Detection Systems at LEAF

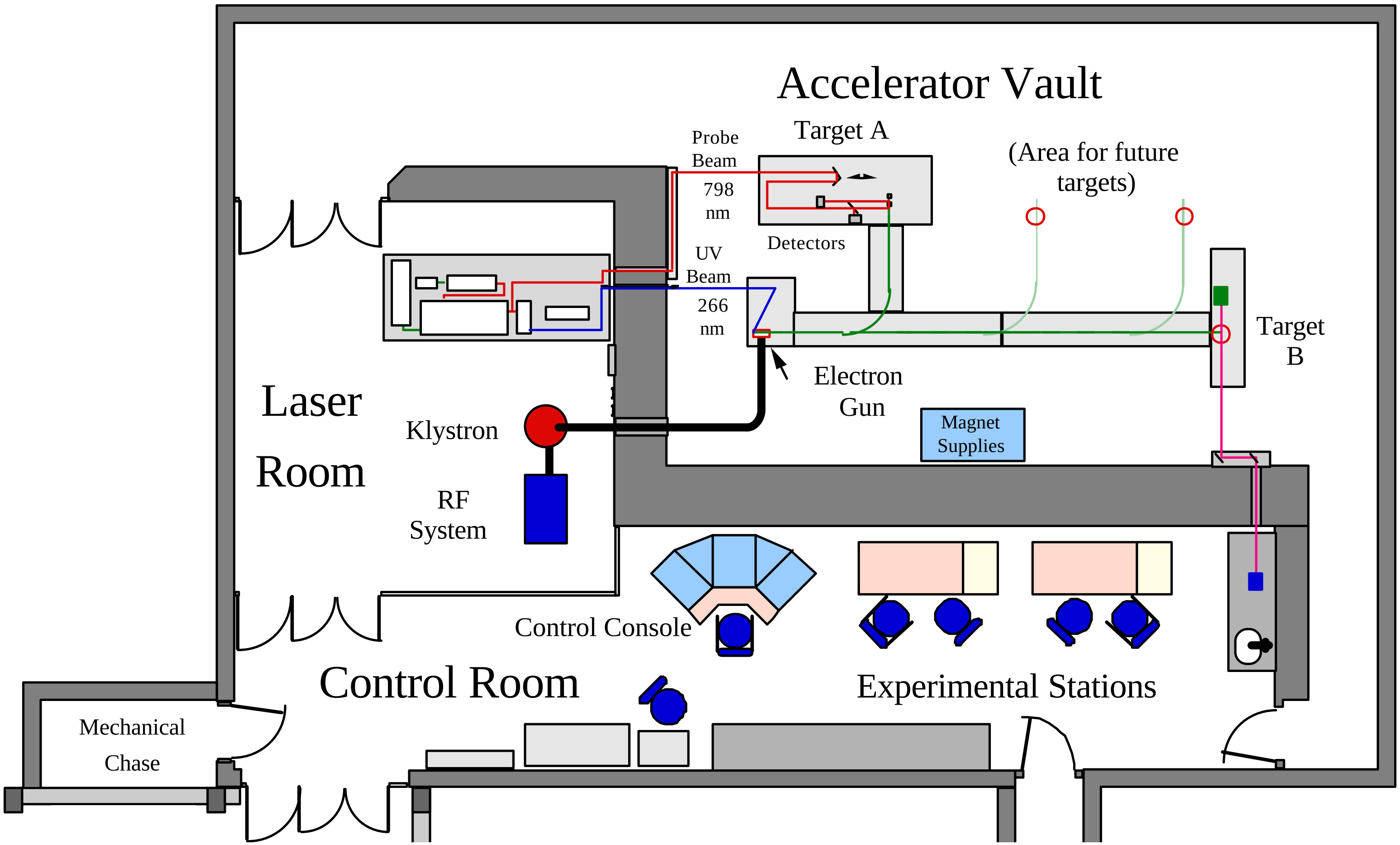
International Symposium on Ultrafast Accelerators for Pulse Radiolysis – June 26, 2004.

Andrew R. Cook

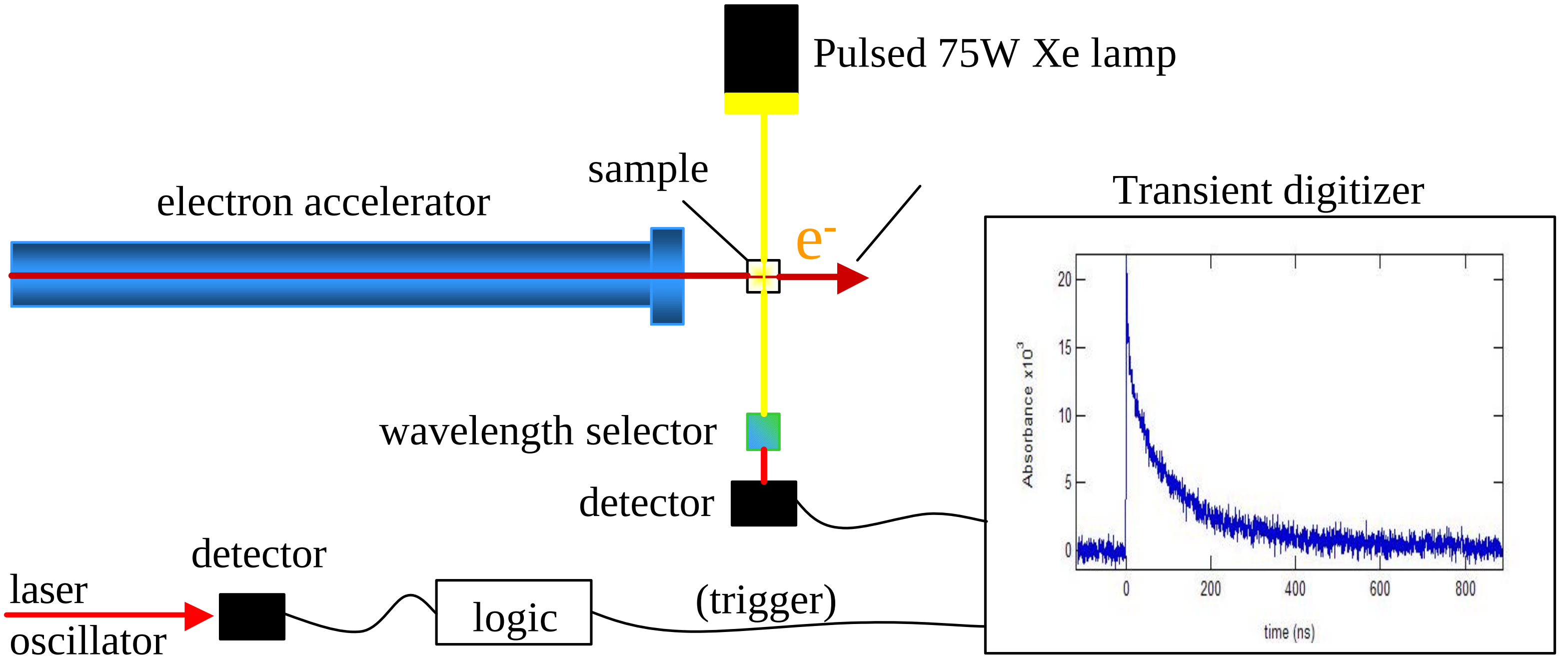
LEAF Detection System Overview

Flashlamp/Digitizer	Operational
Pulse-Probe	Operational
High Pressure	Operational
Transient Conductivity	Operational
Pulse-Pump-Probe	In development: 2004
Ultrafast Single-Shot	In development: 2004-2005

