ULTRAFAST OPTICS

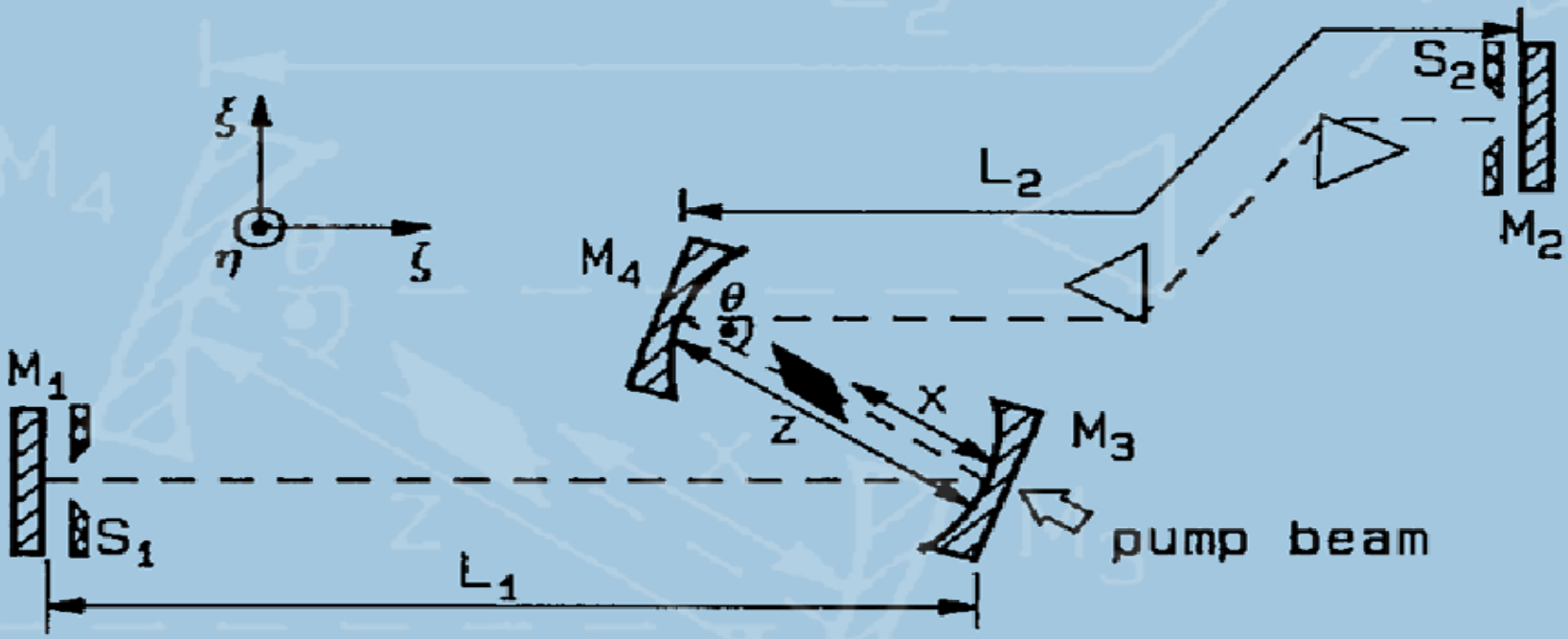
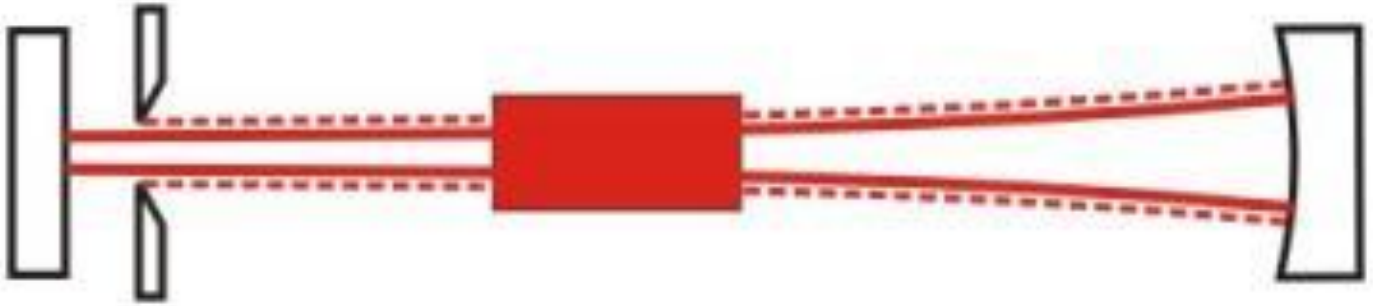


image from G. Cerullo et al., Opt. Lett. 19, 807 (1994), © OSA

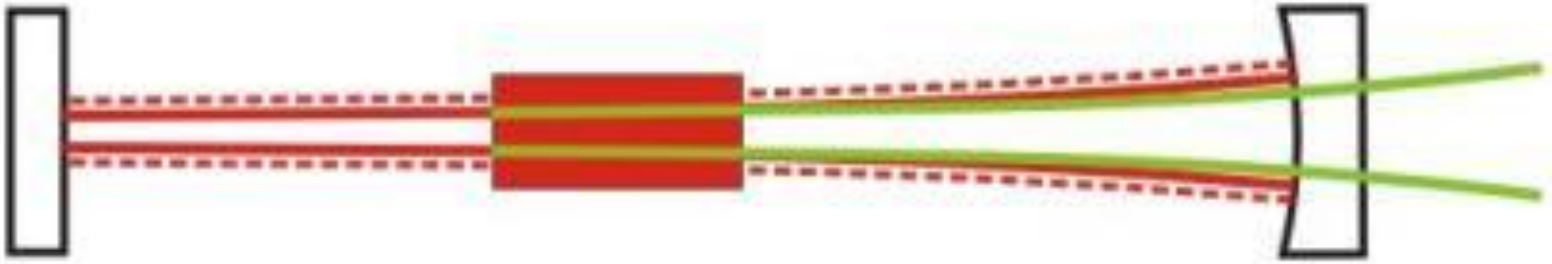
by PIOTR WASYLCZYK

Kerr-lens modelocking in a laser cavity

Dashed line – low intensity cavity spatial mode
Solid line – high intensity cavity spatial mode



Hard aperture



Soft aperture

Yb:KYW

$Yb^{3+}:KY(WO_4)_2$

stands for

ytterbium-doped double (yttrium-potassium) **tungstate**, not vanadate

W – tungsten

V – vanadium

EKSMA Optics

Ultrafast Laser Spectroscopy

How and why ultrafast laser spectroscopy?

Generic ultrafast spectroscopy experiment

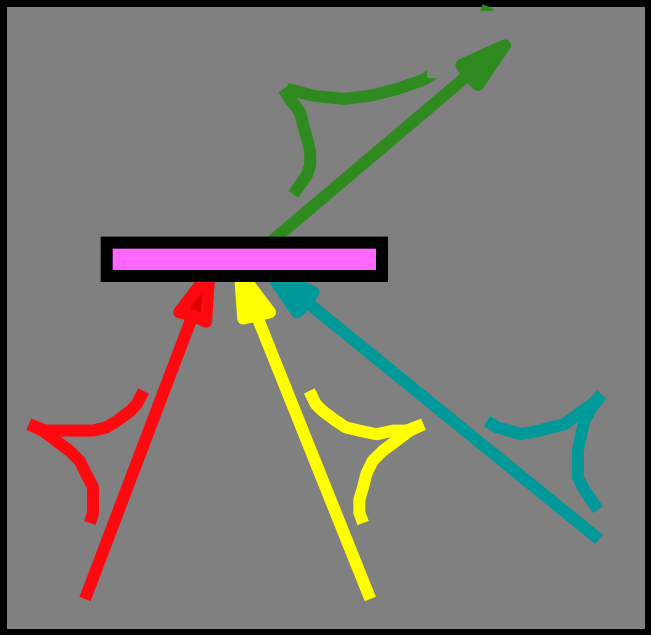
The excite-probe experiment

Transient-grating spectroscopy

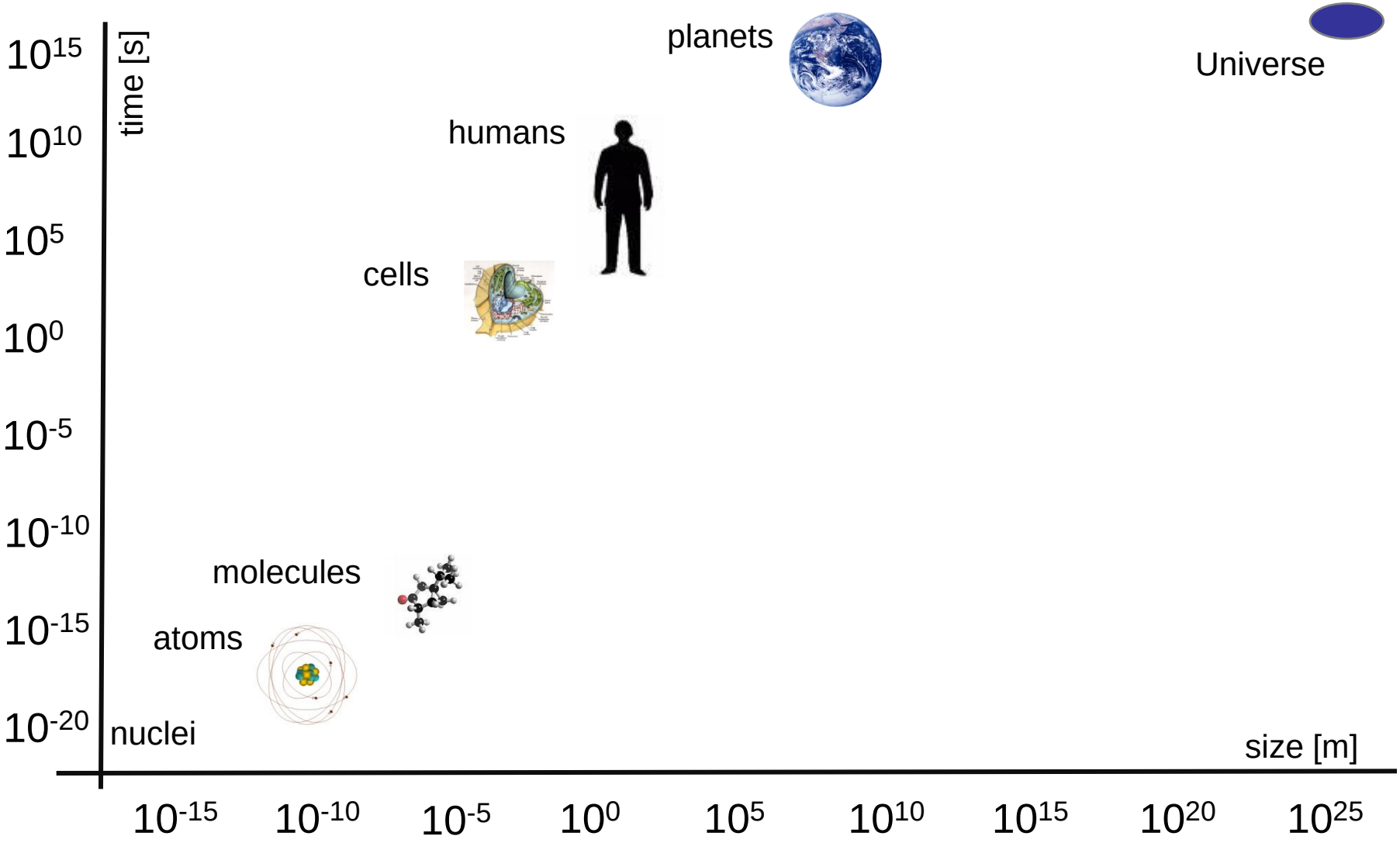
Ultrafast polarization spectroscopy

Optical heterodyne detection (OHD)

