Introduction to Laser Flash Photolysis LP980

By

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Laser Flash Photolysis (LFP)

LFP is a technique for studying the transient chemical and biological species generated by a short, intense light pulse from a nanosecond pulsed laser source (pump pulse).

Transient = short lived

LFP continued…

- Laser based technique
- The light pulse from the laser interacts with a sample
- to creates short lived photo-excited intermediates such as excited states, radicals, and ions.
- Intermediates generated in amounts enough for chemical and physical interactions to occur.
- Direct observation of the temporal absorption characteristics

LFP continued…

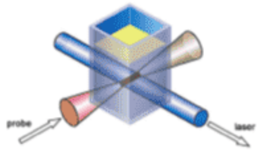
- **Absorption changes recorded spectrally: continuous Xenon lamp (probe source) in a single beamed spectrometer.**
- **Probe source pulsed: enhance photon flux measurements in short time ranges**
- **Spectra measured with temporal resolutions :**

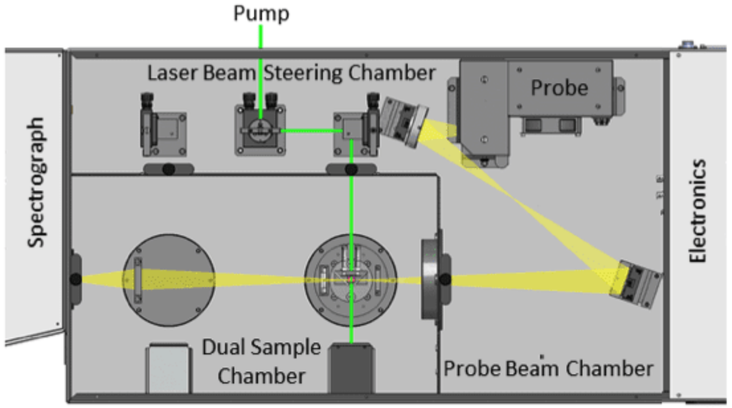
  Pulse mode (nanoseconds to milliseconds)

  Continuous mode (milliseconds to seconds)

Standard Transient Absorption

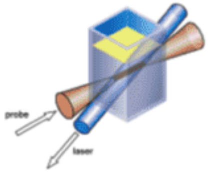
suitable for liquids (shown) and film samples

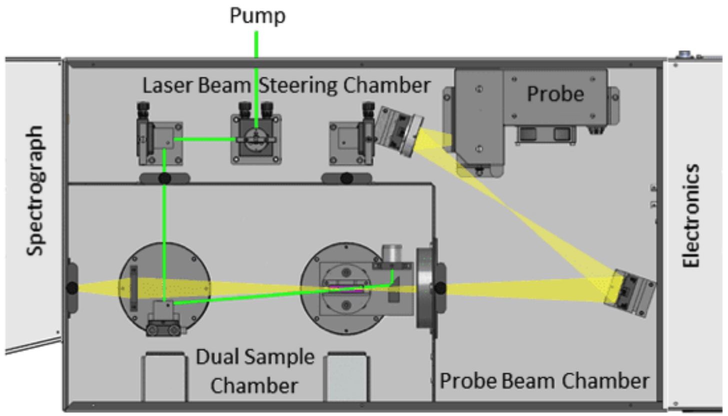




Quasi-Collinear Transient Absorption

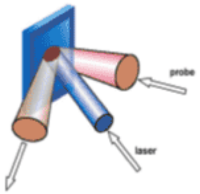
suitable for low absorption liquid and gas samples