LEAF Facility Layout



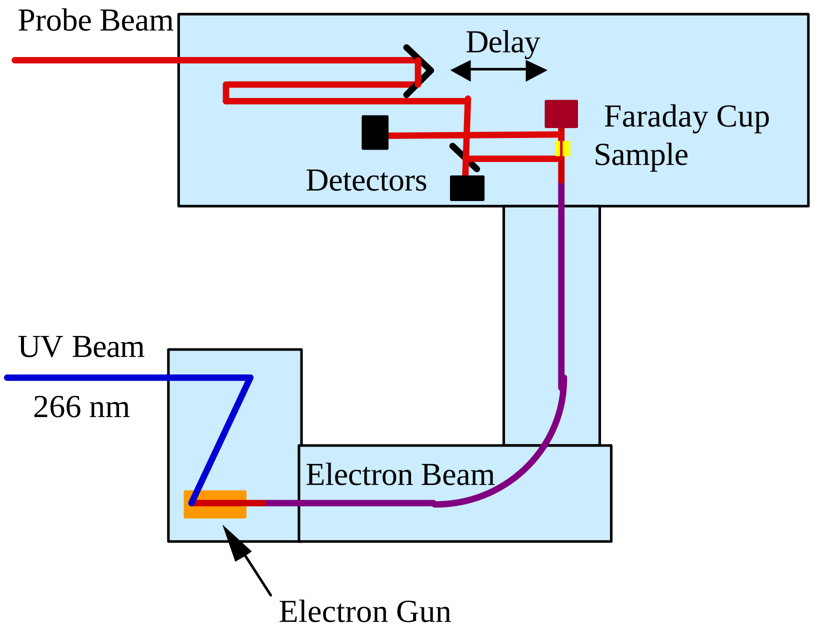
Flashlamp/Transient Digitizer Detection

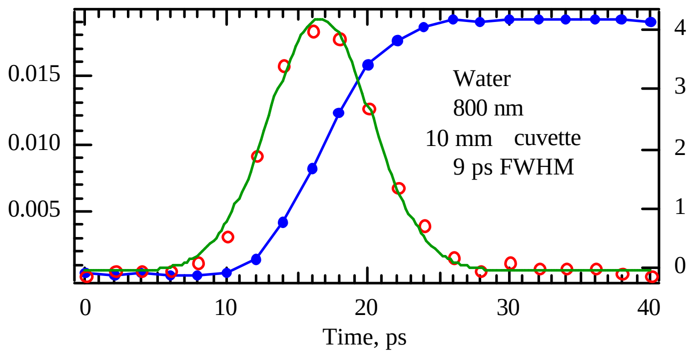


Characteristics:

- Time resolution ~120 ps
- 200 – 2500 nm
- $[e\text{-}]_{aq}$ ~ 4-6 μM (8-10 nC)
- Low jitter trigger
- Temperature control
- High stability lamp pulser
- Selection of detectors, digitizers
- Low repetition rate (SS)
- FCUP dosemetry
- Robot sample automation
- Acquisition: VAX ? LabView

Pulse – Probe Detection





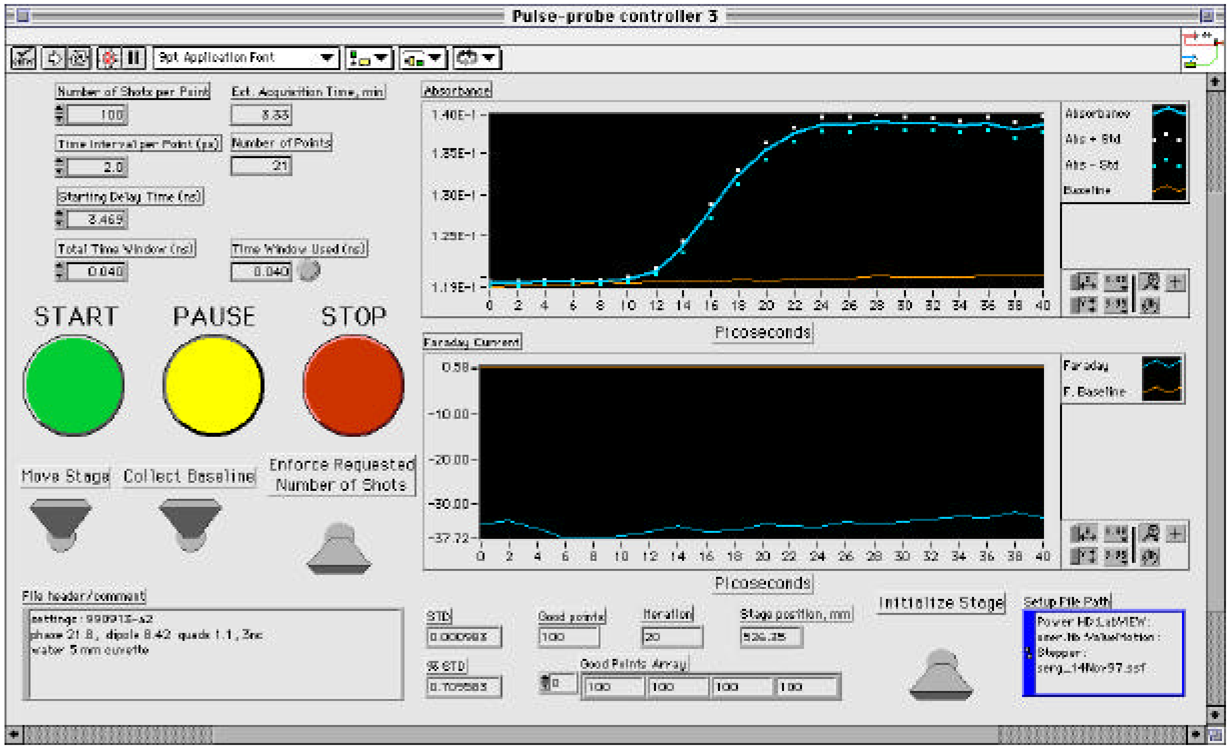
Key Characteristics

- 7 ps time resolution (5 mm cell)
- Synced 800 nm, OPA probe 240-1700 nm (2400 nm)
- Acquisition: digitizer as a boxcar
- Sample flow systems
- $[e\text{-}]_{aq}$ ~ 9 µM max (8 nC) ~ 140 mOD. 2-3X higher signal due to moving sample closer to beam window (0.5 mil foil)

Planned Enhancements

- Improve S/N
  - Explore additional sample arrangement: 2 – 4X greater signals?
  - Balanced detectors
  - Laser beam transport and mode – drift; aperture; imaging ?
  - kHz front end ?
- Make OPA use more routine
- Automated sample changers
- Spectral array detection

