Measurement of luminescence decays: High performance at low cost

Mark Sulkes[a)] and Zoe Sulkes
Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

(Received 2 March 2011; accepted 11 July 2011)

The availability of inexpensive ultra bright LEDs spanning the visible and near-ultraviolet combined with the availability of inexpensive electronics equipment makes it possible to construct a high performance luminescence lifetime apparatus (~5 ns instrumental response or better) at low cost. A central need for time domain measurement systems is the ability to obtain short (~1 ns or less) excitation light pulses from the LEDs. It is possible to build the necessary LED driver using a simple avalanche transistor circuit. We describe first a circuit to test for small signal NPN transistors that can avalanche. We then describe a final optimized avalanche mode circuit that we developed on a prototyping board by measuring driven light pulse duration as a function of the circuit on the board and passive component values. We demonstrate that the combination of the LED pulser and a 1P28 photomultiplier tube used in decay waveform acquisition has a time response that allows for detection and lifetime determination of luminescence decays down to ~5 ns. The time response and data quality afforded with the same components in time-correlated single photon counting are even better. For time-correlated single photon counting an even simpler NAND-gate based LED driver circuit is also applicable. We also demonstrate the possible utility of a simple frequency domain method for luminescence lifetime determinations.

[DOI: 10.1119/1.3620415]

I. INTRODUCTION

In the early 1990s, the ability to measure luminescence lifetimes down to nanosecond timescales was expensive. Although the necessary electronics then cost many thousands of dollars, the single most prohibitive cost was in necessary light sources, almost always lasers. Now, as the result of the availability of many inexpensive ultra bright LEDs spanning the entire visible range, the cost of implementing a visible range nanosecond or even sub-nanosecond pulsed light source can be only a few dollars. Table I summarizes the costs and the properties of readily available light sources across the visible range. While very useful near UV diode lasers (used in Blu-ray devices) are increasingly dropping in price, very cheap near-UV LEDs with equal or greater light output are also available. Although a number of deep-UV LEDs have used as light excitation sources,[1] their cost is currently ~\$60–\$300 for one piece, with prices increasing deeper into the UV.[2]

The availability of electronics instrumentation at low prices combined with the availability of inexpensive ultra bright LEDs can facilitate luminescence decay detection by three different methods—luminescence decay waveform capture,[3] time-correlated single photon counting,[3] and frequency domain lifetime determinations.[3] We will explore methods of implementing each of these methods with the following provisions: total costs in the range of no more than hundreds of dollars, mainly for the purchase of electronics instrumentation; simplicity of operation and implementation, with no skills involved other than knowledge of how to use the electronics and soldering; and no additional capabilities required for construction, such as a machine shop, circuit board etching, and use of surface mount components. Table II summarizes the system needs and the current costs for low cost implementations of the three kinds of systems.

The instrumental resolution of luminescence decay waveform capture and time-correlated single photon counting depends on the duration of the LED excitation pulses. The time resolution for frequency domain measurements depends on the maximum driving frequency possible for the LEDs. Inexpensive LEDs can be driven at hundreds of megahertz or more for frequency domain measurements or can provide nanosecond or sub-nanosecond light pulses for time domain measurements.

II. EXPERIMENTAL NEEDS

Regardless of the method used, a waveform digitizer with a bandwidth of 300 MHz or more is indispensible. Used digitizers from the early to mid 1990s can be found at the prices given in Table II.

Another component necessary in all three methods is a photomultiplier tube (PMT). It is usually possible to find an inexpensive 1P28 PMT. Detector enclosures occasionally are included or sold separately. It is assumed that the enclosure and the base bias circuit will need to be built by hand.

Used mainframe PMT high voltage supplies often can be found for little more than \$100, but it is also possible to buy a new DC to DC HV module in this price range or less. A budget of at least \$100 should be included for the purchase of coaxial cables and connectors and some common electrical components. These needs are less for a simple frequency domain system, more for time-correlated single photon counting or waveform capture systems.

For each of the lifetime determination methods, a similar geometry and sample chamber can be employed, as shown in Fig. 1. The LED illuminates a cuvette containing a luminescing sample in solution. It is simplest to place the cuvette near the LED. Luminescence is collected at 90°. A red pass filter is used to eliminate light from the LED. The PMT can either be placed in close proximity to the red pass filter or the luminescence can be lens coupled into the PMT. A typical sample chamber design can be straightforward (a scheme closely following our Fig. 1 or, for example, Ref. 4, Fig. 4). PMT

Table I. Some ultra bright visible light sources available at \$0.10–\$0.25 each in quantities of 25–100 (less than ≈ \$0.60 each when sold singly). A Blu-ray laser diode is included. Luminous intensities in the visible are commonly specified in millicandela units, MCD, as given in the table.

