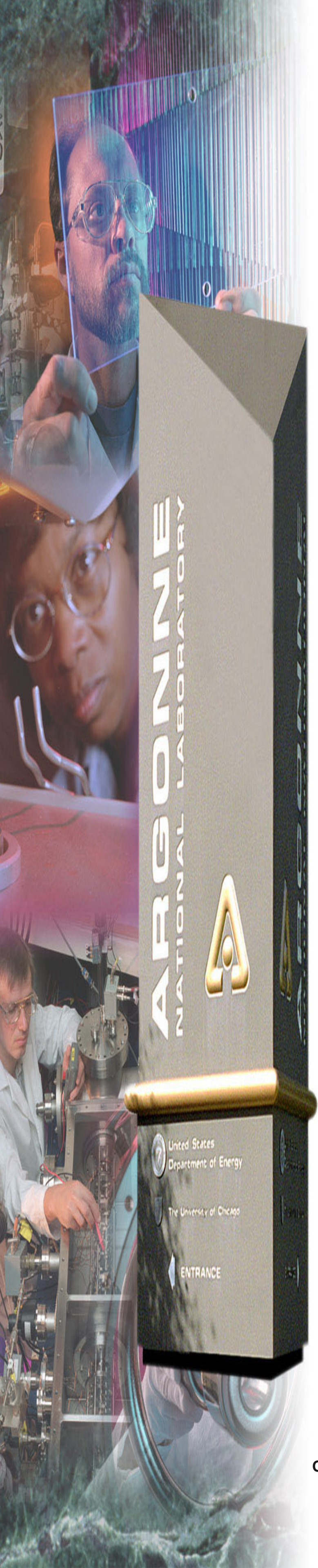


Frequency-Domain "Single Shot" Spectroscopy With Chirped Pulses

Quick & Dirty Method for Ultrafast Transient Absorption Measurements on "Real Systems"

Eli Shkrob

June 26-27, 2004

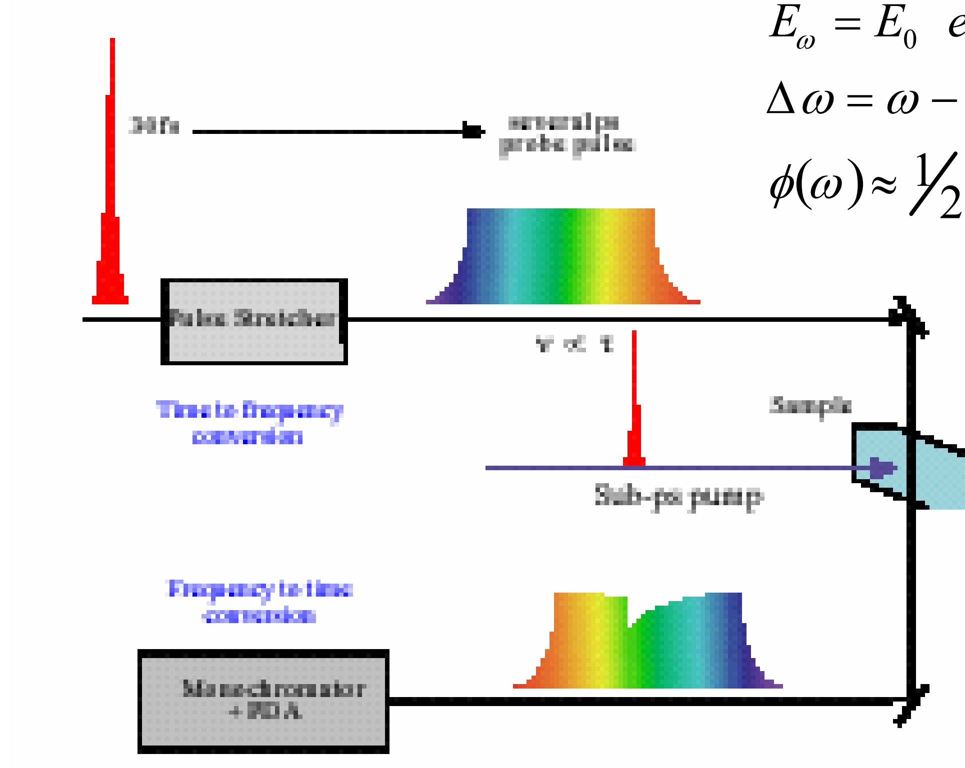
Ultrafast Accelerators for Pulse Radiolysis, BNL

Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy Office of Science Laboratory Operated by The University of Chicago

The idea



$$E_\omega = E_0 \; e^{-\frac{\Delta\omega^2\tau^2}{2}} \; e^{i\phi(\omega)}$$

$$\Delta\omega = \omega - \omega_0$$

$$\phi(\omega) \approx \tfrac{1}{2}\,\phi''(\omega_0)\Delta\omega^2$$

- **Whose idea?** Beddard et al. *CPL* **198**, 641 (1986)
- Used optical fibre to stretch white light supercontinuum pulse. Low GVD: < 5 ps window
- Grating pair compressor can be used to achieve GVD of -1.6 ps^2 (200 ps window)

FDSS catechism:

- **What for?** Tee Cube
- **Single shot?** Not really
- **Why do it?** Low repetition rate, poor pulse-to-pulse stability, elimination of the mechanical movement of the stage
- **What parts needed?** A grating pair (1200 g/mm) on a 1m translation stage, one CCD array, one monochromator.
- **How much?** $30-50k
- **Time window:** 1 to 500 ps (1k channels)
- **Sensitivity:** 50 μOD for 50k shots
- **More than a demonstration?** Yes
- **Better than spatio-temporal methods?** Oftentimes yes; certainly, on the long time scale
- **Better than chirped-pulse interferometry?** Easier to interpret but less informative
- **Limitations:** spectral evolution excluded
- **Serendipous advanatges:** the phase of the complex dielectric function for free