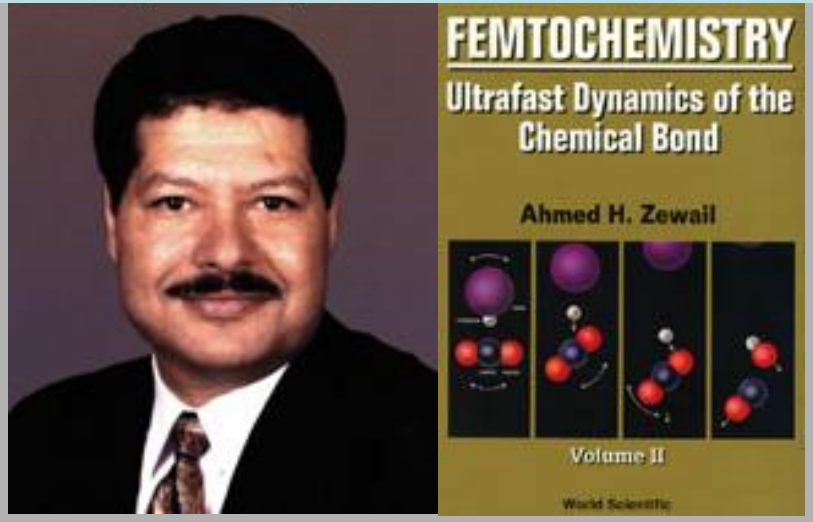
Spectrally resolved excite-probe spectroscopy



Time and space in the Universe



The 1999 Nobel Prize in Chemistry went to Professor Ahmed Zewail of Cal Tech for ultrafast spectroscopy.



Zewail used ultrafast-laser techniques to study how atoms in a molecule move during chemical reactions.

Ultrafast laser spectroscopy: Why?

Most events that occur in atoms and molecules occur on fs and ps time scales because the length scales are very small.

Fluorescence occurs on a ns time scale, but competing non-radiative processes only speed things up because relaxation rates add:

$$1/\tau_{ex} = 1/\tau_{fl} + 1/\tau_{nr}$$

Biologically important processes utilize excitation energy for purposes other than fluorescence and hence **must be very fast**.

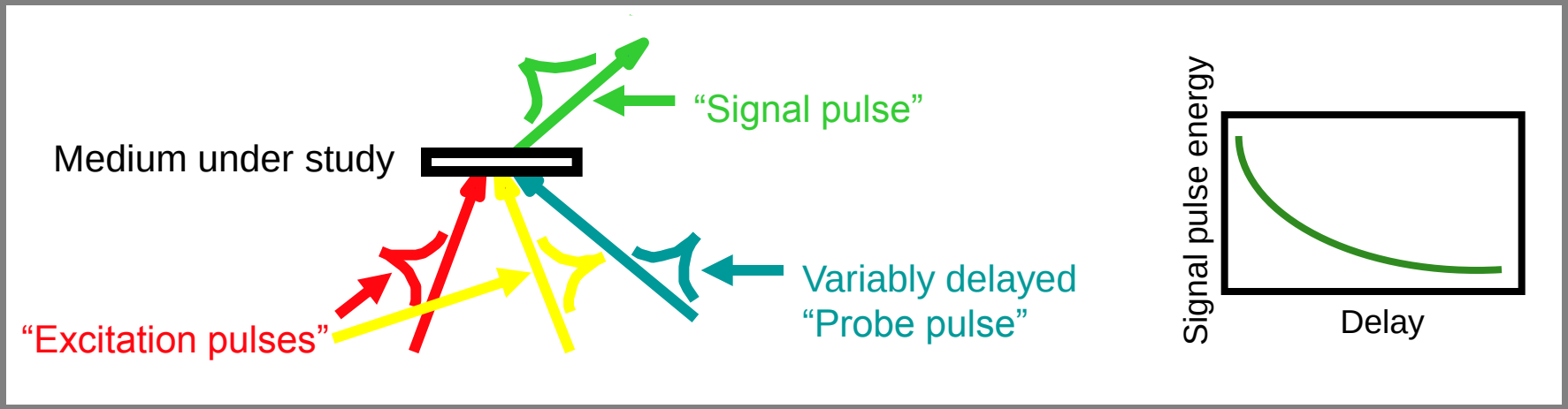
Collisions in room-temperature liquids occur on a few-fs time scale, so nearly all processes in liquids are ultrafast.

Semiconductor processes of technological interest are necessarily ultrafast or we wouldn't be interested.

Ultrafast laser spectroscopy: How?

Ultrafast laser spectroscopy involves studying ultrafast events that take place in a medium using ultrashort pulses and delays for time resolution.

It usually involves exciting the medium with one (or more) ultrashort laser pulse(s) and probing it a variable delay later with another.



The signal pulse energy (or change in energy) is plotted vs. delay.

The experimental temporal resolution is the pulse length.

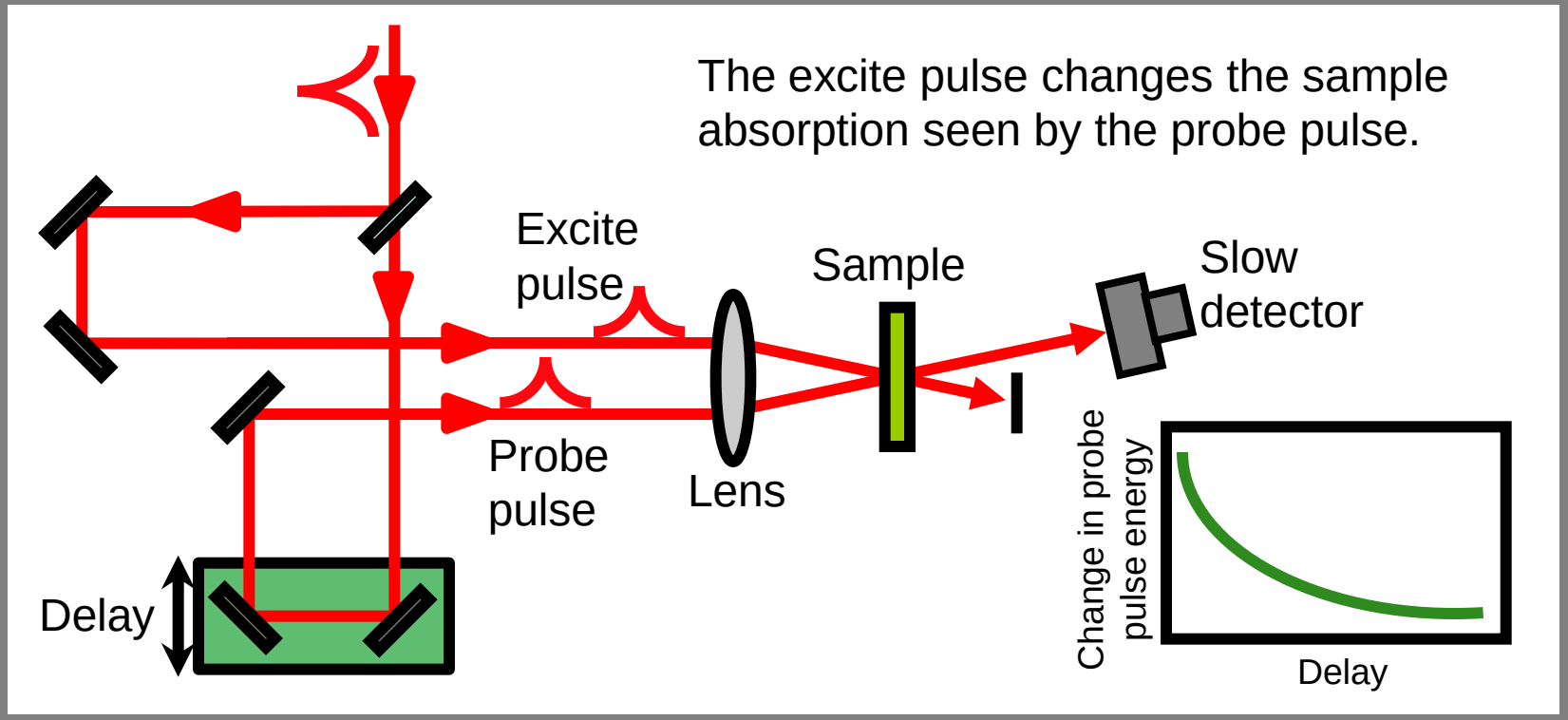
What's going on in spectroscopy measurements?

The excite pulse(s) excite(s) molecules into excited states, which changes the medium's absorption coefficient and refractive index.

The excited states only live for a finite time (this is the quantity we'd like to find!), so the absorption and refractive index recover.

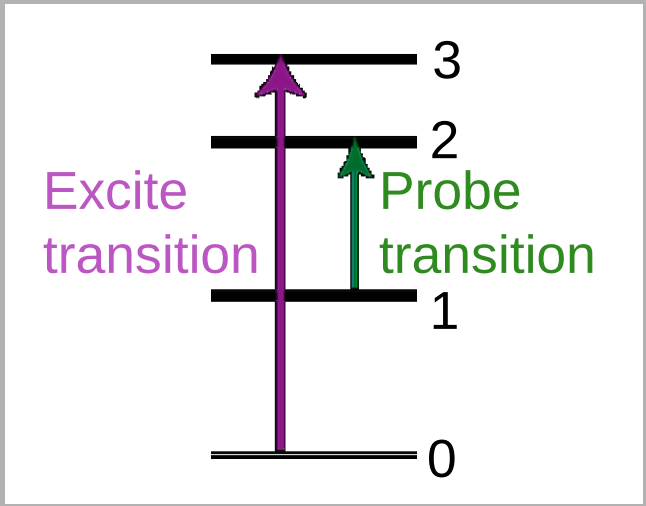
The simplest ultrafast spectroscopy method is *The Pump-Probe (Excite-Probe) Technique*.

Excite the sample with one pulse; probe it with another a variable delay later; and measure the change in the transmitted probe pulse energy or average power vs. delay.

