LASERS4EU Online training on experimental methods and data analysis for femtosecond and attosecond spectroscopies, 9-11 June 2026

Transient Absorption Spectroscopy (TAS)

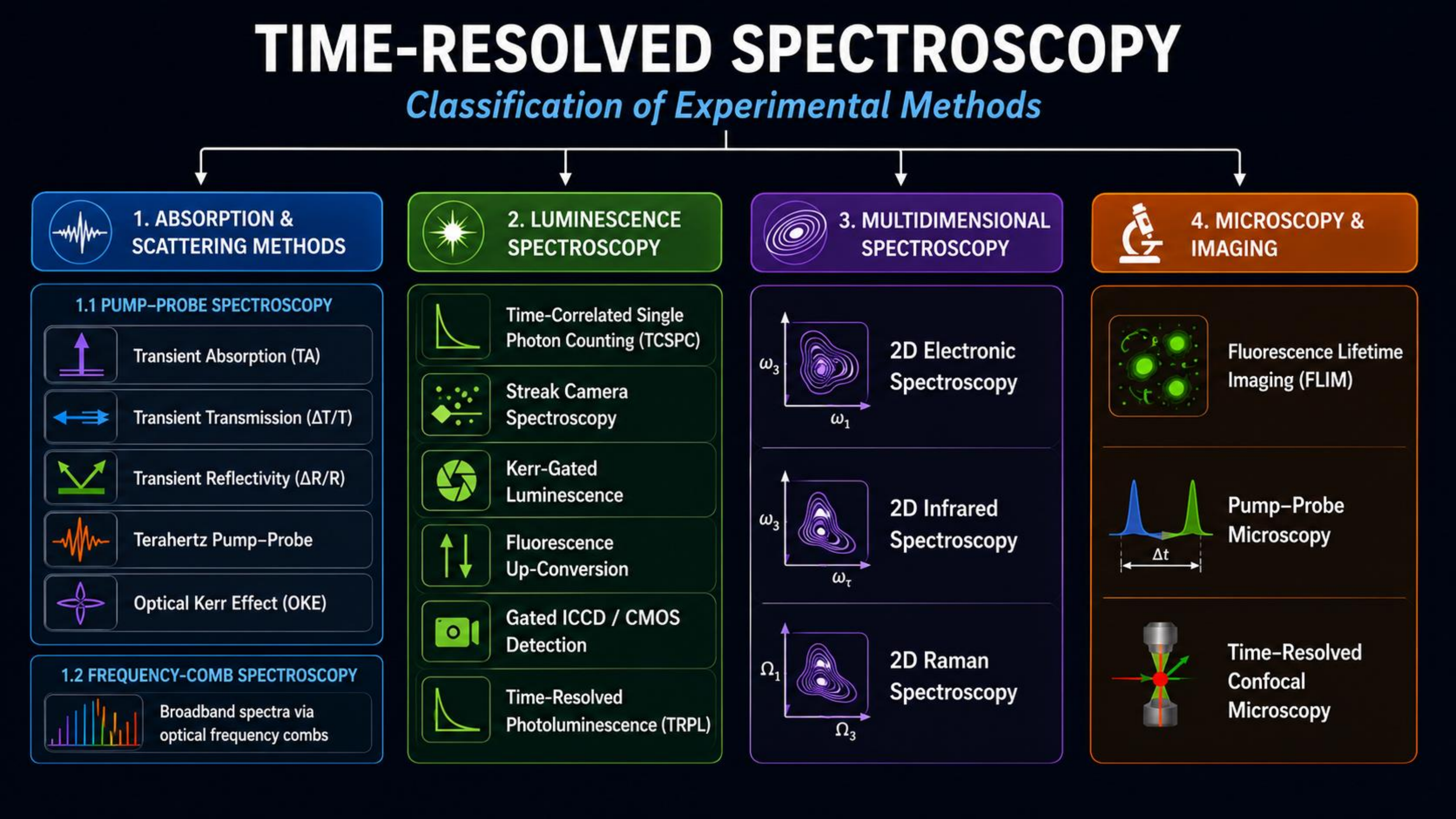
Igor Dmytruk

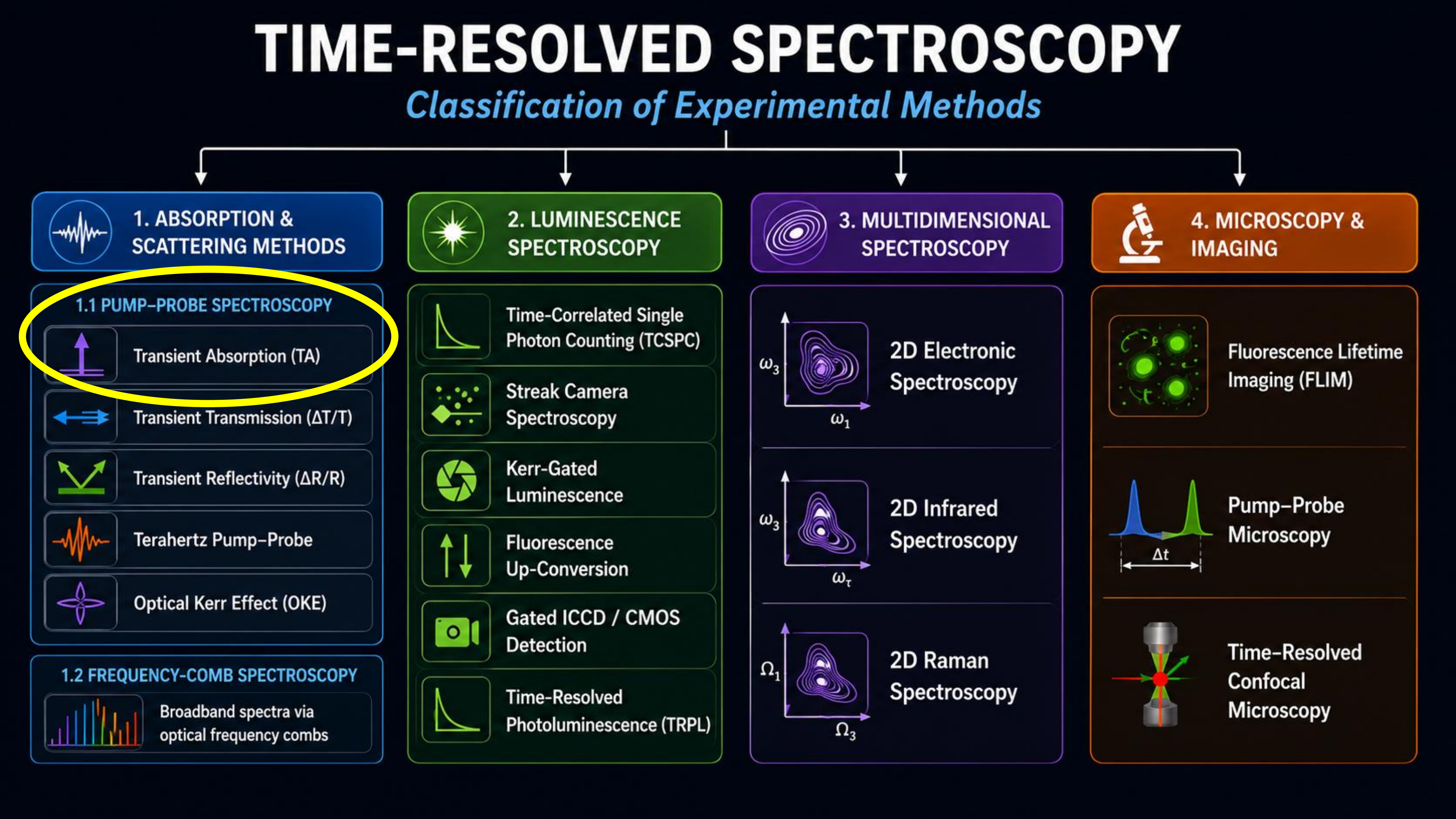
Department of Experimental Physics, Faculty of Physics,
Taras Shevchenko National University of Kyiv

Department of Photonic Processes, Institute of Physics,
National Academy of Sciences of Ukraine

Outline

- Methods of time-resolved spectroscopy:
  - Time-resolved luminescence
  - Pump-probe:
    - Absorption (TAS)
    - Reflection
    - Anisotropy
  - TAS measurement setup
    - Physical principles
    - What values are actually measured
    - Practical realization
    - Pitfalls and workarounds
  - Examples of results
    - Dye molecules
    - Nanoparticles
  - More sophisticated schematics


TIME-RESOLVED SPECTROSCOPY
Classification of Experimental Methods
1. ABSORPTION & SCATTERING METHODS
1.1 PUMP–PROBE SPECTROSCOPY
Transient Absorption (TA)
Transient Transmission (ΔT/T)
Transient Reflectivity (ΔR/R)
Terahertz Pump–Probe
Optical Kerr Effect (OKE)
1.2 FREQUENCY-COMB SPECTROSCOPY
Broadband spectra via optical frequency combs
2. LUMINESCENCE SPECTROSCOPY
Time-Correlated Single Photon Counting (TCSPC)
Streak Camera Spectroscopy
Kerr-Gated Luminescence
Fluorescence Up-Conversion
Gated ICCD / CMOS Detection
Time-Resolved Photoluminescence (TRPL)
3. MULTIDIMENSIONAL SPECTROSCOPY
ω_3
ω_1
2D Electronic Spectroscopy
ω_3
ω_τ
2D Infrared Spectroscopy
Ω_1
Ω_3
2D Raman Spectroscopy
4. MICROSCOPY & IMAGING
Fluorescence Lifetime Imaging (FLIM)
Δt
Pump–Probe Microscopy
Time-Resolved Confocal Microscopy

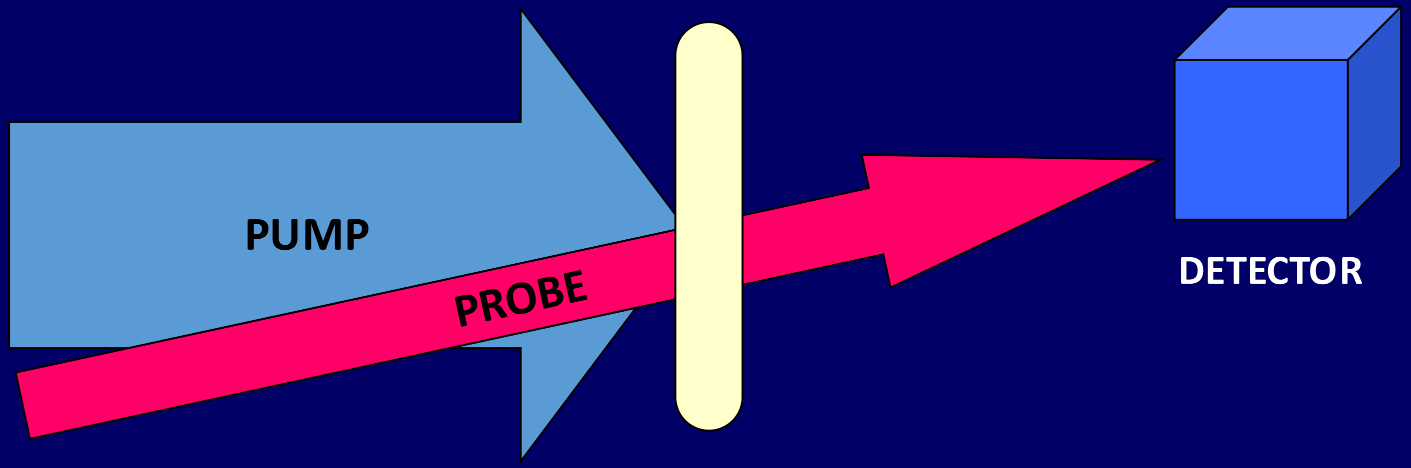

TIME-RESOLVED SPECTROSCOPY
Classification of Experimental Methods
1. ABSORPTION & SCATTERING METHODS
1.1 PUMP–PROBE SPECTROSCOPY
Transient Absorption (TA)
Transient Transmission (ΔT/T)
Transient Reflectivity (ΔR/R)
Terahertz Pump–Probe
Optical Kerr Effect (OKE)
1.2 FREQUENCY-COMB SPECTROSCOPY
Broadband spectra via optical frequency combs
2. LUMINESCENCE SPECTROSCOPY
Time-Correlated Single Photon Counting (TCSPC)
Streak Camera Spectroscopy
Kerr-Gated Luminescence
Fluorescence Up-Conversion
Gated ICCD / CMOS Detection
Time-Resolved Photoluminescence (TRPL)
3. MULTIDIMENSIONAL SPECTROSCOPY
ω_3
ω_1
2D Electronic Spectroscopy
ω_3
ω_τ
2D Infrared Spectroscopy
Ω_1
Ω_3
2D Raman Spectroscopy
4. MICROSCOPY & IMAGING
Fluorescence Lifetime Imaging (FLIM)
Δt
Pump–Probe Microscopy
Time-Resolved Confocal Microscopy

Practical realization

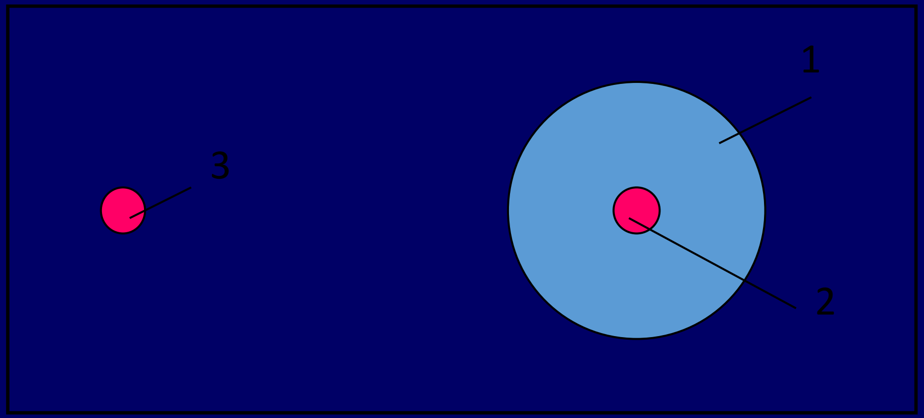
Main idea:

EXCITATION: 150 fs, 400 nm, 1 kHz, up to 10^9W/cm^2

PROBE: 150 fs “white light”, 200 - 1600 nm



Range of delay between pump and probe: 0 fs – 2 ns



1 – pump
2 – probe
3 – reference

Physical principles

- Full optical “gating”
- substitution "time -> distance“
- Absorption, transmission or reflection spectroscopy
- nonlinear element – object of study
- contrast is provided by frequency and spatial separation of pump and probe