Input, Output

People involved:

- Dmitri Oulianov
- Eli Shkrob
- Robert Crowell
- Stanislas Pommeret

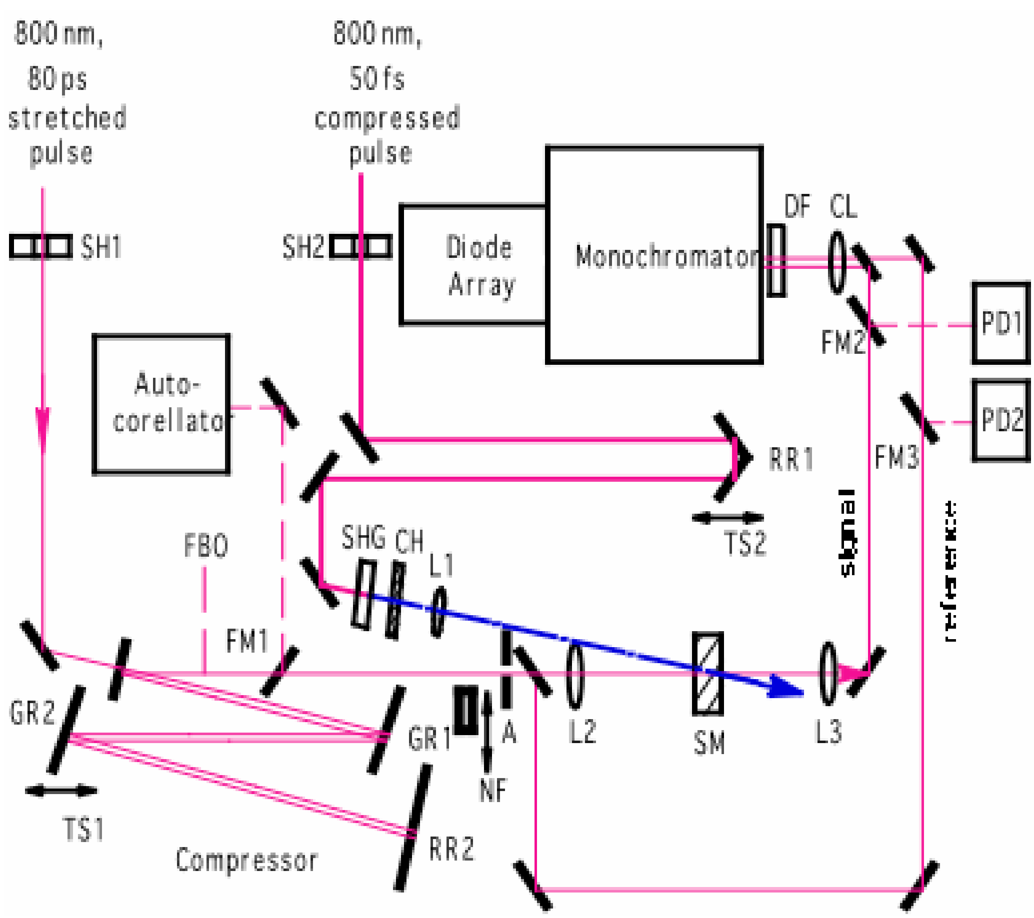
$$$ BES-DOE

Where to read about:

- *J. Appl. Phys.* **95** (2004) **JAPIAU-95-032411**
- http://www.arXiv.org/abs/physics/0401039
  http://www.arXiv.org/abs/physics/0401040

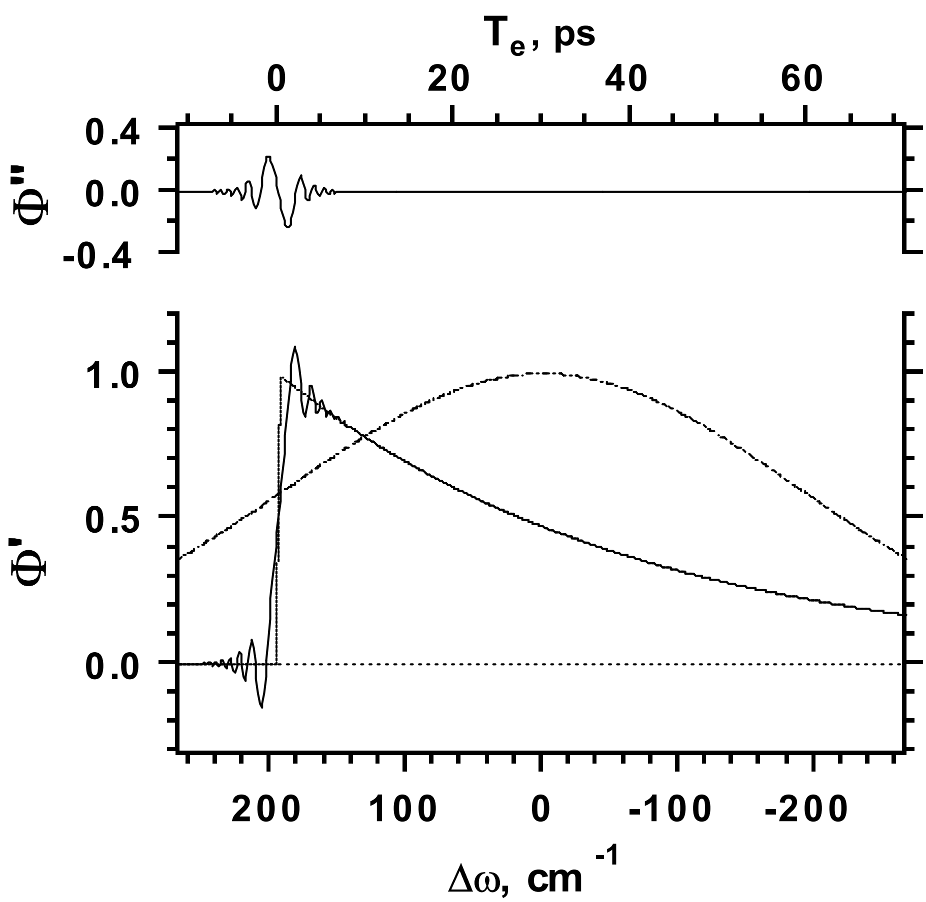
The hybrid setup, or the best of the two worlds.