Pulse – Probe Software Features

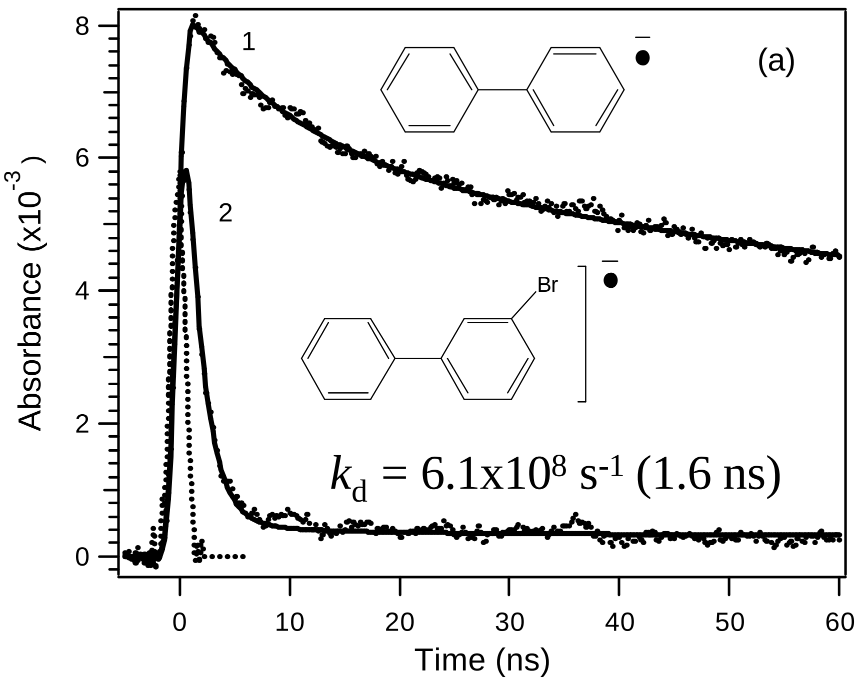


- Interleaved signal and baseline shots
- Faraday cup correction – shot by shot
- Dose depletion: ignore first 5 electron pulses
- Dose stability: constant time between acquisitions
- Point rejection: FCUP and laser intensity
- Coupled to an Igor fitting/analysis suite

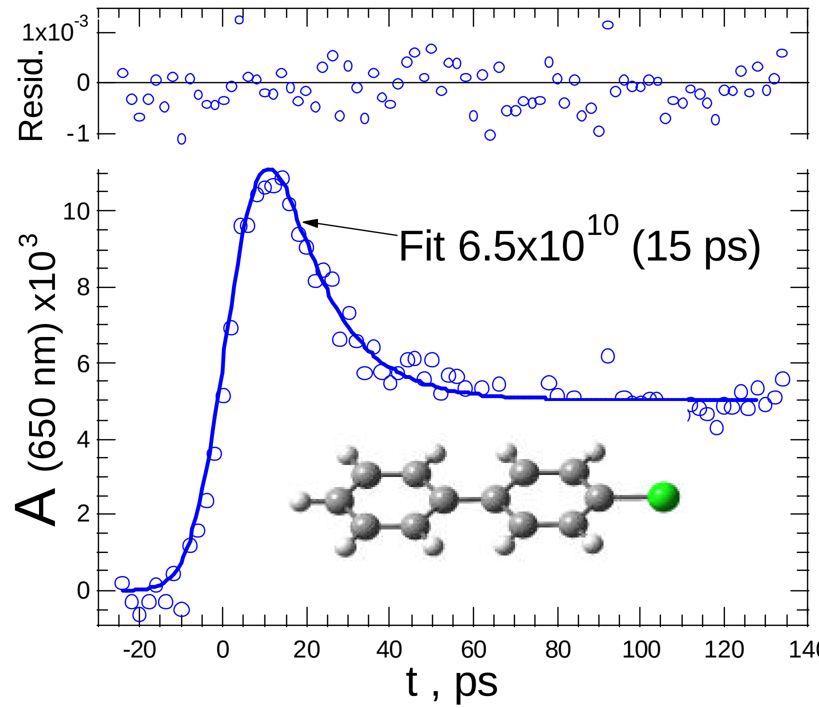
Dissociation of Aryl Halides in Me_4P

$$RX + e^- \xrightarrow{ET} \left(RX^{-\bullet}\right) \xrightarrow{BB} R^\bullet + X^-$$