Data processing

measured quantity – change of optical density of the sample after pump pulse

$$\Delta D = D - D_0 =$$

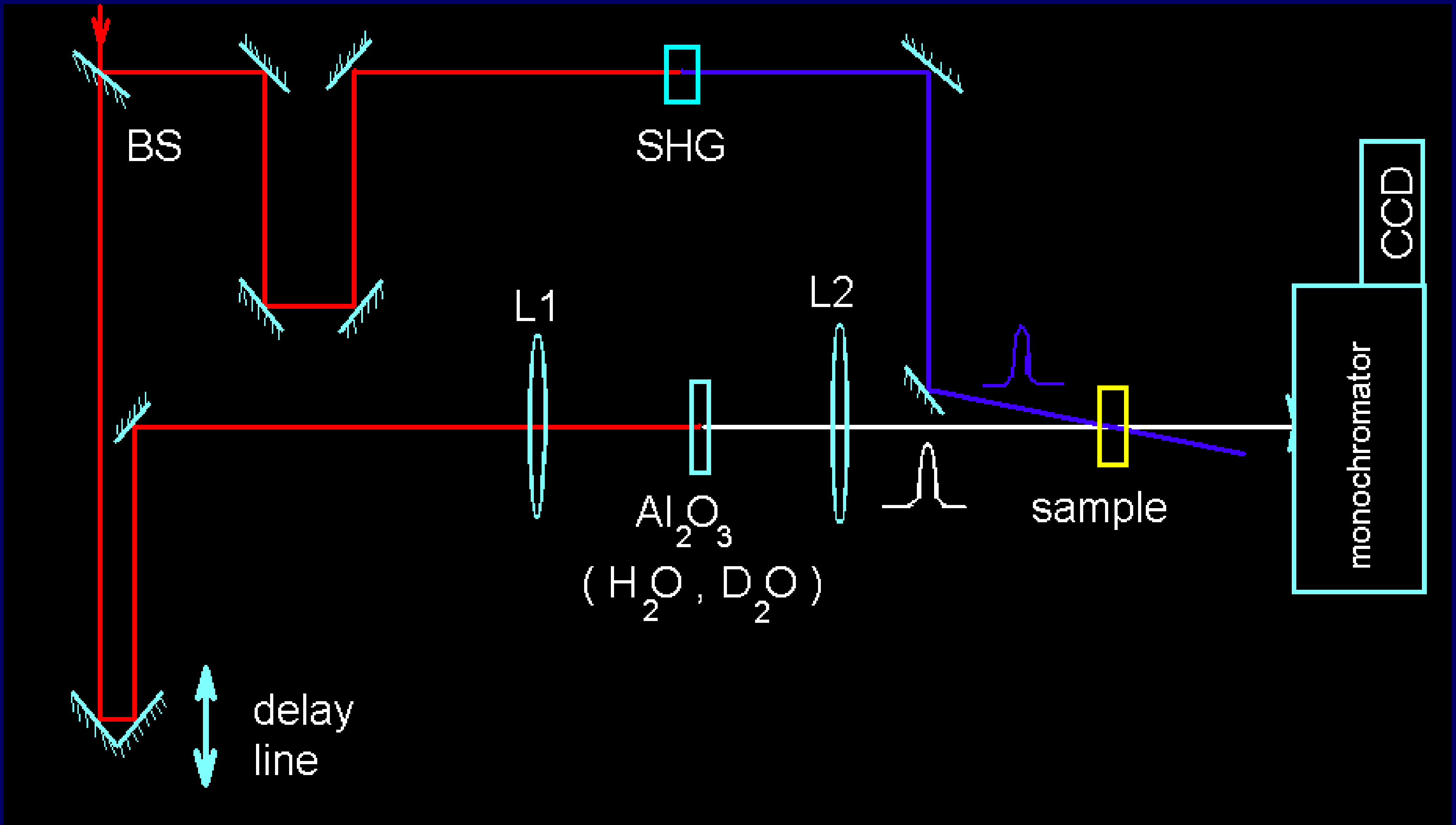
$$= \log \frac{I_0 - I_{background}}{I_{pump-probe} - I_{pump}} - \log \frac{I_0 - I_{background}}{I_{probe} - I_{background}}$$

Requirements to samples

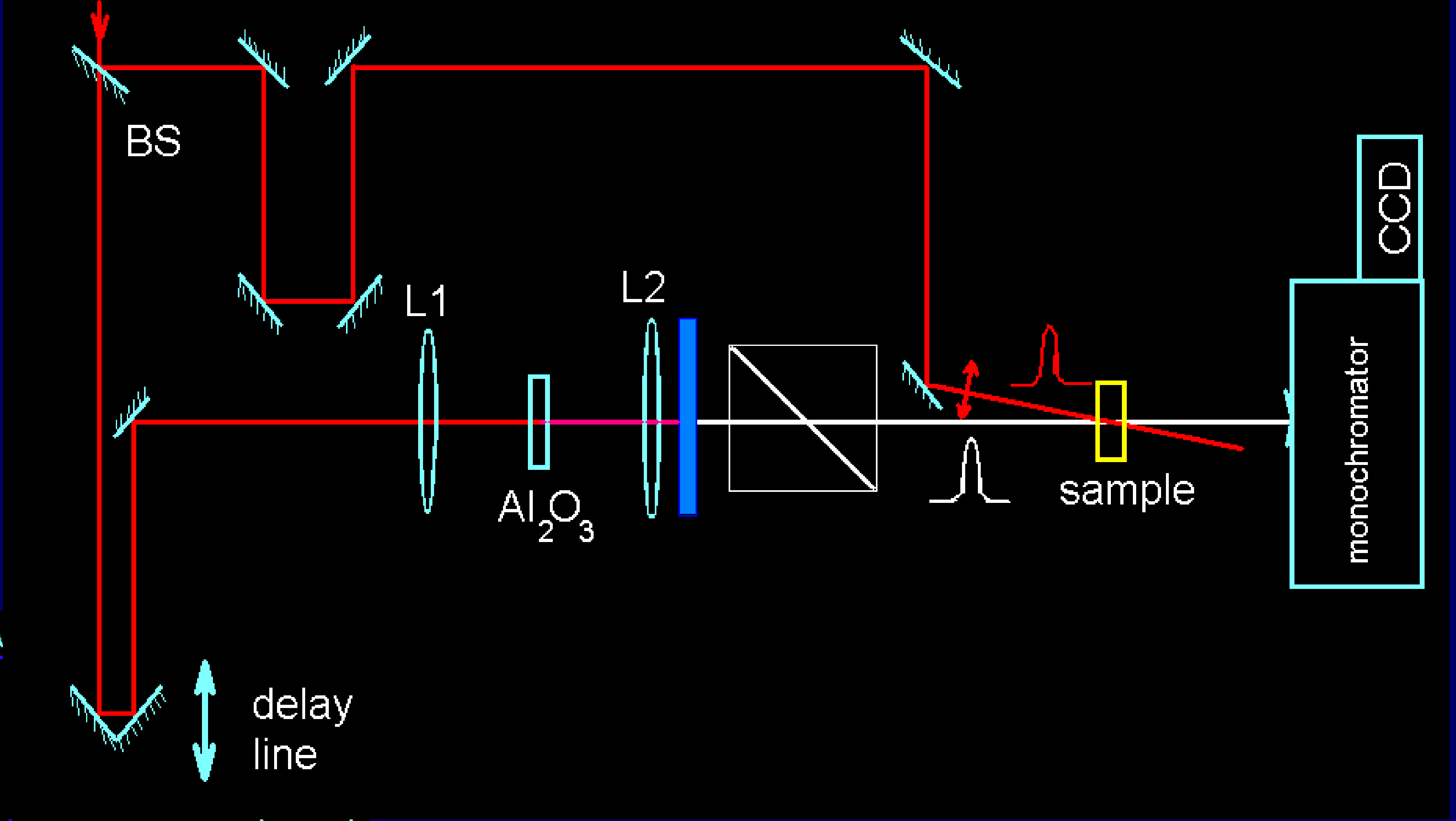
- Stability in pump beam
- low light scattering
- relaxation time < 1ms

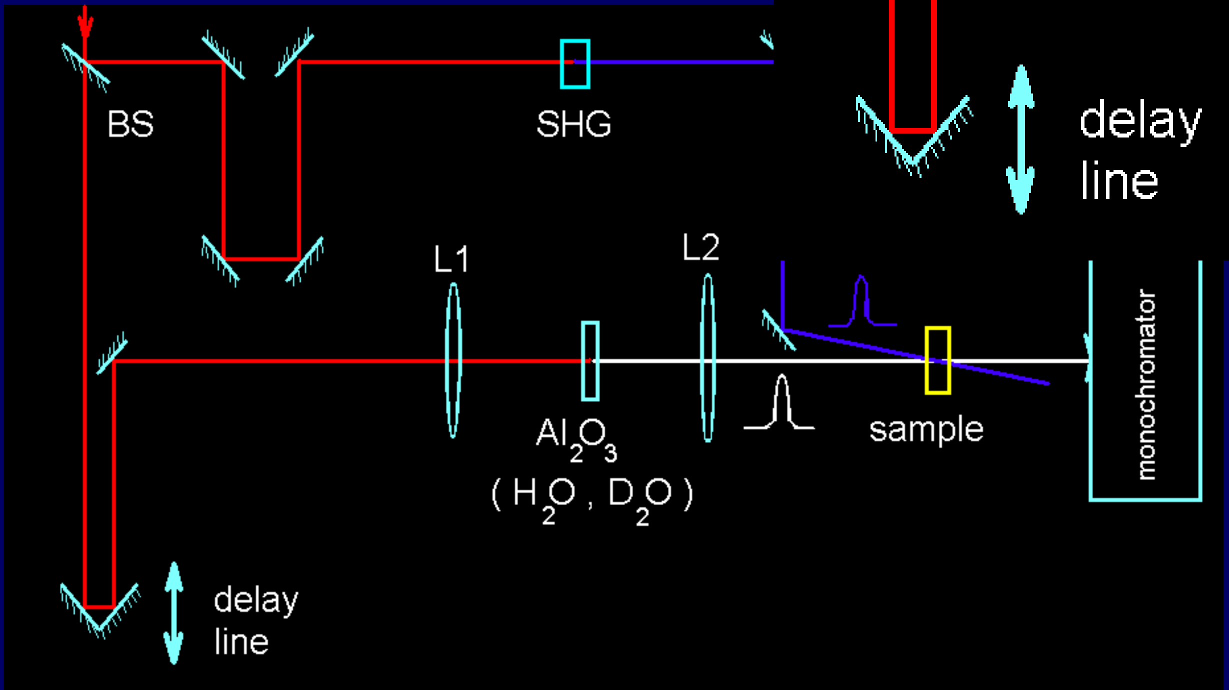
Practical implementation

- Optical schematic



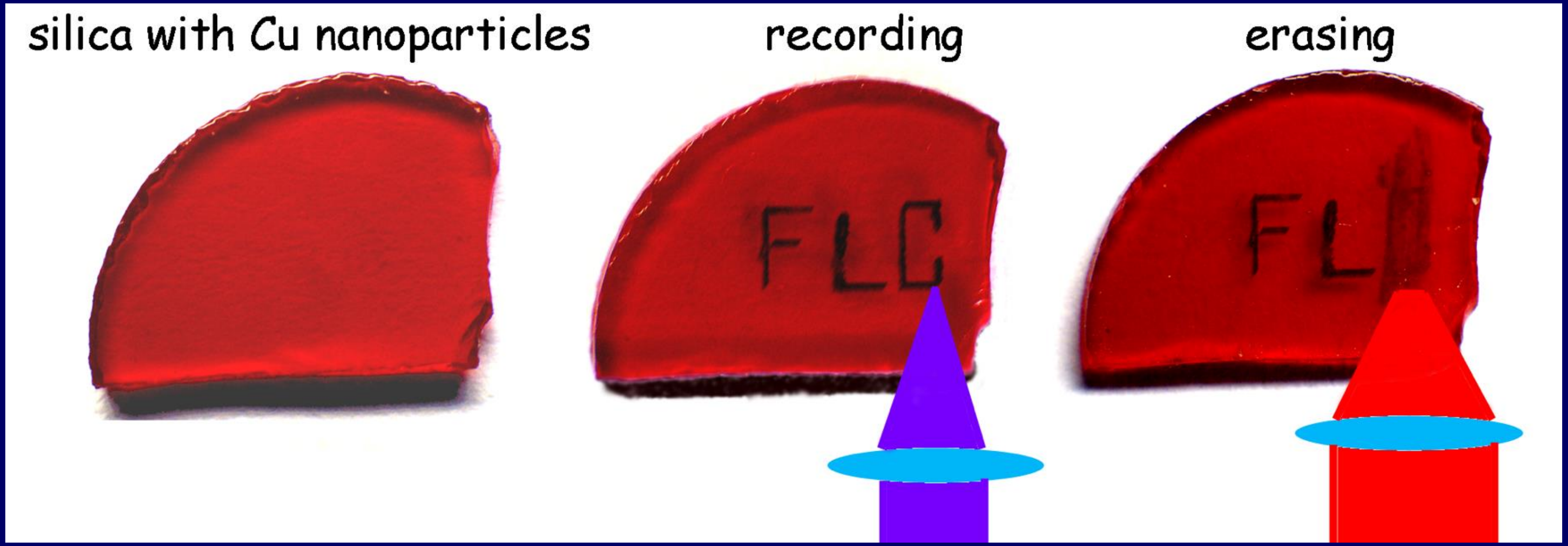
Experimental setup



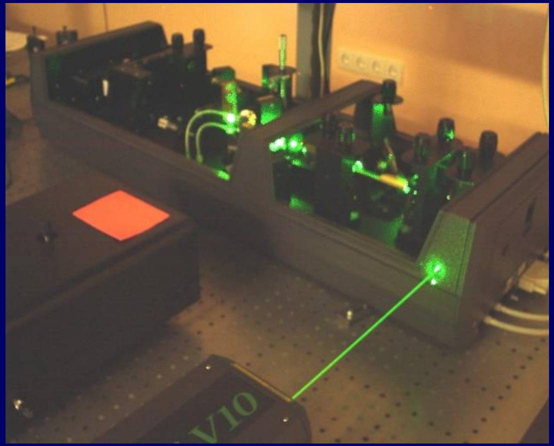


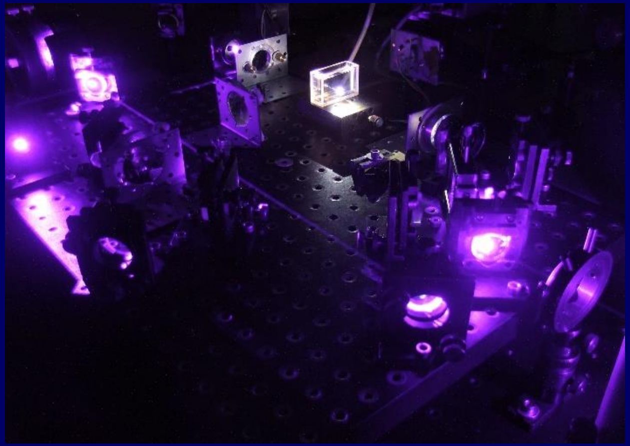
Pitfalls and workarounds

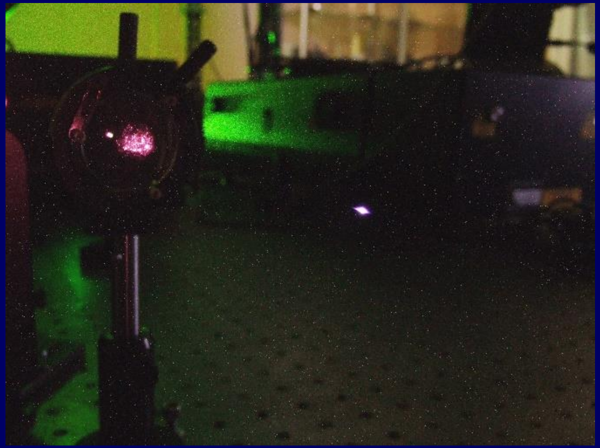
- Sample instability
- Chirp of white light
- Unwanted optical signals (luminescence, scattering)
- Misalignment as delay line moves
- Nonlinear phenomena in the sample



