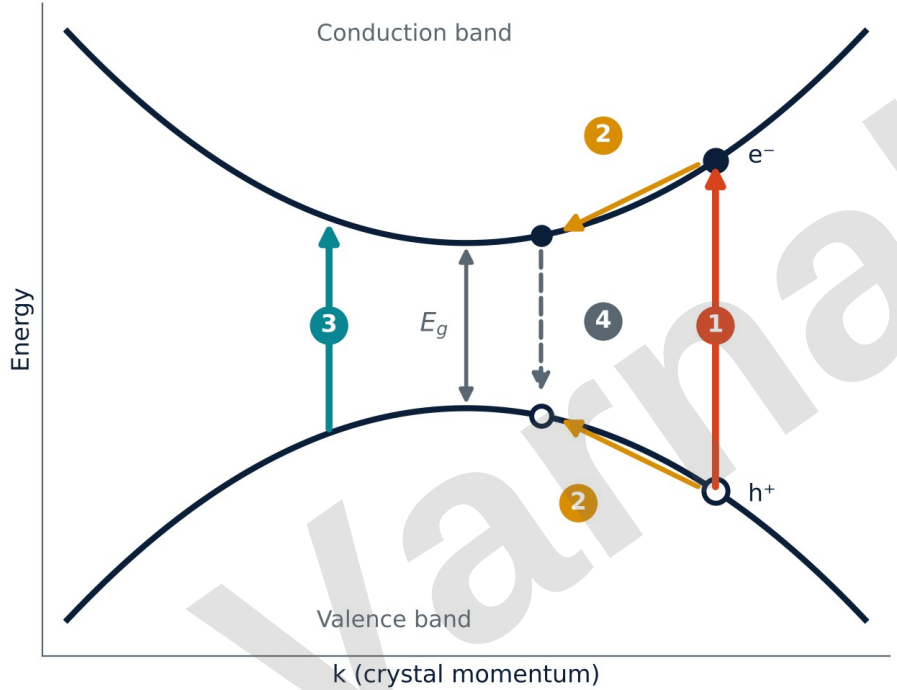
Column: kinetics at one wavelength

Global fit: lifetimes plus species spectra (DAS or EADS)

Blue / red: bleach and SE / induced absorption

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Semiconductors: band-edge state filling



1 Pump above the gap ($h\nu > E_g$)

Creates hot electrons and holes high in the bands

2 Carrier cooling (≈ 0.1 to a few ps)

Carriers shed excess energy and reach the band edges; the bleach grows in on this timescale

3 Band-edge state filling → bleach

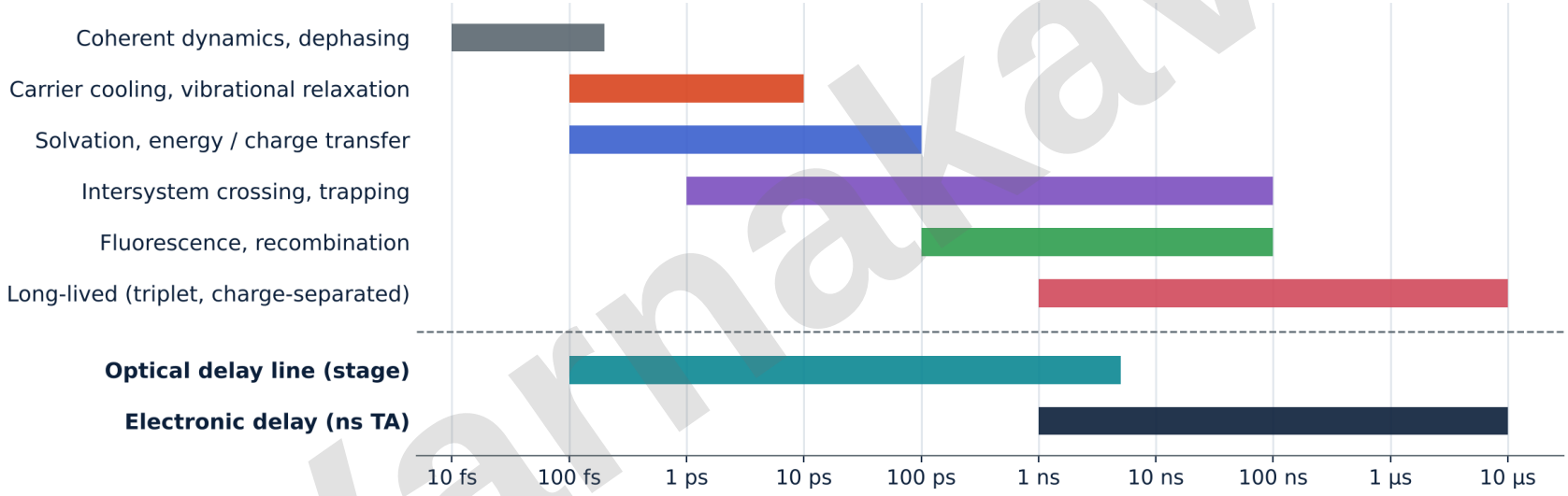
Occupied states block the probe transition: $\Delta A < 0$ at the band edge (excitonic peak in NCs)

4 Recombination and trapping

The bleach recovers; decay times report radiative, non-radiative and Auger channels (check fluence)

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Which processes, which timescales



An optical delay line covers fs to a few ns; electronic delay extends TA to ns–µs and beyond.

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Pitfalls worth checking

1 Pump fluence

Keep linear; avoid multi-exciton effects

2 Photodamage

Stir or flow the sample; re-check absorption

3 Coherent artifact

Spikes near $\Delta t = 0$; do not fit

4 White-light chirp

Different λ reach t_0 at different times

5 Solvent response

Measure cuvette and solvent alone

6 Polarization

Use the magic angle for population kinetics

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Takeaways

1. Pump creates excited states at $\Delta t = 0$
2. Probe, delayed by Δt, measures the change in absorption
3. Negative ΔA: bleach and stimulated emission
4. Positive ΔA: excited-state and product absorption

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