10 mM Bp and 30 mM 3BrBp (1.7M THF added as cation scavenger) @650nm

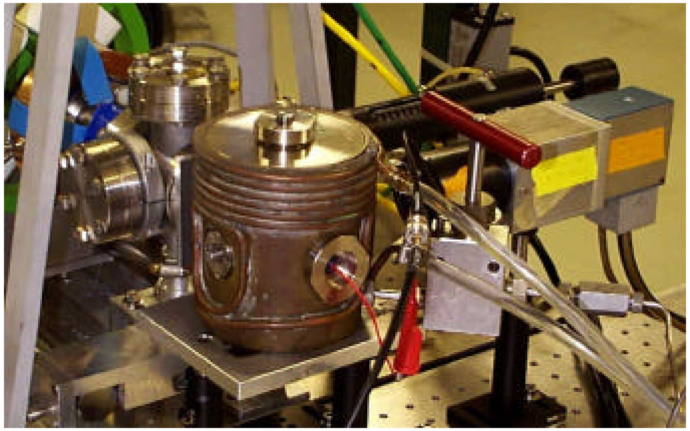


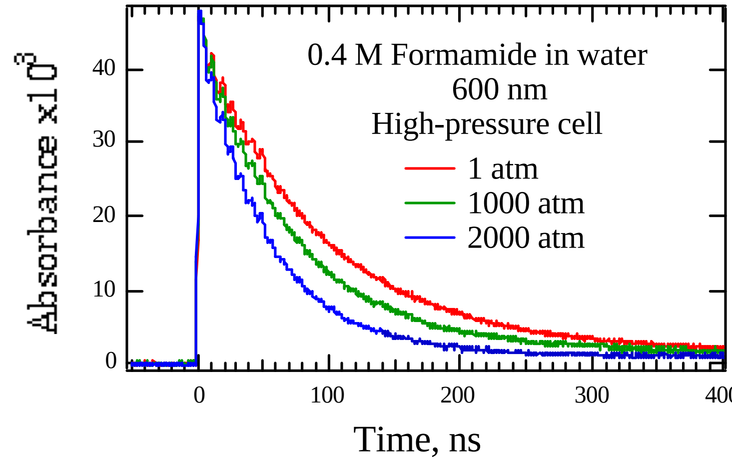
4-BrBiphenyl

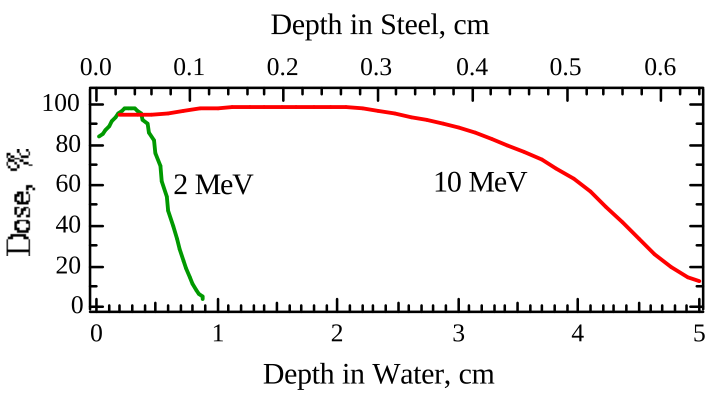


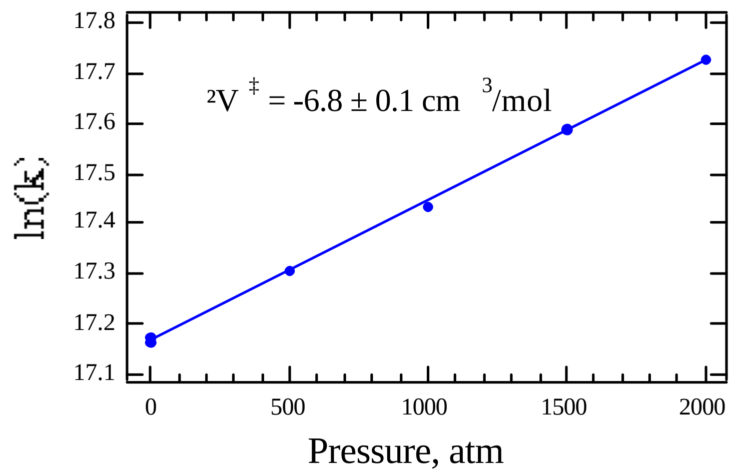
N. Takeda, P.V. Poliakov, A.R. Cook, J.R. Miller,
J. Am. Chem. Soc., 126(13), 4301 (2004).

