Subnanosecond lifetime measurements using inexpensive LED light sources

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Fluorescent lifetime measurements are generally made in the time domain. With the advent of femtosecond laser pulses, this technology has become both impressive and highly specialized, requiring considerable expertise and a sizeable investment. However, many fluorescent materials have lifetimes that do not require such ultra-short time resolution. We have recently developed a simple, inexpensive method of measuring lifetimes. This method has sub-nanosecond time resolution, requires mostly common laboratory equipment, and uses only UV LEDs as light sources.

The method we have developed is based on the phase shift principle. Two unencapsulated LEDs are dc biased and a sinusoidal ripple current is applied at frequencies up to 30 MHz. One LED is used as a reference signal and the other is used to excite the sample. We used Thorlabs PDA 55 silicon photodetectors, which have a 10 MHz bandwidth and built-in, adjustable-gain amplifiers. The signals were averaged using a digital oscilloscope. All of this is general lab equipment, except the detectors, which are cheap.

The lifetime is computed from the phase angle δ between the reference and emitted light signals, the relation being $\tan\delta = \omega\tau$. More precisely, δ is the difference between the detector phase differences with and without the sample in place. For a system with multiple decay channels the measured lifetime τ is generally dependent on the ripple frequency, but in the small ripple frequency limit τ is easily shown to be the arithmetic average relaxation time. This is in contrast to time domain measurements, where the first cumulant of the decay gives the arithmetic average relaxation rate.

It is surprising how well this simple apparatus works: We are easily able to measure lifetimes with sub-nanosecond time resolution, the estimated measurement error being about 200 ps. For example, the lifetime of Coumarin 460 in methanol, was measured to be 1.35 ns at 30 MHz. Our lifetime measurement of Coumarin 500 in methanol (4.71 ns) at 8 MHz is within 160 ps of the published value [1]. The lifetime of the fluorescence standard quinine sulfate dihydrate at 5 MHz (19.1 ns) is within 300 ps of the published value [2].

Finally, the capabilities of this apparatus were tested on phosphors that exhibit simple exponential and stretched exponential decays; as well as laser dyes and quantum dots with multiexponential decays. The phase shift method can be used as an inexpensive alternative to time domain methods for fluorescence lifetime measurements. This technique is simple to use, requires minimal sample preparation, and enables accurate measurements even when the quantum efficiency of the sample is low.

Acknowledgments
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000. Thanks are given to J. Wilcoxen of Sandia Labs for providing quantum dot samples for evaluation.

References

1. S. Nad and H. Pal, "Photophysical properties of Coumarin-500 (CM500): Unusual behavior in nonpolar solvents," *J. Phys. Chem. A.*, **107** [4], 501-507 (2003).
2. W. R. Dawson and M. W. Windsor, "Fluorescence yields of aromatic compounds," *J. Phys. Chem.*, **72** [9], 3251-3260 (1968).