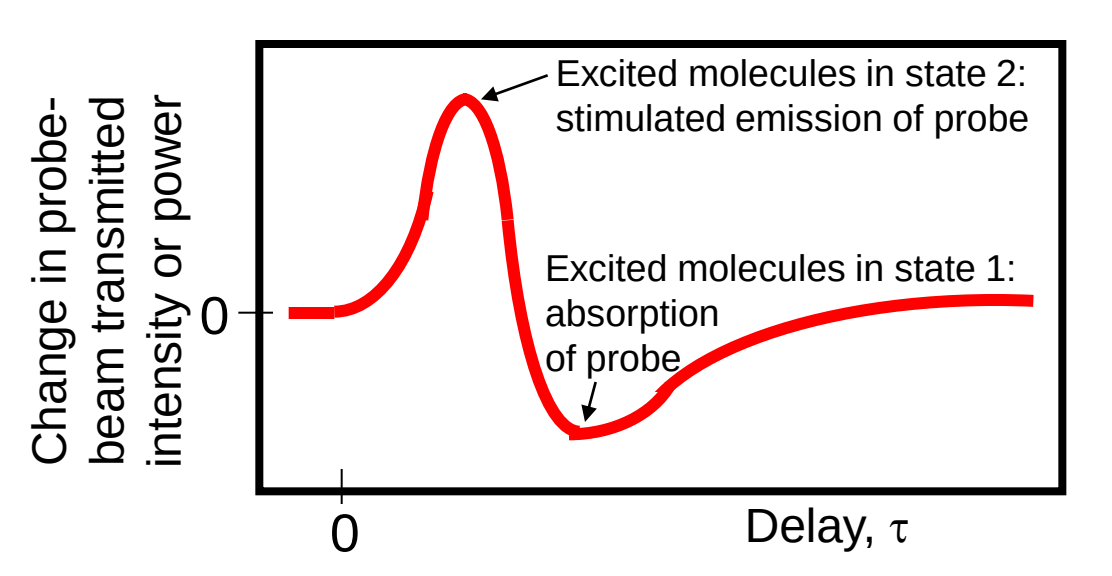


The excite and probe pulses can be different colors.

Modeling excite-probe measurements (cont'd)

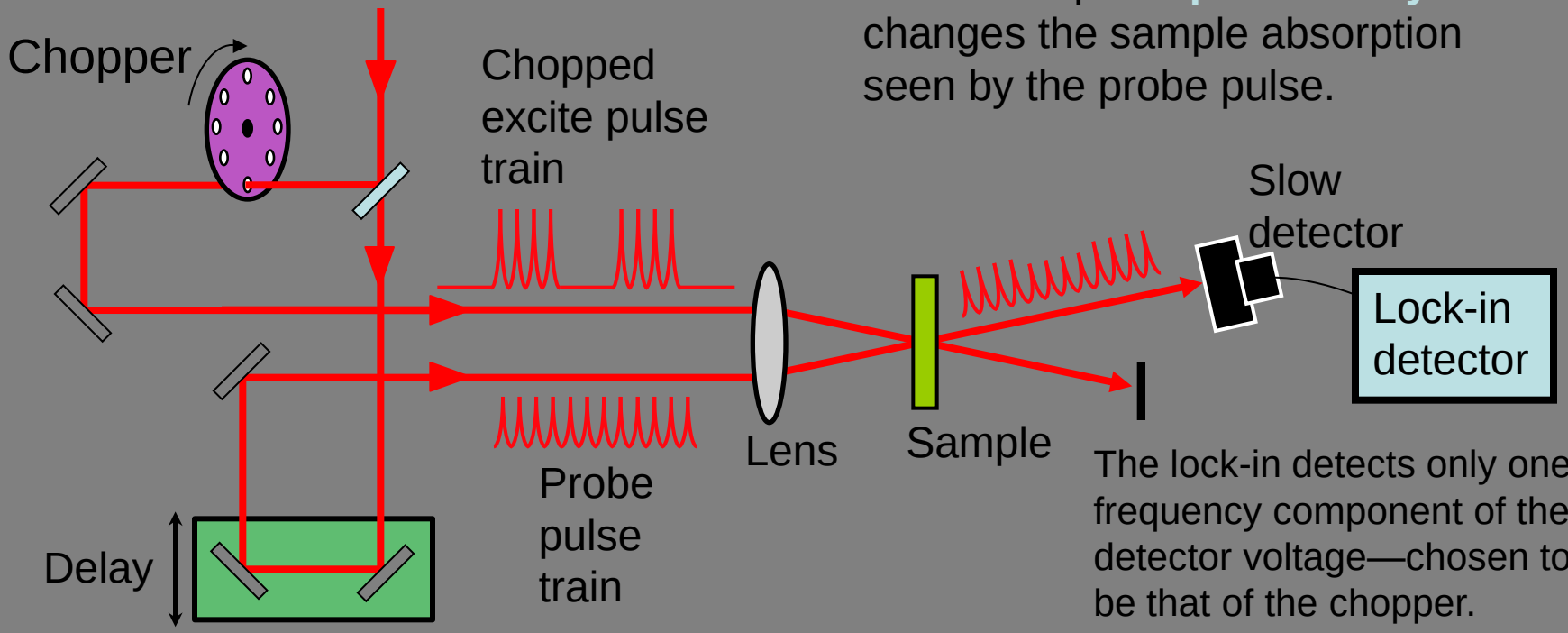


More complex decays can be seen if intermediate states are populated or if the motion is complex. Imagine probing an intermediate transition, whose states temporarily fill with molecules on their way back down to the ground state:



Lock-in Detection greatly increases the sensitivity in excite-probe experiments.

This involves **chopping** the excite pulse at a given frequency and detecting at that frequency with a lock-in detector:



Lock-in detection automatically subtracts off the transmitted power in the absence of the excite pulse. With high-rep-rate lasers, it increases sensitivity by **several orders of magnitude!**

Excite-probe measurements in DNA

DNA bases undergo photo-oxidative damage, which can yield mutations. Understanding the photo-physics of these important molecules may help to understand this process.

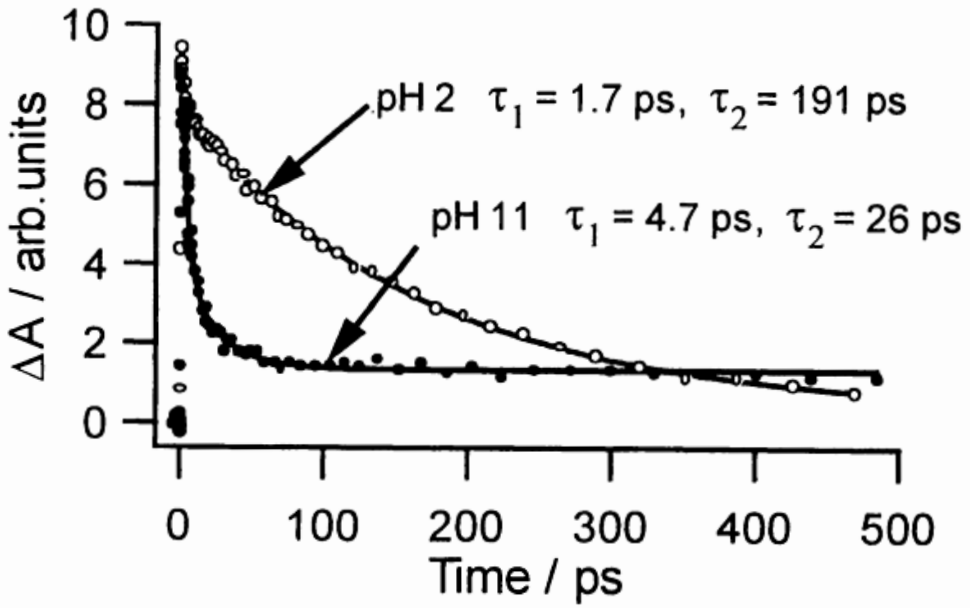
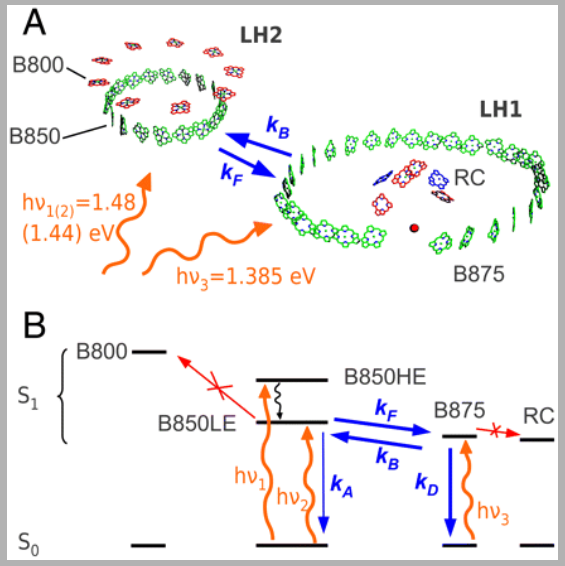


Fig. 1. Transient absorption at 600 nm of protonated guanosine in acidic (pH 2) and basic (pH 11) aqueous solution

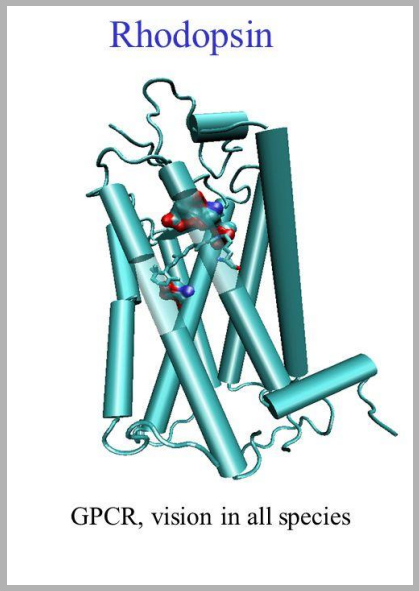
Pecourt, et al., Ultrafast Phenomena XII, p.566 (2000).

Two very efficient processes in nature involving light abosorption:

- photosynthesis,



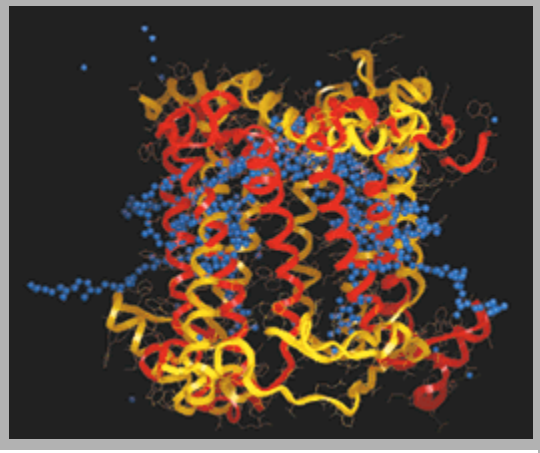
- animal vision.