High-Pressure Radiolysis at LEAF







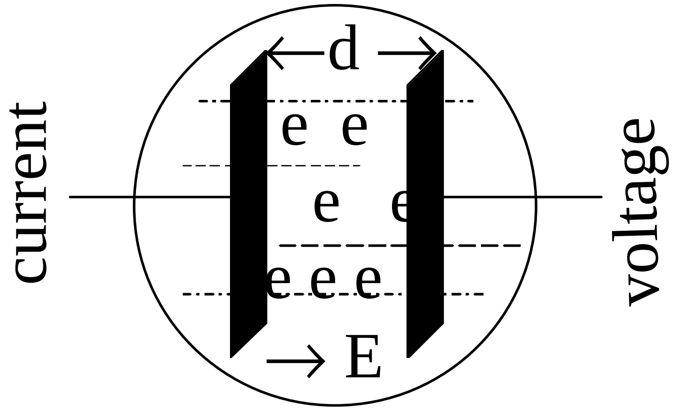


9 MeV gives Uniform penetration

1 - 2000 atm

Temperature controlled

J.F. Wishart, R. van Eldik, R. Holroyd

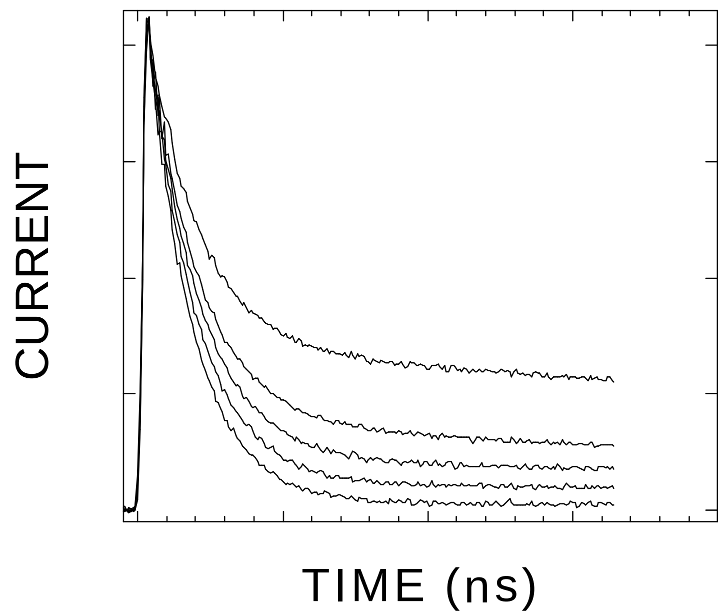


LEAF X-RAY CONDUCTIVITY TECHNIQUE
EG&G preamp 5185
rise time 2 ns

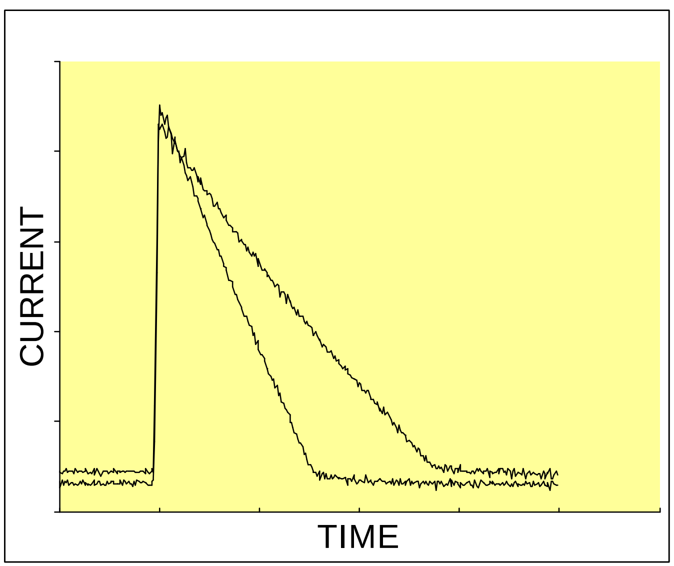
B ELECTRON ATTACHMENT

C ELECTRON EQUILIBRIA

$e^- + CO_2$? CO_2

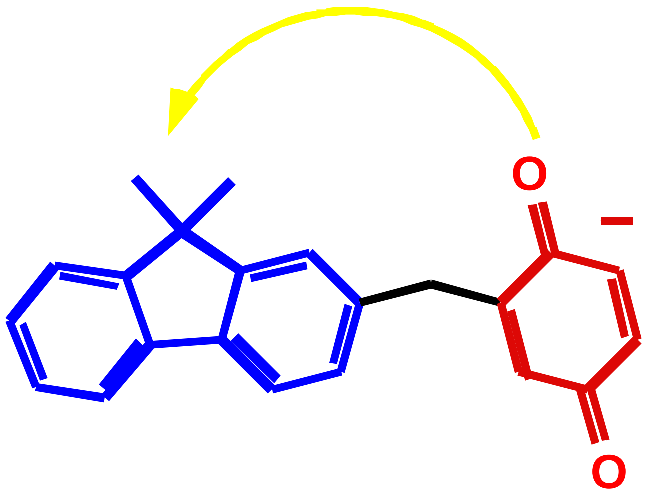


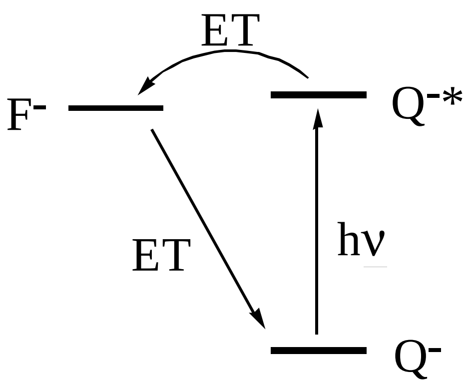
A ELECTRON or ION MOBILITIES



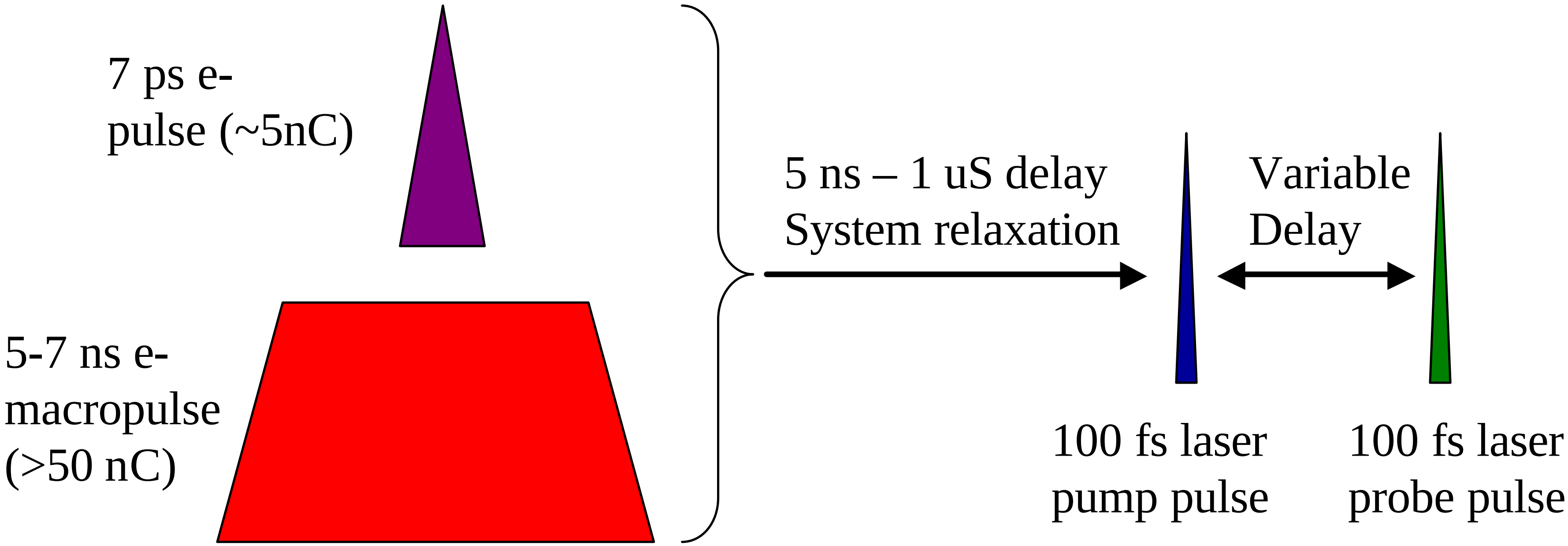
Use excited states of radical ions to gain access to previously unmeasurable ET rates

- Short distances and large electronic coupling, effects of: solvent motions, molecular symmetry, and small reorganization energies
- Maintain desirable characteristics of radiolysis: 1 charge
- Excited states relatively unknown
  - Low energy
  - Short lifetimes
  - Luminescence rare
  - Clean preparation difficult
  - Understand structure and decay mechanisms
- Lifetimes < 1 ps may be sufficient to drive useful chemistry



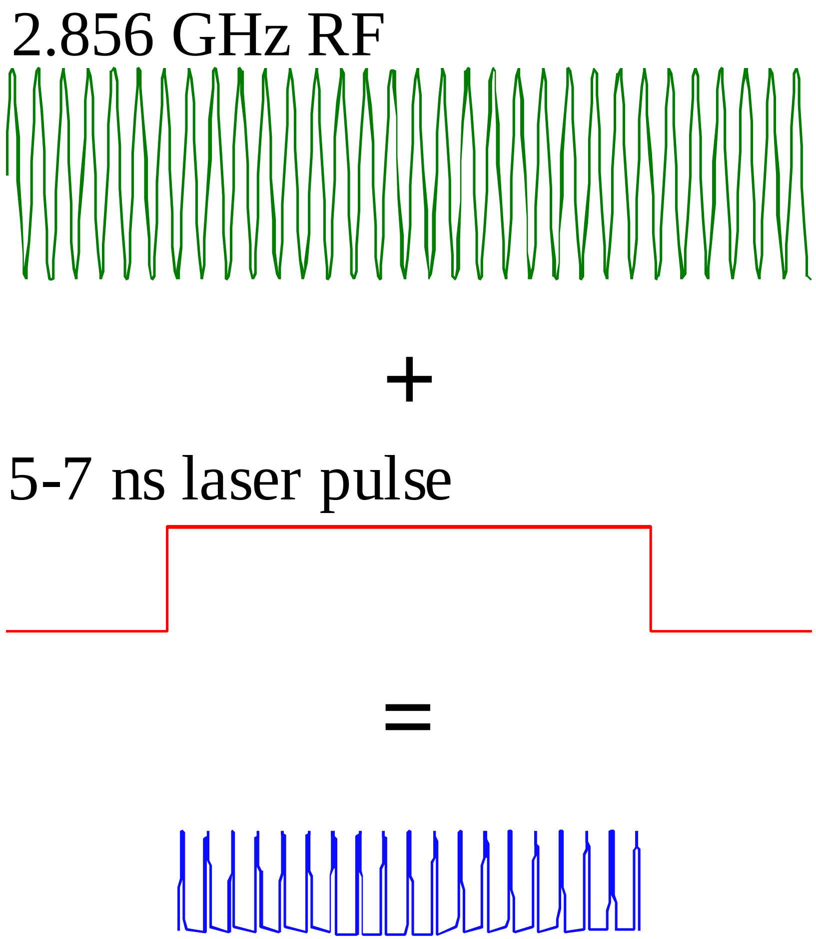


Pulse-Pump-Probe Experiment



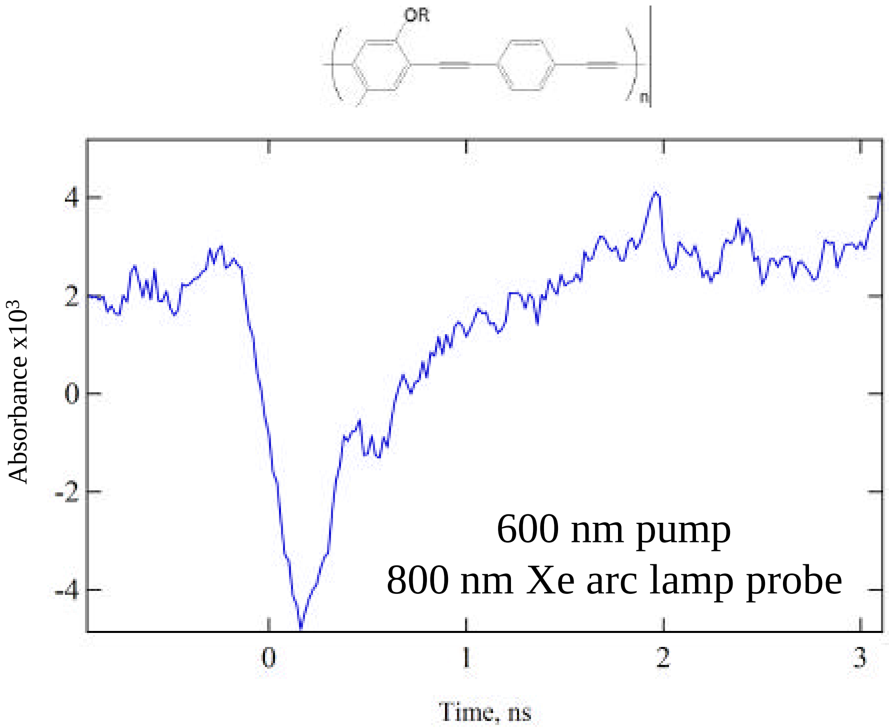
Increase time resolution 100x for systems utilizing excited states of species formed by radiolysis

