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A TECHNIQUE FOR THE MEASUREMENT OF FLUORESCENCE LIFETIMES WITH AN OPTICALLY CHOPPED LASER BEAM

by

A. Watanabe and J.G. Chambers

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ABSTRACT

A technique has been developed for generating a train of short pulses from the output of a CW laser. It is shown that this technique can be used to produce variable length pulses with well defined shapes which are well suited to the measurement of fluorescence lifetimes in a wide range of materials.

INTRODUCTION

The fluorescence lifetimes of electronic transitions in molecules and ions generally fall in the range 10^{-9} to 10^{-3} sec. The basic techniques which have been developed for the measurement of decay times have been discussed by Peterson[1]; essentially a time-varying excitation source and a detector are required. Short pulse discharge lamps have been used[2,3,4], but the pulses from these lamps have long, low intensity tails which can complicate the lifetime determinations. There are available CW lasers capable of exciting the fluorescences of many materials over a wide range of wavelengths[5]. A CW Ar laser whose amplitude was modulated by an electro-optic shutter has been used for the measurement of lifetimes of the order of 10 nanoseconds[6]. A simultaneously Q-switched and mode-locked ruby laser has been used to measure the lifetimes of some dyes[7]. We have developed a technique for generating a train of short, variable width pulses by optically chopping the beam of a CW laser, and have used these pulses for the measurement of the fluorescence lifetime of a sample with a lifetime of several microseconds.

THE GENERATION OF OPTICAL PULSES

A train of pulses was generated by means of the system shown schematically in Figure 1. The essential items are the laser, the rotating prism (or mirror) and the slit. As the prism is rotated, the laser beam is deflected past the slit in the manner of a lighthouse beacon, and a short optical pulse is transmitted through the slit. A similar system has also been employed by Hoffmann and Jovin[8] as a fast risetime chopper for laser light.

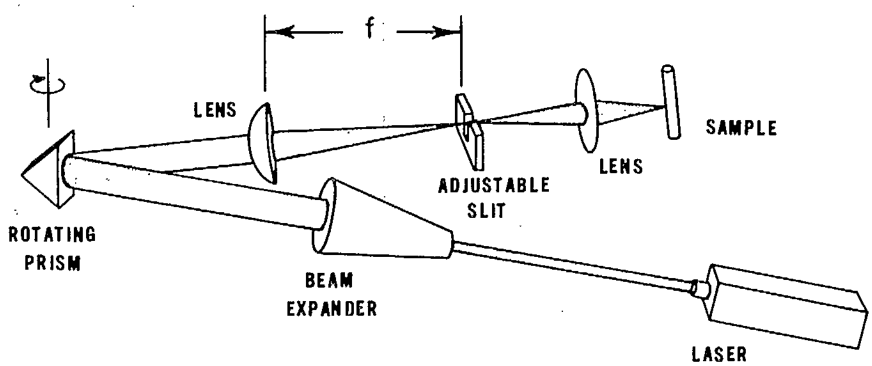

Fig. 1. Diagram of the optical setup to derive short pulses from a CW laser.

These pulses can be made extremely short, and have a predictable shape and pulse width. The intensity distribution of a laser operating in the TEM_{00} mode is approximately Gaussian, and the beam can be focused by means of a converging of focal length f to a spot whose intensity distribution is also Gaussian. The diameter of the spot between $1/e^2$ intensity point is given by $2a_f = \alpha f$, where α is the divergence angle of the laser. Thus the intensity distribution at a point (x,y) in a laser beam centered at (0,0) can be written as

$$I(x,y) = \frac{2P_0}{\pi a^2} e^{-2(x^2 + y^2)/a_f^2},$$

where P_0 is the total output power of the laser.