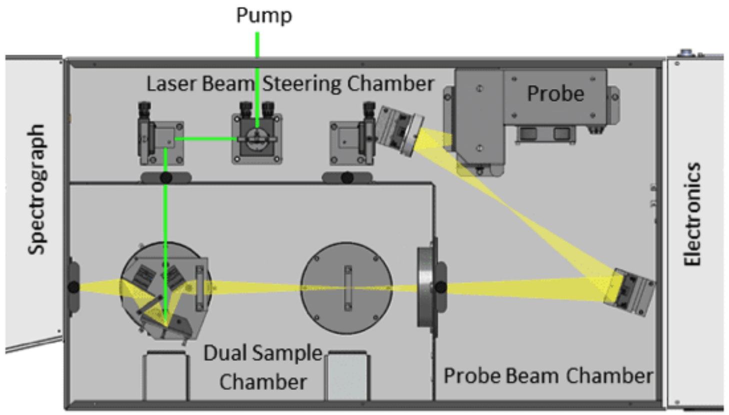




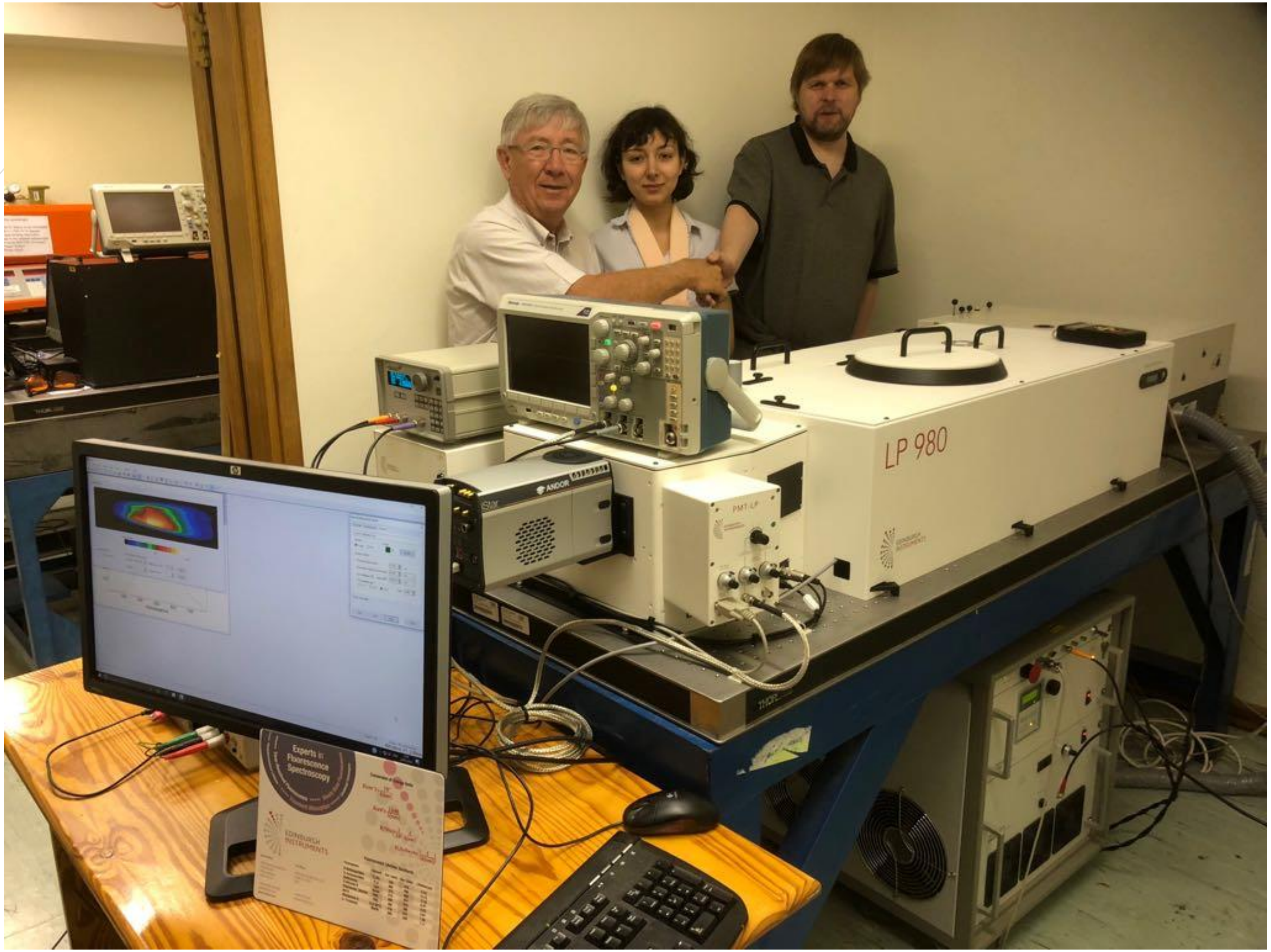
Diffuse Reflectance

suitable for powders and non-transparent film samples





LIQUIDS: The pump beam and the probe beam overlapping orthogonally (transverse excitation).