3–5 mm LEDs	Angle	Max DC current (mA)	Light output	Dominant wavelength(nm)(typical width ± ∼5 nm)
Red	20–25°	20	3000–18000 MCD	625
Orange–Red	20–25°	20	11000 MCD	616
Yellow–Orange	20–25°	20	4000–20000 MCD	590
Green	20–25°	20	17000–19000 MCD	520
Blue	20–25°	20	5000–70000 MCD	470
Near uv	20–25°	20	200–11000 MCD	405
uv	20–25°	20	20 mW	384
White	20–25°	20	15000–255000 MCD	3 (red, green, and blue)
Blu-ray diode laser	Contains very short fl lens at output	30–110	Up to ∼100 mW[a]	405 nm

[a] 100 mW at 405 nm with 1° beam angle corresponds to ∼10000 MCD.

housings can be constructed from PVC or ABS pipe and cap pieces.

III. SIMPLE IMPLEMENTATION OF FREQUENCY DOMAIN DETERMINATION OF LUMINESCENCE LIFETIMES

When a sinusoidally modulated light source excites a luminescent sample, the emission is also sinusoidal but is delayed by a phase shift φ relative to the excitation.[3] For a single exponential decay with lifetime τ, $\tan \varphi = \omega\tau$, where $\omega = 2\pi f$ is the exciting light modulation (angular) frequency. There is also a decrease in the amplitude of the modulated emission relative to the modulated excitation. A sophisticated frequency domain system measures both of these factors as a function of frequency. As a result of the fitting of one or both of these experimental curves to an analytical form for the decay, precise values of τ can be obtained for single exponential decays. For a fit involving several exponential contributions, values can be obtained for each τ and each fractional single exponential contribution component.[3]

LEDs, whether driven at high frequencies or by short duration pulses, yield high harmonic content and are excellent light sources for frequency domain measurements. Complete LED based frequency domain systems have been described.[4–7] These systems yield phase angle and

Table II. The basic components needed to construct a luminescence lifetime detection system. It is assumed that a computer is already available.

Primary components (sufficient for waveform capture)	Approximate cost	Notes
TTL pulser avalalanche transistor driver circuit DC supply for V$^+$(includes all project electronics parts and components)	\$150	1
Optical components	\$80	2
PMT	\$15	3
PMT enclosure, light tight sample chamber	\$15	4
Waveform digitizer, ≥300 MHz	\$200–\$350	
GPIB PC card	\$10–\$120	5
GPIB cable	\$15	
HV power supply	\$100	
Additional components for frequency domain detection (LED pulser and pulser ancillaries not needed)		
rf signal generator (to ∼1 GHz)	\$300–\$600	
Additional components for time-correlated single photon counting		
Powered NIM bin	\$250	
Quad NIM discriminator	\$150	6
NIM time to amplitude converter (TAC)	\$200–\$300	7
Multichannel analyzer	\$300–\$600	6
Switchable cable delays, 0–50 ns	\$100	8

1\. Includes allowance for purchase of transistors, capacitors, resistors, pc board, solder, various high intensity LEDs, socket for PMT, several bulkhead BNC and MHV connectors for PMT, several pre-made RG58 cables of various lengths. For V$^+$, a 0–400 V DC supply is very useful for initial testing, but a simple transformer/diode bridge/capacitor supply with one or two fixed voltage outputs is sufficient once operating conditions are established. Adjustable voltage mainframe supplies can be obtained for \$100–\$250. Alternatively, another DC to DC HV modular supply can be purchased for V$^+$. The pulser, avalanche driver circuit, and V$^+$ supply are not needed for the frequency domain system.

2\. Red pass color filters typically must be bought new and are ∼\$30–\$50 each. A glass cuvette is ∼\$15.

3\. 1P28 PMTs are commonly available at low cost. Sometimes surplus PMTs with better red response are also available. The PMT base bias circuit will be user wired.

4\. Materials include PVC or ABS pipe and a cap for PMT enclosure, ABS or black plastic for sample chamber, and black silicone sealant for both. It is simplest and most practical to operate with the LED directly against a side of the excitation cuvette.

5\. A GPIB card supported only by the DOS operating system is available at the low end of this price range. In this case a digitizer control program would need to be written in a language such as Quick Basic. A GPIB card that is supported by Windows is at the high end of this price range.

8\. Switchable cable boxes are available occasionally. If one is not available, it is possible instead to buy or construct RG58 50 Ω cables of different lengths for this purpose.

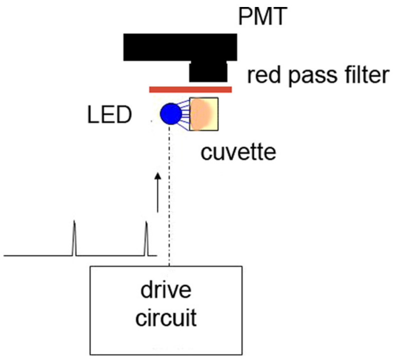

Fig. 1. Basic luminescence lifetime geometry (overhead view). The LED is placed near or against the cuvette. Luminescence is collected by a PMT at 90°. A red pass filter is placed between the cuvette and PMT to prevent excitation light from reaching the PMT. In both of the time domain setups, a hand built drive circuit sends pulses to the LED, as shown here. In the frequency domain setup, the drive circuit is, instead, a frequency generator producing sinusoidal output.

modulation as a function of frequency. The relatively low cost system described by Yuan *et al.*[7] was estimated to cost ~\$2000 to implement.[7] However, the implementation time and the technical expertise needed are both fairly large.