In the system shown in Figure 1, a slit of width d is placed in the focal plane of the lens, and the laser beam is rotated by the prism rotating at s rps. At the slit the beam appears to be rotating about an axis passing through the optical center of the lens and at a rate of 2s rps. Thus the linear rate of travel of the beam across the slit is given by $4\pi sf$. By taking the x-axis in the direction of deflection of the laser beam and assuming that the center of the slit lies at x = 0, we can express the x co-ordinate of the center of the beam as $x(t) = 4\pi sft$. The time variations in the power transmitted by slit can be written as

$$P(t) = \int_{-\infty}^{\infty} dy \int_{-d/2}^{d/2} I(x - 4\pi sft, y)\,dx$$

$$\frac{P(t)}{P_0} = \frac{1}{2}\left\{\mathrm{erf}\left[\frac{1}{\sqrt{2}}\left(2\frac{d}{d_0} + 4\frac{t}{t_0}\right)\right] + \mathrm{erf}\left[\frac{1}{\sqrt{2}}\left(2\frac{d}{d_0} - 4\frac{t}{t_0}\right)\right]\right\} \qquad \text{.....(1)}$$

where erf is the error function, $d_0 = 2a_f$ is the focused diameter of the Gaussian beam, and $t_0 = a_f/2\pi fs = \alpha/4\pi s$ is the time taken for the laser beam to be deflected through a distance equal to d_0. In Figure 2 $P(t)/P_0$ is plotted versus t/t_0 for several values of d/d_0. It is seen that, as d/d_0 is increased, the peak power of the pulse increases until $P(0)/P_0$ reaches the maximum value of 1 for $d/d_0 = 1.5$. At the same time the pulse width at the half power points increases from a lower limit of approximately 0.59 t_0. For $d/d_0 > 1$, the pulse width can be written as

$$\tau_{\frac{1}{2}} = \frac{d}{d_0}\, t_0 = \frac{d}{2a_f}\,\frac{\alpha}{4\pi s} = \frac{d/f}{4\pi s} \qquad \ldots\ldots(2)$$

and the rise time of the pulse between the 10% and 90% intensity points is given approximately by

$$\tau_{10 \rightarrow 90} = 0.38\,\frac{\alpha}{4\pi s}\ .$$

Thus it is seen that for cases where the rise time of the pulse is of importance, or where narrow slits are used in order to obtain a very narrow pulse, the divergence angle should be minimized. The dashed line in Figure 2 is a plot of $P(0)/2P_0$ versus $\tau_{\frac{1}{2}}/2t_0$; thus it describes the relationship between $P(0)$ and $\tau_{\frac{1}{2}}$ as d/d_0 is varied. The case for $d/d_0 = 1$, i.e., when the Gaussian spot diameter and the slit width are equal, appears to give a good combination of maximum peak power and narrow pulse width. For this case the pulse width is given approximately by $\tau = \frac{\alpha}{4\pi s}$. Shorter pulses could be obtained without sacrificing the peak power only by increasing the rotational speed or decreasing the divergence angle. On the other hand longer pulses could be obtained either by decreasing the rotational speed to get a longer pulse of the same shape or by increasing the slit width to get a longer, flat-topped pulse without an increase in the rise time.

The system shown in Figure 1 was used to verify equations (1) and (2). The laser was a HeNe laser with a divergence angle of 10^{-3} rad, which was decreased to approximately 1.3×10^{-4} rad by means of a beam expander. The converging lens had a focal length of 500 mm and the adjustable slit was set for a width of approximately 0.067 mm to correspond to the case $d/d_0 = 1$. The rotating prism was driven at 2243 rps to obtain pulses of width 7 nsec, in agreement with the τ calculated from equation (2). An oscilloscope photograph of one of these pulses is shown in Figure 3. The detection system consisted of a photomultiplier tube with a 10 ohm load connected directly to the oscilloscope. The pulse shown is somewhat distorted by the mismatch between the load resistor and oscilloscope and by the rise time of the oscilloscope, which was about 3 nsec. In order to verify the pulse shape some pulses were photographed for s = 533 rps; one of these pulses is shown in Figure 4. A comparison of the shape of this pulse with the theoretical shapes shown in Figure 2 shows that the observed pulses follow the predicted shape reasonably closely.

