

# Combined Stationary Fluorescence and Nanosecond Time Resolved Laser Flash Photolysis Setup

*Nele Lange<sup>1</sup>, Martin Regehly<sup>1</sup>*

<sup>1</sup> *University of Applied Sciences Wildau, Hochschulring 1, 15745 Wildau, Germany  
nele\_sophie.wandel@th-wildau.de*

## Summary:

This paper presents a novel, adaptable setup for characterizing photoactive molecules, focusing on the determination of triplet state lifetimes and fluorescence spectra. The setup incorporates a custom-designed chopper wheel, which reduces the need for complex time control electronics. This configuration is easy to replicate and applicable across diverse fields. Initial tests with tetraphenylporphyrin demonstrate reliable lifetime and fluorescence measurements.

**Keywords:** laser flash photolysis, triplet state, fluorescence spectroscopy, chopper wheel

## Motivation

The characterization of photoactive molecules is essential for numerous applications, including volumetric 3D printing [1], solar cells [2] or nanocircuitry [3]. Investigating triplet state properties, such as lifetime, can aid in designing molecules that are more efficient for targeted applications.

This laser flash photolysis setup is designed to be highly versatile, allowing for continuous modifications to meet specific experimental needs. It allows not only the determination of excited state lifetimes within the nanosecond range but also acquisition of fluorescence spectra.

## Setup

The setup (Fig. 1.) primarily consists of standard laboratory components used in pump probe setups. Other components, like the cuvette holder, can easily be 3D printed. The laser must be capable of being triggered by the chopper controller.

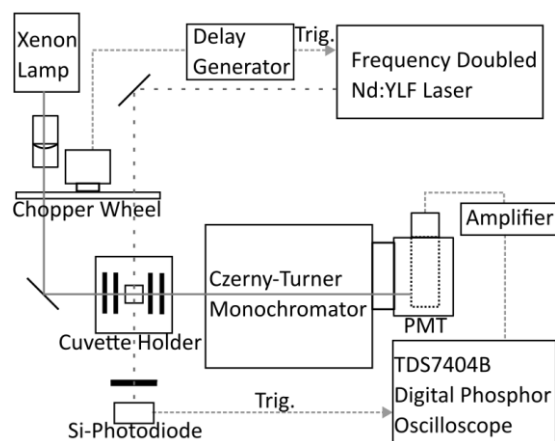


Fig. 1. Schematic drawing of the measurement setup

The pump beam is created by a diode-pumped, intercavity frequency doubled Nd:YLF laser that produces pulses exceeding 100 ns with single pulse energies between 0.1 mJ and 9.6 mJ. It passes through the chopper wheel, exciting the sample before reaching the Si-photodiode, which triggers the oscilloscope. The probe beam, generated by a xenon lamp, passes through the chopper wheel, reflects off a mirror, intersects the sample and the pump beam at a 90° angle, then continues through the Czerny-Turner monochromator before reaching the photomultiplier tube. The photomultiplier has a rise time of 2.2 ns. An amplifier transmits the data to the digital phosphor oscilloscope.

To acquire the laser-induced fluorescence spectrum, the xenon lamp and the chopper wheel are switched off and the monochromator is scanned across the desired wavelength range.

A key innovation of this setup is the chopper wheel (Fig. 2.) where both the probe and pump beam pass through at the same height, but in different locations.

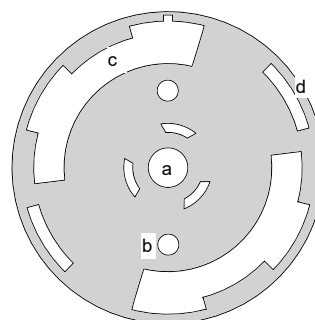


Fig. 2. Chopper wheel geometry a) mounting cut-out, b) pump laser openings, c) probe beam openings, d) feedback slots

The chopper wheel triggers the laser, allowing the pump laser frequency to be reduced by selectively opening sections in the inner ring of the disk (b). The chopper wheel also defines the measurement timing by opening and closing the probe beam path at precise intervals (c).