A simple but still serviceable implementation is possible if one is willing to accept some compromises. In such a system, employing the geometry in Fig. 1 (see also Fig. 4 of Ref 4), a sinusoidally driven LED directly adjacent to a sample cuvette excites the luminescent sample. The emission is detected by a PMT. For highly luminescent samples a photodiode can be used for detection.

In our simplified system, we measure only the phase shift between the LED excitation and the detected output signal, both of which are acquired (averaging mode) on a digitizing oscilloscope. Measurements should ideally be done at several driving frequencies. An illustrative measurement is shown in Fig. 2 for a sample of $[(bpy)_2Ru(pyr\text{-}bpy)]Cl_2$ dissolved in aerated water (absorption maximum 458 nm and emission maximum 630 nm).[8] This sample was chosen because of its microsecond regime decay time, which means that a RF signal generator is not needed. Excitation was done using a 460 nm LED with emission passed through a 630 nm red pass filter. Multiple phase shift measurements in the range of 50 kHz to several hundred kilohertz yielded single exponential lifetime values in the range of 1.5–1.7 μs. These values are consistent with single exponential fits of data acquired using time-correlated single photon counting (same value range for fits from this data). The range in the determined values of τ could be the result of a decay that has small multiexponential components.

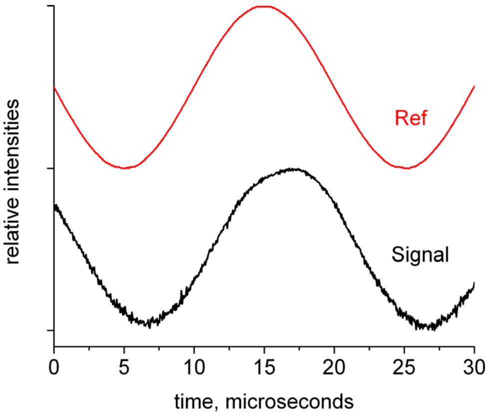

Fig. 2. Reference versus luminescence signal for $[(bpy)_2Ru_9pyr\text{-}bpy)]Cl_2$ dissolved in aerated water with excitation from an LED driven at 50 kHz. The signal was detected using a 1P28 PMT and signal averaged with a Tektronix 2440 digitizer. The PMT signal shown has been inverted to compensate for a 180° phase factor (negative PMT signal for positive LED drive signal). In this frequency range, there is a negligible phase shift between the reference drive signal and the detected light signal from the LED. In this example, the phase shift is 27.6°, which corresponds to a single exponential lifetime of 1.67 μs.

Higher driving frequencies are associated with larger phase delays. As φ increases toward 90°, the tan ϕ factor in the expression of tan $\varphi = \omega\tau$ is subject to larger errors for the same accuracy of ϕ; the best single ω value determinations of τ are for $\varphi < \sim 50°$.The modulated LED signal must be measured to be sure that it is sinusoidal; if the offset on the driver signal is not adjusted properly, the LED light signal amplitude could be clipped. As long as the frequency range is less than about 100 kHz, there should be little phase shift between the driver signal and the detected LED signal (as is the case in our measurements). If so, the driver signal can be used as the reference in this frequency range. However, particularly at higher frequencies, it is necessary to measure the reference LED signal directly. In a simple setup, all delays would be equal if the same detection arrangements were used for both the luminescence signal and reference. For reference signal measurements, the luminescent sample cuvette can be replaced by a cuvette containing a scatterer and the red pass filter removed. The rms current for a typical LED should be limited to less than 20 mA.

The value of the foregoing frequency domain lifetime determination setup, which may offset its limitations is its simplicity and low cost, particularly for microsecond regime decays. Without the need for a relatively expensive RF signal generator or a high bandwidth digitizer, microsecond and even sub-microsecond decays can be measured. For example, with a single exponential with a τ of 0.5 μs, the predicted φ is 17.4° at 100 kHz. The price paid in diminished performance manifests itself in less precisely determined τ values, especially if more than one single exponential component contributes significantly.

IV. TIME DOMAIN METHODS AND IMPLEMENTATIONS

There are two time domain methods, luminescence decay waveform acquisition and time-correlated single photon counting. We discuss some of the pros and the cons of each and then the details of their implementation.

