Picosecond Fluorescence Spectroscopy
with a Streak Camera


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Abstract

Streak cameras have enabled kinetic data in the picosecond time regime to be obtained from single laser shots. Digitization of the streaked image with an optical multichannel analyser results in accurate fluorescent decay curves from which accurate fluorescence lifetimes may be calculated, and in which non-exponential decays are readily detected. This paper describes the characteristics of the picosecond laser system at the University of Melbourne. For excitation, a Nd3+: glass mode-locked laser, Pockels cell pulse selector and various harmonic generators are used; a streak camera/OMA system linked directly to a computer is used to detect fluorescence.

1. Introduction

While the technology of producing light pulses of picosecond duration is now well established, the application of this technology to the study of fluorescence emission on this time scale has been somewhat inhibited by the lack of a convenient detector. Point-by-point measurements of fluorescence intensity as a function of time, using an ultra-high-speed (c. 10 ps) light gate, was the first method used to study directly fluorescence decay on a picosecond time scale. However, such measurements are intrinsically inaccurate because of the high background intensity caused by fluorescence leaking through the crossed polarizers during the entire fluorescence decay. Reid has calculated that, for a CS2 shutter, even with crossed polarizers having an extinction ratio of 10^-5, the signal-to-background ratio cannot exceed 10:1, even in the most intense region of the fluorescence emission, and decreases during the decay in proportion to the fluorescence intensity. Thus the combination of tedious point-by-point measurements, their correction for capricious shot-to-shot variations in laser intensity, and the high intrinsic background have limited the usefulness of the light gate technique to semi-quantitative estimates of fluorescence lifetimes. In the following paper of this series, there is an example of a case in which subtleties in the decay curve have been observed which have been missed by light gate techniques.

2 Bradley, D. J., Opto-electronics, 1974, 6, 25.
Phase shift methods\textsuperscript{6} suffer from the inability to measure the exact shape of the decay function and are, furthermore, limited to the $\geq 100$ ps time scale.

Use of a stacked plate echelon to interrogate the decay of the absorption spectrum of an excited electronic state\textsuperscript{7} avoids the background problem and the tedium of the point-by-point determination in the light gate experiments. However, there is an inherent difficulty in absorption measurements as compared with emission measurements, in that the sensitivity is limited by the ability to differentiate between two signals of comparable intensity. This fact, coupled with the discrete temporal spacing of the interrogating pulses, causes the echelon technique also to be a somewhat inaccurate method for measuring the exact time evolution of an excited electronic state.

Many interesting experiments require a detailed knowledge of non-exponential fluorescence decay functions. For example, time-dependent fluorescence depolarization experiments are a source of non-exponential fluorescence decay when the rotational correlation time for the excited molecule is comparable to its fluorescence decay time.\textsuperscript{8} These and other non-exponential decays will be the subject of study in many future experiments, and their detection will require a rather more precise technique than any of those so far used. This paper describes in detail the picosecond fluorescence instrumentation recently set up at the University of Melbourne, using for detection a high-speed streak camera which employs an image converter (ICT), image intensifier (IIT) and optical multichannel analyser (OMA). Subsequent papers will describe applications of the instrumentation.\textsuperscript{5,9}

2. Picosecond Laser System

\textit{(a) Laser Oscillator and Amplifier}

Stability of laser alignment is critical for reliable operation of a mode-locked laser: the laser and its associated optics are mounted on a rigid, steel-topped aluminium 'honeycomb' table (Modern Optics, U.S.A.)—the rigid structure is necessary for stable laser alignment, while the steel top allows the use of magnetic bases for mounting of optical components. The laser is of conventional semi-confocal design and consists essentially of two mirrors, a Nd\textsuperscript{3+} : glass rod housed in a water-cooled laser head, and a mode-locking dye cell containing a solution of Eastman 9860 dye. Each of these components will now be described in more detail.