Femtosecond Laser Complex for collective use at Institute of Physics of National Academy of Sciences of Ukraine

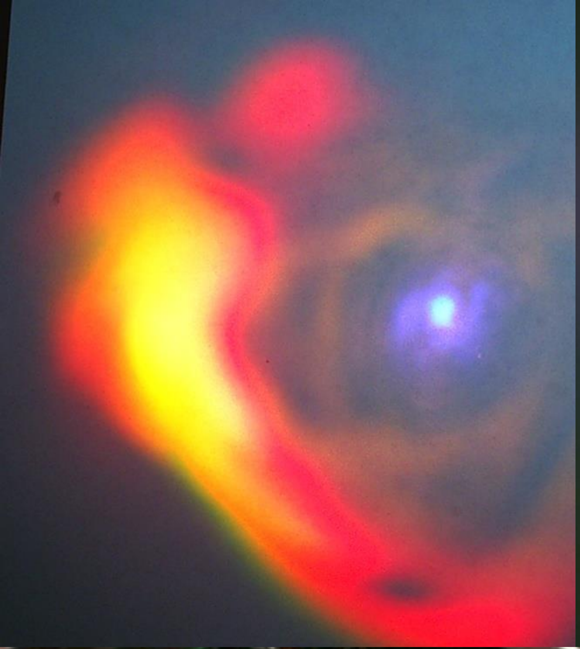




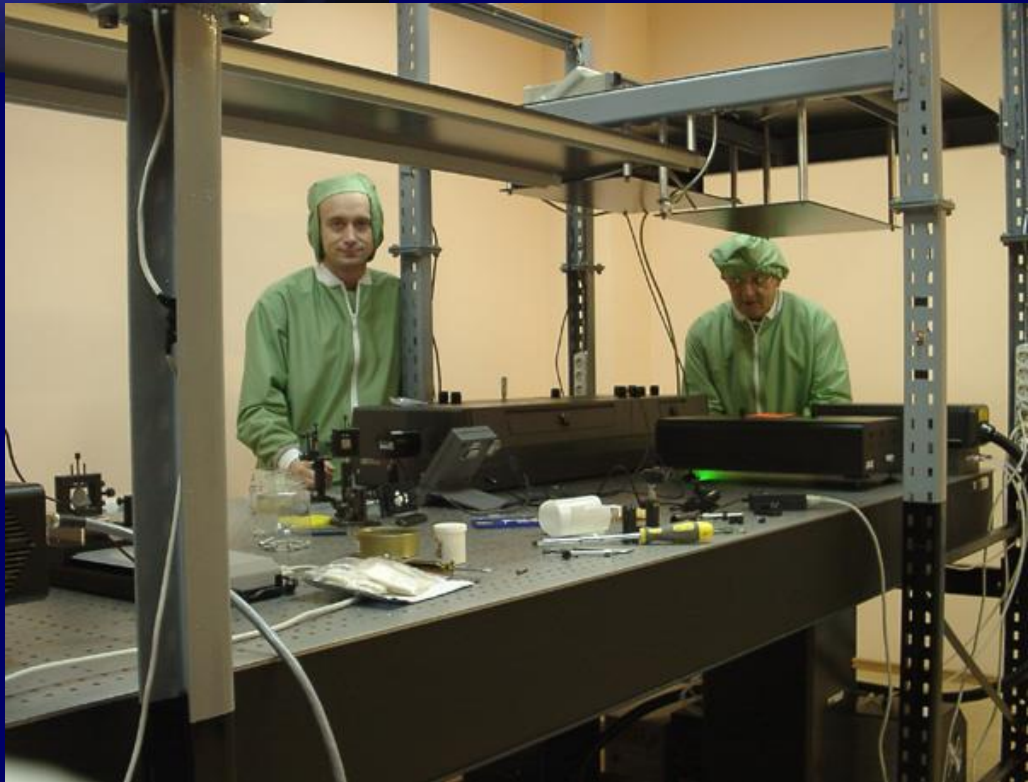


Characteristics

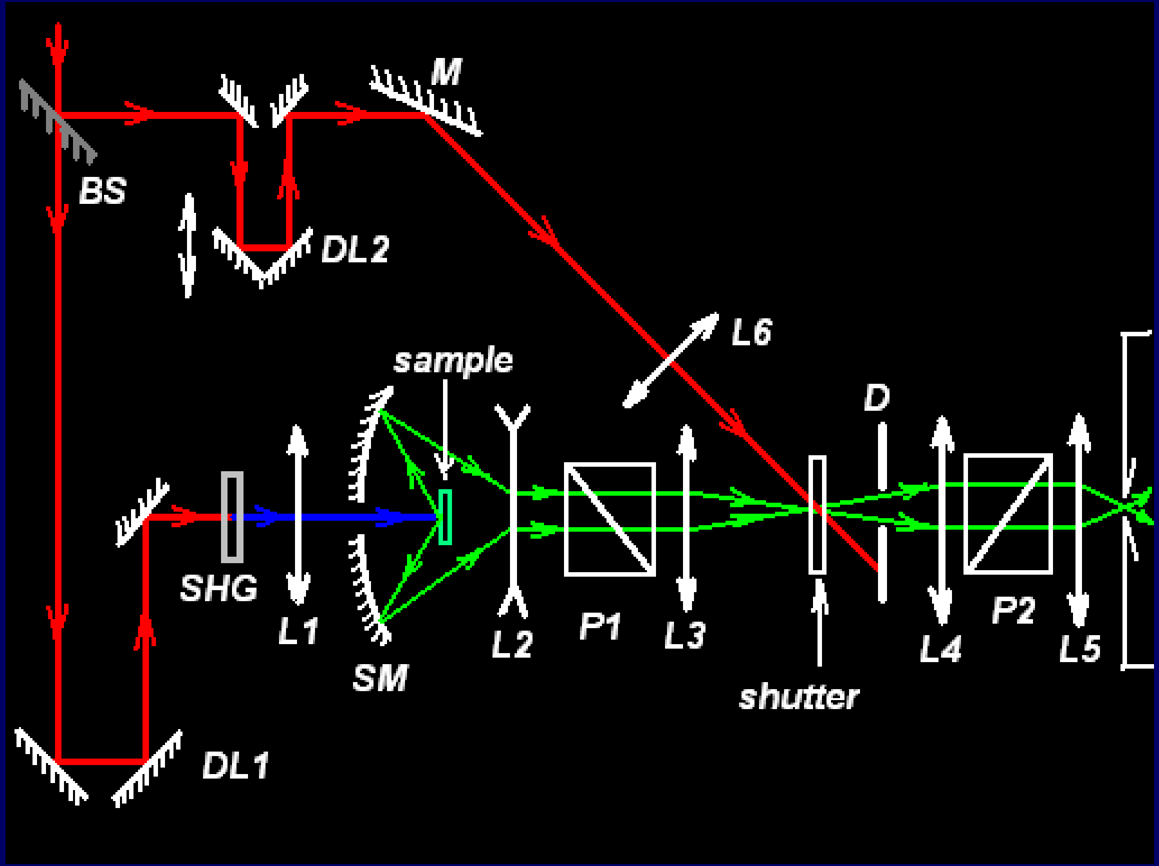
- time range – up to 2 ns
- repetition rate up to 1 kHz
- scanning step – 0.1 µm (~0.7 fs)
- time resolution – ~150 fs
- spectral ranges:
  - pumping – 750-800-900 nm (1 mJ)
  - 375-400-450 nm (0.2 mJ)
  - 250-267-300 nm
  - OPA and its harmonics, DFG
  - probing – 250-1100-1600 nm



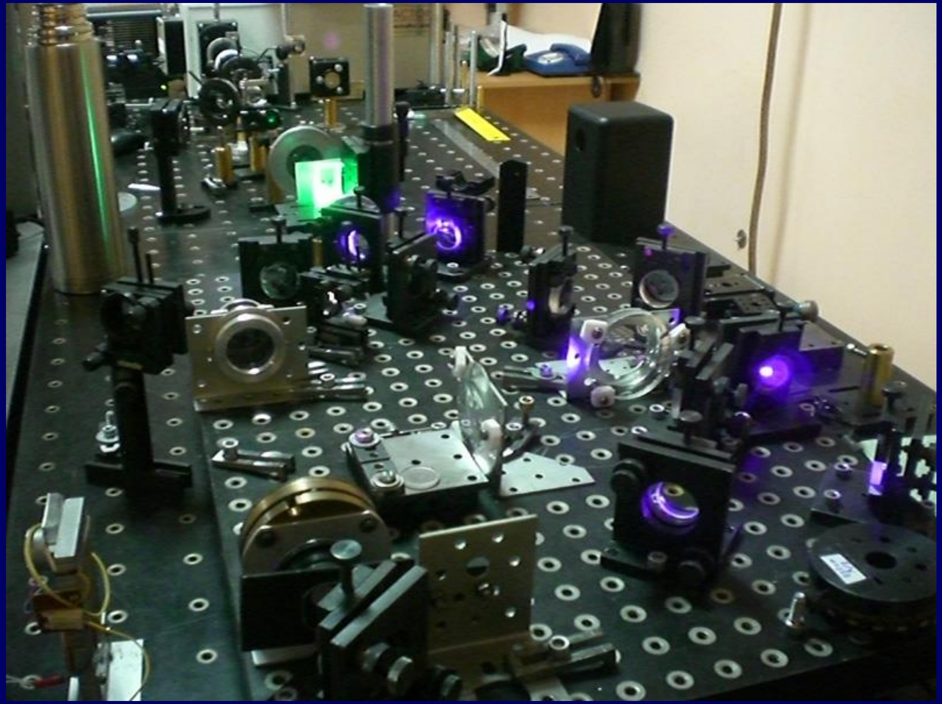

Legend



Time-resolved luminescence

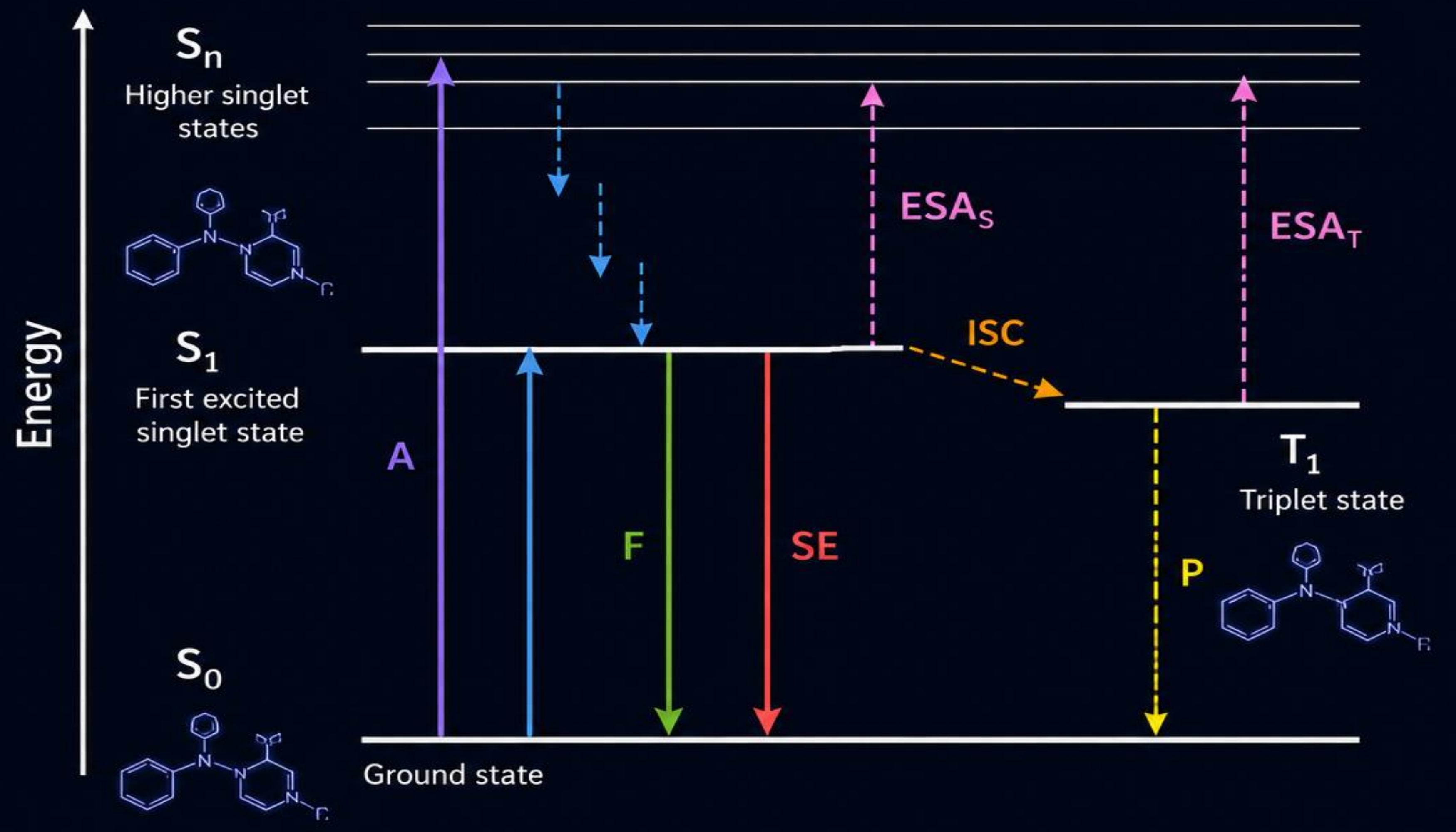


Optical Kerr gate



Electronic Transitions in a Dye Molecule Studied by TAS

Key pathways contributing to pump–probe (transient absorption) signals



- A — Absorption (pump or probe)
- Nonradiative relaxation (vibrational relaxation, internal conversion)
- F — Fluorescence ($S_1 \rightarrow S_0$)
- SE — Stimulated emission ($S_1 \rightarrow S_0$)
- ISC — Intersystem crossing ($S_1 \rightarrow T_1$)
- P — Phosphorescence ($T_1 \rightarrow S_0$)
- ESA — Excited-state absorption (S_1 or $T_1 \rightarrow S_n$)

Contributions to TA signal (ΔA)

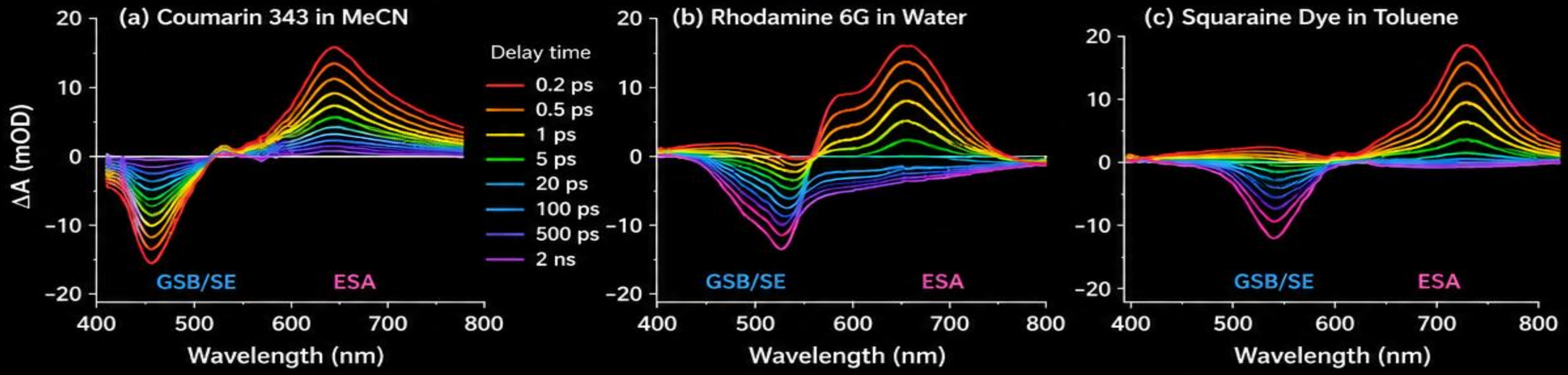
ESA_S	Positive (bleach at λ_{probe})
ESA_T	Positive (absorption)
GSB	Negative (bleach)
SE	Negative (emission)

TAS monitors changes in absorbance (ΔA) as a function of probe wavelength and pump–probe delay time, reflecting population dynamics among these electronic states.