The luminescence decay waveform acquisition method is also simple (layout of Fig. 1). Short duration light pulses excite the luminescent sample. After each pulse, the ensuing decay waveform detected by the PMT is sent to a digitizer for averaging. The system time resolution is the convolution of the time profile of the light pulse, the PMT time response (transit time spread), and the digitizer frequency response (1–2 ns). Although a side-on PMT (1P28 type) with typical dynode base biasing usually has a transit time spread of 2–3 ns, it is possible to employ a PMT base dynode biasing scheme that brings this response to ≤ 1 ns.[9] We will describe a simple driver circuit for LEDs that results in bright LED excitation pulses of ~1 ns duration—less if the circuit is constructed with more care. The advantages of this system are that it is simple and inexpensive (the digitizer is the major cost), employing inexpensive excitation sources (ultra bright LEDs) spanning the visible range down to near UV. The disadvantages are that it is difficult to eliminate PMT ringing, which degrades performance in the low nanosecond range, and there are inherent limitations with analog signal acquisition. Nonetheless, the performance for the effort and cost can be quite good.

Time-correlated single photon counting is a digital, not an analog, technique.[3] Essentially it is a method where the excitation pulse turns on a "stopwatch" [time-to-amplitude converter (TAC)] and a single PMT detected luminescence photon turns off the "stopwatch." (There is an advantage to recording data with the start and stop pulses reversed, by delaying the start pulses sufficiently to make them stop pulses.) A histogram of the number of "stopwatch" times falling within various time bins is recorded by a multichannel analyzer (MCA). The system time resolution depends on the convolution of the excitation pulse duration and the PMT transit time spread. A typical multidynode PMT transit time spread is 2–3 ns, although subject to some reduction as mentioned. For very expensive microchannel plate PMTS it can be as little as ~20 ps.

The advantages of time-correlated single photon counting are numerous and include excellent time resolution, absence of PMT ringing effects, and very high sensitivity. In particular, the absence of analog limitations means that the longer data are acquired, the more precise the decay waveform becomes. The disadvantages are higher cost than waveform acquisition, less practicality in the use for decays longer than ~1 μs, and difficulty in readily obtaining all the necessary electronics components at low cost. The major components needed are nuclear electronics, including zero crossing discriminators, a TAC, and a MCA. The single module that is the most difficult to find is a TAC. However, the availability of used NIM (nuclear instrumentation module) electronics may be improving.

V. TIME DOMAIN LED DRIVER CIRCUITS AND MEASUREMENTS

The avalanche transistor circuits (see the following) must be driven by a logic pulse signal generator or a simple TTL pulser circuit, which might employ a NE555 (see NE555 application notes for a circuit). There should be an optoisolator between the drive circuit and the avalanche transistor board. If the TTL drive circuit is not isolated and is also used to trigger the waveform digitizer for data acquisition, it is possible that RF noise could affect the waveforms collected.

A. LED driver circuit for time-correlated single photon counting

A common rule-of-thumb in time-correlated single photon counting is that the detected luminescence photon rate should be no more than 10^{-2} of the light pulse excitation rate;[3] high pulse excitation repetition rates are desirable. For example, a 4 MHz light excitation rate (250 ns pulse interval) would still allow an MCA collection rate up to 4×10^4/s.

A simple and inexpensive LED driver circuit capable of megahertz rates was proposed and demonstrated by O'Hagan *et al.*[10] They used it to drive LEDs and reported measured light pulses in the range of 1.9–3.6 ns for three different LEDs.[10] This driver circuit is useful for time-correlated single photon counting, resulting in a system resolution of ~5 ns or less using a 1P28 PMT.

We wished to see if further improvements in time resolution are possible for their circuit. We used a 300 MHz digitizing oscilloscope (Tektronix 2440) for measurements on a version of the circuit constructed on a prototyping board and found output pulses of ≤5 ns FWHM (full width at half maximum) for the circuit in Fig. 3 using a 74AC00 IC, as used in Ref. 10. We obtained somewhat better performance using a 74F00, with a measured FWHM of 4 ns. Considering that a 300 MHz oscilloscope has a rise time of ~1.2 ns, the output drive pulse widths are consistent with the reported light pulse durations. (The light pulses might be expected to be somewhat shorter in duration than the driving pulses, if only because of the ~0.6 voltage drop across a typical LED.) A simple modification to this circuit using the RG174 cable delay shown in Fig. 3 might produce shorter drive pulses. The idea of the circuit is to send a logic H pulse directly to one of the two inputs of the final NAND. The H signal is simultaneously sent through another NAND, resulting in a L pulse which is sent to the second input of the final NAND. This L signal is slightly delayed relative to the H signal at the other input due to the propagation delay through the first NAND, resulting in coincident H signals at the two final NAND inputs for several nanoseconds. We used short lengths of RG174 cable to delay the H pulse to the first input of the final NAND by ~1 ns. In principle, the result should be a shorter duration of coincident H signals at the two inputs of the final NAND, potentially resulting in a shorter L output pulse. However, there was no discernible change in FWHM of the output pulses, at least as observed on the Tektronix 2440. If the RG174 delay was increased further, the output pulse amplitude decreased but the width appeared unchanged. The somewhat limited bandwidth of our oscilloscope may have obscured the observation of small decreases in the pulse width.