LP 980
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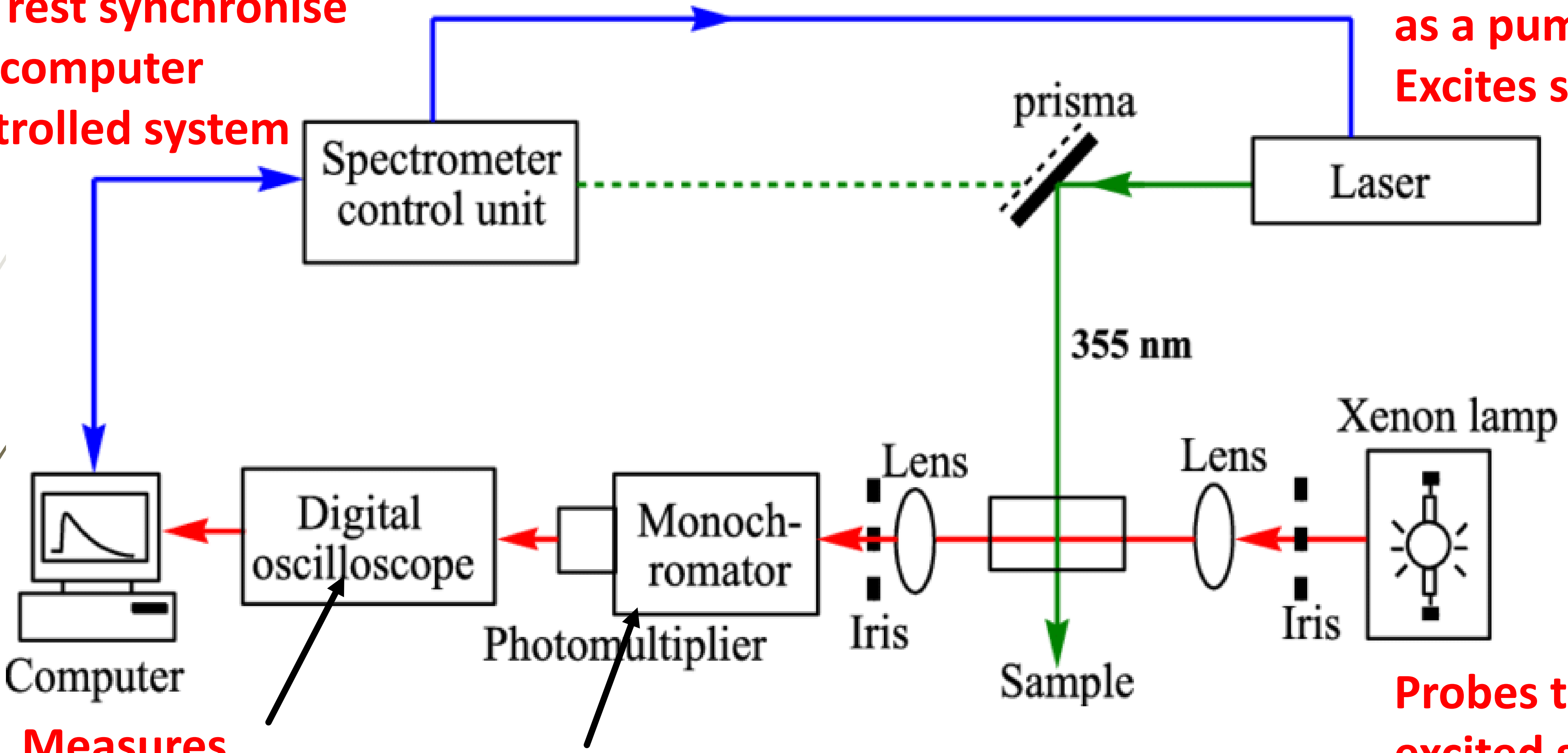
LFP Instrumentation