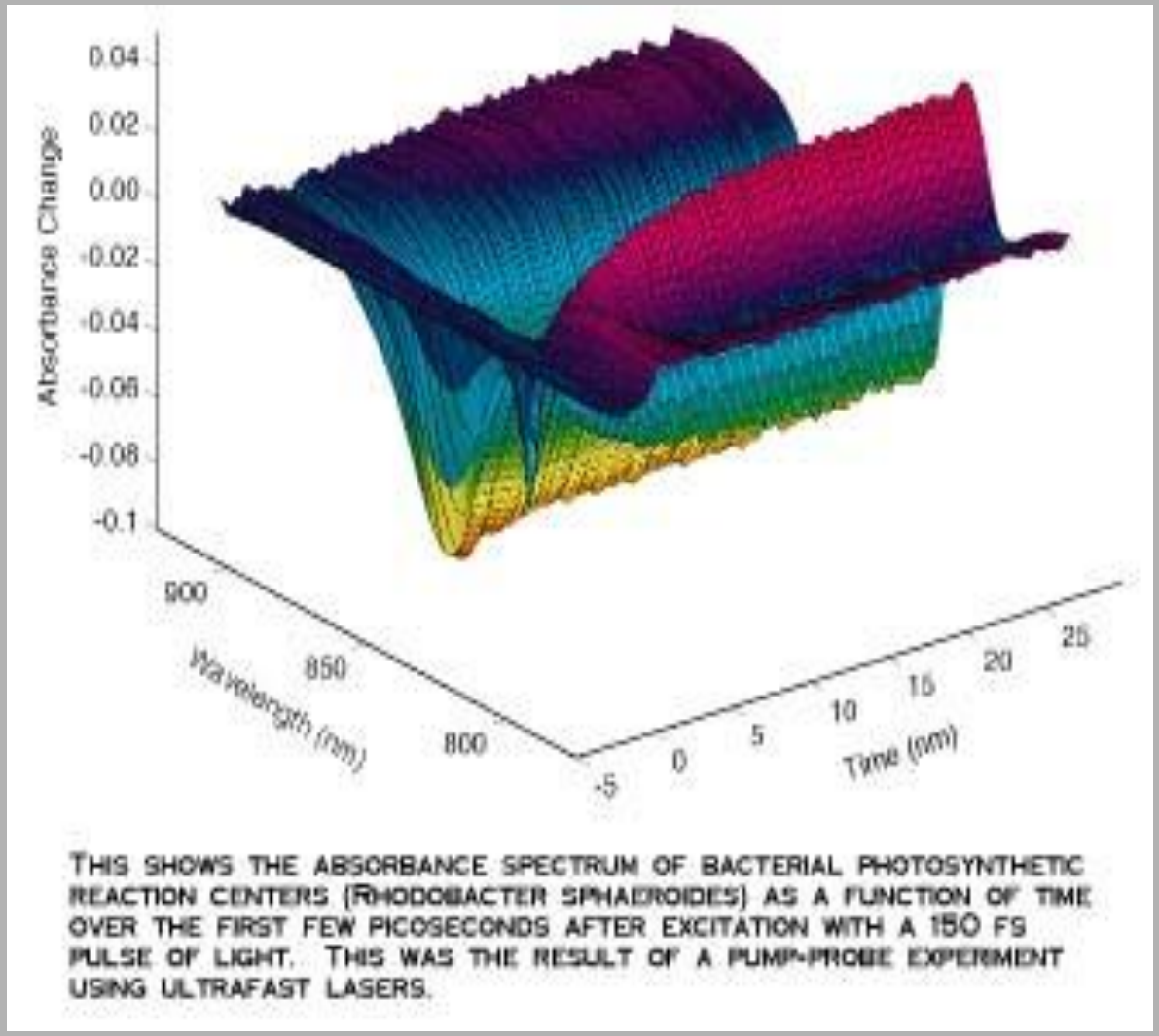
Both involve ultrafast energy transfer – before the energy from the excitation photon can be distributed among many degrees of freedom (and lost), it is transferred and used in the process of interest.

Ultrafast Spectroscopy of Photosynthesis

The initial events in photosynthesis occur on a ps time scale.



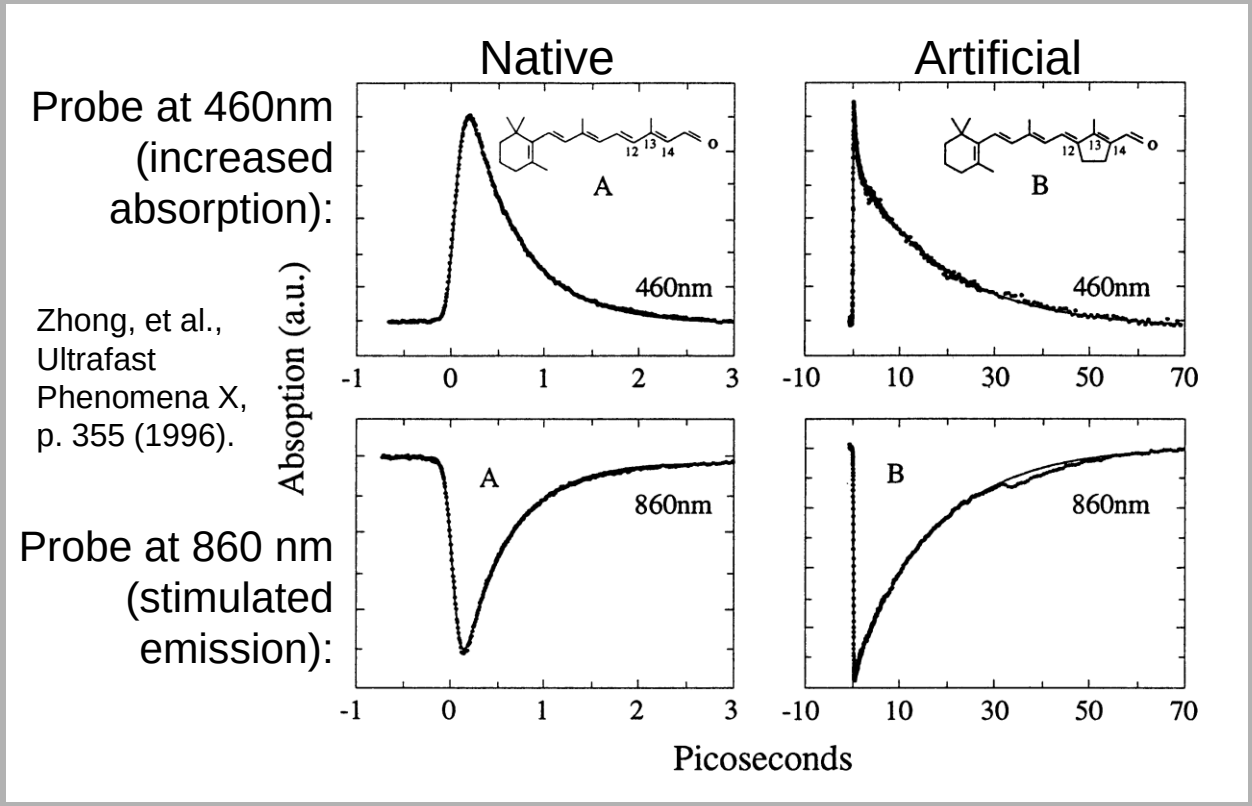
During Photosynthesis, energy absorbed by the antenna is passed to the reaction center where a charge separation occurs. This is a picture of the reaction center of a purple non-sulfur bacterium.



This shows the absorbance spectrum of bacterial photosynthetic reaction centers (Rhodobacter sphaeroides) as a function of time over the first few picoseconds after excitation with a 150 fs pulse of light. This was the result of a pump-probe experiment using ultrafast lasers.

Excite-probe measurements of bacterio-rhodopsin

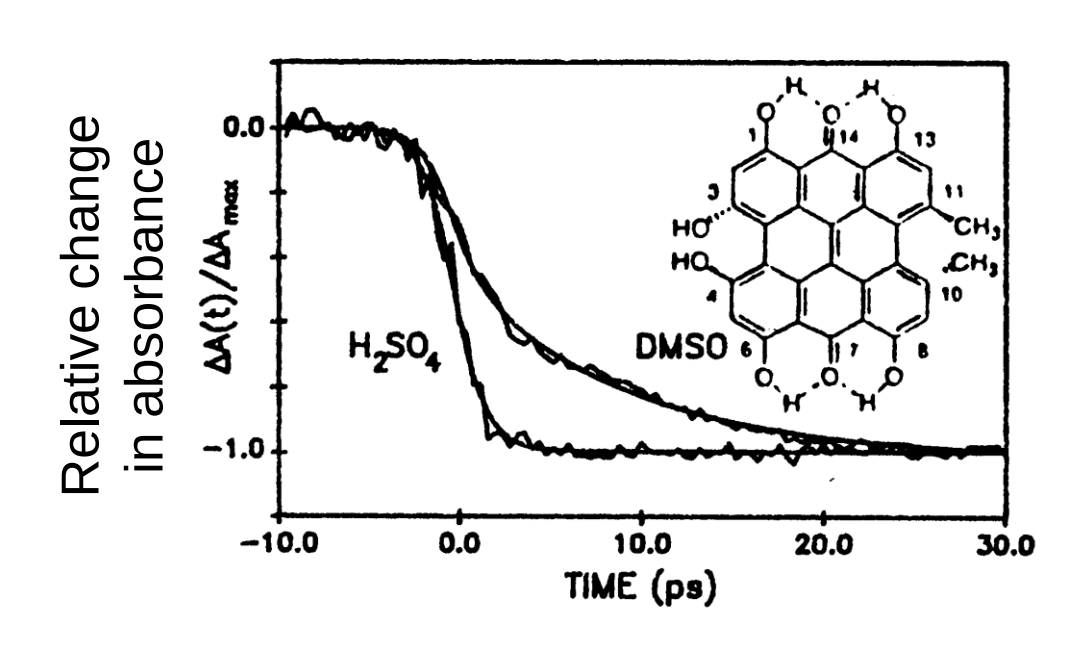
Rhodopsin is the main molecule involved in vision. After absorbing a photon, rhodopsin undergoes a many-step process, whose first three steps occur on fs or ps time scales.



Excitation populates a new state, which absorbs at 460nm and emits at 860nm. It was thought that this state involved motion of the carbon atoms (12, 13, 14). But an artificial version of rhodopsin, with those atoms held in place, also reveals this change on the same time scale (the rise time is the same)!

Excite-probe measurements of Hypericin, an anti-viral substance

When excited by light, Hypericin deactivates HIV.
So it would be nice to understand how it works.