We concluded, consistent with Ref. 10, that the NAND circuit is an excellent LED driver for an inexpensive implementation of time-correlated single photon counting and may be subject to some improvement. However, it is not a good LED driver circuit for a waveform capture system. In our evaluations we used the circuit to drive a 70000 MCD (millicandela units) blue LED at 2000 Hz. Even with the room lights off, very little light from the LED was visible to the eye. In contrast, at 2000 Hz with an avalanche transistor pulser circuit (described in the following) the LED output was highly visible to the eye even with the room lights on.

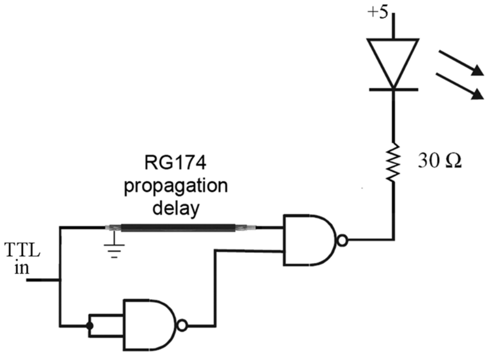

Fig. 3. Dual NAND nanosecond pulse generation circuit. The circuit is shown with inclusion of a ~1 ns RG174 delay to reduce final pulse output.

The avalanche pulser circuits can also be applied to time-correlated single photon counting, provided that long term stable operation continues at high repetition rates.

B. Avalanche pulser LED driver circuit for waveform acquisition systems

Overall system response depends on the light pulse duration, the PMT response (2–3 ns, possibly down to ∼1 ns), and the digitizer time response (∼1 ns). In order not to increase the overall instrumental time response significantly, optimum time resolution waveform capture calls for light pulses of ∼1 ns or less. In waveform acquisition, a low repetition rate can be tolerated (tens of hertz, as with some pulsed lasers), but a repetition rate of at least kHz is desirable. We also require that the driving circuit must be inexpensive and require no special technical skills or special equipment to construct. Avalanche transistor drive circuits can satisfy all these criteria.

Avalanche breakdown pulse operation in transistors was known even in the 1950s and has been exploited extensively since the 1960s. A number of avalanche transistor circuits have been described that can be used to drive LEDs.[11–15] Some component tweaking is usually necessary to obtain an inexpensive hand built circuit that performs optimally.

Transistors explicitly specified to avalanche are available (Zetex FMMT415 or 417 would be appropriate) but are somewhat expensive (∼$13 each for small quantities). However, a number of small signal NPN transistors can exhibit avalanching, with performance similar to transistors specified to avalanche. According to our observations and those of others, their operation in avalanche mode is stable and long term.[12,14,15] These transistors have a typical unit costs of $0.05. Although many small signal transistors can exhibit avalanching, the presence of avalanching and the observed performance depend on the manufacturer and production lot; two of the same numbered transistors from different sources might exhibit different behavior. For example, Gallant obtained excellent avalanche operation results using an inexpensive NPN transistor, 2N2369a.[15] In contrast, the 2N2369a transistors that we tested did not avalanche.

It is useful to employ a simple circuit to test for avalanching. We used the circuit in Fig. 4(a). As V^+ (see Fig. 4) is increased, avalanching, if it occurred, generally began in the $V^+ = 100$–150 V range, evidenced by the appearance of a high amplitude (40–80 V) fast rise time pulse. The RG174 delay line shuts off avalanching as follows: the avalanche pulse propagates down the delay line, is reflected back with inverted amplitude and, on its return at the collector, stops avalanching. The pulse duration depends on the length of the delay line. We chose a cable length of around 9”, because the output avalanche pulse FWHM on the Tektronix 2440 did not decrease visibly for smaller cable lengths, although the pulse amplitude decreased. With this circuit, the observed FWHM on the oscilloscope for avalanching pulses was 4–5 ns. (It would likely be larger for higher power NPN transistors found to avalanche.) Figure 4(a) also shows a typical test circuit voltage waveform for a transistor that