- **Such a setup can be used both for pump-probe spectroscopy (PPS) and FDSS**
- **Chirped 800 nm pulse is taken from Ti:sapphire stretcher and then overcompressed**
- **Advantages: easy to switch tp and fro, excellent dynamics range for GVD**
- **Disadvantages: limited to 800 nm probe wavelength**

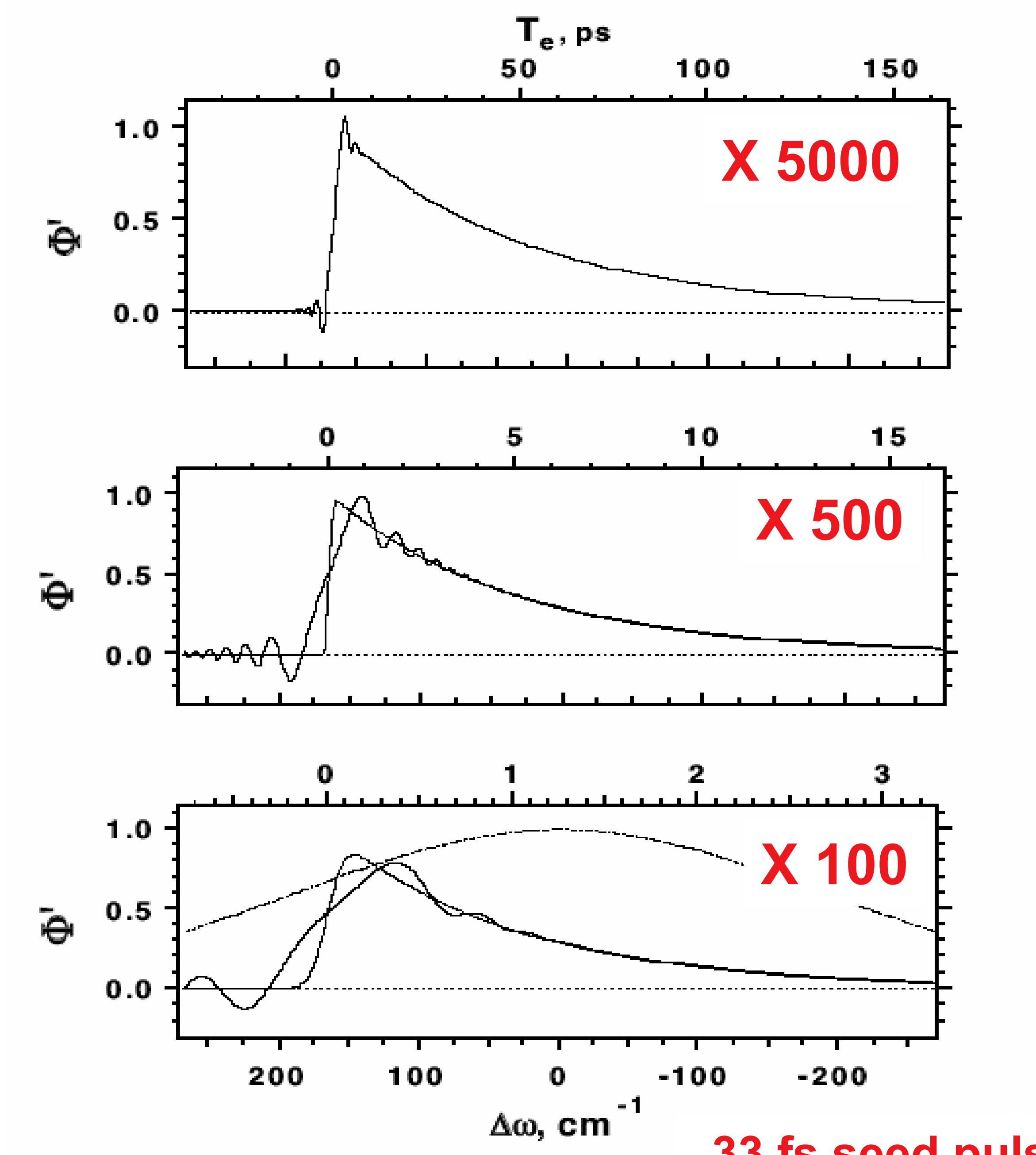


The theory: interference of quasimonochromatic components

- **For large GVD, most of the kinetics is free of oscillations (compression x 2k for 33 fs fwhm seed 800 nm pulse in the figure)**