\textit{Laser Mirrors}

Mirrors manufactured by Valpey Corporation (U.S.A.) have proved very reliable and are mounted in Aerotech AOM 100 precision mirror mounts. Both mirrors consist of dielectric coatings deposited on glass substrates and are E-beam hard-coated to withstand the high light intensities generated with the laser cavity. The intracavity side of the rear mirror is coated for maximum reflection at the laser wavelength (c. 99\% at 1.06 $\mu$m), while that of the output mirror is coated for c. 50\%

\textsuperscript{6} Ware, W. R., in 'Creation and Detection of the Excited State' (Ed. A. A. Lamola) Vol. 1A (Marcel Dekker: New York 1971).
\textsuperscript{8} Tao, T., \textit{Biopolymers}, 1969, 8, 609.
transmission at 1.06 µm. An output mirror with a transmission in the range 45–55% gives long, flat pulse trains (800–1000 ns duration) with reliable mode-locking. The extracavity surface of the output mirror substrate is wedged at c. 1° to prevent unwanted reflected light from re-entering the cavity and interfering with the mode-locking, and also to spatially separate the reflected images of the He–Ne alignment laser for much more convenient alignment. The rear mirror is also slightly concave to compensate for negative thermal lensing effects within the laser rod. Mirrors having 5-m and 10-m radii of curvature work well, whereas if a flat mirror is used, laser alignment is much more critical and operation less reliable.

**Laser Heads and Laser Rods**

Two laser oscillators are currently in use in our laboratory, a Korad Kl laser and an Apollo laser. The power supplies of both lasers have been modified so that the laser can be fired when the voltage on the storage capacitor has leaked down to a preset level (± 1 V). This gives a fine control on the energy dumped into the flashlamp. In addition, we have a Quentron Optics (Australia) QP25-A laser amplifier. The properties of the lasers and the four different types of laser glass are listed in Table 1. Owens–Illinois EV-2 and Hoya LSG-91H are both silicate glasses; Owens–Illinois EV-2 and Hoya LHG-5 are the newly developed phosphate glasses.

**Table 1. Laser parameters**

<table>
<thead>
<tr>
<th>Laser head</th>
<th>Make</th>
<th>Type</th>
<th>Flash duration (µs)</th>
<th>Size (in.)</th>
<th>Configuration A</th>
<th>Nd (º)</th>
<th>Threshold B (J)</th>
<th>Max. gain C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Korad Kl</td>
<td>osc</td>
<td>1000</td>
<td>7.5 by 0.5</td>
<td>B-B</td>
<td>EV2.3</td>
<td>1.062</td>
<td>3.1</td>
<td>1600</td>
</tr>
<tr>
<td>Apollo</td>
<td>osc</td>
<td>300</td>
<td>8.5 by 0.5</td>
<td>B-B</td>
<td>EV2.3</td>
<td>1.062</td>
<td>3.1</td>
<td>455</td>
</tr>
<tr>
<td>Apollo</td>
<td>osc</td>
<td>300</td>
<td>8 by 0.5</td>
<td>B-B</td>
<td>LHG-5</td>
<td>1.056</td>
<td>3.3</td>
<td>295</td>
</tr>
<tr>
<td>Quentron</td>
<td>AMP</td>
<td>350</td>
<td>8 by 0.5 p-p</td>
<td>LHG-91H</td>
<td>Hoya</td>
<td>1.062</td>
<td>3.1</td>
<td>9</td>
</tr>
<tr>
<td>Quentron</td>
<td>AMP</td>
<td>350</td>
<td>7 by 0.5 6° wedge</td>
<td>LHG-5</td>
<td>Hoya</td>
<td>1.056</td>
<td>3.3</td>
<td>14</td>
</tr>
</tbody>
</table>

A B-B, Brewster–Brewster; p-p, plano–plano.
B Cavity parameters: 10 m RC 100% mirror; 50% output mirror; 1 m cavity; optical density of dye 0.12 at 1.06 µm; calculated as CV2/2.
C Measured for whole pulse train, 3000 J input energy to amplifier flashlamp.
D Kindly loaned by Quentron Optics Pty Ltd, Adelaide.

With identical laser rod and cavity parameters, the smaller input energy required for lasing in the Apollo laser compared with the Korad laser is very marked. The mode-locking of the Apollo is also much more reliable, a fact we attribute to the shorter pumping flash duration and consequent lower total energy input. Thermal distortion effects within the laser rod are thus minimized. The output energy of the Apollo oscillator is reproducible to within 10% over long periods after careful alignment; under similar conditions the shot-to-shot variation of the Korad is about 30%. Despite these differences, the duration (800–1000 ns) and average output energy (150–200 mJ) of the pulse train is very similar for both lasers and independent of the particular laser glass. The higher gain of the newer phosphate glass relative to that of the silicate glass is shown in Table 1, both by the lower threshold for lasing when used in the oscillator, and by the increased amplification factor when used in the amplifier.