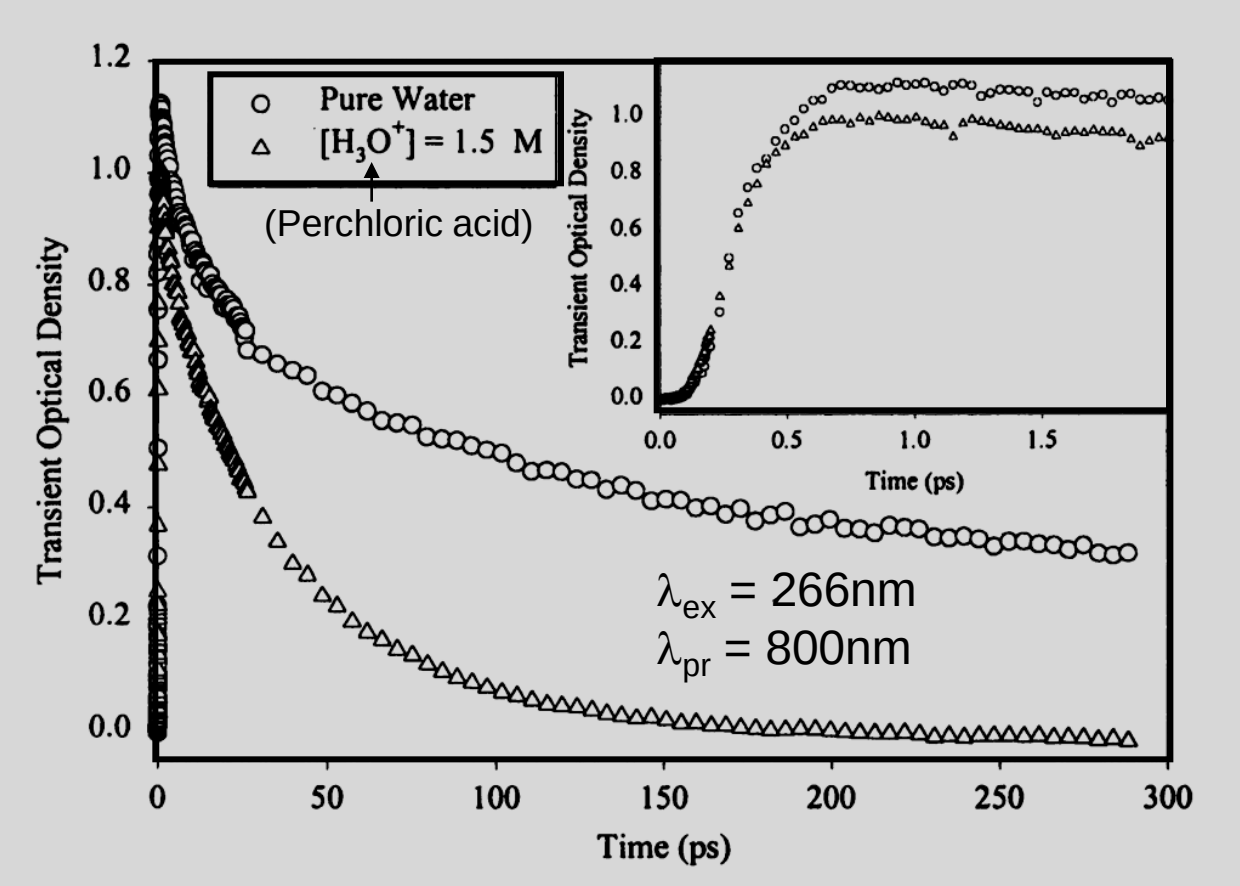


These curves (for two different solvents) show the rise time for a proton-transfer process important in its biological activity.

M.J. Fehr, et al., Ultrafast Phenomena IX, pg. 462 (1994).

Excite-probe measurements of Terawatt femtosecond UV pulses in water

High-intensity UV ultrashort pulses may someday be used in surgery.
So understanding what these pulses do to water is important.
Hydrated electrons are formed in very high concentrations (0.01 molar).

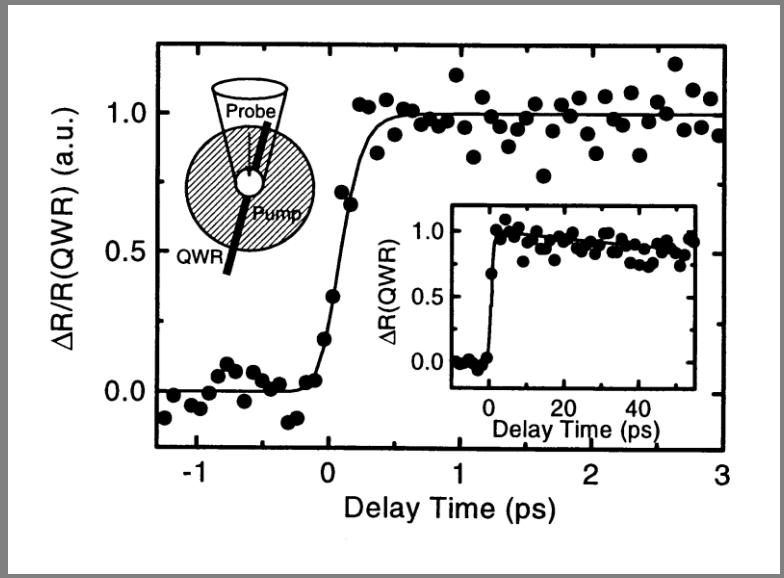


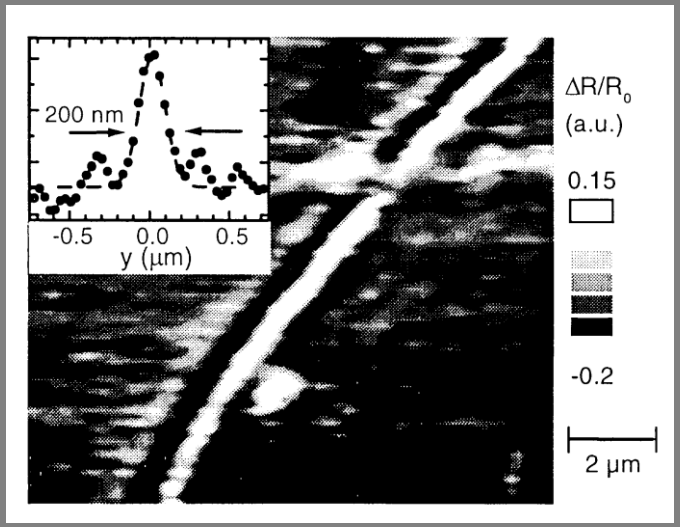
The induced absorption seen here is very high!

Pommeret, et al., Ultrafast Phenomena XII, p. 536 (2000).

Excite-probe reflection spectroscopy

Exciting a surface and probing its reflectivity later reveals surface physics.
Here, a quantum wire is studied using ultrashort pulses in a near-field scanning optical microscope to yield 200-nm spatial resolution, too!



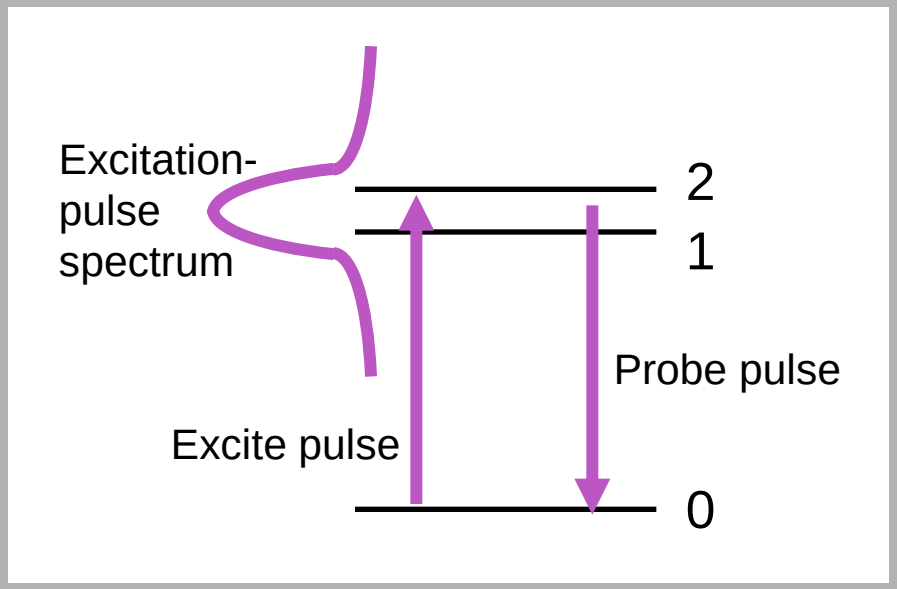


ΔR/R vs. x and y for a delay of 10 ps

Emiliani, et al., Ultrafast Phenomena XII, p. 256 (2000).

Excite-probe measurements can reveal quantum beats: Theory

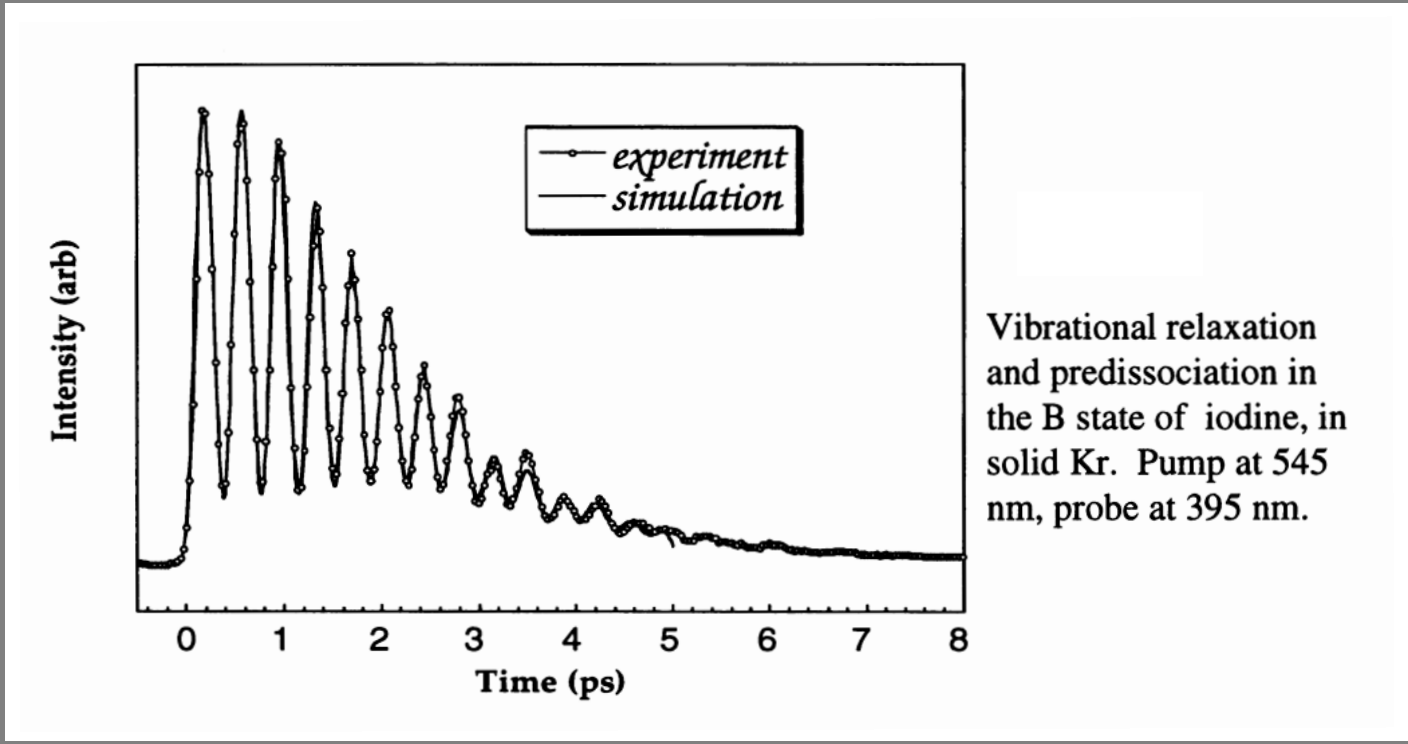
Since ultrashort pulses have broad bandwidths, they can excite two or more nearby states simultaneously.



Probing the 1-2 superposition of states can yield quantum beats in the excite-probe data.

Excite-probe measurements can reveal quantum beats: Experiment

Here, two nearby vibrational states in molecular iodine interfere.

