

Long Photoluminescence Lifetimes with the Fluorolog-QM



Technical Note
FLTN260101

Introduction

Traditionally, long photoluminescence lifetime measurements have been conducted with either Boxcar or Multi-Channel Scaling (MCS) techniques. In addition to offering these traditional techniques, HORIBA also provides a more efficient Single-Shot Transient Digitizer (SSTD) method, which offers some unique benefits. Specifically, SSTD is the fastest of the three techniques as it captures entire PL decays in real-time with each flash of a pulsed light source, is not limited by photon counting statistics and requires no additional detection electronics.

All three techniques utilize pulsed light sources, such as microsecond Xe flash lamps, variable pulse duration LEDs (e.g. HORIBA's SpectraLEDs) and a variety of lower repetition rate lasers (e.g. DPSS, Q-switched, nitrogen/dye etc.). These techniques work well for a lifetime range from microseconds to tens of milliseconds but gradually become inefficient or unusable for lifetime ranges extending to hundreds of milliseconds and seconds. One reason is that a relatively short excitation pulse will not populate efficiently a long lifetime excited triplet state, so it is advantageous to increase the duration of the excitation cycle to attain the absorption/emission equilibrium (Fig. 1). Another reason is an electronic limitation of the longest time range available with the pulse excitation techniques, typically up to ~10 s.

In this note we discuss how the Fluorolog-QM can provide exquisite phosphorescence decays across the widest possible range of lifetimes from microseconds to seconds and beyond.

Materials and Methods

Figure 1 illustrates the excitation and phosphorescence emission cycle for a typical aromatic molecule at 77K. The phosphorescence intensity levels off after about 20-40 s illumination, the excitation shutter is rapidly closed after 40 s resulting in a clean, exponential decay on the time scale of seconds.

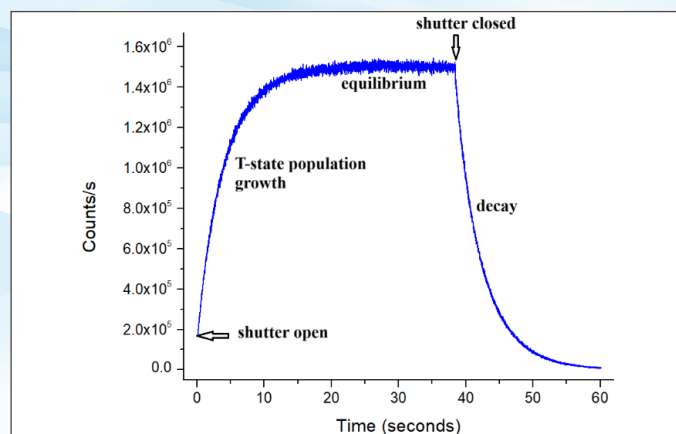


Figure 1. Excitation and emission cycle of a long-lived phosphorescent aromatic at 77K illuminated for 40 s by shutter-controlled Xe lamp

Such experiment can be set up with the Time-Based (kinetic) mode of Felix FL software. The excitation shutter opening and closing is under software control, and the duration of the excitation and phosphorescence signal acquisition can be set according to the time scale of the sample decay. The Fluorolog-QM digitizer electronics allows acquisition rates from 2×10^5 to 1 point/s, which is sufficient to cover typical ranges of phosphorescence decay. The acquisition can be repeated and multiple traces accumulated to improve signal-to-noise.

Figure 2 shows the fluorescence and phosphorescence spectra and the phosphorescence decay at 465 nm of biphenyl in 2-propanol glass at 77K using 100 points/s and yielding $\tau = 4.28$ s.

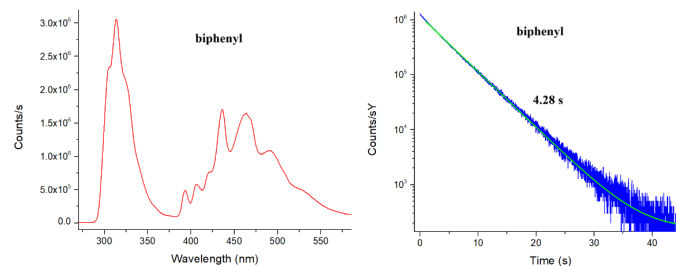


Fig. 2 Fluorescence and phosphorescence spectra and decay of biphenyl in 2-propanol glass matrix at 77K measured with the steady-state setup of Fluorolog-QM. The 100 points/s (10 ms) digitization was used for the decay

A more challenging case is phosphorescence of anthracene in ethanol glass at 77K presented in Fig. 3. The phosphorescence spectrum is very weak, requires filtering off the much more intense fluorescence and the use of wide excitation and emission slits. The phosphorescence decay, resulting in $\tau = 39.8$ ms, two orders of magnitude shorter than that of biphenyl, was determined using 1000 points/s digitization rate and accumulating 5 repeats to improve signal-to-noise.