Mode-Locking Dye Cell

The mode-locking dye cell has a path length of 1 cm and is oriented at Brewster's angle to the optic axis; it is placed about 15 cm from the output mirror, but the position is not critical for reliable operation. A concentration of Eastman 9860 dye corresponding to an absorbance of 0.12 at 1.06 \( \mu \text{m} \) (measured at normal incidence) consistently gives reliable mode-locked pulse trains. If the dye concentration is increased slightly, the total energy output of the oscillator also increases; Fig. 1 shows a plot of the total energy output as a function of the dye absorbance. At too low a dye concentration, mode-locking will be poor because the dye cannot act as an effective shutter. If, on the other hand, the dye concentration is too high, mode-locking becomes less reliable and reproducible and shorter pulse trains are produced. At much higher dye concentrations the output becomes a single giant pulse of 30–50 ns duration with considerable modulation superimposed. In between these two extremes there is, however, a reasonable range of dye concentrations where mode-locking is reliable.

![Fig. 1. Total output energy of the oscillator as a function of the absorbance of the mode-locking dye solution (Eastman 9860 in dichloroethane). Absorbances were measured at 1.06 \( \mu \text{m} \) in a 1-cm cell.](image)

There has been much discussion in the literature about the mode-locking dye cell. A relationship between cell length and the width of the resulting light pulses has been reported which limits pulsewidths to \( \geq 8 \text{ ps} \) for cells \( \geq 1 \text{ cm} \) in length. Our 1-cm cell produces pulses between 6 and 9 ps (FWHM), within the first 200–300 ns of the pulse train. There seems to be little dependence of the pulsewidth on position in the pulse train, for the first third of the pulse train. It has been reported that thick cells not in contact with one of the laser mirrors give satellite pulses. This is certainly not true for either of our oscillators.

(b) Pulse Selection

Excess total light entering the streak camera can cause distortions of the fluorescence decay curves (see section on Streak Camera/OMA Detection System). For this reason, we extract a single exciting pulse from the mode-locked pulse train. The selection of single picosecond pulses has been discussed by several authors.

13 Yu, W., and Alfano, R. R., Opto-electronics, 1974, 6, 243.
described by von der Linde et al.,\textsuperscript{14} in conjunction with a Pockels cell (Lasermetrics 1973, 15 mm aperture) and Glan–Taylor polarizers (Electro-Optic Developments, 15 mm aperture). The measured extinction ratio (cw at 633 nm) of this combination is 600:1. After harmonic generation, the intensity ratio of selected to discarded pulses improves to better than 1000:1 due to the non-linearity of this process.

It is well-known\textsuperscript{10–12} that the duration of the laser pulses increases as the pulse train evolves. Concomitant with this is an increase in the spectral bandwidth of the individual pulses.\textsuperscript{10,13} These effects have been explained in terms of self-phase modulation, linear dispersion within the laser rod, and the finite amplification bandwidth of the neodymium glass rod.\textsuperscript{16} This degradation of pulse duration and shape may lead to ambiguities in the interpretation of experiments involving integration of the entire pulse train. Therefore it is important to select a pulse early in the pulse train. The choice of which pulse is selected can be controlled to some extent by varying the attenuation of the beam focussed into the spark gap.

The trigger pulse for the streak camera can be derived from a coaxial attenuator\textsuperscript{17} inserted in the sheath of the charging cable. A pulse of c. 10 V amplitude with a risetime of c. 2 ns is obtained. Pulse requirements for streak camera triggering are further discussed in Section 3a.