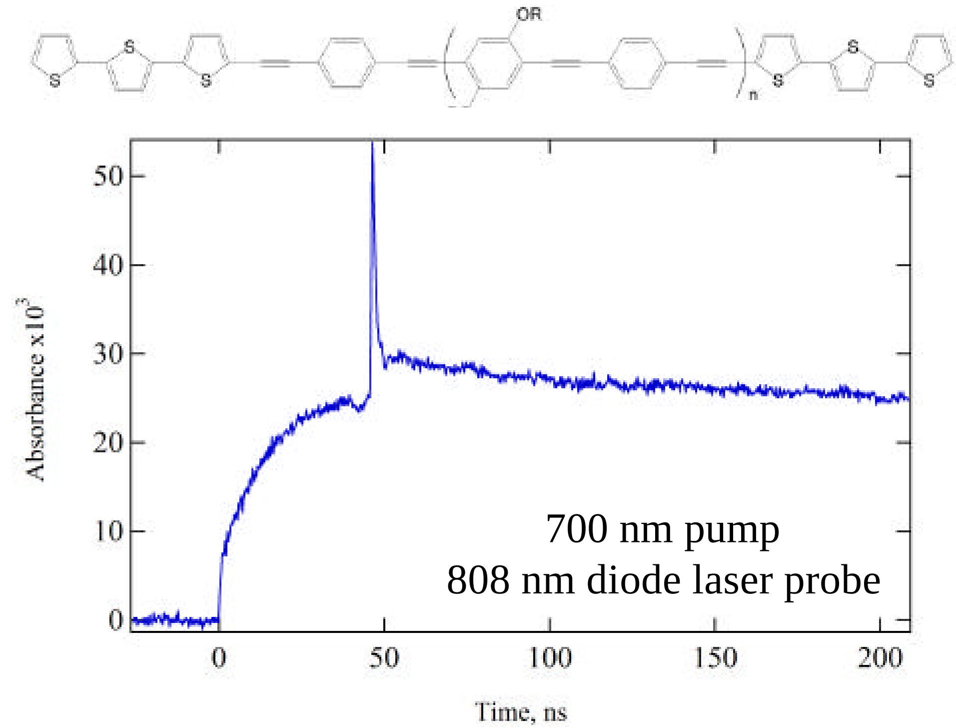
Large Charges in Electron Macropulses



- Produced a train of 15-20 short electron pulses with Nd:YAG 266 nm laser pulse
- 100 nc / macropulse produced at cathode; more may be possible
- First attempt yielded ~50 nc at sample; with optimization improved transport is expected.

Pulse-Pump-Digitizer Probe



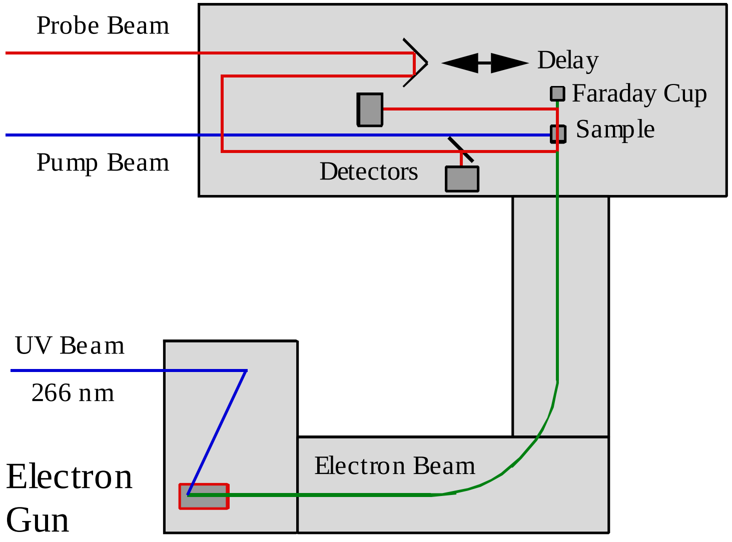


- Triplet species produced by radiolysis in toluene
- Higher energy excited state formed by photo excitation
- Longer transient due to two photon absorption by the sample
- Pulsed diode lasers as probes: lots of light, small spots, fast VIS/NIR detectors

A. Funston, A.R. Cook, J.R. Miller, E. Silverman, K. Schanze

Plan for Pulse-Pump-Probe Detection

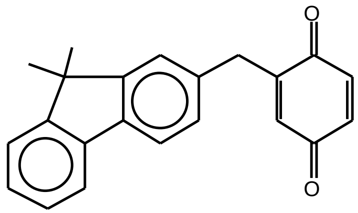
* 100 fs time resolution *

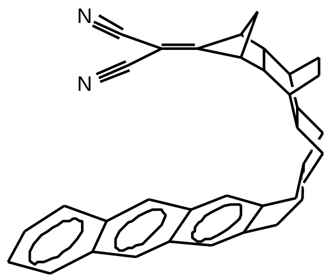


Major Components

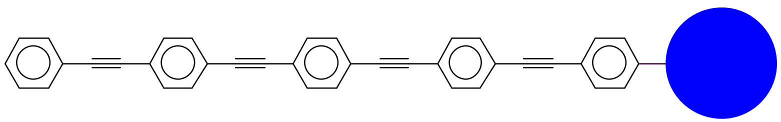
- Integrate with existing pulse-probe system; adding to existing detection system
- High charge electron macro pulses will allow for arbitrary pulse-pump delay
- Possibly build additional Ti:Sapphire amplifier stage
- High power OPA for excitation
- Existing OPA or white light continuum probe