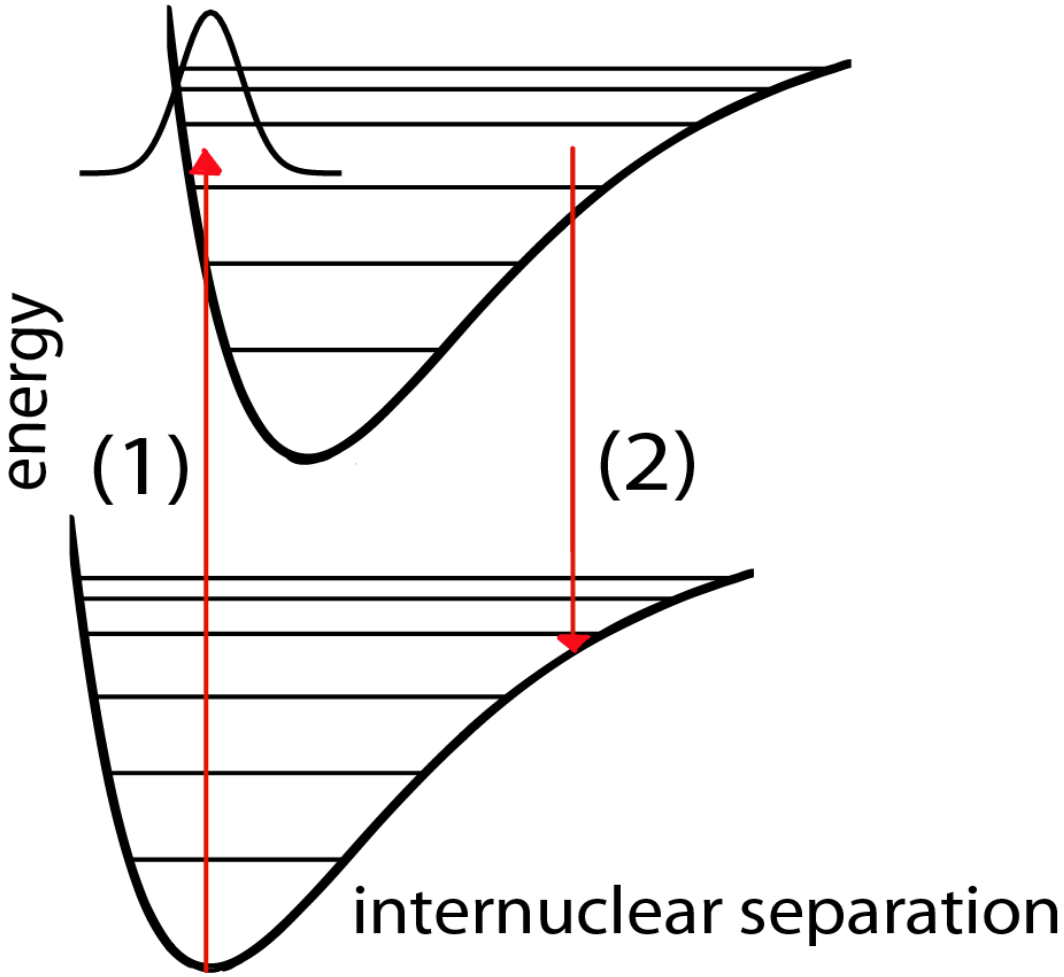


Vibrational relaxation and predissociation in the B state of iodine, in solid Kr. Pump at 545 nm, probe at 395 nm.

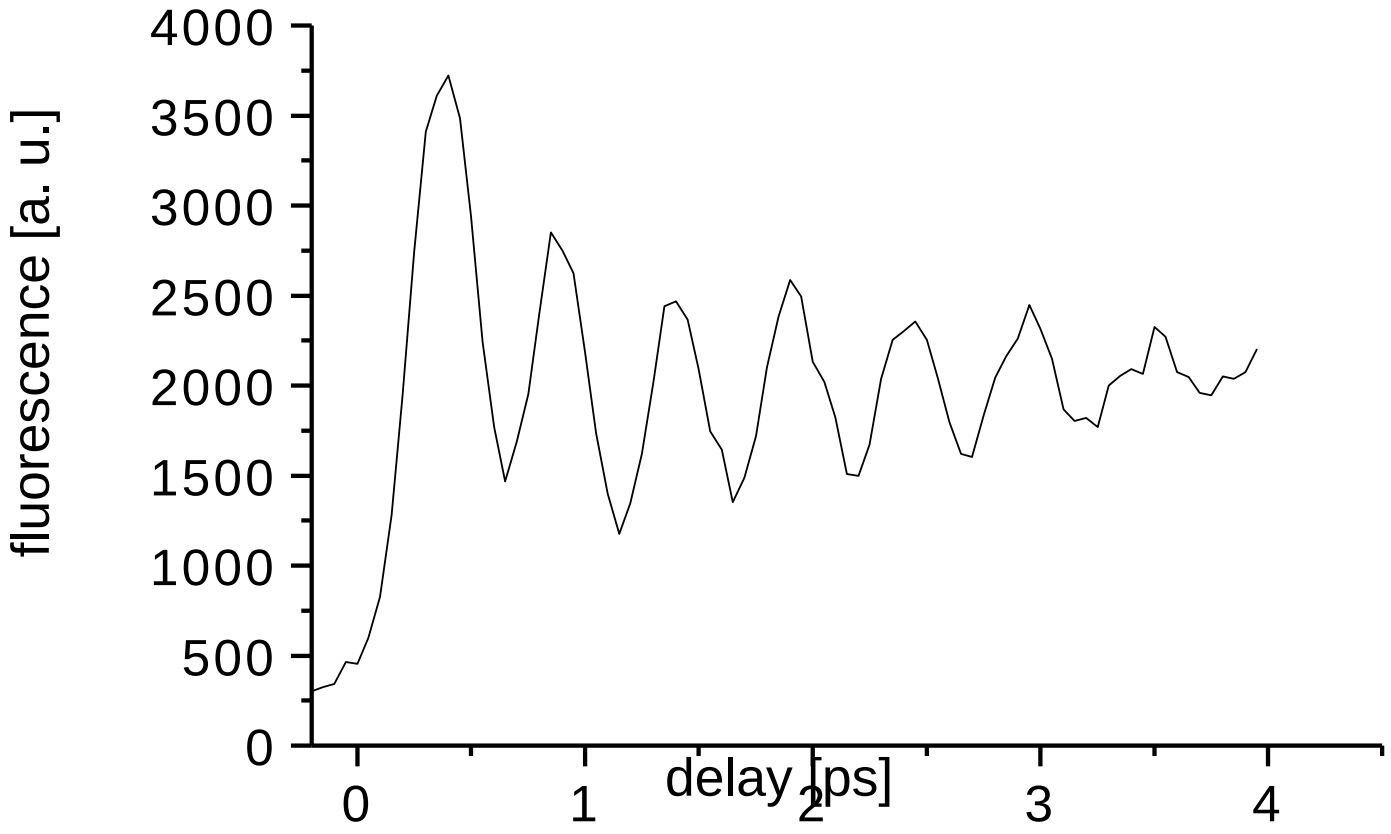
These beats also indicate the motion of the molecular wave packet on its potential surface. A small fraction of the I_2 molecules dissociate every period.

Zadoyan, et al., Ultrafast Phenomena X, p. 194 (1996).

Coherent exitation of a wavepacket

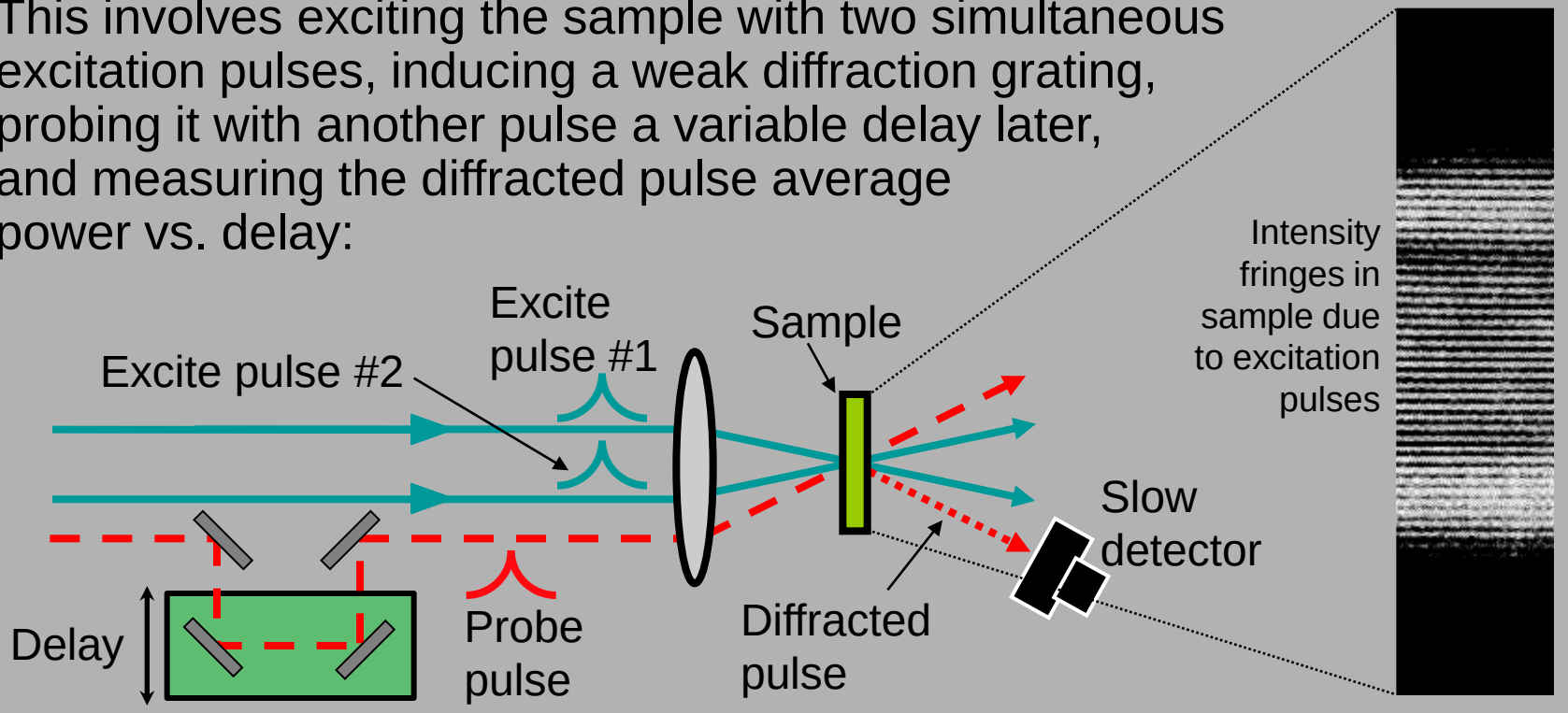


„Real-time” molecular vibrations (wavepacket) measurements

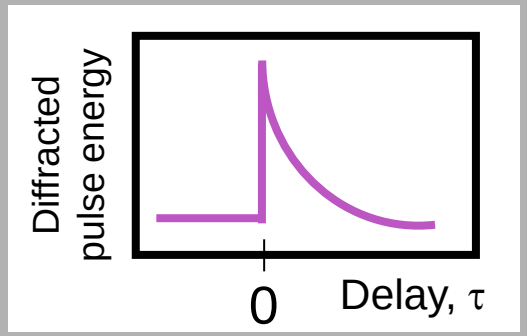


A background-free ultrafast spectroscopy method is *The Transient-Grating Technique*.