The rest synchronise the computer controlled system

Nd: YAG laser as a pump. Excites sample



Probes the excited sample

Measures output signal from detector

Detect and convert acquired signals

Sample Preparation

- **Standard (known molar extinction coefficient)**
- **Sample of interest**

Cross over wavelength using the Q-BAND of both the sample and the standard: put the value in your keypad

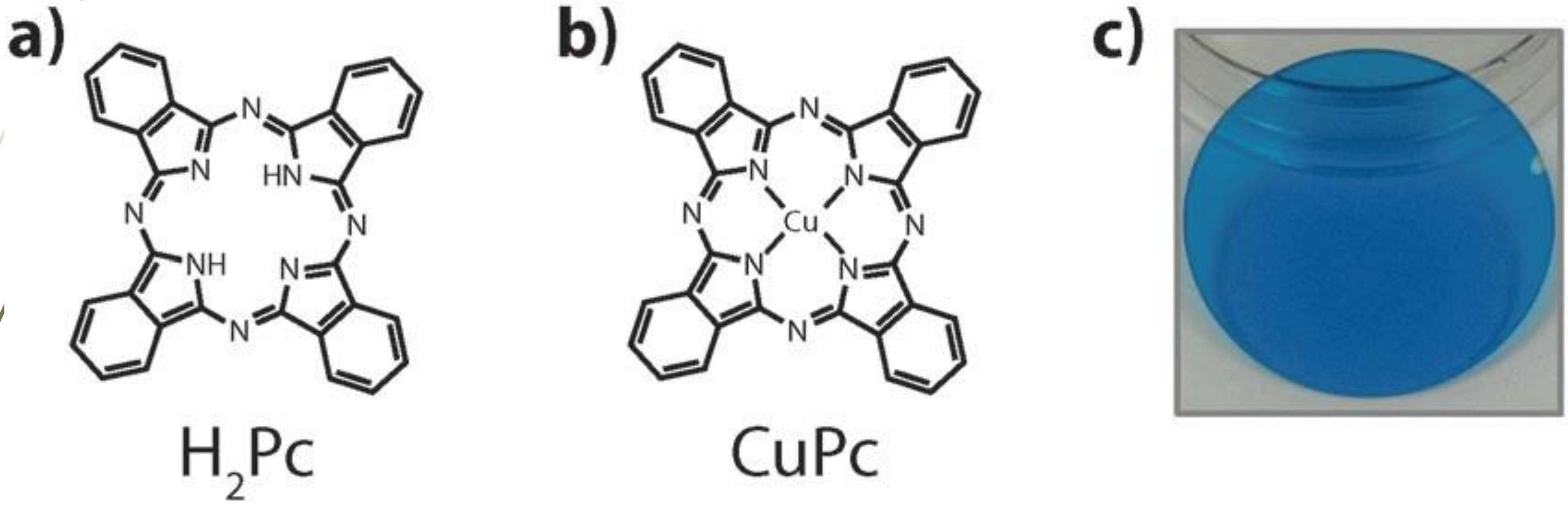