Need for ultrafast single shot detection methods





- Fast electron transfer
- Through solvent ET
- Molecular wires

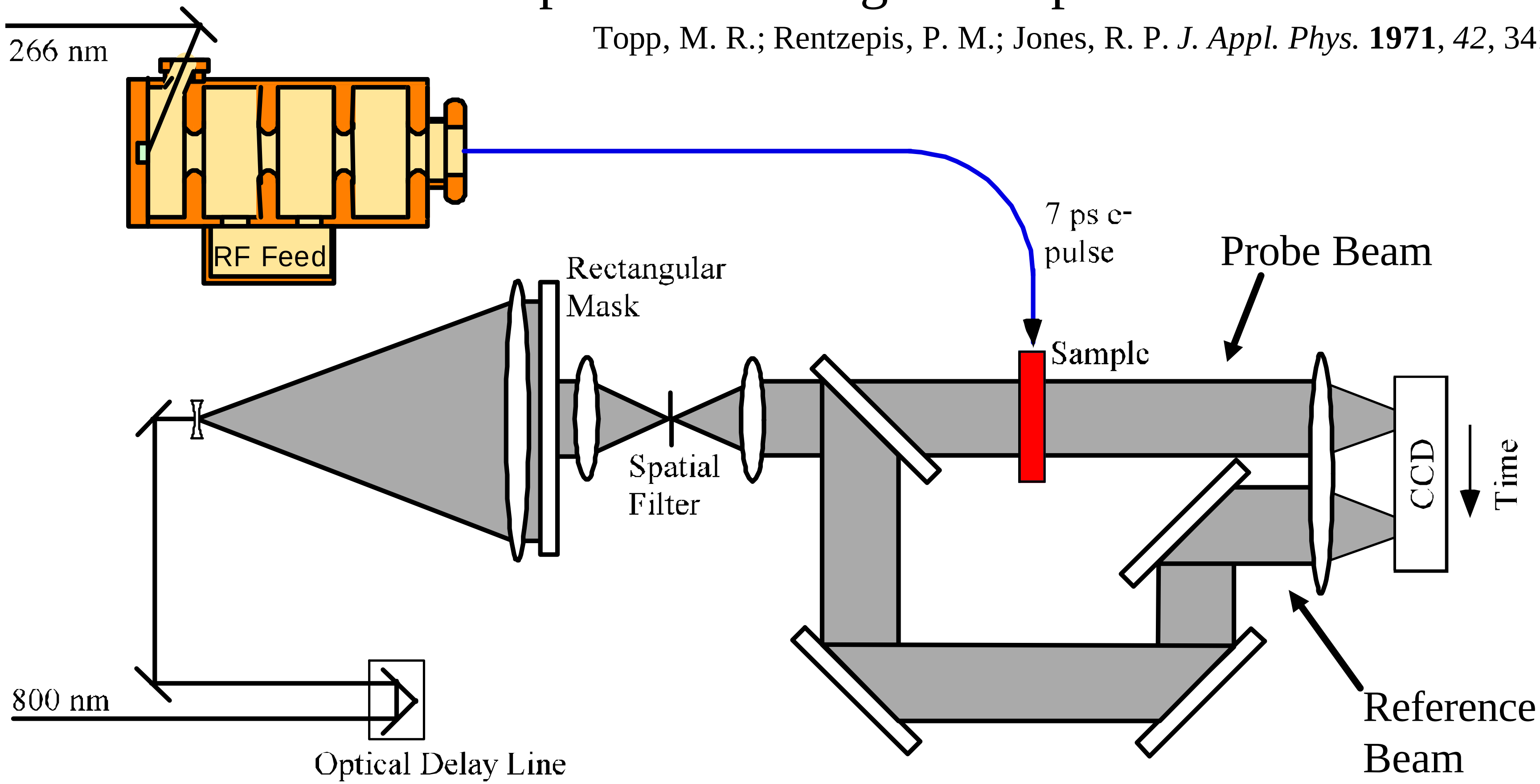


	Pulse Probe	UFSS
Sample:	1 gram flowed solution	1-5 mg liquid, solid, ionic liquid
e- pulses:	10^4	1
Scan time:	1 hour	< 5 minutes
Spectra:	days	1-2 hours

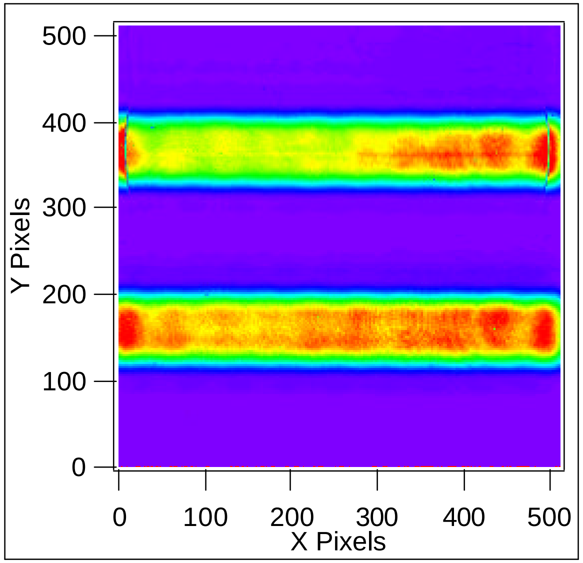
Ultrafast single shot detection

Spatial encoding of temporal information

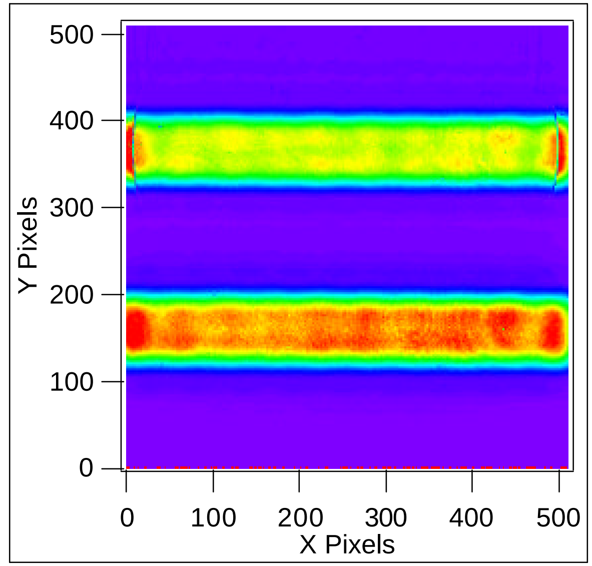
Topp, M. R.; Rentzepis, P. M.; Jones, R. P. *J. Appl. Phys.* **1971**, *42*, 3415.