Transient Absorption Spectra and Time Traces of Dye Molecules

Examples of TAS Measurements

Broadband TAS Spectra (ΔA)



How to read TAS spectra

Positive ΔA (above zero):

- Excited State Absorption (ESA)
- Ground State Bleach (GSB)

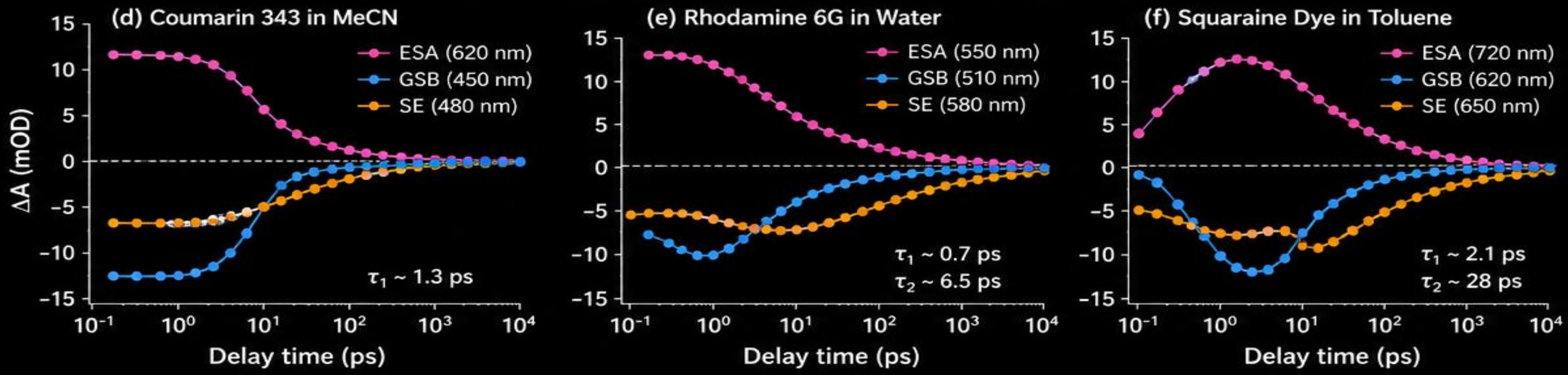
Negative ΔA (below zero):

- Stimulated Emission (SE)

Delay time

Early → Late

Kinetic Time Traces (ΔA vs pump–probe delay time)



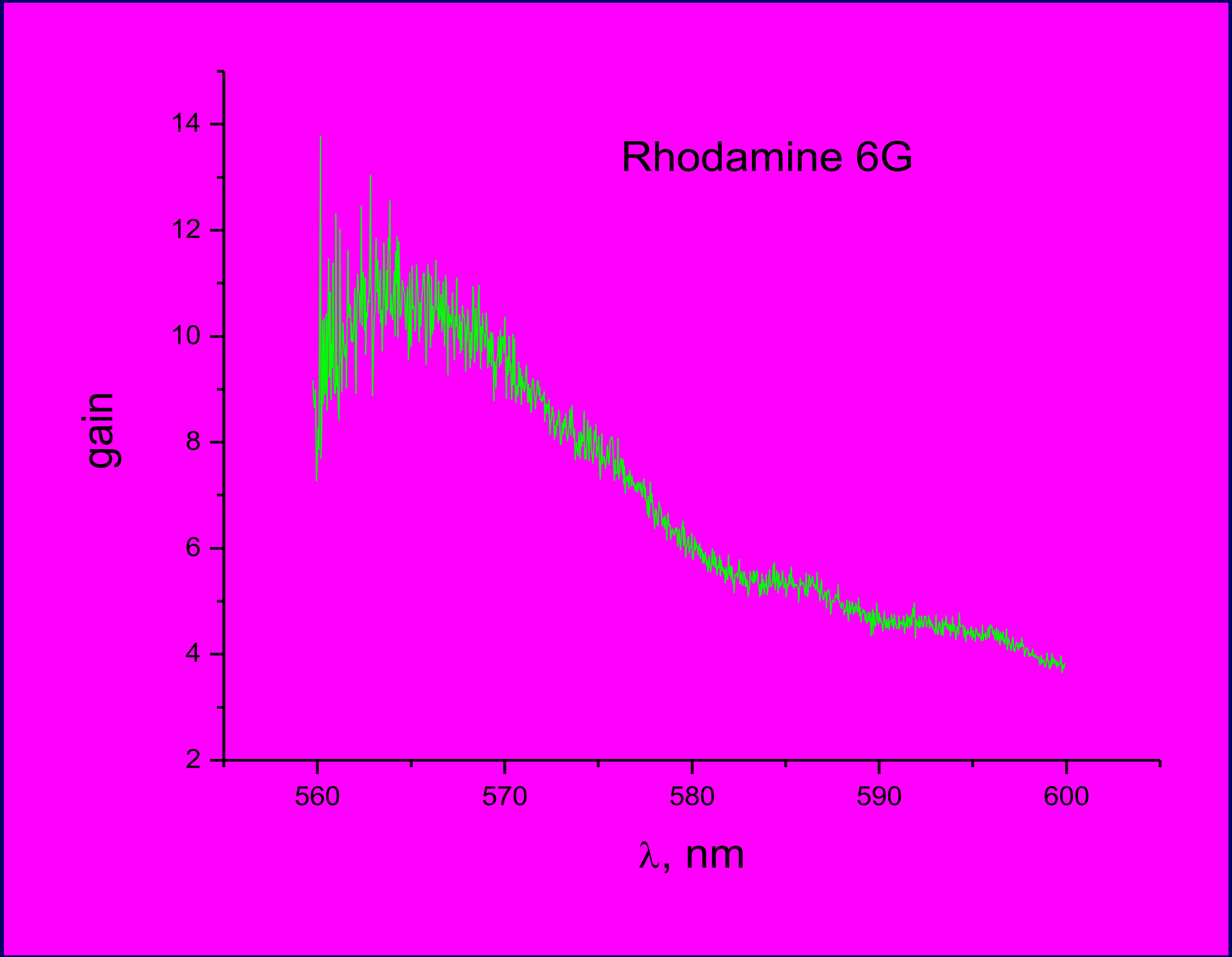
What time traces tell us

- Rise and decay of excited state absorption (ESA)
- Recovery of ground state (GSB)
- Stimulated emission (SE) dynamics
- Extract lifetimes and kinetic models

TAS provides a "molecular movie" of excited state proceses:

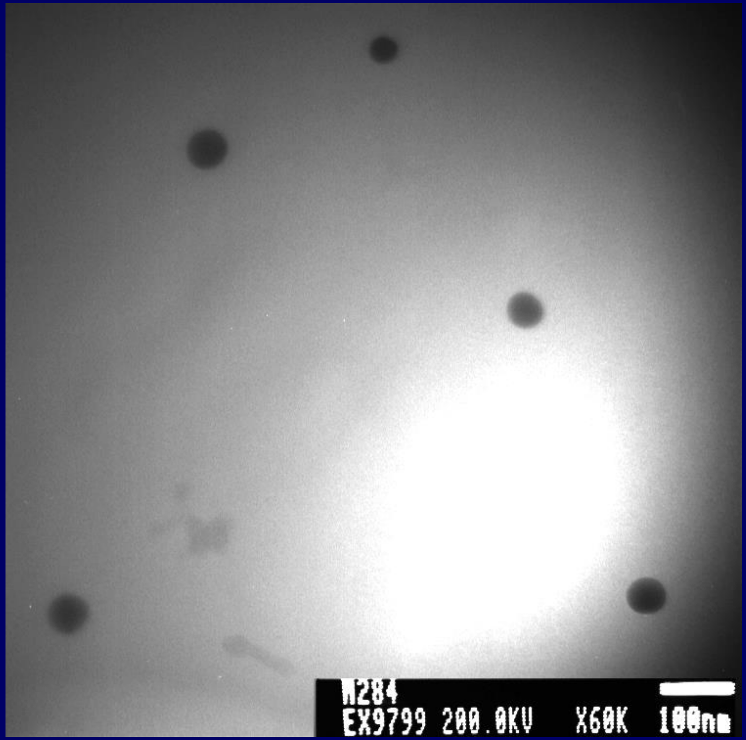
✓ Excitation ✓ Relaxation ✓ Energy transfer ✓ Charge transfer ✓ Nonradiative decay

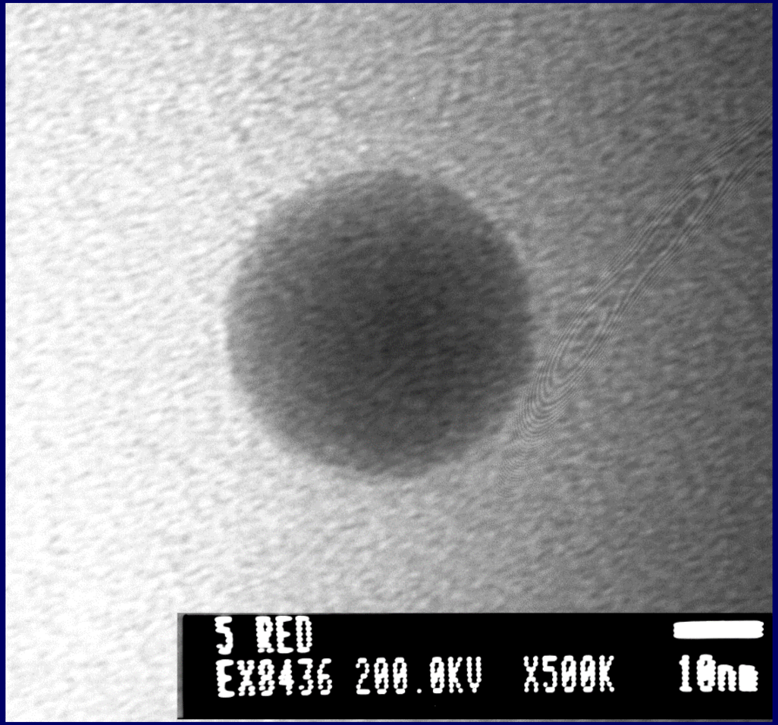
Gain in Rhodamine 6G



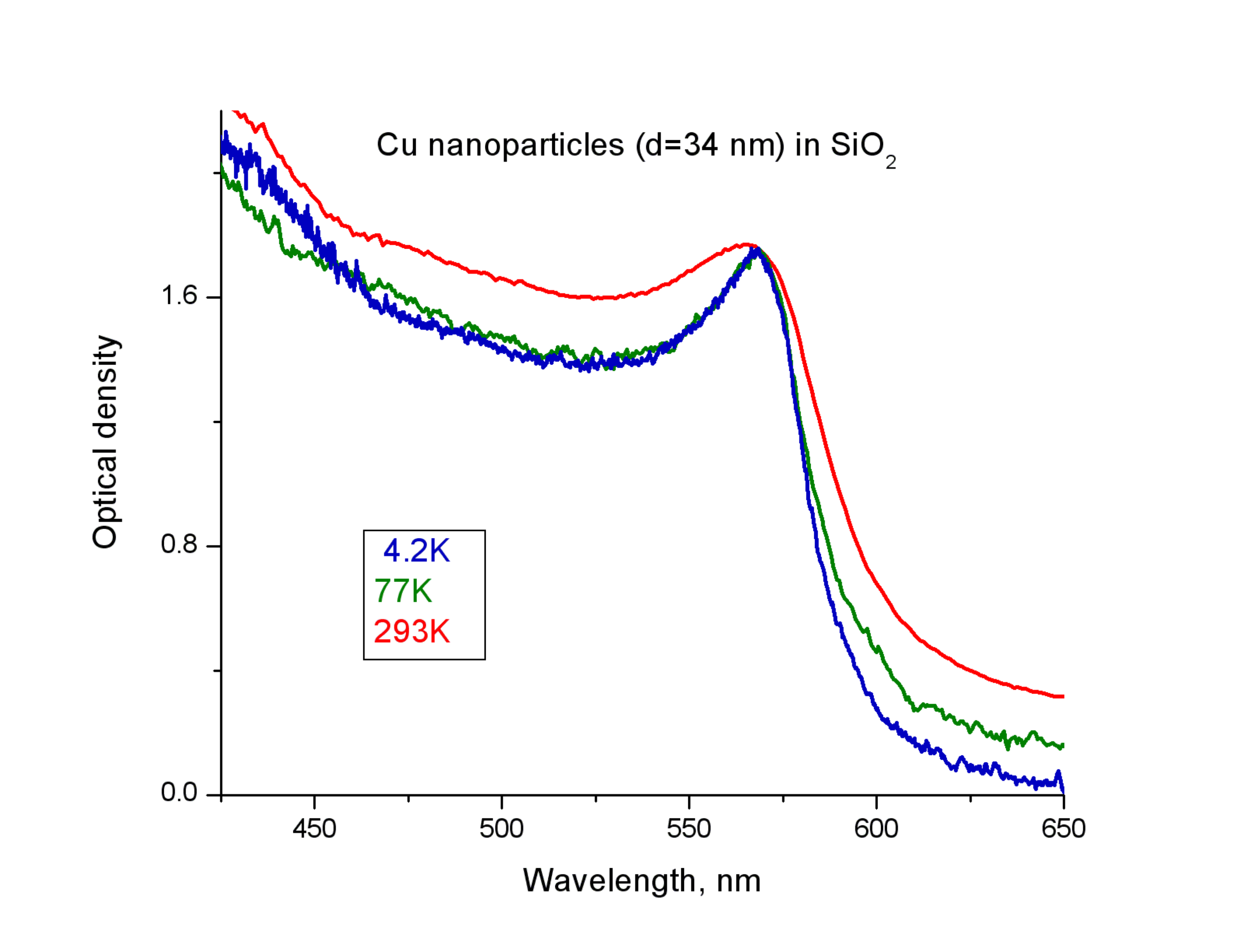
Samples preparation and characterization