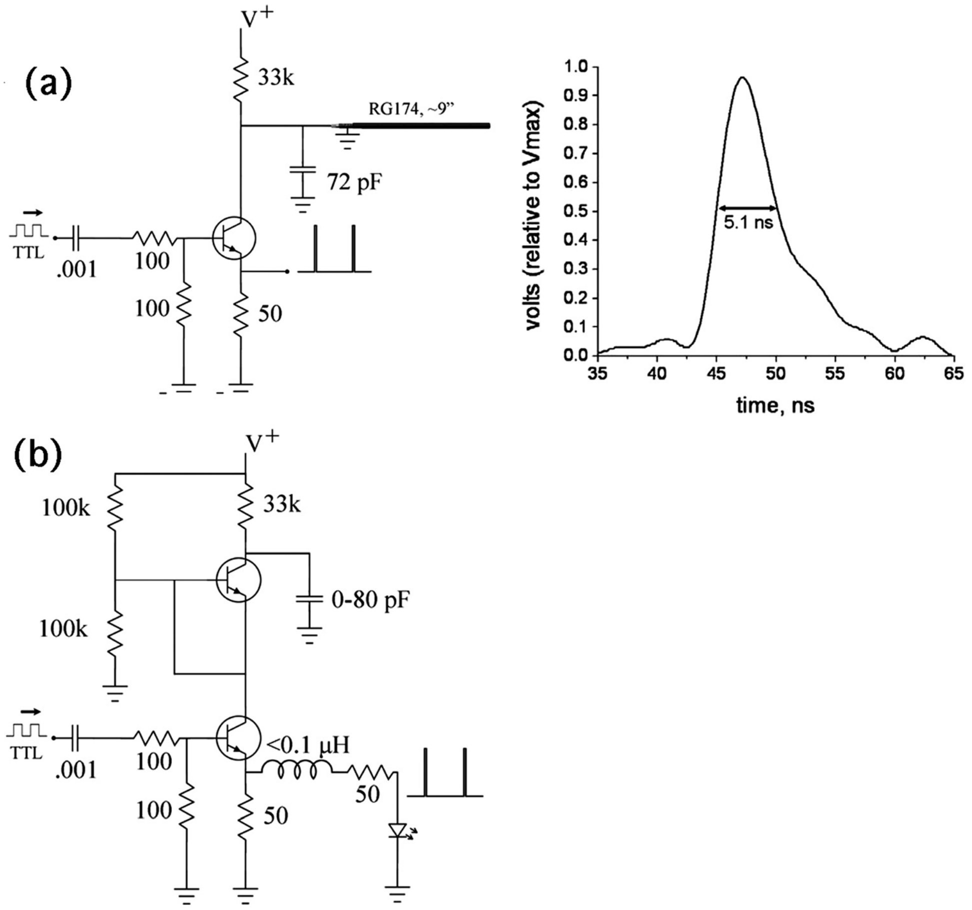

Fig. 4. (a) Test circuit for transistor avalanching with typical avalanching waveform. The accompanying waveform was measured using a 10 × 50 Ω attenuator, into a 50 Ω input to a Tektronix 2440 digitizer. (b) Final drive circuit. In our version the pF capacitor at the transistor collector was removed.

avalanched. Of the ten small signal transistors we tested, those we observed to avalanche were 2N2222, 2N3904, 2N4401, 2N4424, and 2N5551. In addition, Gallant obtained avalanching with 2N2369a transistors.[15] Multiple transistors of each avalanching type should be tested to select the best performing ones.

Measurements of the voltage output waveforms with the Tektronix 2440 were non-optimum because of its inadequate bandwidth. Although a sampling oscilloscope (typical 3 GHz performance) for observing the output pulses would have served well, adequately resolved direct time domain measurements of the light pulses, which we carried out, were as good or arguably better. To obtain an undistorted time domain recording of the light pulses, we employed time-correlated single photon counting with a Hamamatsu R3809 microchannel PMT, giving an overall system time response of less than 0.1 ns. We performed our measurements for driving circuits built on a prototyping board, which allowed for rapid changes in the circuit, beginning with the circuit in Fig. 4(a). All circuits drove a 70000 MCD blue LED. We found that removing the delay line and the 72 pF capacitor decreased the width of the light pulses but also decreased the voltage amplitude of the driving pulses. We tried various features of the circuits of Araki and Misawa,[13] Franzen and Day,[12] Gallant,[15] and Vanderwall *et al.*[14] Because some of the features that decreased the measured time width of the LED pulses also decreased the driving pulse amplitude, our final improved circuit in Fig. 4(b) employed two stacked avalanche transistors (additive avalanching voltages; 2N3904 used). The purpose of the 100k series resistors was to distribute the potential drop from V^+ between the two transistors. For higher voltage pulses, additional transistors can be stacked (for example, the circuit described by Krishnaswamy[16] stacked eight), but two were adequate for our purposes.

Several features of the circuit in Fig. 4(b) are not specified precisely and probably should be optimized in each built version. We obtained the best time width by removing the 0–80 pF capacitor entirely at the expense of less, but still highly adequate, pulse amplitude. It might be possible to add small capacitors to increase the driving pulse amplitude with little sacrifice in time width. Following Gallant,[15] we also found some improvement in the time domain pulse width by using a very small inductance, though less than indicated by Gallant.[15] If L was 0.5 μH, as used by Gallant, we observed significant degradation in the light pulses, with satellite pulses appearing. Fairly small changes in the circuit or passive component values can result in the appearance of one or more small satellite light pulses, behavior that was also observed by Uhring *et al.*[17] This fact underlines the need for measuring the light pulses before using the circuit for luminescence decay measurements. Figure 5 shows a photograph of the avalanche pulser as constructed on a prototyping board, driving a 11000 MCD 405 nm LED. This circuit was used for the measurements described in the following.