(c) Harmonic Generation

The fundamental wavelength of the neodymium glass laser (c. 1.06 μm) is not suitable for the electronic excitation of the majority of molecules of interest to photophysicists. Thus crystals with non-linear dielectric properties are used to produce harmonics of the fundamental frequency. The techniques for frequency mixing have improved considerably over the last few years due to the appearance of new non-linear crystals and in the more general use of temperature tuning rather than angle tuning to achieve phase matching. Temperature tuning utilizes crystals cut at 90° to the optics axis; this allows efficient doubling of beams with much larger beam divergence than is possible by angle tuning.\textsuperscript{18}

| Process | Type | Crystal | Angle | Temp. (°C) | Efficiency (%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1060 → 530</td>
<td>I</td>
<td>KH₂PO₄</td>
<td>40° 31’</td>
<td>room</td>
<td>11\textsuperscript{4}</td>
</tr>
<tr>
<td>1060 → 530</td>
<td>I</td>
<td>CsH₂AsO₄</td>
<td>90°</td>
<td>c. 43</td>
<td>25\textsuperscript{b}</td>
</tr>
<tr>
<td>1060 + 530 → 353</td>
<td>II</td>
<td>NH₄H₂PO₄</td>
<td>61° 12’</td>
<td>room</td>
<td>&lt;1\textsuperscript{a}</td>
</tr>
<tr>
<td>1060 + 530 → 353</td>
<td>I</td>
<td>RbH₂PO₄</td>
<td>57° 54’</td>
<td>room</td>
<td>12\textsuperscript{b}</td>
</tr>
<tr>
<td>530 → 265</td>
<td>I</td>
<td>NH₄H₂PO₄</td>
<td>90°</td>
<td>c. 48</td>
<td>10\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Data for ED2.3 silicate glass. \textsuperscript{b} Data for LHG-5 phosphate glass.

Table 2 summarizes the results we have obtained for various crystals. For frequency doubling, caesium dihydrogen arsenate (Quantum Technology Ltd) is more efficient than potassium dihydrogen phosphate, although there does appear to be some variation in the damage threshold of caesium dihydrogen arsenate.

crystals. One crystal shows some slight damage and has been used only with the unamplified oscillator (c. 0.1 GW cm$^{-2}$), whereas a second identical crystal has withstood the full power of the oscillator–amplifier combination (c. 1 GW cm$^{-2}$) with no sign of damage.

Various authors$^{19-21}$ have reported that type II (e + o → e) third harmonic generation is an efficient method for the production of ultraviolet light (0.35 μm) from neodymium glass lasers. Our attempts to use an ammonium dihydrogen phosphate crystal (Electro-Optics Developments) for this purpose resulted in disappointingly low conversion efficiencies (<1 %), probably caused by the appreciable absorbance of ammonium dihydrogen phosphate at 1.06 μm. Recent experiments$^{22}$ using a type I (o + o → e) angle-tuned rubidium dihydrogen phosphate crystal (Quantum Technology Ltd) have proved much more successful.

To produce ultraviolet light at 0.265 μm, a temperature-tuned ammonium dihydrogen phosphate crystal (Electro-Optics Developments) is used to frequency double the 0.53 μm output of the caesium dihydrogen arsenate doubler ('frequency quadrupling').

The spectral properties of the various harmonics have several interesting features; these are described in full elsewhere,$^{22}$ but are summarized in Table 4, p. 2351.

3. Streak Camera/OMA Detection System

(a) Streak Camera

The most straightforward method of measuring the temporal properties of a light pulse is to use a photodiode (or photomultiplier)/oscilloscope combination. Photomultipliers with rise- and fall-times of 100 ps have recently become available (e.g. Varian VPM 148), whilst photodiodes with similar risetimes have been available for several years (e.g. ITT 4000). Real-time oscilloscopes with risetimes of c. 70 ps have been reported,$^{23}$ but the fastest commercial oscilloscopes have risetimes of the order of 0.8 ns (e.g. Tektronix 7904).

Development of the streak camera has enabled electron–optical methods of light pulse measurement to be extended into the picosecond regime. Both the fastest commercially available streak cameras were developed by Bradley and coworkers. With their Photochron II design (produced commercially by Electrophotonics Ltd, Northern Ireland) a time resolution of <1 ps can be obtained at wavelengths close to the photocathode cut-off.