- Sol-gel technique based on hydrolysis of tetraethoxysilane
- doping with Cu salt
- addition of silica powder
- gelation, drying
- annealing in air and/or hydrogen

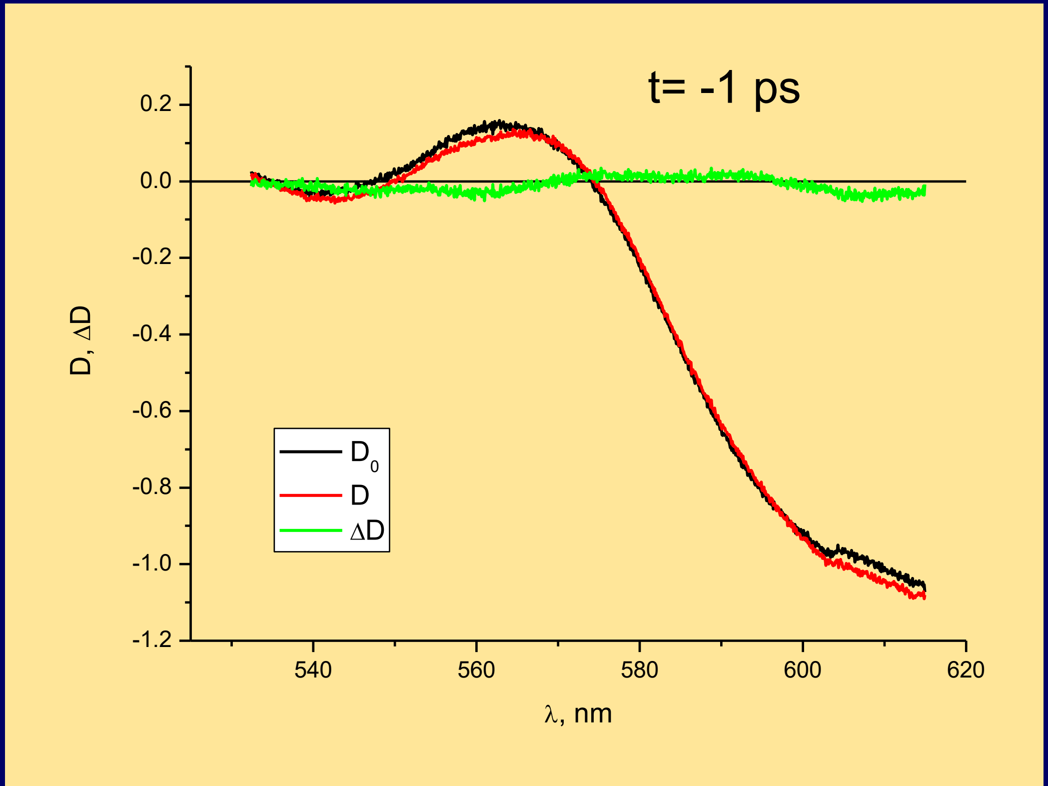


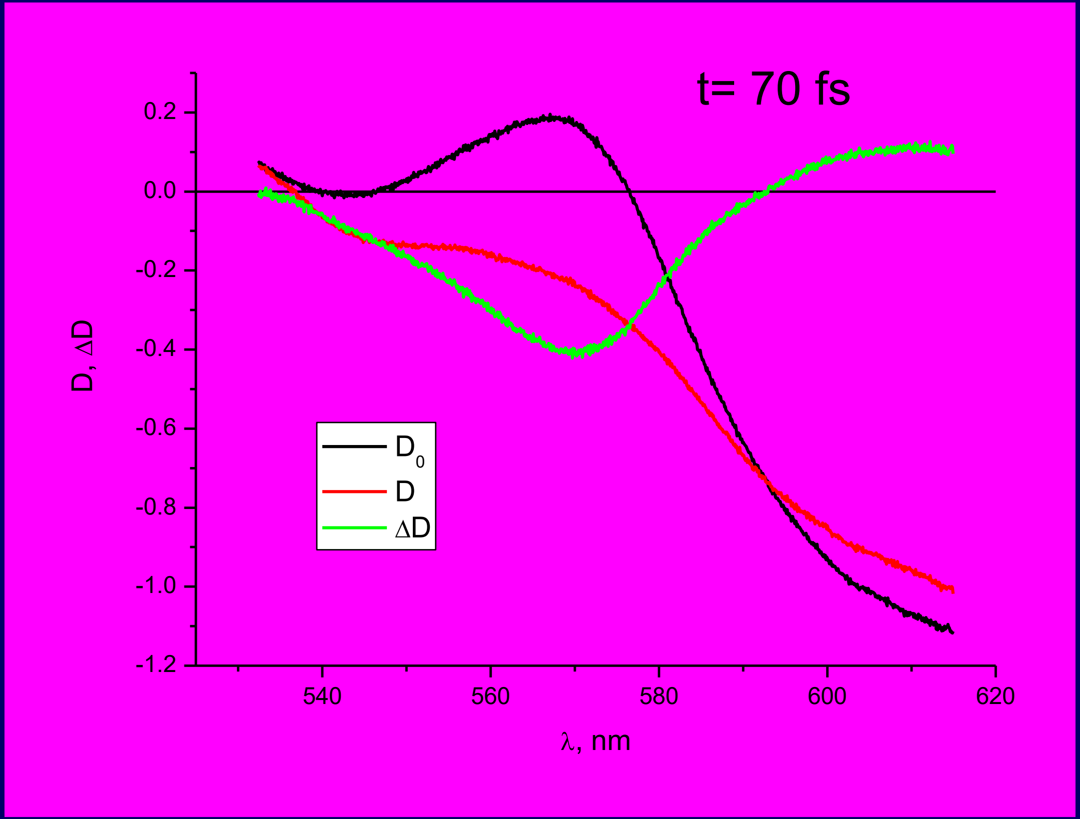


Absorption spectra

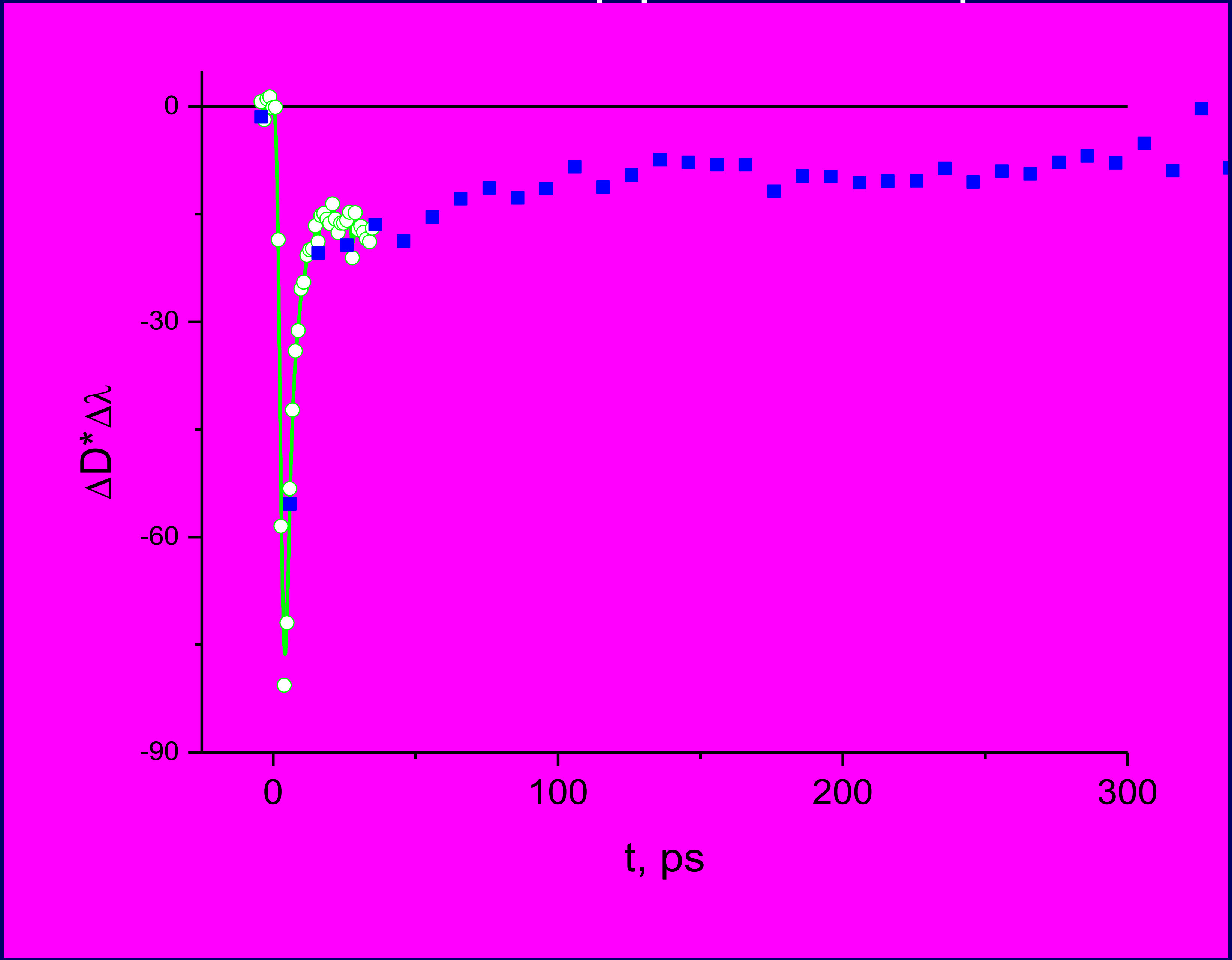


Copper nanoparticles in SiO2 matrix

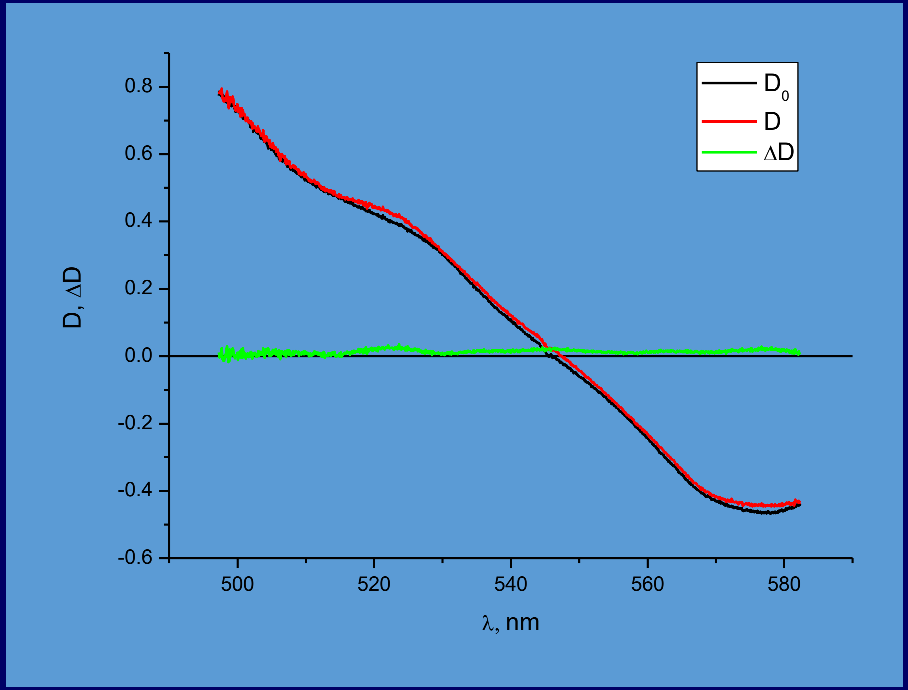




