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 create 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)
LIQUIDS: The pump beam and the probe beam overlapping orthogonally (transverse excitation).
Nd: YAG laser as a pump. Excites sample.

The rest synchronise the computer controlled system.

Measures output signal from detector.

Detect and convert acquired signals.

Probes the excited sample.
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

a) \( \text{H}_2\text{Pc} \)

b) \( \text{CuPc} \)

c) Image of a solution
Jablonski Diagram

\[ \text{Pc} \xrightarrow{\text{hv}} \text{Pc}^* \]
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.

\[ \tau_T = \text{triplet lifetime} \]

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.
Excited at : 660 nm

Wavelength of maximum triplet absorption

Wavelength of maximum singlet transition
Calculation of triplet quantum yield ($\Phi_T$) and lifetime ($\tau_T$)

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

$$\varepsilon_{T\,std} = \varepsilon_{S\,std} \frac{\Delta A_{T\,std}}{\Delta A_{S\,std}} \quad \text{(standard)}$$

$$\Phi_T = \Phi_{T\,std} \frac{\Delta A_T \cdot \varepsilon_{std \, T}}{\Delta A_T \, std \, \varepsilon_T}$$
Factors that might result in errors in quantum yield ($\Phi_T$) and life times ($\tau_T$)

- 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