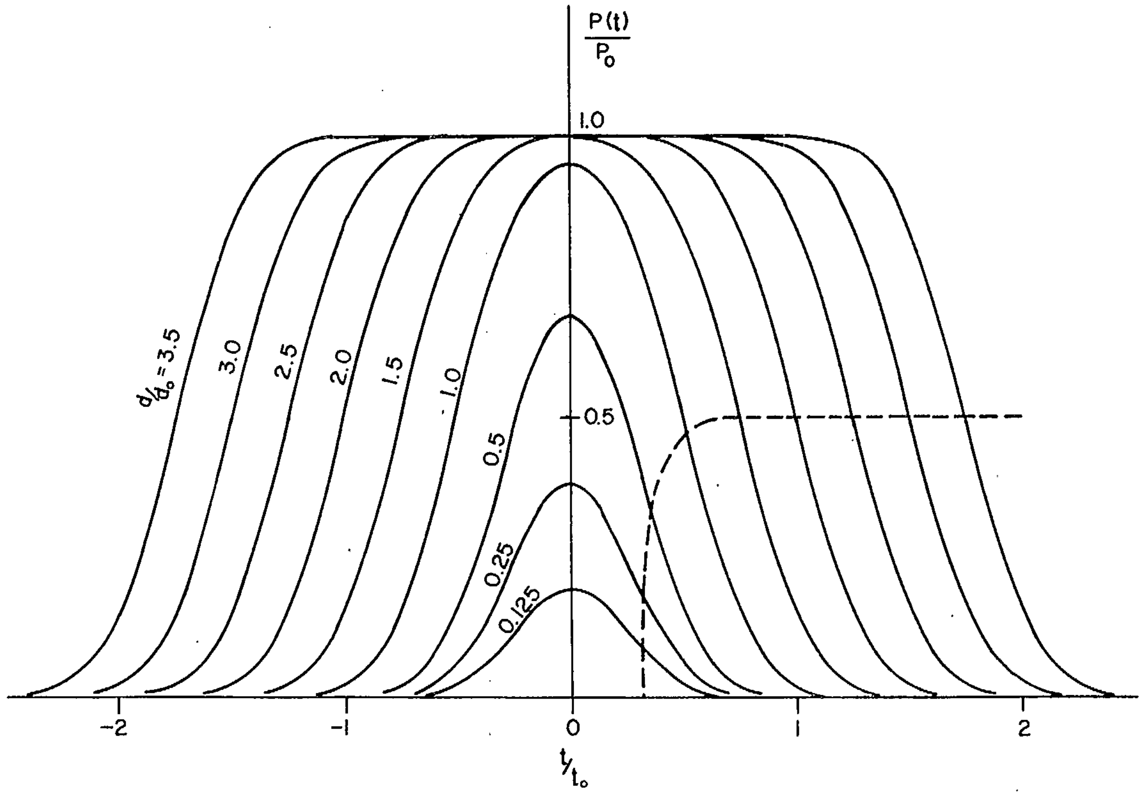

Fig. 2. The normalized output power $(P(t)/P_0$ versus normalized time t/t_0 for a series of values of the normalized slit width d/d_0. The dashed line gives the relationship between normalized peak power and normalized pulse width. The curve is a plot of $P(0)/2P_0$ versus $\tau/2t_0$.

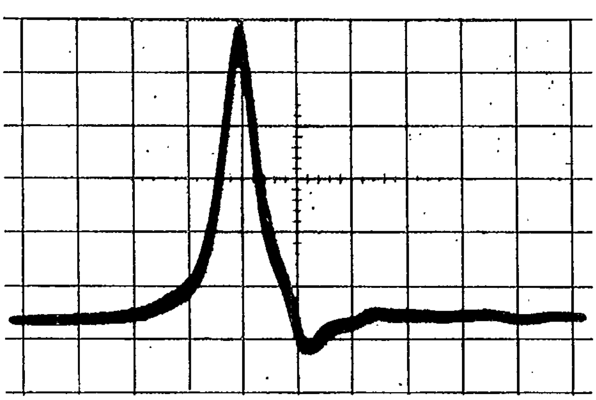

Fig. 3. Oscillogram of the short pulse obtained from a HeNe laser. 1 div = 10 nsec.