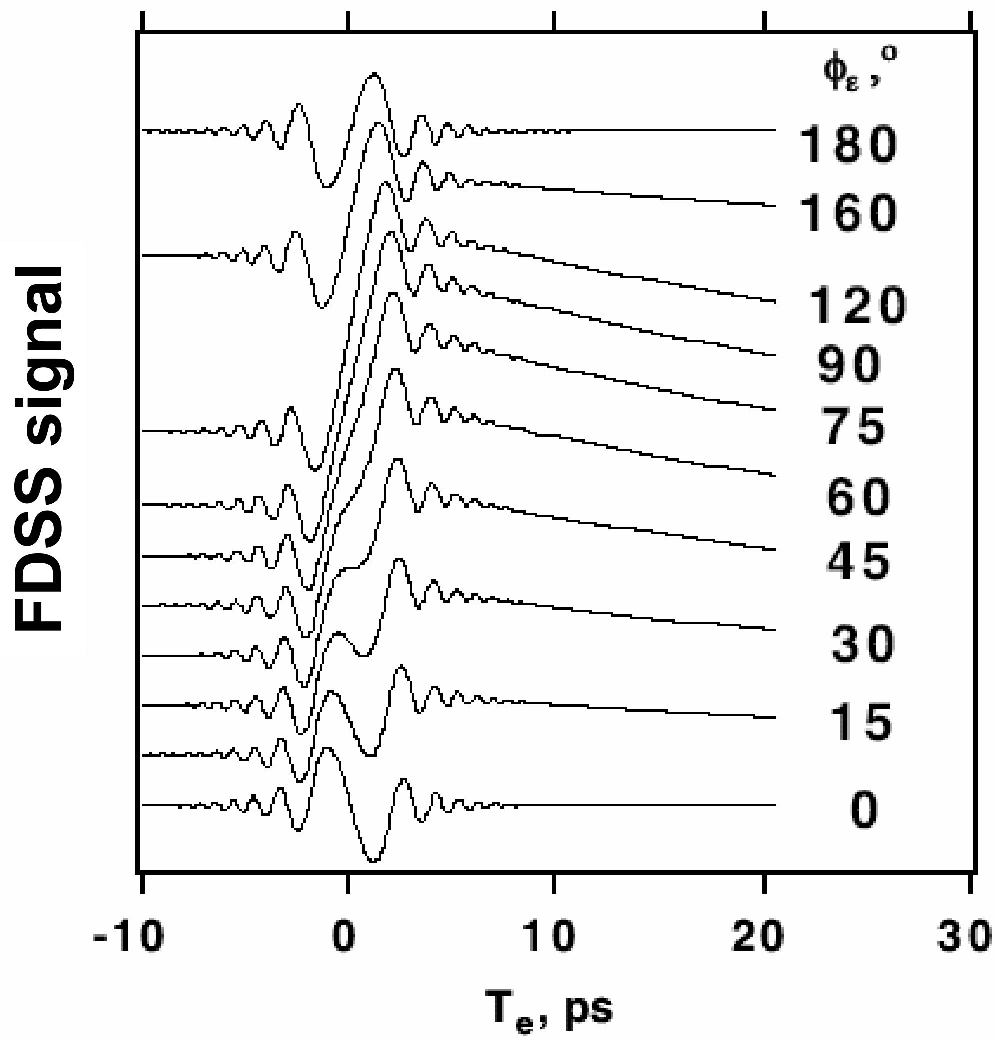
GVD: oscillations & compression factor. The more, the merrier.



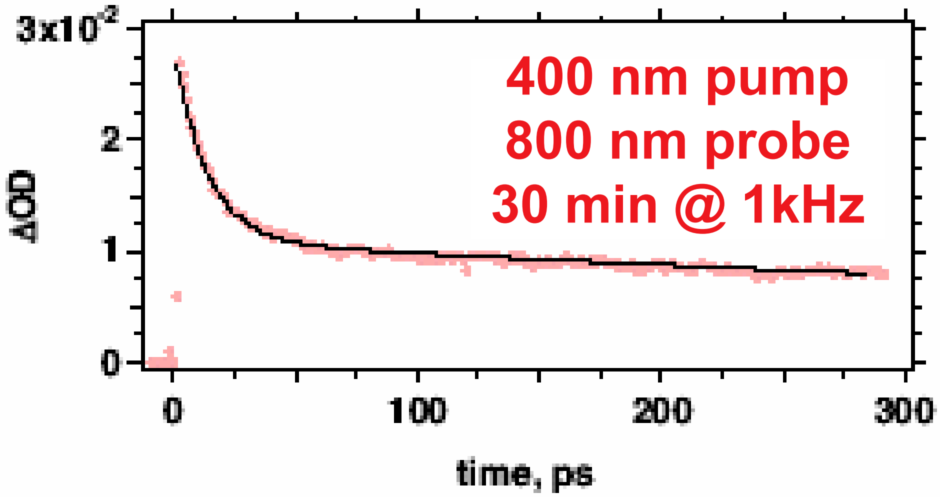
33 fs seed pulse

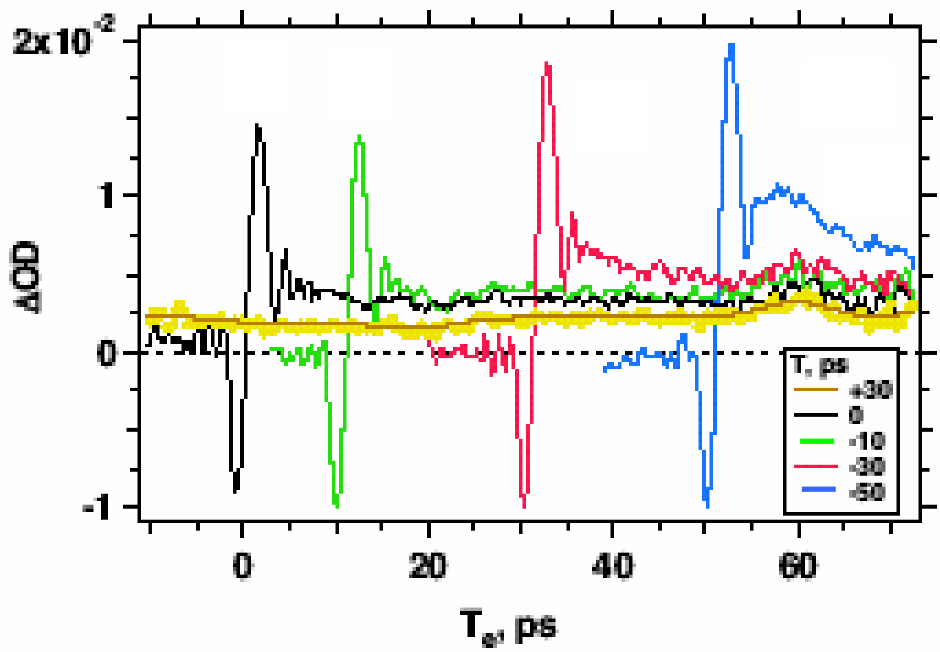
Are these oscillations “bad”?