Copper nanoparticles in SiO2 matrix

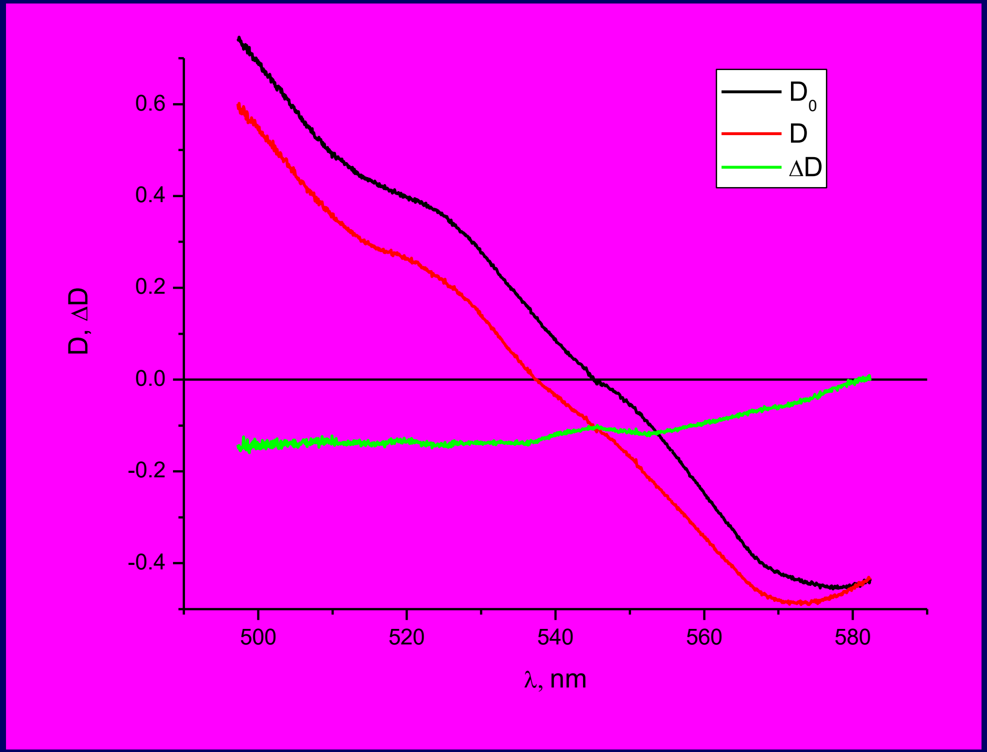


Colloidal solution of CdSe nanoparticles

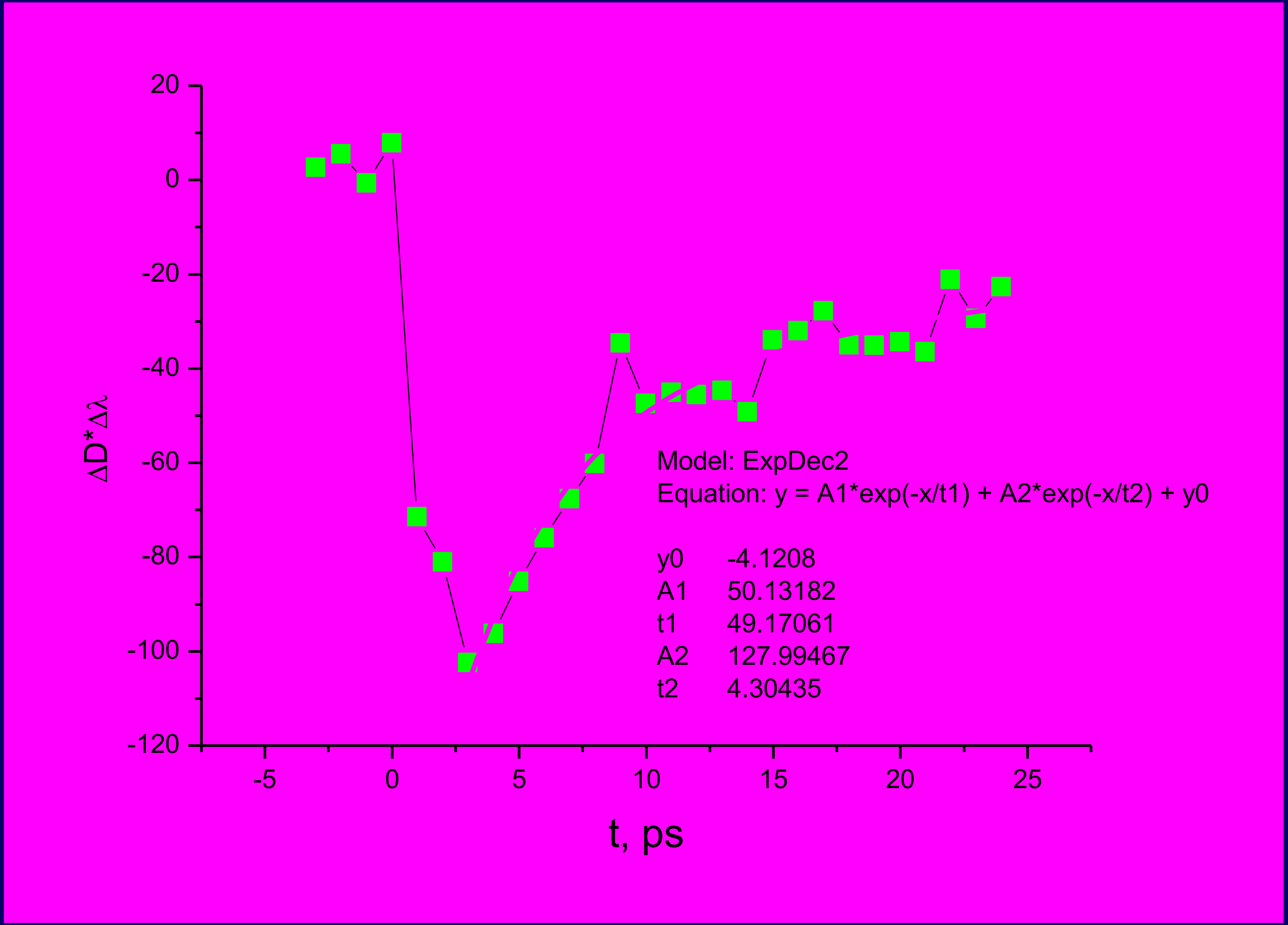


← t= -3 ps

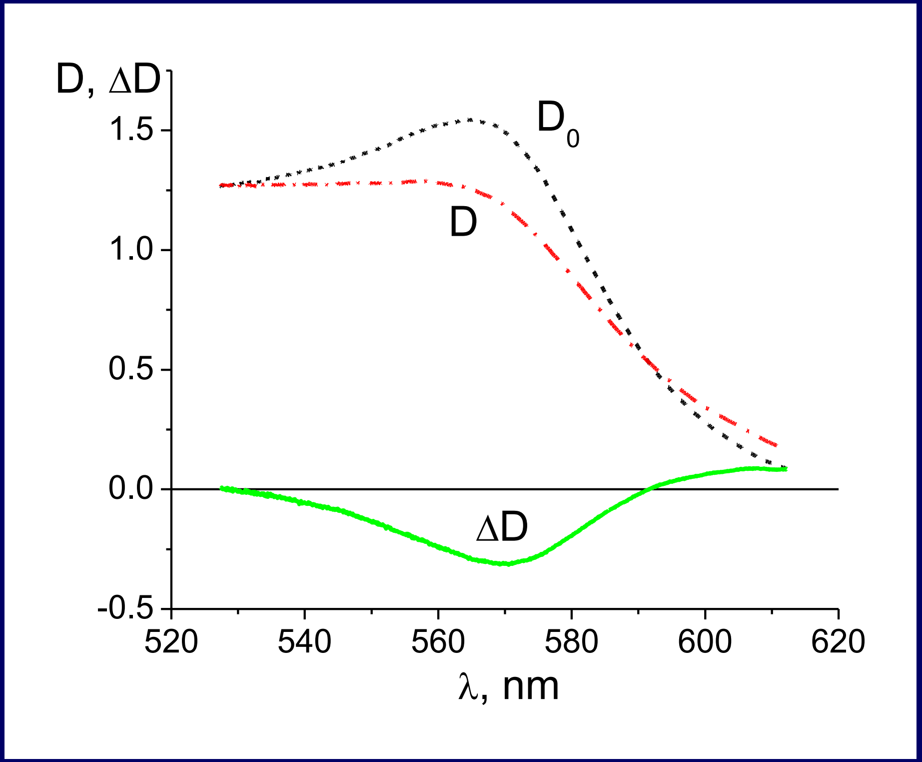
t= 3 ps →

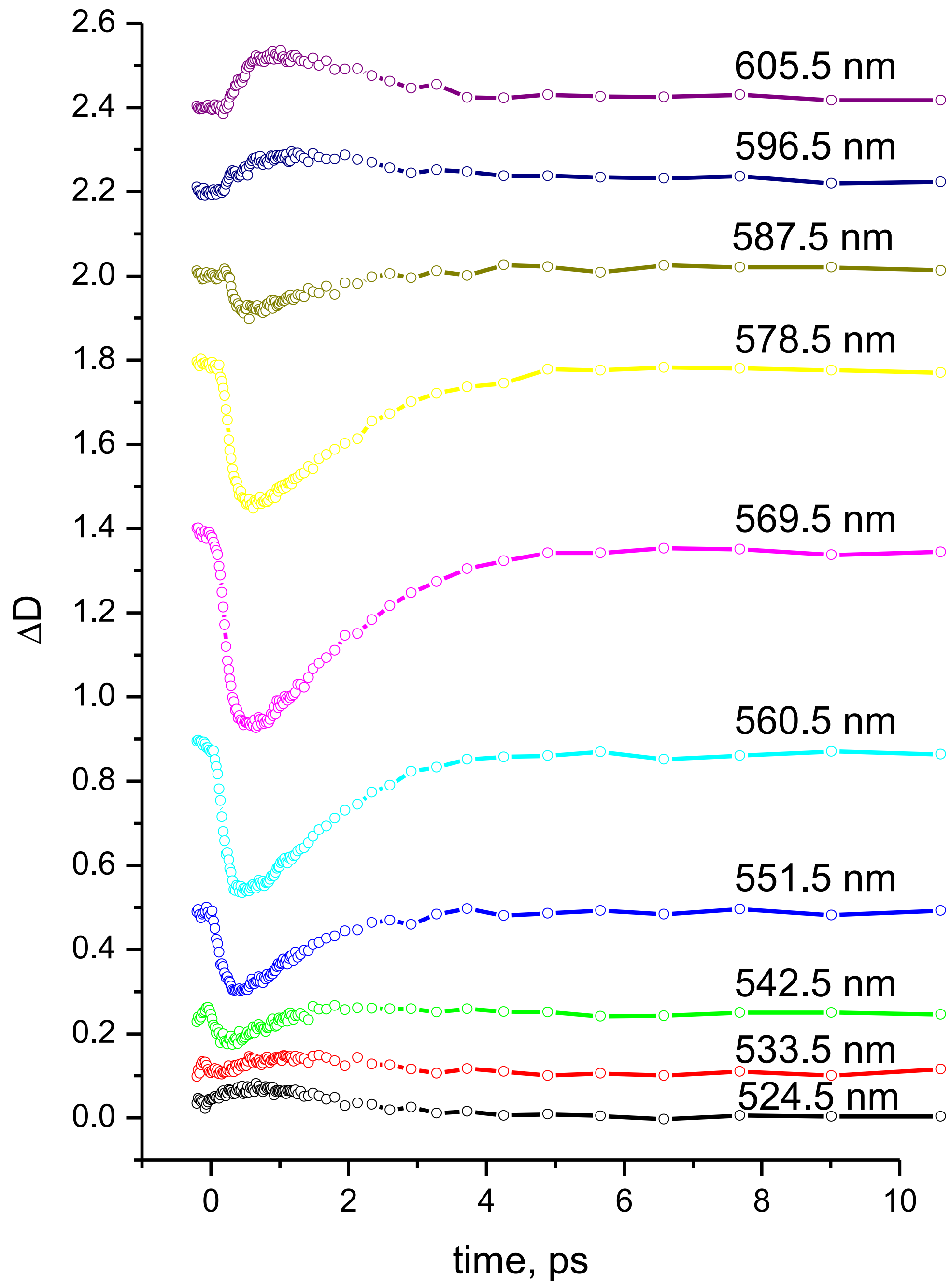


Colloidal solution of CdSe nanoparticles



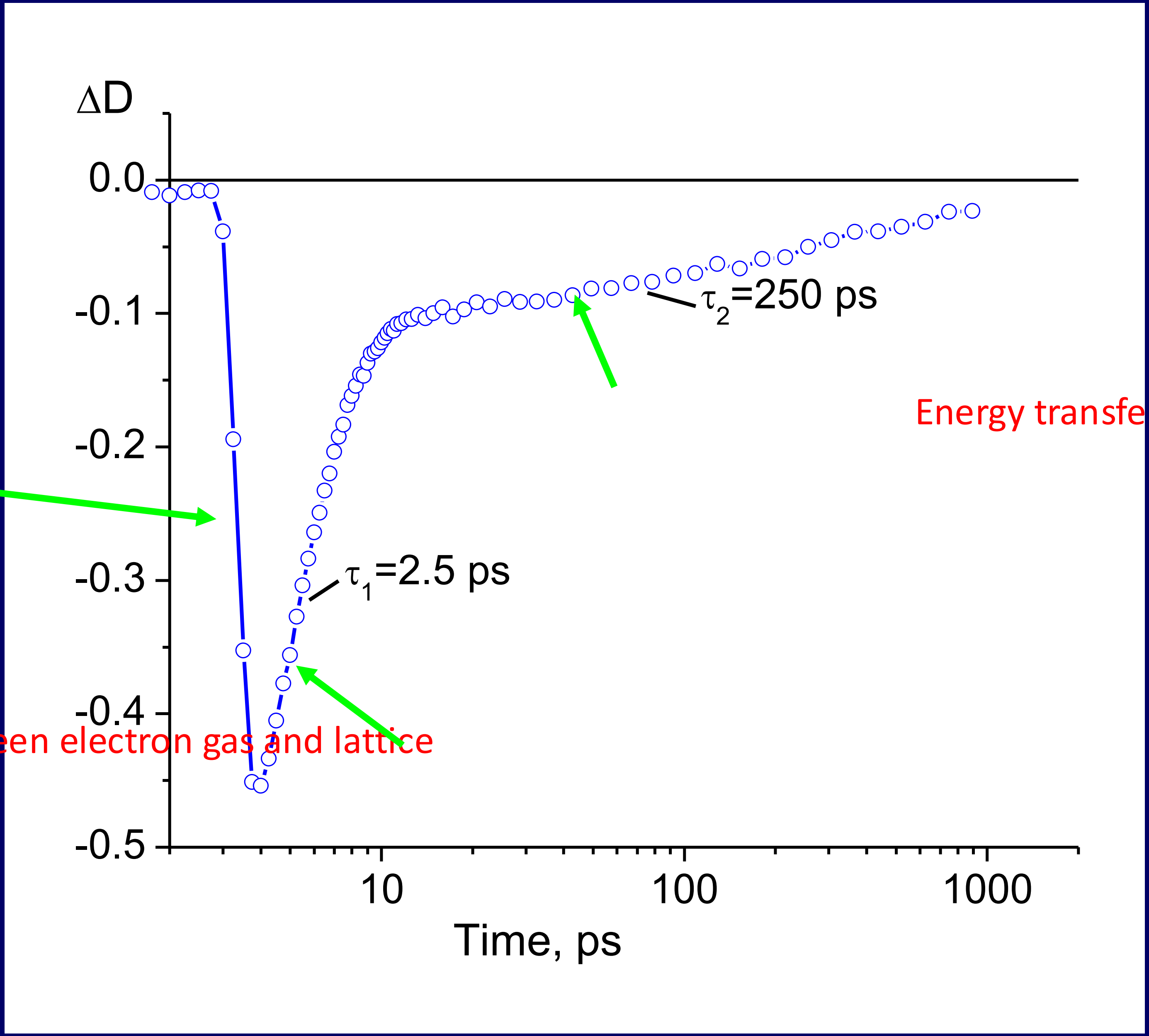
Ultrafast spectroscopy of copper nanoparticles in silica matrix