The setup's time resolution depends on the pump pulse duration and the photomultiplier rise time. The time window is defined by the slowest achievable repetition rate, with extended probe beam durations allowing for measurements over a broader timeframe.

### Nanosecond Laser Flash Photolysis Results

Fig. 3. shows how the chopper wheel provides precise measurements with clear on/off intervals, offering the 0% and 100% transmission values.

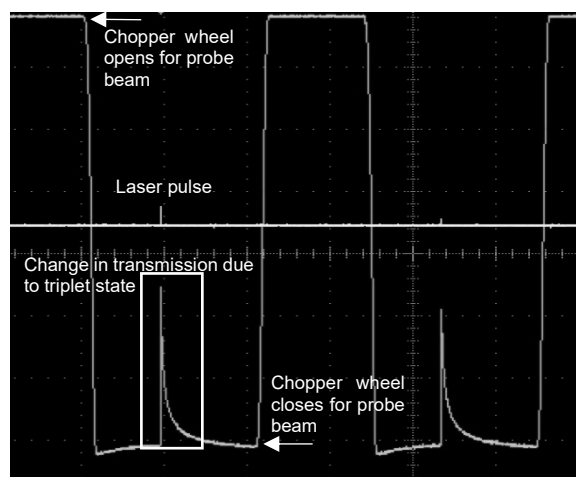


Fig. 3. Oscilloscope screenshot showing triplet state lifetime measurement

Upon excitation to the triplet state, tetraphenylporphyrin, exhibits a change in optical density influenced by the pump laser's energy and surrounding  $O_2$  levels. This change is observed on the oscilloscope as a loss of intensity caused by the reduced transmission.

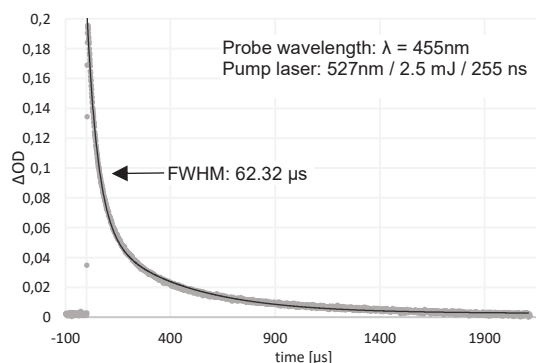


Fig. 4. Triplet state lifetime of tetraphenylporphyrin in toluene under nitrogen atmosphere

The change in optical density at a specified time  $\Delta OD_t$  can be calculated using equation (1):

$$\Delta OD_t = -\log\left(\frac{I_t - I_0}{I_{max} - I_0}\right) \quad (1)$$

The results of the change in optical density can be seen in Fig. 4. A double-exponential curve fit yielded a half-life of 62.32  $\mu s$  for the triplet state.

### Steady State Fluorescence Results

Tetraphenylporphyrin has a distinct fluorescence emission spectrum which was captured using this setup. Relative radiometric calibration was used to correct the data set, resulting in accurate fluorescence spectra, as illustrated in Fig. 5.

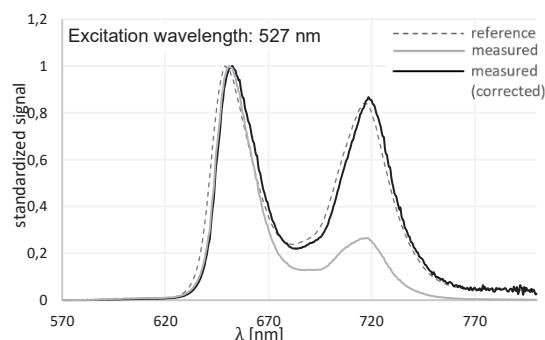


Fig. 5. Fluorescence spectrum of tetraphenylporphyrin in toluene

### Conclusion

This work successfully demonstrates a versatile measurement setup capable of performing nanosecond laser flash photolysis spectroscopy and capturing steady state laser-induced fluorescence spectra, making it ideal for diverse applications. The innovative chopper wheel design and straightforward setup make replication feasible in any laboratory setting.

### References

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