- Their pattern yields the phase of the complex refraction index of photoinduced species



Electrons in photoexcited ZnSe

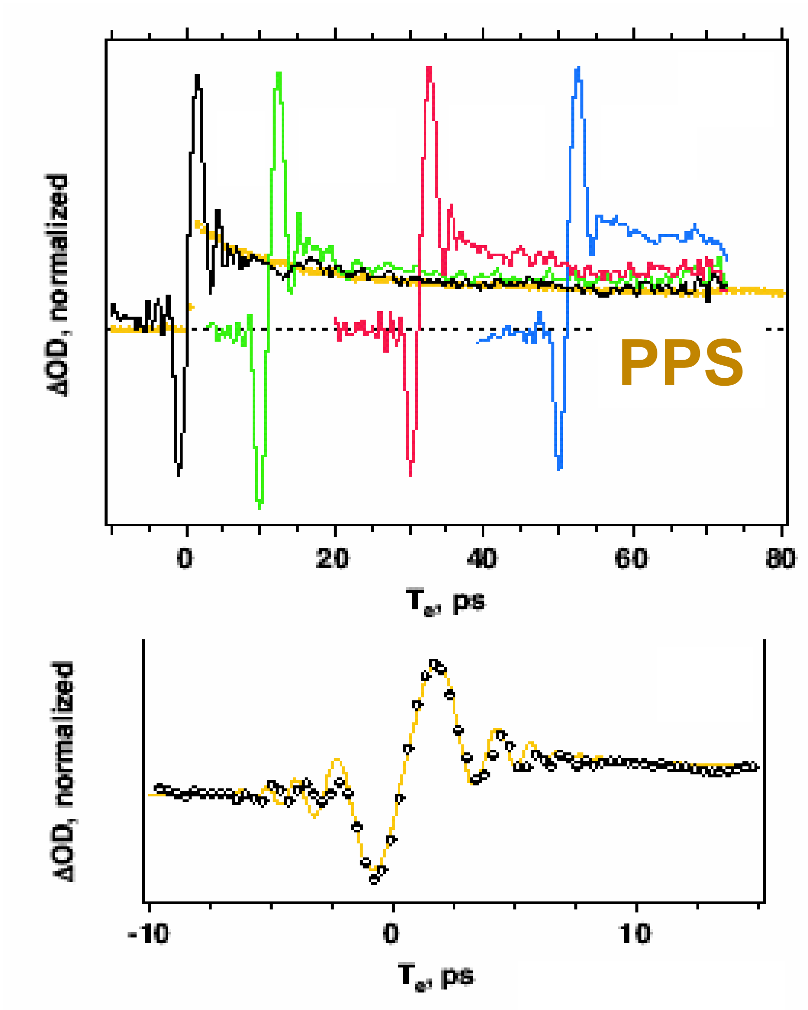




Almost all of the “TA” signal is actually due to the refraction of 800 nm light by free electron carriers in the photoexcited semiconductor

FDSS kinetics in ZnSe

- Each FDSS kinetics was aquired in 5 min
- The actual signal is 2 mOD
- Phase of ε determined with accuracy of 1°