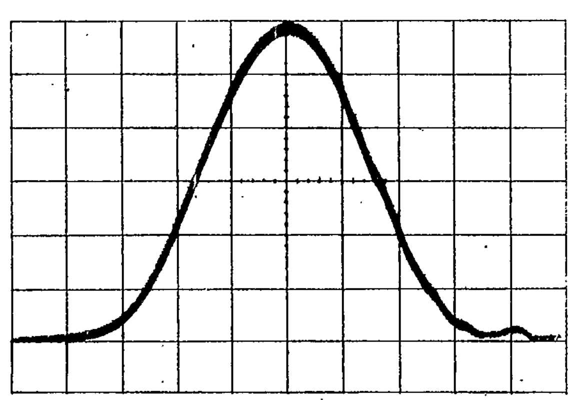

Fig. 4. The pulse shape for a lower rotational speed of the Q spoiler prism. 1 div = 10 nsec.

THE MEASUREMENT OF FLUORESCENCE LIFETIMES

The technique was employed with a 2 watt CW Ar laser to generate a train of pulses to measure the fluorescence decay time of the $^3P_0$ level of the Pr^{3+} ion in the solvent system $SeOCl_2:SnCl_4$. The 4880 A line of the Ar laser is absorbed by the $^3H_4 \rightarrow {}^3P_0$ transition of the Pr^{3+} ion and intensely excites the fluorescence of the $^3P_0$ state. The pulse width was adjusted to be approximately 100 nsec in order to optimize the coupling of excitation energy into the sample. In order to extract the values of short decay times it is often necessary to process the signal by sophisticated methods. If an intense source of short excitation pulses is available the signal processing can be simplified considerably. In the present case the lifetime was measured simply by viewing the time-varying fluorescence displayed on an oscilloscope screen. The fluorescence decay curve for a typical sample under pulsed excitation is shown in Figure 5. The value obtained for the lifetime of the $^3P_0$ level was 1.8 μsec. This measurement of the lifetime made it possible to calculate the radiative efficiency of the $^3P_0$ level[9].

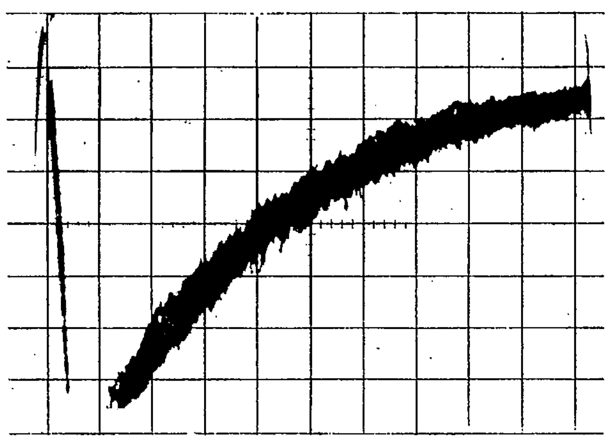

Fig. 5. Fluorescence decay curve for the $^3P_0$ level of the Pr^{3+} ion in a liquid solvent. 1 div = 0.5 μsec.

REFERENCES

1. Peterson, G.E. *Transition metal chemistry*. (R.L. Carlin, ed.) Marcel Dekker, Inc., New York, 1966, p 202.

2. Bennett, R.G. Rev. Sci. Instrum. 31, 1275 (1960).

3. Hundley, L., Coburn, T., Garwin, E. and L. Stryer. Rev. Sci. Instrum. 38, 488 (1967).

4. Studer, M.C., Wild, U.P., and H.H. Gunthard. J. Phys. E: Sci. Instrum. 3, 847 (1970).

5. Damen, T.C., Porto, S.P.S., and F. Varsanyi. Bull. APS 12, 273 (1967).

6. Haug, A., Kohler, B.E., Priestley, E.B. and G.W. Robinson. Rev. Sci. Instrum. Instrum. 40, 1439 (1969).

7. Mack, M.E. J. Appl. Phys. 39, 2483 (1968).

8. Hoffman, G.W. and T.M. Jovin. Appl. Opt. 10, 218 (1971).

9. Watanabe, A. and J.G. Chambers. Bull. APS 16, 70 (1971).