- **Degas with argon**

Things to consider during measurements

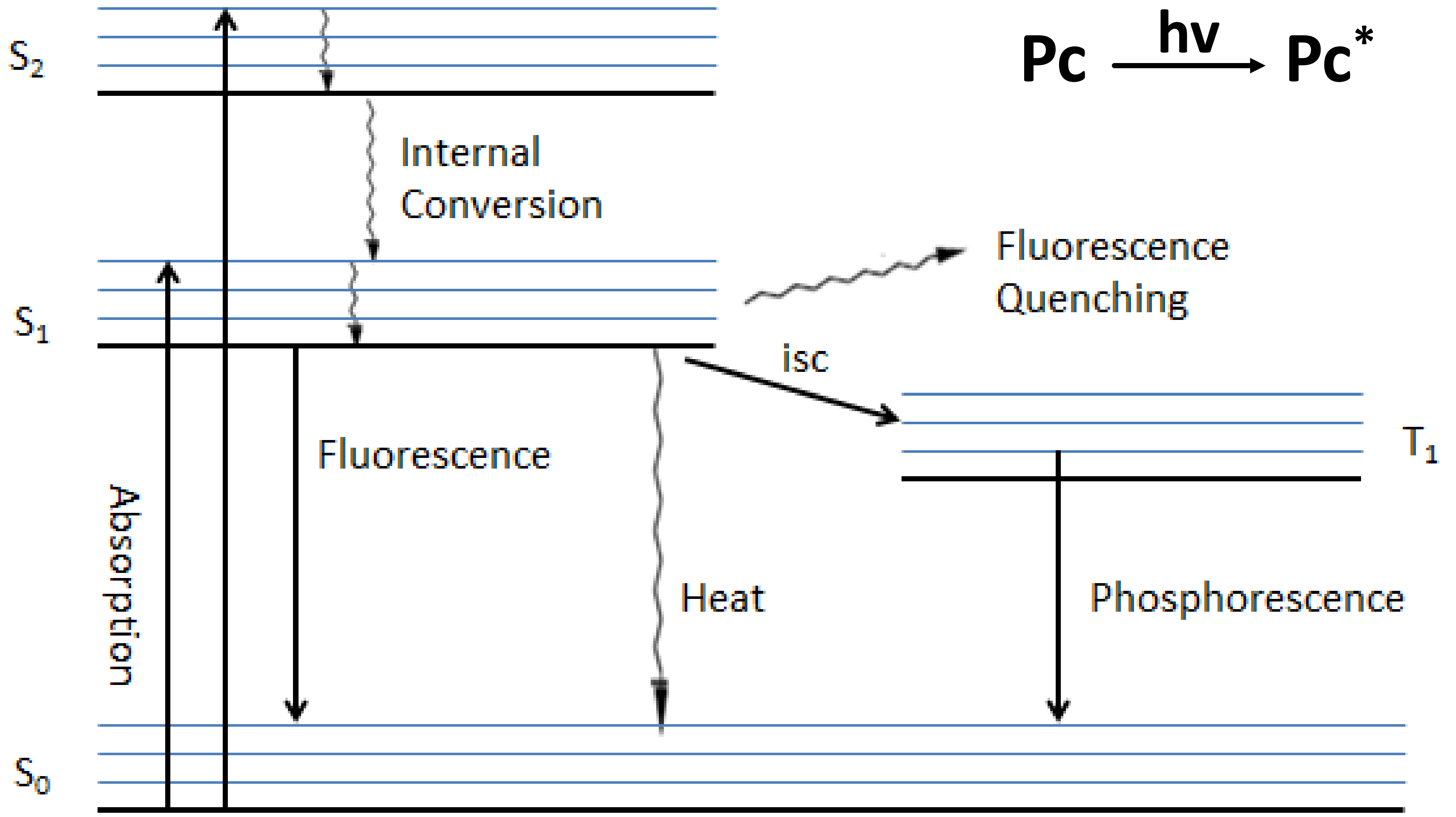
- Excitation should occur where ground state absorption occurs
- **Laser pulse must be half the length of the reaction**
- Sufficient energy to cause excitation
- The flash must cover spectrum of frequencies being covered : the flash produces intermediates unknown and source of spectroscopic analysis.