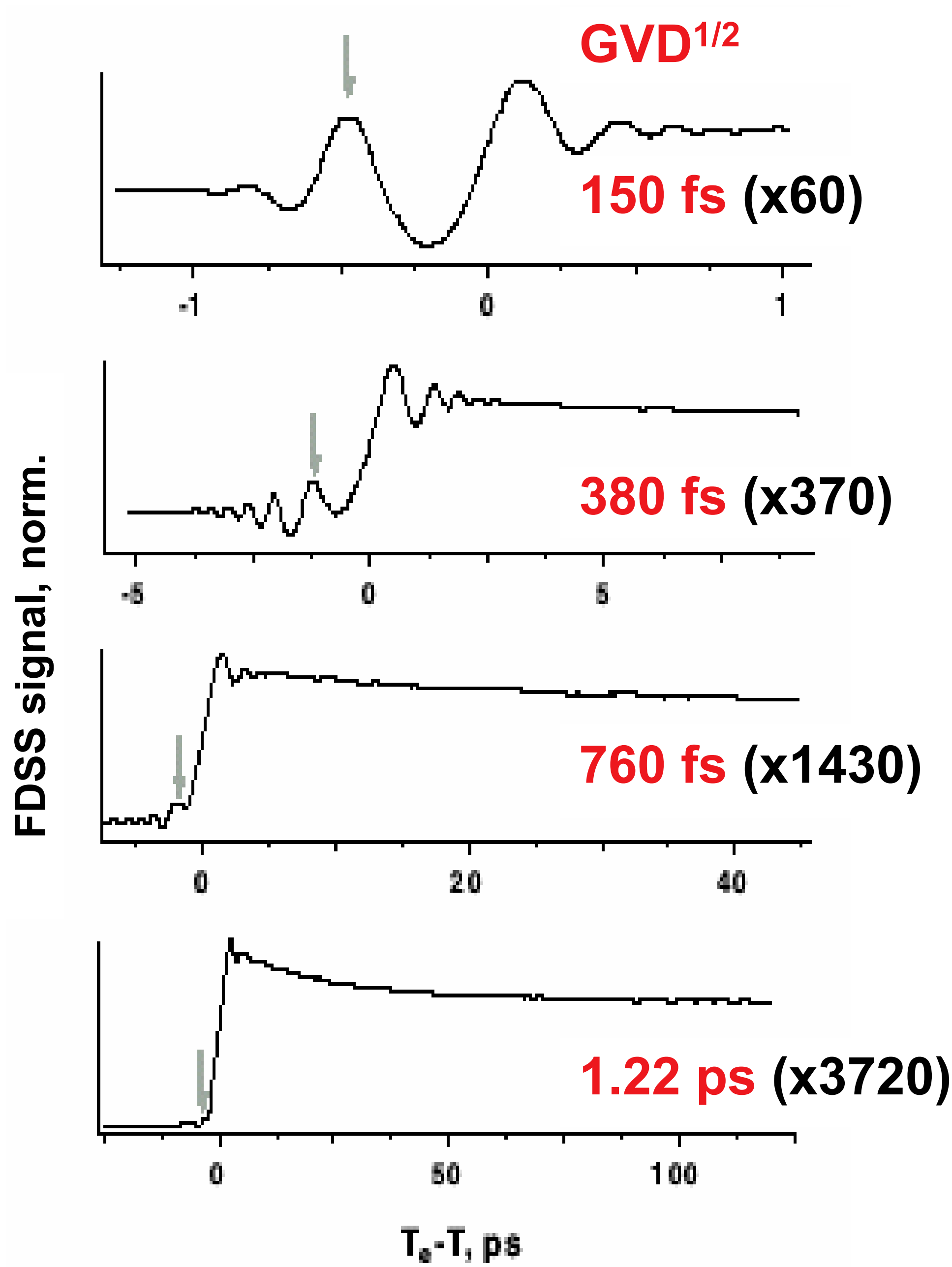


Drude plasma:

$$\cot \phi_\varepsilon = -\omega\tau_e$$
$$\tau_e \approx 171 \pm 1°$$

Free e⁻ plasma dumping time (2.8 fs) in a single measurement! Thanks to the wiggles.

Solvated e⁻ by 2x400nm excitation of aqueous iodide: a CTTS system

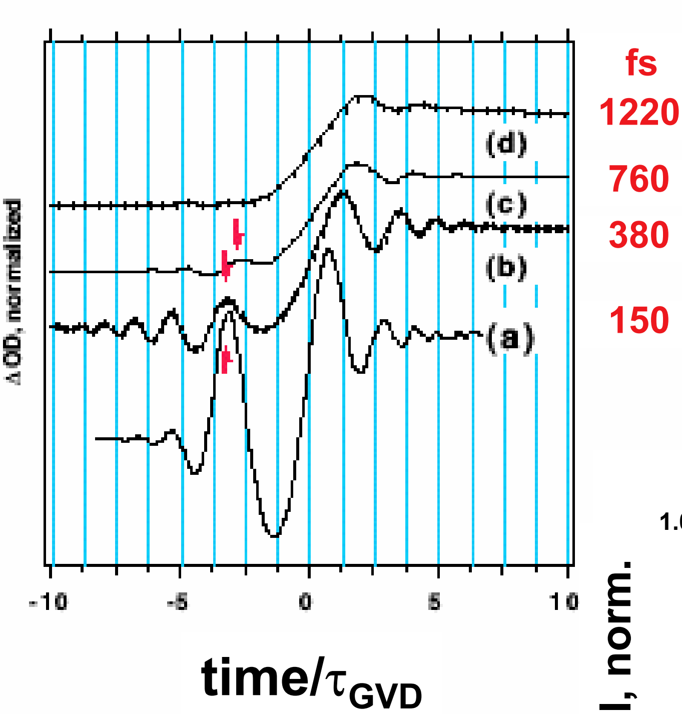


75 mM NaI; 90k shots; 33 fs seed pulse

100 mOD; 0.3 TW/cm^2

The oscillations are telling a story

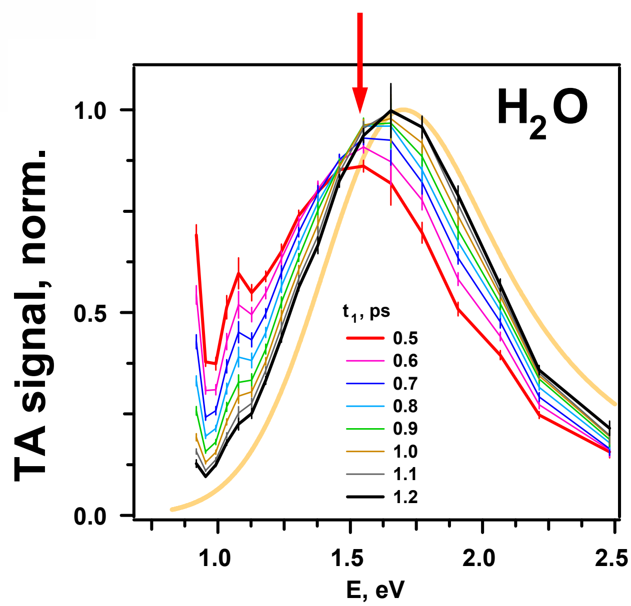
- **Oscillation asymmetry is due to the change in the complex refraction index during electron solvation on the femtosecond time scale**
- **The phase swings from negative to positive as the absorbance peaks passes through 800 nm**