LED light pulse detection using a PMT and 300 MHz digitizer should be sufficient to discern satellite light pulses or any other undue degradation of the LED pulses. Such a plot is shown in Fig. 6(a). We used a 1P28 PMT with the fast response base biasing scheme described by Beck.[9] Beck reported no ringing for his dynode biasing method when constructed on a custom circuit board in lieu of a standard base socket. Our implementation using a standard PMT socket showed some ringing in the analog decay waveforms. The overall FWHM of the scattered light waveform was 5.0 ns, including the rise time of the Tektronix 2440. It can be seen that some broadening occurred due to the ringing effects. Without ringing, the recorded FWHM would have been 3.7 ns. Overall, even with ringing, the system response was sufficient to begin to resolve lifetimes of $\sim$5 ns. Those seeking the best results with waveform capture should make the effort to build a circuit board implementation of the base biasing scheme, as discussed by Beck. Figure 6(b) shows the recorded LED light pulses with an instrumental time resolution of less than 0.1 ns (time-correlated single photon counting detection, R3809U PMT). The FWHM was 1.16 ns.

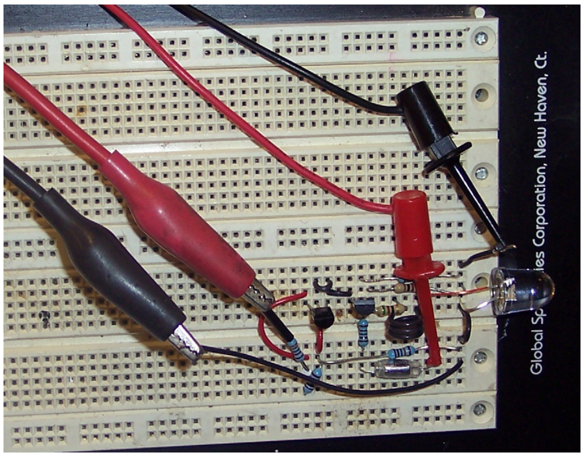

Fig. 5. Photograph of the final drive circuit as constructed on a prototyping board.

There is a high level of operational stability in the avalanche LED pulser described. We operated our pulsing circuit at 2000 Hz for $\sim$100 h with no observed degradation.

C. Avalanche pulser LED/1P28 detection in waveform acquisition and time-correlated single photon counting

Figure 6(a) shows the time resolution of the LED pulser/1P28 system when used in waveform acquisition with the Tektronix 2440. Some improvement can be obtained by eliminating or reducing ringing. The use of the same LED pulser/1P28 in time-correlated single photon counting offers significant improvements. PMT single photon pulses for the time-to-amplitude converter are obtained by sending amplified PMT pulses into a discriminator (triggering on leading edge) so that ringing effects are eliminated. Bandwidth effects of the digitizer also are no longer present. The data histogram in the MCA is digital, governed by Poisson statistics.

To illustrate these improvements in Fig. 7 we show a measured fluorescence lifetime for a less than 10 ns lifetime chromophore, tetraphenylporphyrin in toluene. The decay was fitted to a single exponential τ of 4.58 ns. The FWHM system response was 2.0 ns.

D. Optional improved performance of the avalanche pulser using better construction techniques

We note that no further improvement is necessary for a waveform acquisition system. However, some improvement in time-correlated single photon counting performance can be obtained with shorter LED light pulses.

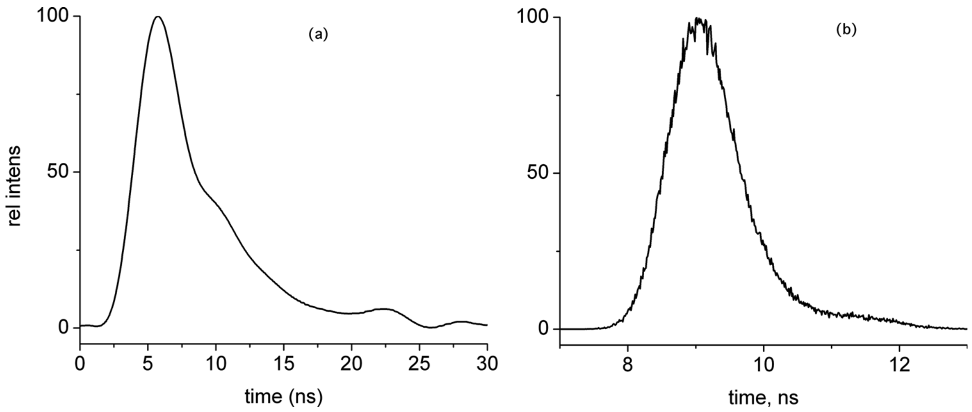

Fig. 6. Scattered light response from an avalanche pulser driven LED. (a) Detection with a 1P28 PMT using waveform acquisition (Tektronix 2440). The FWHM was 5.0 ns. With deconvolution of the ringing, the FWHM was 3.7 ns. (b) Detection using time-correlated single photon counting with a R3809U microchannel PMT (system response better than 0.1 ns). In this case, the FWHM was 1.16 ns.