Bringing it home

Phthalocyanines



Jablonski Diagram

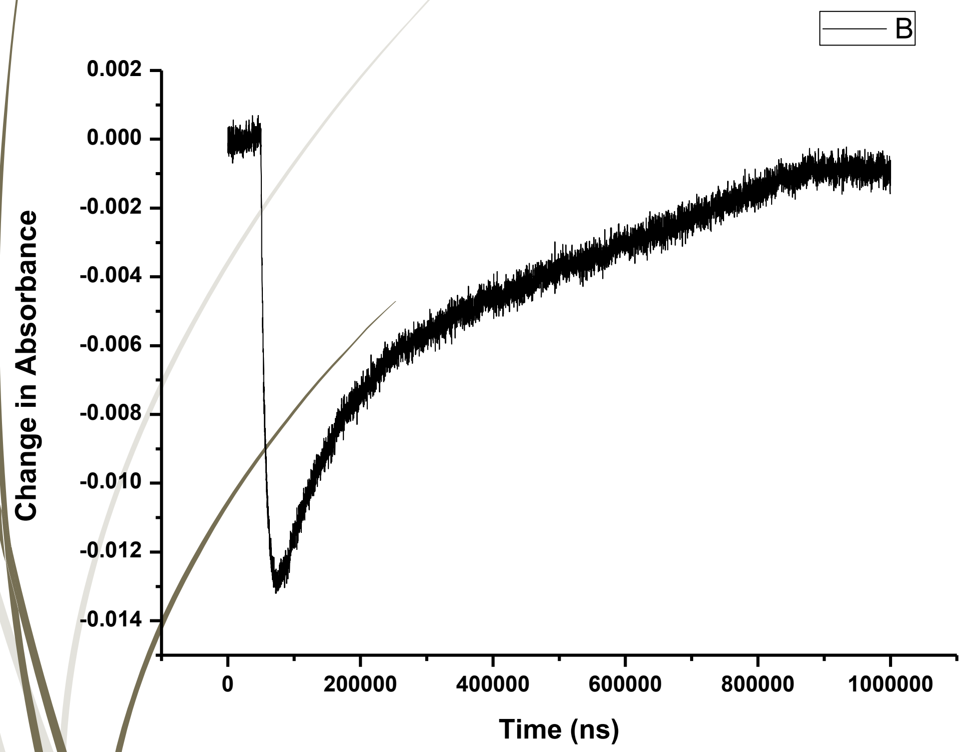


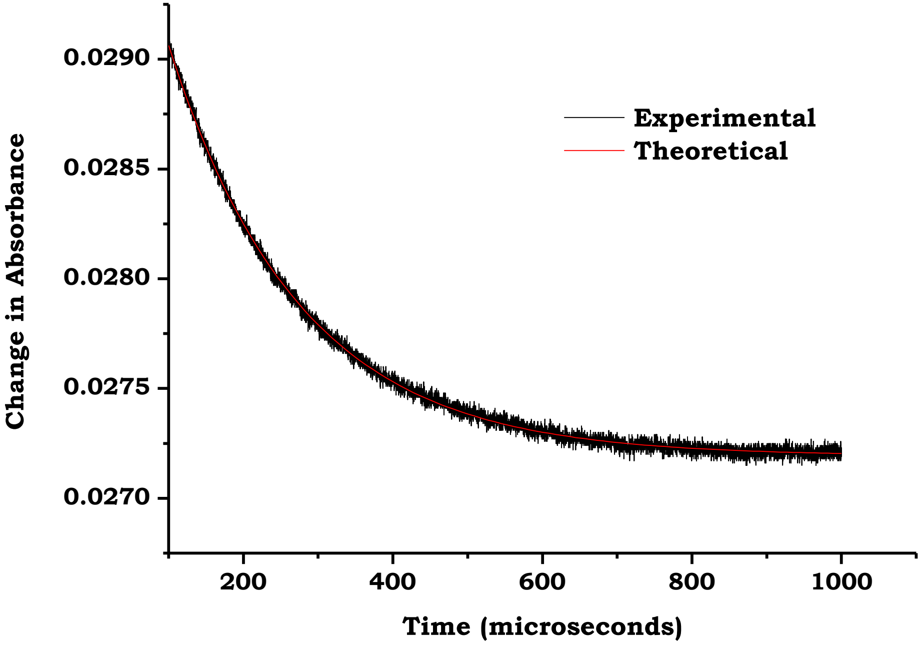
Data acquisition/Types of Modes

1. Kinetic Mode

Transient Absorption decays are recorded at a single wavelength as a function of time using a photodetector and a digital storage oscilloscope.

Transient Absorption





Depletion of your single state to populate the triplet.