The operation of the streak camera can be understood by reference to Fig. 2. The light pulse, incident on a 50-μm slit, produces an image of the slit on the photocathode of the image converter tube (ICT). The resultant photoelectrons are accelerated very rapidly (to reduce transit-time dispersion) by a fine mesh extraction electrode placed very close (c. 0·5 mm) to the photocathode and pass through a hole in the anode. A fast voltage ramp is applied to the deflection plates of the image converter tube. This voltage ramp converts intensity information along the line of sight of the observer into intensity information normal to the line of sight of the

observer. The resultant 'streaked' photoelectrons form an image on a phosphor screen. The width of an image in the streak is therefore proportional to the duration of the incident light pulse. The photoelectron current in the image converter tube must be kept low to avoid image distortion and loss of spatial resolution arising from space charge effects. For this reason, the output phosphor of the image converter is optically coupled to a high-gain image intensifier tube, which is, in turn, optically coupled to the Vidicon detector of the optical multichannel analyser (OMA). The individual components of the Electrophotonics Photochron II streak camera will now be described in more detail.

Fig. 2. Schematic diagram of the streak camera. S, entrance slit; L, lens; C, photocathode; M, extraction mesh; CO, cone; A, anode; DE, deflection electronics; DP, deflection plates; B, baffle; P, phosphor; MA, magnetic focusing coils; ICT, image converter tube; IIT, image intensifier tube.

**Photochron II Image Converter Tube (ICT)**

The major difference between the Photochron II image converter tube (Instrument Technology Ltd) and previous designs is in the increased extraction field at the photocathode. This allows for a high time resolution (<2 ps) over the entire spectral range of the photocathode, and a resolution of <1 ps at wavelengths close to the photocathode cut-off.

The image converter tube can be operated in two ways. The 'focus' setting applies no deflection voltage, so that the photoelectrons are transmitted directly to the ICT phosphor, thus allowing camera focus and external optical alignment to be optimized. Two 'operate' settings apply a constant voltage to deflect the image off the phosphor; deflection by the voltage ramp returns the image onto the phosphor.

**Streak Deflection Voltage Ramp**

The streak deflection voltage ramp is produced by an avalanche transistor–krytron circuit. The fastest streak velocity is obtained when the krytron is connected directly to the ICT deflection plates; slower streak velocities are obtained by interposing calibrated plug-in units between the krytron and the deflection plates. The available streak velocities are in the range $4 \times 10^5$–$8 \times 10^7$ m s$^{-1}$ over a streak length of c. 45 mm.

The avalanche transistor–krytron circuit requires a trigger pulse of about 1–10 V into 50 Ω with a risetime of c. 1 ns. A portion of the laser output diverted onto a pin photodiode (Hewlett-Packard 5082–4203) provides a suitable signal. Synchroni-
zation between the deflection ramp and the light pulse is achieved by varying the length of the cable between the photodiode and the deflection circuit. With a new krytron (EG&G KN-22) the delay between triggering and ramp generation is 40–50 ns, varying with individual krytrons. When the photodiode is used as a trigger source, the jitter is c. 500 ps. As krytrons age both jitter and delay can increase dramatically. If a single pulse is selected from the mode-locked pulse train, the arrival of the selected pulse must be delayed by c. 50 ns to compensate for the delay between krytron triggering and ramp generation. We reduced the optical delay necessary by deriving a trigger pulse from the spark gap transmission line (see Section 3b) and interposing a cable delay between the spark gap and the Pockels cell. Although this technique has proved successful in most respects, it has not been an entirely satisfactory solution. The jitter is increased to 1–2 ns; we believe this is mainly attributable to jitter in the spark gap breakdown but the slower risetime (c. 2 ns) of the trigger pulse probably also contributes. This jitter in the timing of the deflection ramp can be a serious problem on the faster sweep speeds where the total time span of the sweep is small compared with the jitter; the light pulse may be completely missed on some shots.

The Image Intensifier Tube (IIT)

The image converter tube is coupled with about 2% efficiency to an image intensifier tube, an f/1·4 80 mm focal length lens being used. The image intensifier tube (EMI 9912) is a magnetically focused four-stage cascade image converter tube; the S20 photocathodes and P11 phosphors are each 50 mm in diameter. The maximum gain of the IIT is $10^6$.

Although both the IIT and ICT are magnetically shielded, the focus of this combination is sensitive to external magnetic fields. We have found that the presence of a magnetic base within 50 cm of the streak camera both moves and distorts the image of the slit on the final phosphor of the IIT; some image rotation was also observed. To avoid these problems, all optical equipment within 70 cm of the camera is mounted on an optical bench.