Construction and layout of the LED driver circuit are critical for attaining the shortest drive pulses. Even our non-optimal construction on a prototyping board is sufficient for attaining ~1 ns pulses. The best results are obtained by employing etched trace copper clad boards. Those seeking the highest level of performance should invest in PCB-CAD layout software to design an etched circuit board. Even without a copper trace board, better results can be obtained by avoiding prototyping boards or wire wrapping. Instead, components can be mounted and connected on a solder board, avoiding long leads and using a common ground point. This method of construction is illustrated in a photograph by Gallant.[15] His measured drive voltage pulses, as displayed on a high speed oscilloscope, were roughly 1 ns FWHM, including instrumental rise time. With the foregoing drive pulses, the LED pulses should easily be sub-nanosecond. Further, performance improvement would probably result from using surface mount transistor packages, commonly available for small signal NPN transistors.

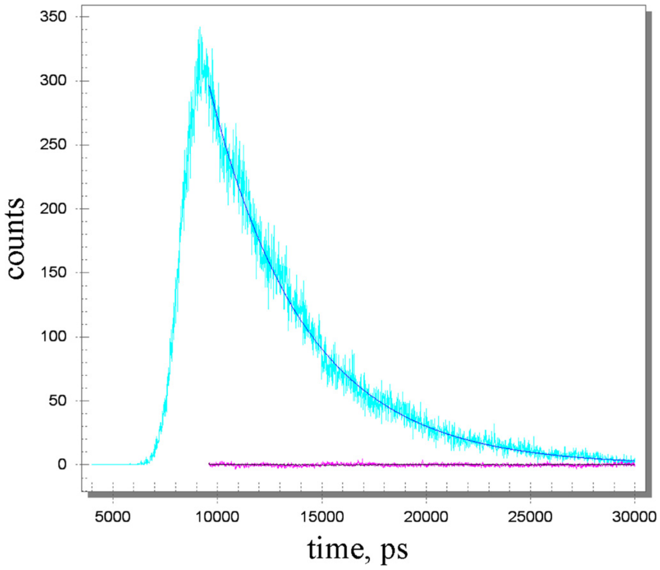

Fig. 7. Lifetime decay of tetraphenylporphyrin (tpp) in toluene fitted to a single exponential decay with weighted residuals for the fit also shown (bottom curve). At the concentration of tpp in the cuvette, the fitted τ was 4.58 ns. Excitation was with an 11000 MCD 405 nm LED. The luminescence collected at 90° was sent through a 495 nm red pass cutoff filter before reaching a 1P28 PMT. Data acquisition was done using time correlated single photon counting.

E. MHz avalanche pulser operation for time-correlated single photon counting

The LED should not limit repetition rates to below MHz levels, even with ~100 V amplitude pulses. The rated CW LED current is 20 mA. Using a two transistor avalanche pulser producing ~1 ns LED pulse width and ~100 V amplitude pulses, the repetition rate that produces an average current of 20 mA should be in the megahertz range. Similarly, the driver circuit should be capable of MHz operation. For each transistor in the avalanche pulser, a 1 MHz rate corresponds to an average power of ~10^2 mW, which is within the specified 625 mW maximum for a 2N3904 or similar small signal transistor. At a minimum, as found by Araki and Misawa[13] and us, long term operation at 10 KHz is possible, which would allow tolerable time-correlated single photon counting operation.

Commercial LED drivers are available that can operate in the megahertz range, which produce light pulses of ~100 ps or better. Vendors include PicoQuant, Picosecond Pulse Labs, and Hamamatsu. However, the cost is in the multi-thousand dollar range. In the absence of a microchannel plate PMT, overall system response would not be substantially improved for LED pulses well under 1 ns in contrast to ~1 ns.

VI. POSSIBILITIES FOR UV EXCITATION FOR THE THREE SYSTEMS

Inexpensive LEDs are presently available only in the visible and near-visible range (none below 384 nm), with deeper UV LEDs available only at higher cost.[2] The UV LEDs available typically have CW light outputs of only 0.3 mW,[2] considerably less than the output of ultra bright LEDs in the visible range, but adequate for time-correlated single photon counting. They can also be used in waveform capture systems, but care in attaining maximum possible luminescence collection would be important.

ACKNOWLEDGMENTS

The authors have incorporated results from a science project by Zoe Sulkes at Benjamin Franklin High School, New Orleans, LA 70122.

[a] Electronic mail: cm06acf@tulane.edu

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Synchronous Spark Timer. In the venerable Behr free-fall apparatus, first made by Cenco in the late 1930s, a metal bob falls between two wires. A high-voltage spark jumps between the two wires 120 times per second and melts a tiny bit of white wax on the surface of a strip of red paper between the bob and one of the wires. The high voltage signal is obtained from this synchronous spark timer that is driven by the 60 Hz power line. Every year I used to hit the high voltage with my hand, and it was high enough to wake me up! The instrument is first listed in the 1940 Cenco catalogue at $47.50. This example is in the Greenslade Collection, along with the Behr apparatus. (Notes and photograph by Thomas B. Greenslade, Jr., Kenyon College)