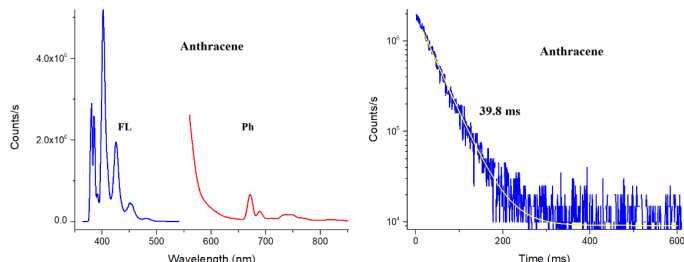


Fig. 3 Fluorescence and phosphorescence spectra and phosphorescence decay of anthracene in ethanol glass matrix at 77K measured with the steady-state setup of Fluorolog-QM. For the decay measurement 1000 points/s (1 ms) digitization was used. A 500-nm long pass filter and fully open slits were used for phosphorescence spectrum and decay measurements

While the highest digitization rate of 2×10^5 points/s ($5 \mu\text{s}$) is fast enough to potentially measure lifetimes in the tens of microseconds range, the excitation shutter closure speed is the limiting factor. In the Kinetics mode we can illuminate and then close the shutter and subsequently analyze the decay after the shutter has been fully closed.

To verify the feasibility of shorter lifetime measurements with the kinetic scan, the fluorescence decay of Er^{3+} ion was measured with the steady-state kinetic scan as well as with the standard SSTD technique using a pulsed Xe lamp excitation. In both cases an InGaAs solid state detector operating in the analog mode was used. With SSTD the InGaAs detector can measure lifetimes down to $\sim 5 \mu\text{s}$. The results from both experiments are compared in Fig. 4.

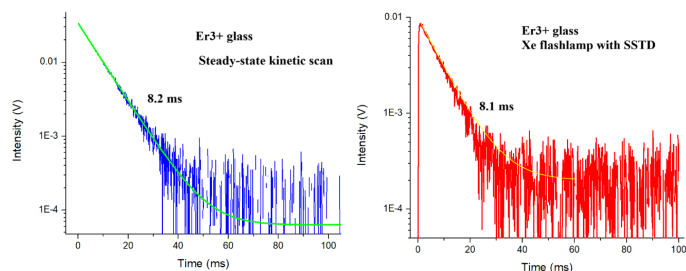


Fig. 4 Fluorescence decay of Er^{3+} -doped glass measured with the steady state kinetic scan (10000 points/s digitization rate) and with SSTD using a pulsed Xe lamp (ex = 980 nm, em = 1536 nm). Solid state InGaAs detector was used for both measurements.

Both methods yield very similar lifetime, 8.1-8.2 ms, thus proving that the kinetic scan method can be used successfully for lifetimes down to < 10 ms.

Conclusion

The results presented in this note show that the Fluorolog-QM with its standard kinetic scan mode can be used for long PL lifetime measurements without requiring any pulsed light source or special signal processing electronics. Due to the fast steady-state digitization rate (up to 2×10^5 points/s) and the software-controlled excitation shutter, the instrument can measure lifetimes ranging from < 10 ms to seconds or longer. This covers the lifetime range of phosphorescence lifetimes of most organic fluorophores and longer fluorescence lifetimes of some lanthanides. When combined with its unrivalled SSTD technique, the instrument is an excellent choice for PL lifetimes from $\sim 5 \mu\text{s}$ and longer with either photomultipliers or solid-state NIR detectors, using photon counting or analog detection, without any extra electronics.

info.sci@horiba.com

www.horiba.com/scientific

USA: +1 732 494 8660
UK: +44 (0)1604 542 500
China: +86 (0)21 6289 6060
Taiwan: +886 3 5600606

France: +33 (0)1 69 74 72 00
Italy: +39 06 51 59 22 1
India: +91 80 41273637
Brazil: +55 (0)11 2923 5400

Germany: +49 (0) 6172 1396 0
Japan: +81(75)313-8121
Singapore: +65 (0)6 745 8300
Other: +33 (0)1 69 74 72 00