(b) Optical Multichannel Analyser (OMA)

In the past, the image from the image intensifier phosphor of the streak camera has usually been photographed and a microdensitometer trace taken. Obviously it is desirable to have a detector with a larger dynamic range than film, linear response to light intensity, and analogue-to-digital conversion. This would increase both the precision and ease of data acquisition. A commercial instrument with these attributes is the optical multichannel analyser (OMA, Princeton Applied Research Corp.). This consists of a standard silicon Vidicon detector (RCA 4532) or silicon intensified target detector (SIT RCA 4804) connected through a preamplifier to the analogue-to-digital converter and memory of the console unit.

The operation of the OMA can be understood by reference to Fig. 3. The signal electrode (SE) is operated at a positive potential with respect to the back of the target (PT), which is charged to the cathode potential by the electron beam (EB). When light falls on the photoconductive target, electron–hole pairs are formed, which causes an increase in conductivity of the illuminated area. The back of the target becomes more positively charged in these areas; a scanning electron beam
then 'reads' the signal by depositing electrons on the positively charged area. This provides a capacitively coupled signal at the signal electrode. Each scan of the target takes 32.8 ms and is divided into 500 'channels'; repetitive scanning of the target is necessary because only a fraction of the signal is removed in a single scan. The dark current due to thermal effects is subtracted by sampling an area adjacent to the area on which the light falls and performing an analogue subtraction. However, even with this correction the baseline is still not flat. A second subtraction (after A/D conversion), using the two console memories and two separate accumulations with and without signal, gives a flat baseline.

The OMA may be set to respond to light signals in two ways:
(i) *Real time.*—The memory is cleared and displayed after each scan. With the streak camera ICT on the 'focus' setting, this gives a real-time display of the intensity of light incident on the streak camera slit. In this way the external optics can easily be adjusted for maximum light collection.
(ii) *Accumulate.*—In this mode of operation, the OMA will accumulate into the memory for a present number of scans after a trigger signal is received. A delay (i.e. a preset number of inactive cycles) can be interposed between the accumulation cycles if desired. This is the normal mode of operation when detecting transient light signals.

**Coupling of the OMA to the Streak Camera**

To optically couple the streak camera to the OMA, the image on the phosphor of the final stage of the ICT must be reduced in size, since the length of the scanned area of the Vidicon target is only 12.5 mm compared with the 45 mm streak length. For this purpose we use a 50 mm focal length camera lens in an Electrophotonics Ltd mount. The mount allows for rotation and lateral motion to facilitate focusing of the OMA on an image of the streak camera slit with the OMA in the real-time mode.
A series of laser pulses viewed at a slow streak speeds (Fig. 4) shows that the image of the slit is then in focus across the entire OMA. A shorter focal length coupling lens is desirable since at present only about 2/3 of the available IR image length can be imaged on the Vidicon target.

The Two-Dimensional Option

The two-dimensional option of the OMA allows scanning of the Vidicon target in up to 256 tracks of reduced width. In principle, this allows different regions along the slit height to be recorded in different tracks. This would seem like a good way of resolving the temporal behaviour of an event with respect to wavelength, making possible the collection of time- and frequency-resolved data in a single shot. However, if more than two tracks are used, an external fast-access mass-data-storage system is necessary. Furthermore, the analogue subtraction cannot be used with the two-dimensional option, so that the information must be extracted from the Vidicon before the dark current becomes excessive. A cooled detector seems essential if more than about four tracks are used.

We have used the two-dimensional option (i) to ensure that the sweep of the electron beam of the OMA is aligned parallel to the streak, and (ii) to scan only the centre portion of the streak to attain the best time resolution. This removes the effect of slit image curvature (Fig. 5) which would otherwise reduce time resolution on the faster sweep speeds. Division of the slit length into tracks reduces the sensitivity, and so care must be taken not to overload the streak camera.

![Fig. 5. Artist's reproduction of the streak image produced by two pulses generated from a single pulse by reflection off the front and back surfaces of a glass plate. The separation between the two pulses is c. 15 ps. Two shots are shown; in both the slight curvature of the slit image at this streak speed (8 x 10^7 ms^-1) may be seen. Time increases from the bottom to the top of the Figure.]