This involves exciting the sample with two simultaneous excitation pulses, inducing a weak diffraction grating, probing it with another pulse a variable delay later, and measuring the diffracted pulse average power vs. delay:

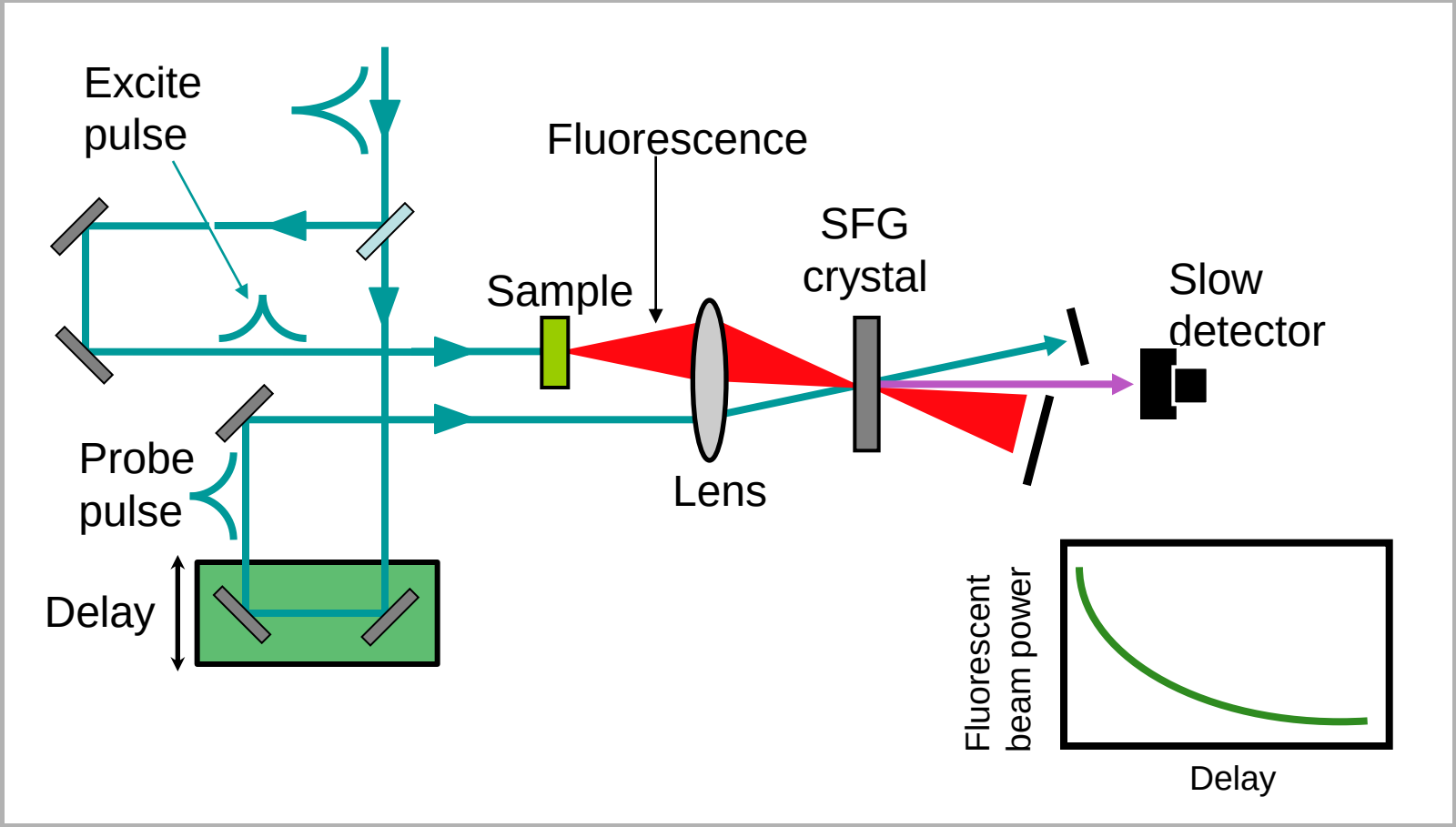


The excite pulses have a spatially sinusoidal energy deposition in the sample. The sample absorption and refractive index will now vary sinusoidally in space.



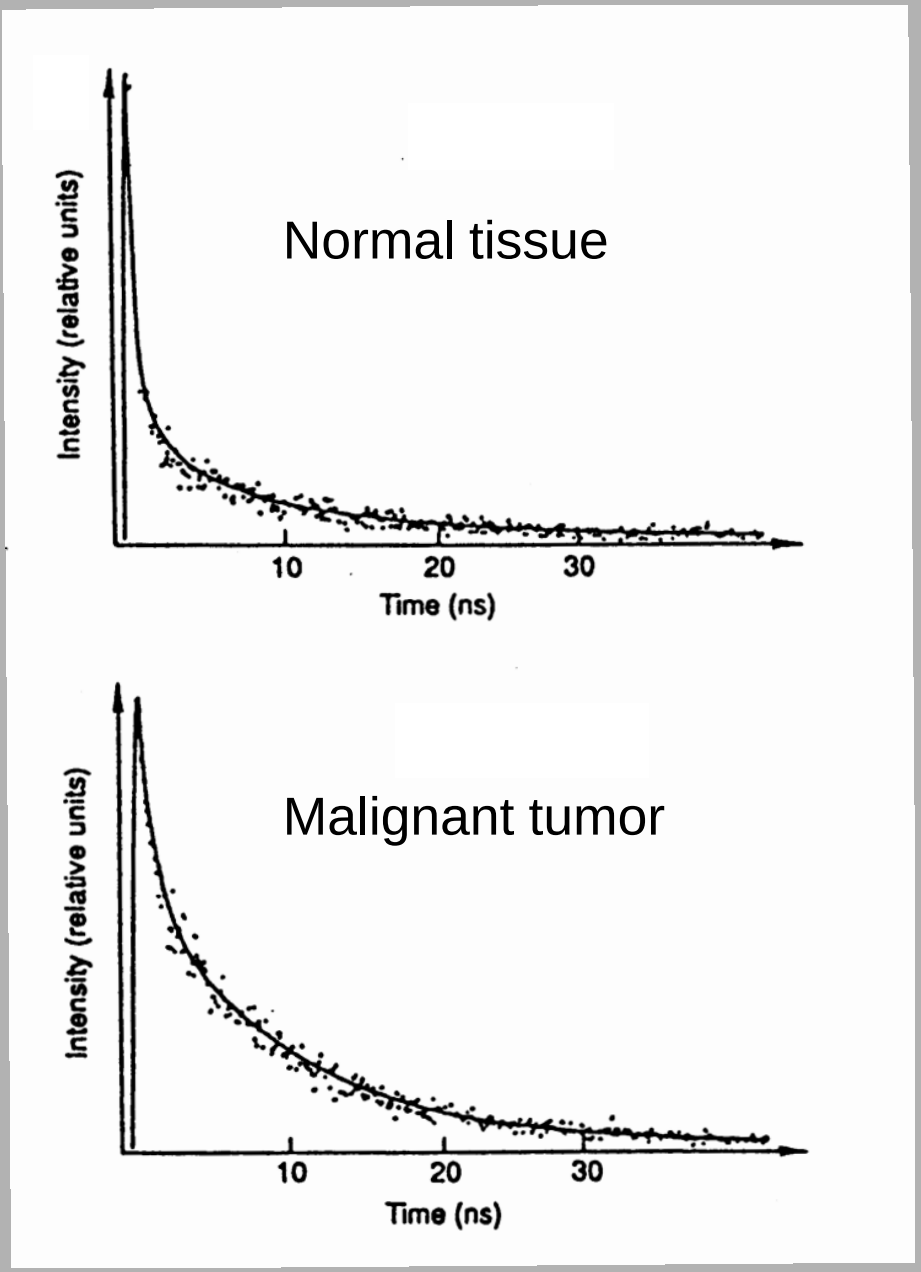
Time-resolved fluorescence is also useful.

Exciting a sample with an ultrashort pulse and then observing the fluoresccence vs. time also yields sample dynamics. This can be done by directly observing the fluroescence or, if it's too fast, by **time-gating** it with a probe pulse in a SFG crystal:



Time-resolved fluorescence decay

When different tissues look alike (i.e., have similar absorption spectra), looking at the time-resolved fluorescence can help distinguish them.

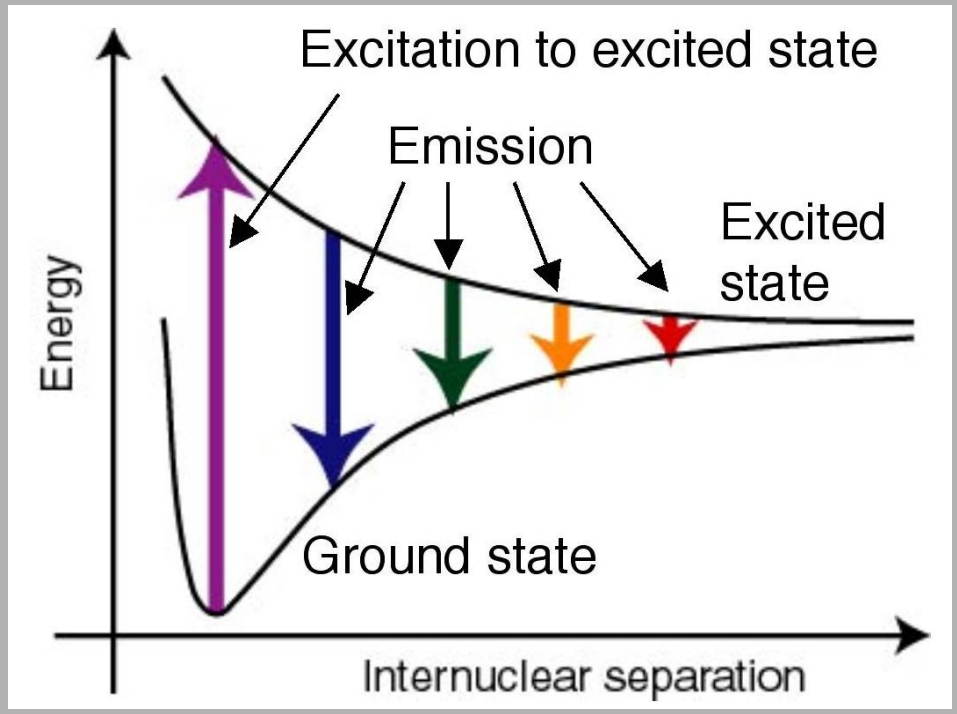


Here, a malignant tumor can be distinguished from normal tissue due to its longer decay time.

Svanberg, Ultrafast Phenomena IX, p. 34 (1994).

Temporally and spectrally resolving the fluorescence of an excited molecule

Exciting a molecule and watching its fluorescence reveals much about its potential surfaces. Ideally, one would measure the time-resolved spectrum, equivalent to its intensity and phase vs. time (or frequency).