$$\tau_{GVD} = \sqrt{\phi''(\omega_0)}$$

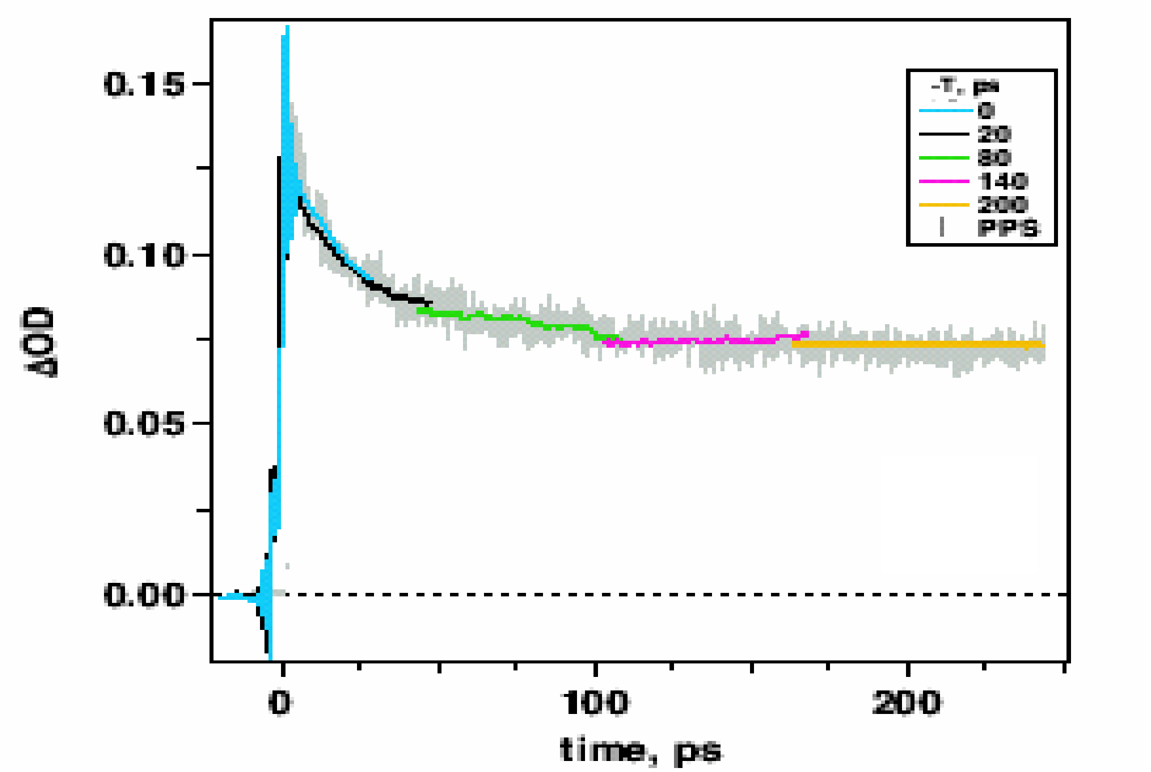
Solvated electron generated in bi- 400 nm photon excitation of 75 mM iodide