Kinetics of induced transparency

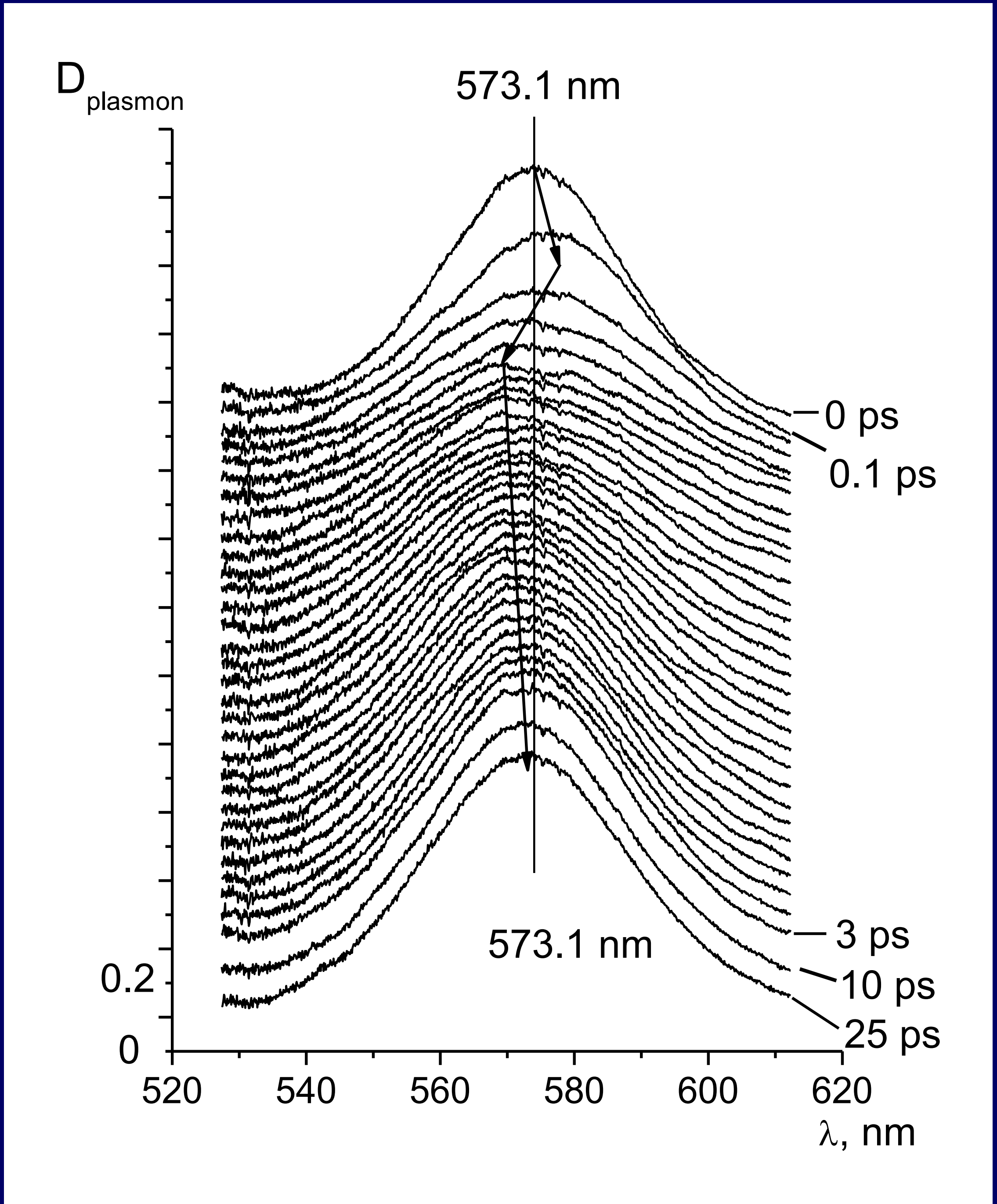
Energy absorption and electron-electron scattering

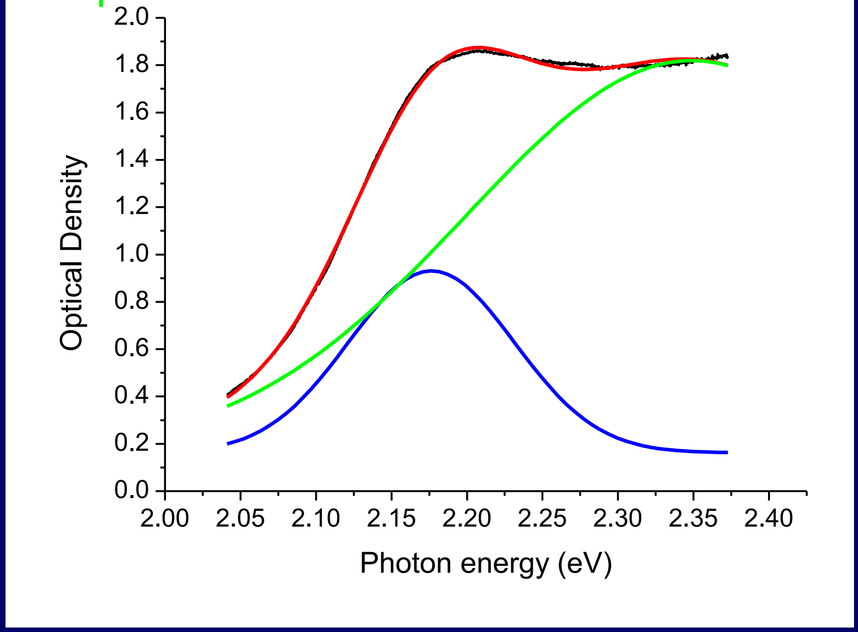


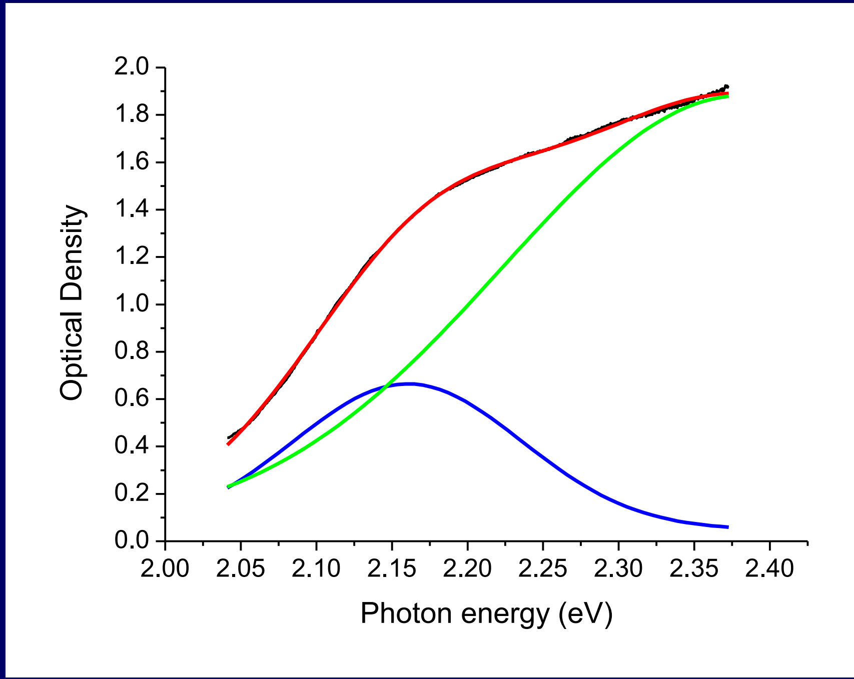
Energy transfer to the matrix

Energy exchange between electron gas and lattice

Plasmon peak parameters



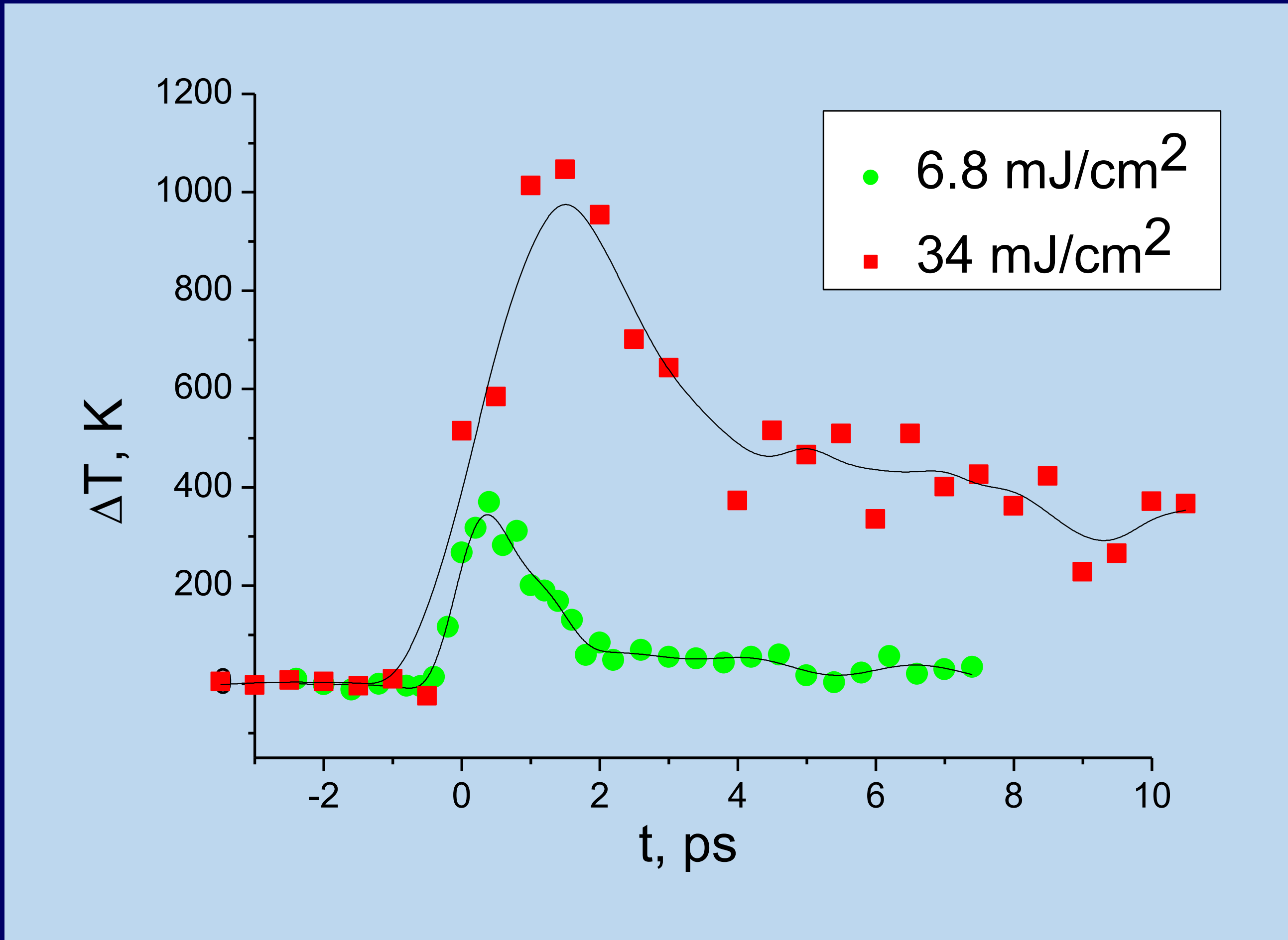




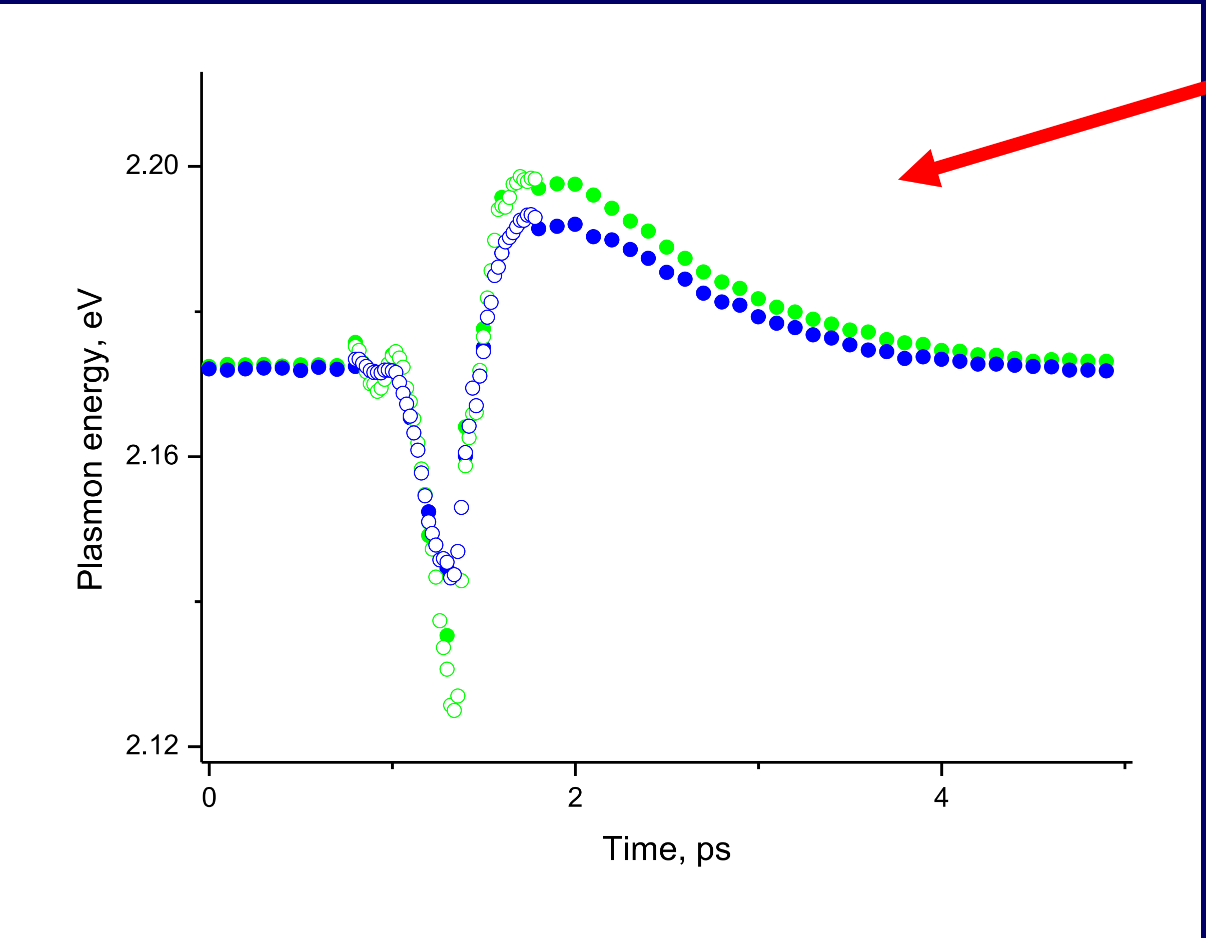
Observed phenomena

- surface plasmon excitation and scattering
- band-to-band transitions (d→p, d→s)
- heating and termalization of electron gas
- electron-lattice relaxation
- excitation of vibrational mode
- energy transfer to matrix