UFSS CCD Images



Signal: with e- pulse



Baseline: no e- pulse

Sample beam

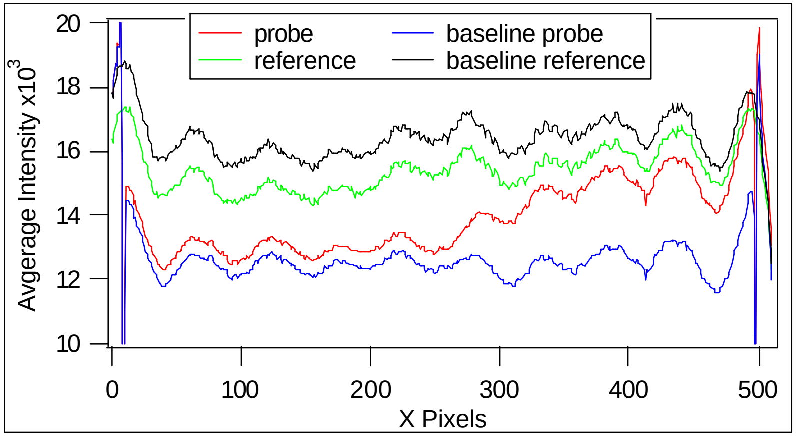
Reference beam

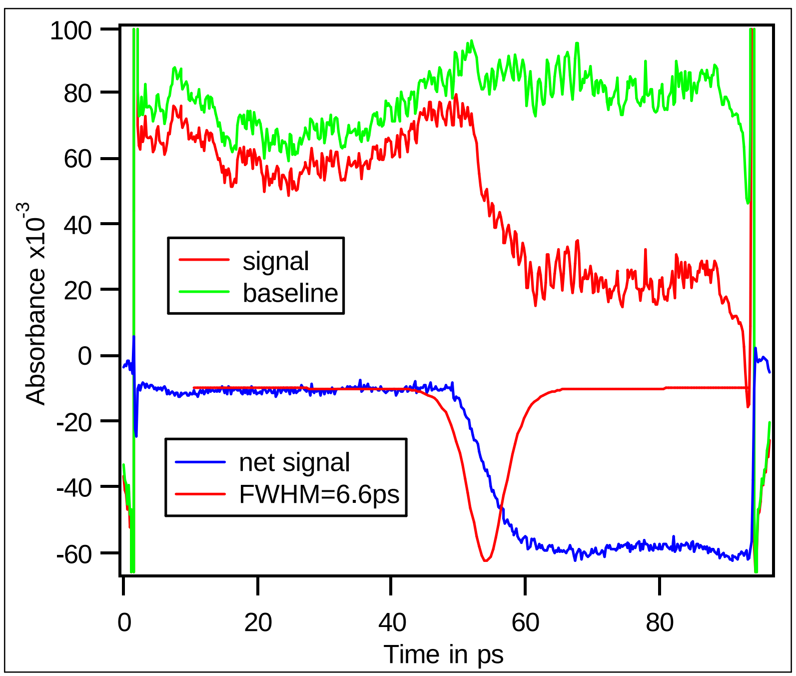
Average all y-pixels at a particular x for each stripe.

Final signal: $f(x) =$

$$-\log(\mathrm{Signal}_{sample}/\mathrm{Signal}_{ref}) + \log(\mathrm{Base}_{sample}/\mathrm{Base}_{ref})$$

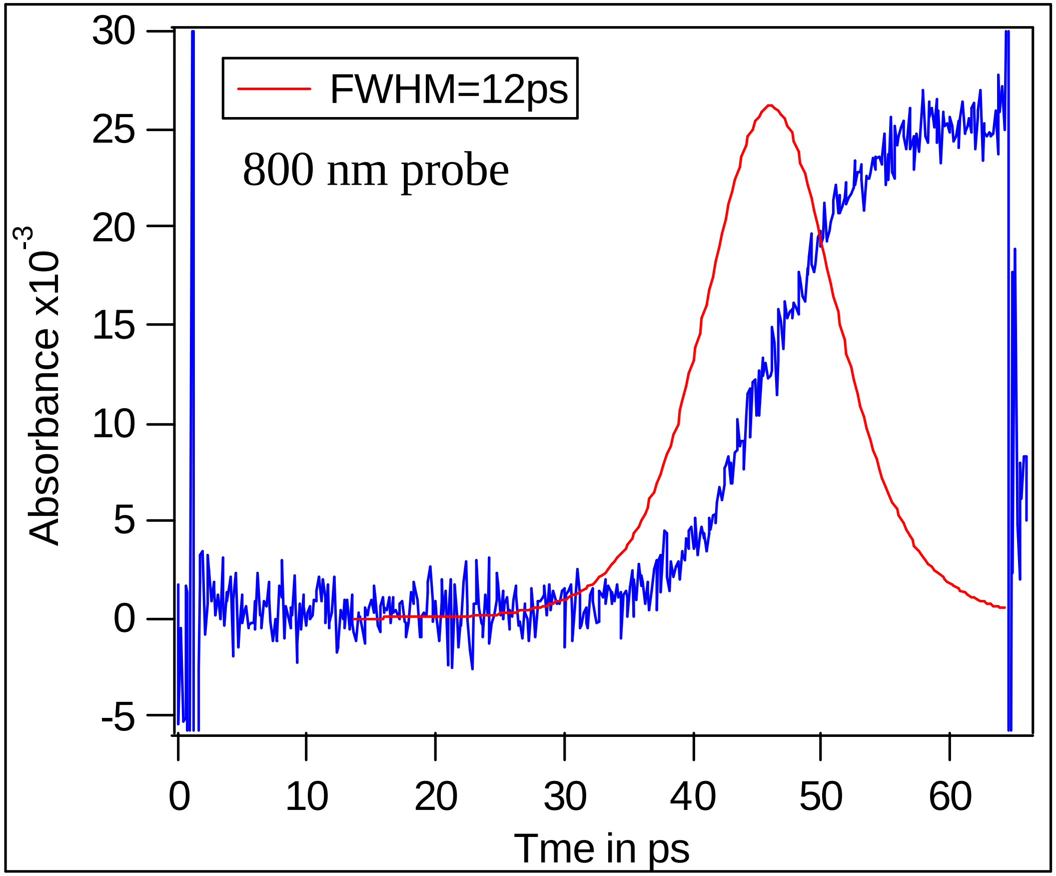
Absorption of IR125 dye with optical pump





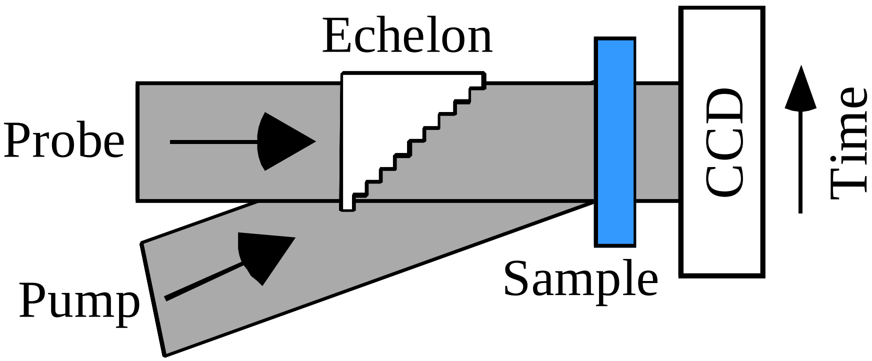
- Rise time of signal ~6-7ps is limited by sample thickness of 2 mm along probe direction.
- Getting ~1-2 mOD noise. “normal PP data” noise level is 0.5-1mOD past T=0, 0.2-0.3mOD before.
- Similar pulse-probe data would require 10^4+ shots, and take > 1 hour to collect!

Absorption of e$^-$ in water in *1* e$^-$ shot!



- 1 e- shot replaces many thousands
- Good S/N: no laser and e- pulse shot-shot noise; inherent signal averaging
- Limitations:
  - Temporal dynamic range
  - Time resolution
- Bottom line: UFSS viable

Echelon UFSS for sub-ps time resolution



- “Stair-Step” optical delays
- Step Δ = 10+ fs
- Use 2 crossed echelons
- Time windows < 20 ps

- Technique demonstrated in other labs
  Wakeham, G. P.; Nelson, K. A. *Opt. Lett.* **2000**, *25*, 505.
- With PPP experiment: 100 fs time resolution, mg samples

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