bi- 200 nm pump
800 nm probe



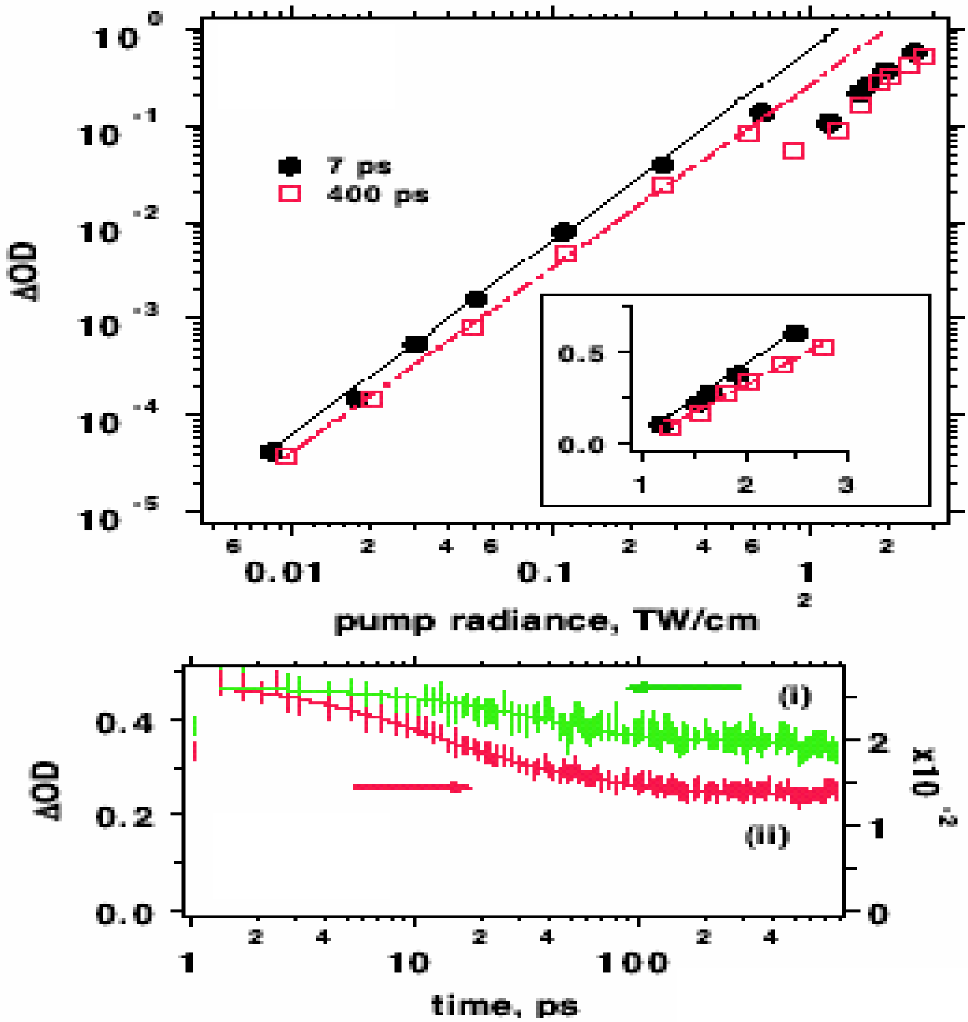
Averaging efficiency & splicing

- One pump-probe trace took more time than five FDSS traces and still shows worse S/N ratio
- Flow instability, pump variations, nonlinear regime all have lower impact on FDSS
- Splicing the FDSS kinetics further increases the observation window



75 mM NaI; 50k shots/trace

Cranking the power up.

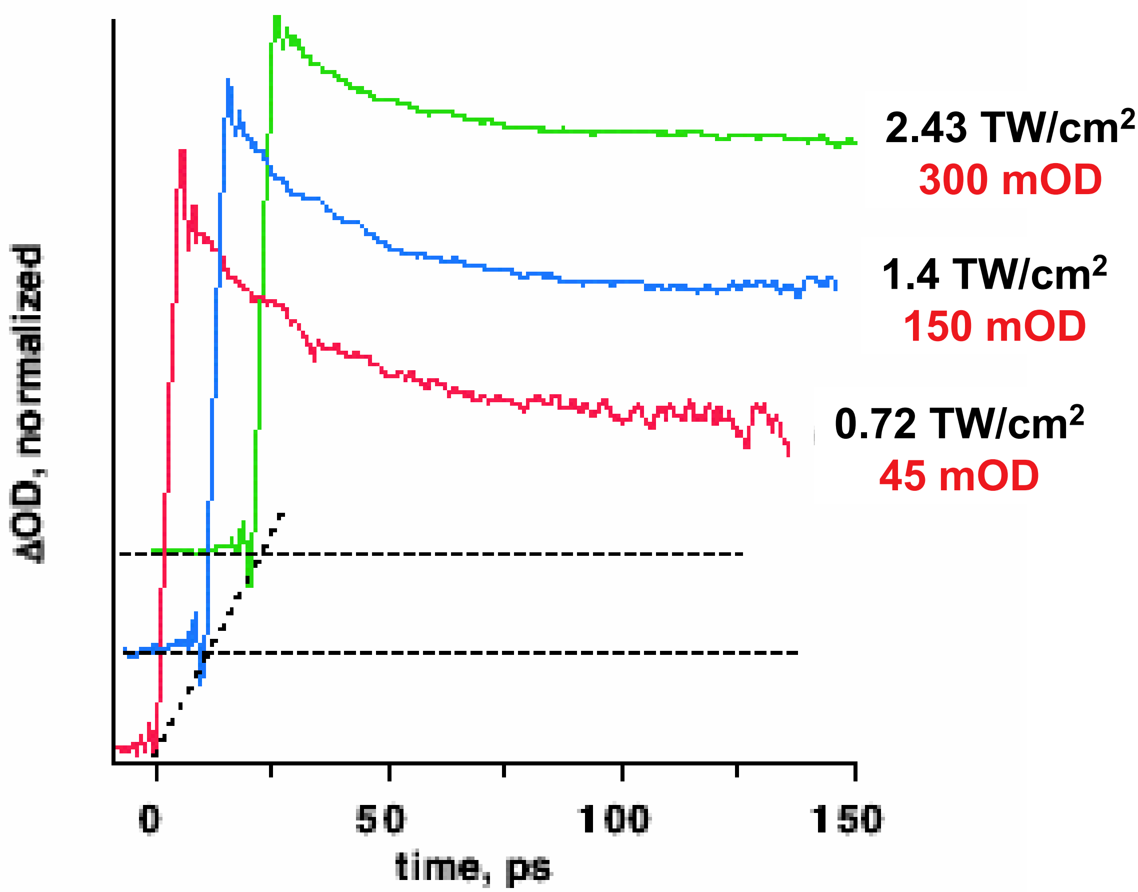


Geminate recombination kinetics of hydrated electron is power dependent in the TW regime:

Heat effects, 3-photon water ionization, above-threshold ionization, etc.

Terawatt regime, FDSS way

- **Mapping how kinetics change as a function of power by the PPS is laborious & tedious**
- **Using FDSS, it is no brainer: the whole kinetic vs. power map was obtained in 30 min**



75 mM NaI; 75k shots; 160 μm jet; 10 m/s; GVD 1.6 ps^2

Conclusion: FDSS works.
We will run FDSS @ Tee Cube

- Long travel distances of probe light are tolerable
- Easy to implement in confined spaces
- Easy to correct for charge fluctuations
- Sensitivity is fine for our expected charge and dose regime, 50 pC ++ (1 nC update)
- Not too good for VERY fast measurements, fine on the *picosecond* time scale
- Which is actually unexplored
- For fast (fs) measurements SS chirped-pulse interferometry would work well
- But fs regime is hard to achieve in pulse radiolysis of condensed matter systems
- 800 nm limitation is not currently an issue
- Could be problematic if rapid spectral evolution occurs on the scale of 300 cm^{-1}
- Thermal spiking in the spur mayprove be fatal for the frequency-coding approach !

Thank you for your attention.