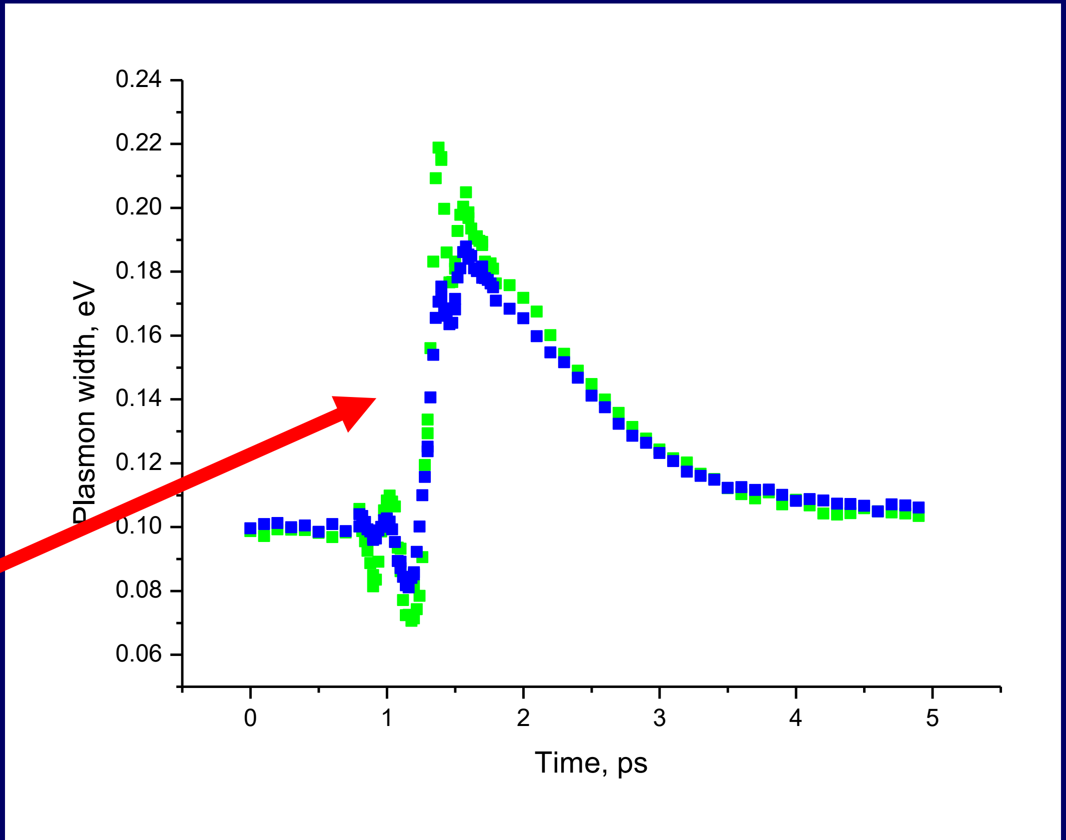
Time evolution of electron gas temperature



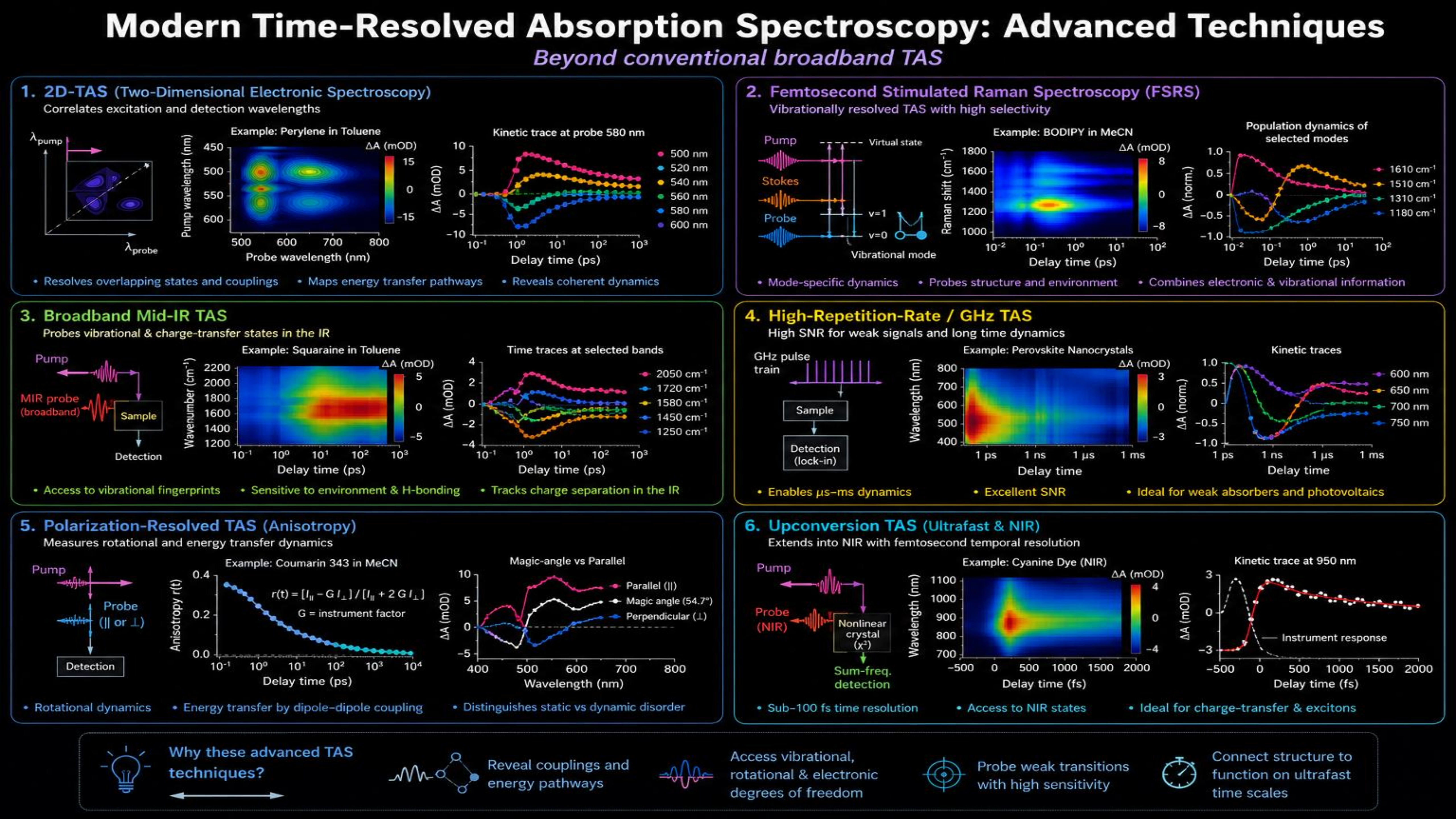
Polarization measurement results



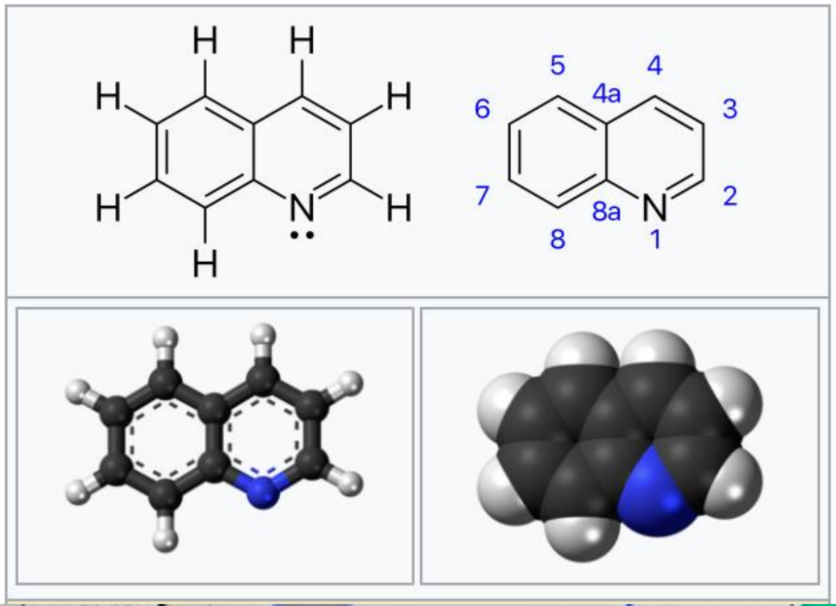
Plasmon peak position

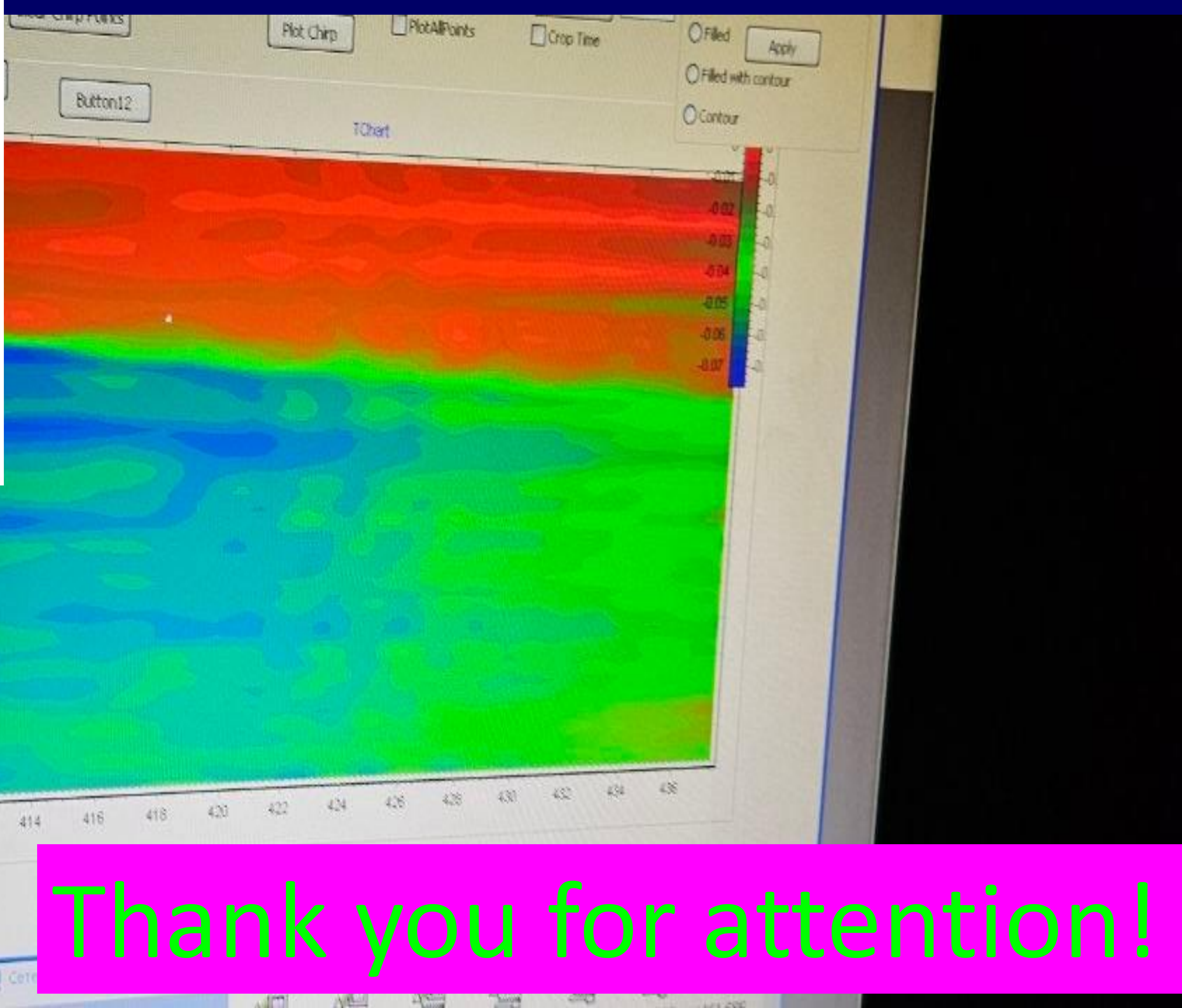


Half-width of the plasmon peak


Modern Time-Resolved Absorption Spectroscopy: Advanced Techniques
Beyond conventional broadband TAS
1. 2D-TAS (Two-Dimensional Electronic Spectroscopy)
Correlates excitation and detection wavelengths
λpump
λprobe
Example: Perylene in Toluene
Pump wavelength (nm)
Probe wavelength (nm)
ΔA (mOD)
Kinetic trace at probe 580 nm
ΔA (mOD)
Delay time (ps)
500 nm
520 nm
540 nm
560 nm
580 nm
600 nm
• Resolves overlapping states and couplings
• Maps energy transfer pathways
• Reveals coherent dynamics
2. Femtosecond Stimulated Raman Spectroscopy (FSRS)
Vibrationally resolved TAS with high selectivity
Pump
Stokes
Probe
Virtual state
v=1
v=0
Vibrational mode
Example: BODIPY in MeCN
Raman shift (cm⁻¹)
Delay time (ps)
ΔA (mOD)
Population dynamics of selected modes
ΔA (norm.)
Delay time (ps)
1610 cm⁻¹
1510 cm⁻¹
1310 cm⁻¹
1180 cm⁻¹
• Mode-specific dynamics
• Probes structure and environment
• Combines electronic & vibrational information
3. Broadband Mid-IR TAS
Probes vibrational & charge-transfer states in the IR
Pump
MIR probe (broadband)
Sample
Detection
Example: Squaraine in Toluene
Wavenumber (cm⁻¹)
Delay time (ps)
ΔA (mOD)
Time traces at selected bands
ΔA (mOD)
Delay time (ps)
2050 cm⁻¹
1720 cm⁻¹
1580 cm⁻¹
1450 cm⁻¹
1250 cm⁻¹
• Access to vibrational fingerprints
• Sensitive to environment & H-bonding
• Tracks charge separation in the IR
4. High-Repetition-Rate / GHz TAS
High SNR for weak signals and long time dynamics
GHz pulse train
Sample
Detection (lock-in)
Example: Perovskite Nanocrystals
Wavelength (nm)
Delay time
ΔA (mOD)
Kinetic traces
ΔA (norm.)
Delay time
600 nm
650 nm
700 nm
750 nm
• Enables μs–ms dynamics
• Excellent SNR
• Ideal for weak absorbers and photovoltaics
5. Polarization-Resolved TAS (Anisotropy)
Measures rotational and energy transfer dynamics
Pump
Probe (|| or ⊥)
Detection
Example: Coumarin 343 in MeCN
$r(t) = [I_{\parallel} - G I_{\perp}] / [I_{\parallel} + 2 G I_{\perp}]$
G = instrument factor
Anisotropy r(t)
Delay time (ps)
Magic-angle vs Parallel
ΔA (mOD)
Wavelength (nm)
Parallel (||)
Magic angle (54.7°)
Perpendicular (⊥)
• Rotational dynamics
• Energy transfer by dipole–dipole coupling
• Distinguishes static vs dynamic disorder
6. Upconversion TAS (Ultrafast & NIR)
Extends into NIR with femtosecond temporal resolution
Pump
Probe (NIR)
Nonlinear crystal (χ^2)
Sum-freq. detection
Example: Cyanine Dye (NIR)
Wavelength (nm)
Delay time (fs)
ΔA (mOD)
Kinetic trace at 950 nm
ΔA (mOD)
Instrument response
Delay time (fs)
• Sub-100 fs time resolution
• Access to NIR states
• Ideal for charge-transfer & excitons
Why these advanced TAS techniques?
Reveal couplings and energy pathways
Access vibrational, rotational & electronic degrees of freedom
Probe weak transitions with high sensitivity
Connect structure to function on ultrafast time scales

Quinoline[1]





Thank you for attention!