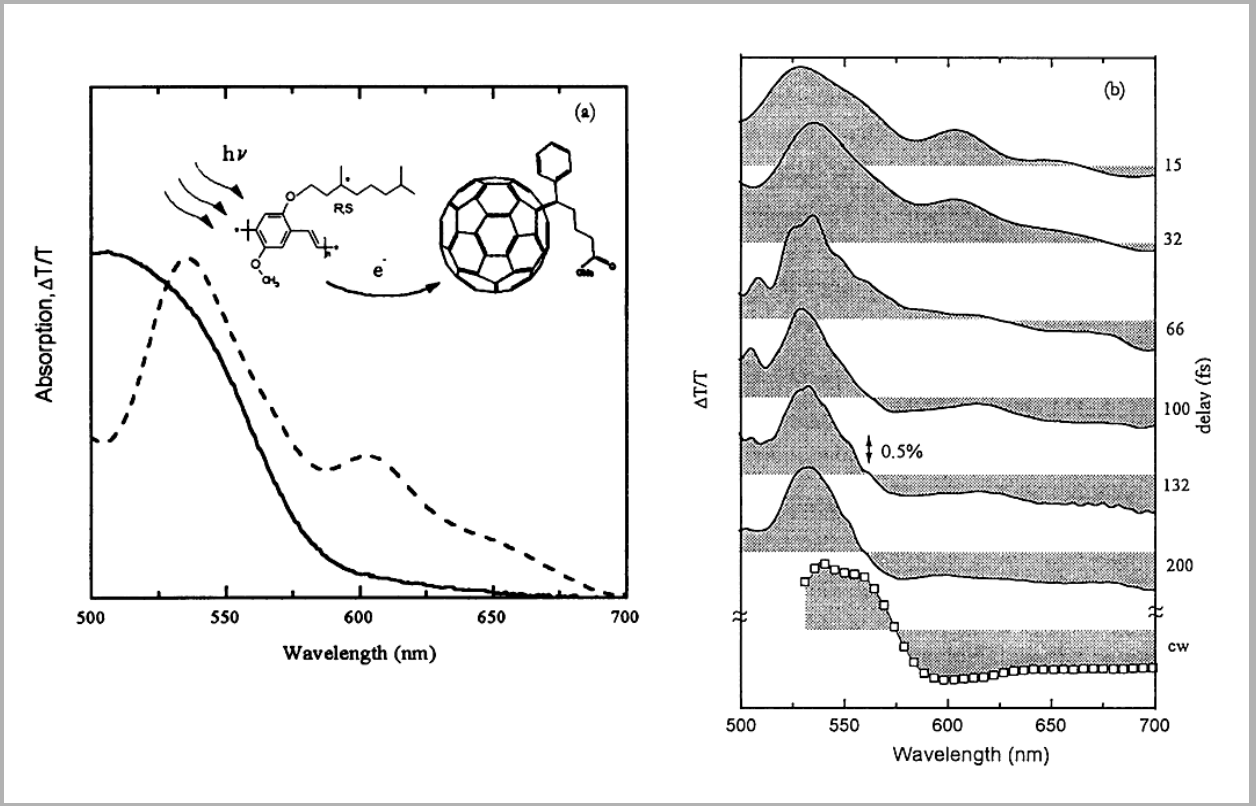


Here, excitation occurs to a “predissociative state,” but other situations are just as interesting. Analogous studies can be performed in absorption.

Time-frequency-domain absorption spectroscopy of Buckminster-fullerene

Electron transfer from a polymer to the buckyball is very fast.

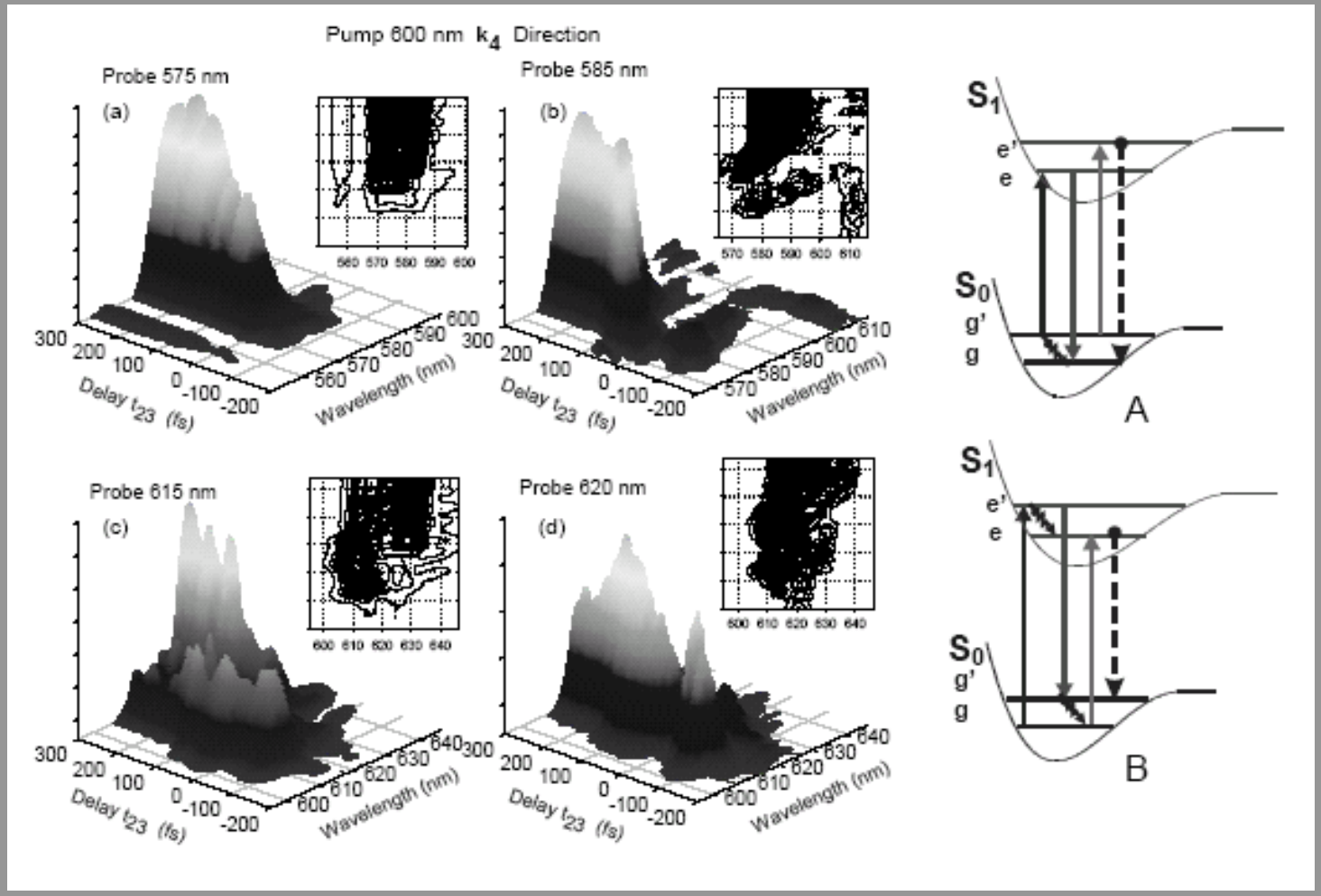
It has applications to photo-voltaics, nonlinear optics, and artificial photosynthesis.



Brabec, et al., Ultrafast Phenomena XII, p. 589 (2000).

Multi-dimensional nonlinear spectroscopy

Measure signal out vs. various input delays and wavelengths

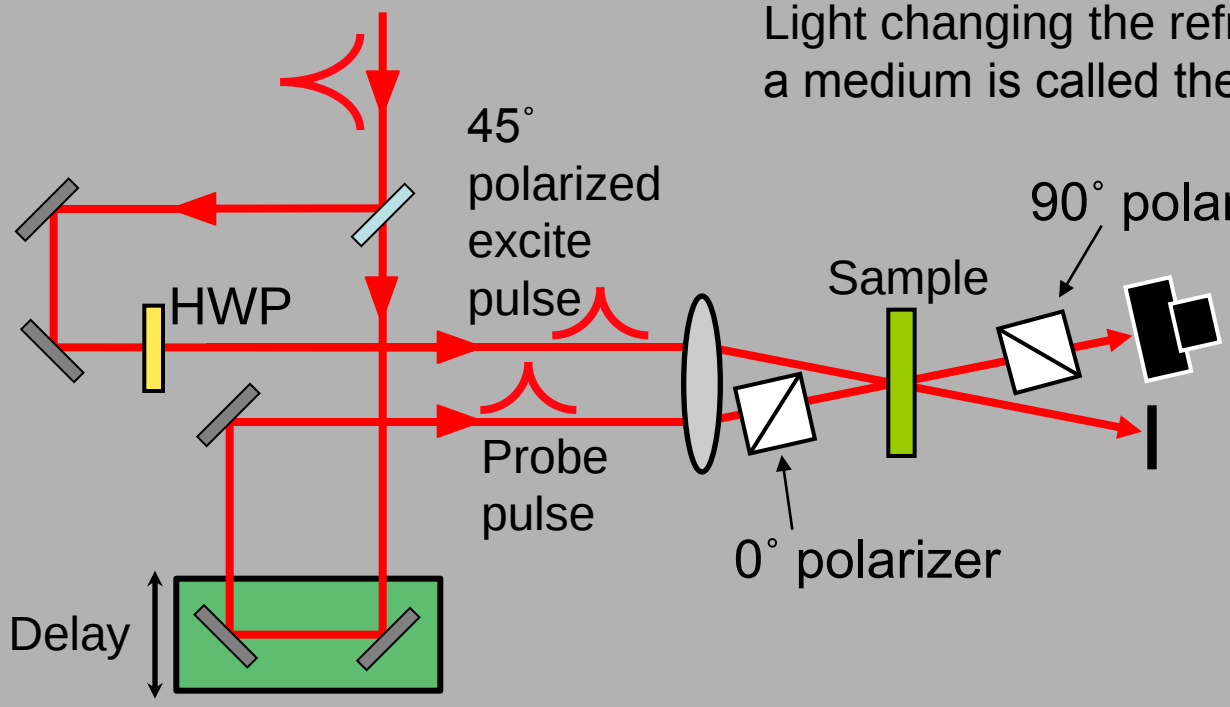


Cresyl violet

Hannaford and coworkers, UP 2004

Ultrafast Polarization Spectroscopy

A 45˚-polarized excite pulse will induce birefringence in an ordinarily isotropic sample. A variably delayed probe pulse between crossed polarizers can watch the birefringence decay, revealing the sample orientational relaxation.



It’s also possible to change the absorption coefficient differently for the two polarizations. This is called an “induced dichroism.” It also rotates the probe polarization and can also be used to study orientational relaxation.

Nice features of ultrafast polarization spectroscopy

It's as easy to set up as excite-probe (just cross two beams in space and time).

It's almost background-free (crossed polarizers transmit as little as 10^{-6} of the incident light).

Unlike excite-probe, it measures both absorption and phase effects.

It can use lock-in detection.

And simultaneously, it can use "optical heterodyne detection," which optimizes the signal-to-noise ratio.