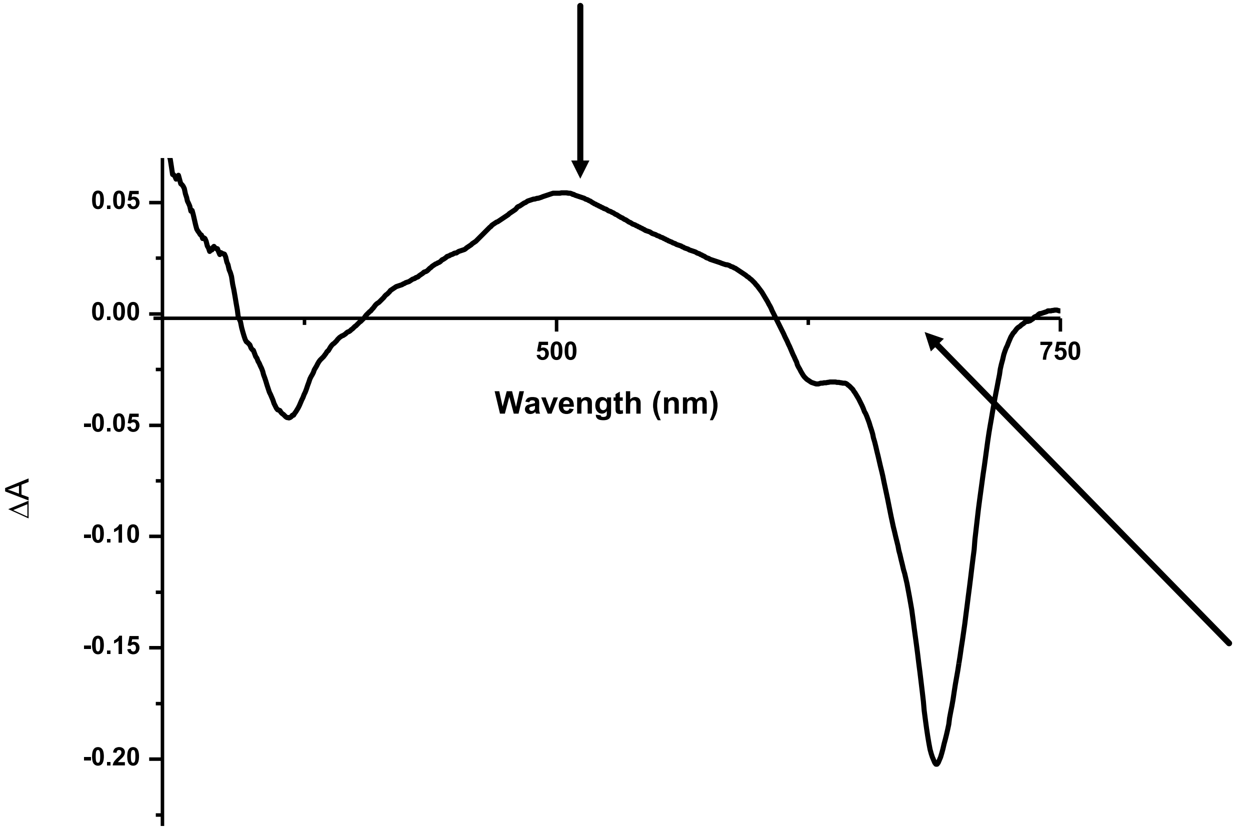
$\tau_{T=triplet\ lifetime}$

Obtained by fitting the experimental data to a mono – exponential function

2. Spectral data acquisition

Time-gated transient absorption spectra are measured at a specific time after excitation using an ICCD detector. Spectral mode measurements provide the full picture of the transient spectral features by exposing the sample to only a few laser shots.

Wavelength of maximum triplet absorption



Wavelength of maximum singlet transition

Excited at : 660 nm

Calculation of triplet quantum yield (Φ_T) and life times (τ_T)

$$\varepsilon = \varepsilon_S \frac{\Delta A_T}{\Delta A_S}$$ **(sample)**

$$\varepsilon_T{}^{std} = \varepsilon_{S^{std}} \frac{\Delta A_T std}{\Delta A_S std}$$ **(standard)**

$$(\Phi_T) = (\Phi_T)^{std} \frac{\Delta A_T . \varepsilon^{std} T}{\Delta\ A_T\ std\ \varepsilon_T}$$

$\Phi\ T^{std} = known$

$\varepsilon_{S,T}$ = molar extinction coefficient

Factors that might result in errors in quantum yield (Φ_T) and life times (τ_T)

- **In-sufficient de-gassing of sample and standard**
- **Wrong value of molar absorption coefficient of the sample**
- **Equipment Handling**
- **Data acquisition and processing**

Singlet Depletion

- All non fluorescing molecules undergo intersystem crossing
- The absorption of the single excited state and triplet states at the working wavelength are negligible when compared to that of the ground singlet state