Dynamic Range, Linearity and Lag

The A/D converter limits the maximum signal that can be extracted from the OMA in a single scan to 750 counts. When used for detecting weak light pulses, great care must be taken to ensure that the OMA is linear over this range. Because the OMA has been traditionally used in a signal averaging mode with CW signals, little information about its use with single-shot pulsed signals can be obtained from the currently available instruction manual.\(^{24}\) Our instrument, when it arrived, was found to be markedly non-linear for pulsed light sources. This was caused by a phenomenon called lag—the electron beam takes a finite time, dependent on incident light

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intensity, to restore the charge on the target. In the silicon Vidicon, lag is purely a capacitative effect. This means that the recharging of the target has an associated \( RC \) time constant. Since resistance of the silicon increases with decreasing light intensity, lag also increases (see Fig. 11.9 in ref.25). As delivered, our OMA removed only about 9\% of the signal per scan. By increasing the cathode voltage from 2 to 6 V this figure was increased to 30\%. Linearity of the whole detection system was tested by using a photographic electronic flash unit (pulsewidth c. 1 ms) with the sc in the focus mode. Incident intensity was varied using calibrated neutral density filters. Under these conditions, the sc/OMA combination was found to be linear within ±5\% from 150 to 2200 counts (OMA delay setting of 1, 6 accumulations).

<table>
<thead>
<tr>
<th>Number of scans</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counts: delay 0</td>
<td>16</td>
<td>42</td>
<td>62</td>
<td>73</td>
<td>116</td>
<td>124</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>57</td>
<td>—</td>
<td>101</td>
<td>131</td>
<td>141</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 3 shows the increase in signal as the number of scans is increased; it also shows that delay setting of 1 (i.e. an inactive cycle between each read-out cycle) increases the signal in this mode of operation. The image intensifier tube has a P11 phosphor (\( \tau \approx 200 \mu s \)) but there is some lag associated with the tube, and we expect the millisecond flash-lamp to duplicate reasonably the situation when the streak camera is viewing sub-nanosecond fluorescence. It is to be noted that lag is a serious problem in obtaining accurate decay curves, as different intensity regions of the curve will have different lag. That is, lag must not be significant in the tail of the decay if this is to be considered in the analysis.

With the standard Vidicon detector, we reject curves with a maximum of more than 1500 counts (6 scans, delay 1) and noise is typically c. 20 counts. This means that the maximum linear dynamic range of the streak camera/OMA detection system is c. 100. Use of a SIT Vidicon tube, which has a gain c. 200 times higher than the standard Vidicon, will not increase the dynamic range because the A/D conversion of the OMA will fail at a correspondingly lower level. It is, however, useful if the entire signal is weak.

**Synchronization of the OMA with the Laser**

The flash-lamp capacitor is charged to a voltage slightly above the preset firing voltage. When the capacitor voltage crops to the present level (by leakage through a large resistor) a voltage comparator gives a signal to start the OMA accumulating. The OMA has its own internal clock, and only starts to accumulate on the first of its own 32-ms cycles following the receipt of an 'accumulate' signal; therefore the laser must be fired from the OMA in synchronization with the OMA internal cycle.* The laser is triggered during an inactive OMA cycle (i.e. when the electron beam is not scanning the target) in order to remove the 'skew lag' effect.24 If the laser fires during

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* Optical isolators are used on both the comparator signal and the fire signal to prevent electrical noise from the flash-lamp firing circuits from upsetting the OMA.

a read-out scan, some of the low numbered channels are read out once more than the remaining channels, which results in too much signal in these low numbered channels.

Transfer of Data to the Computer

Through the serial output of the OMA, the data is transmitted to a NOVA 2/10 located in a remote part of the building. The OMA appears to the computer as an additional teletype—the standard teletype interface board was modified to accept a voltage signal rather than the 20 mA current loop of a teletype. The data transfer rate is 4800 baud, requiring 20 s for the transfer of 500 data channels. Our NOVA supports a number of terminals used by students and other research staff for BASIC programming: data transfer takes place in the background, causing minimal interruption to other users of the computer. The transfer is controlled from one terminal situated in our laboratory; thus we are above to perform simple analyses of the data immediately. The data are stored on a disc and are also plotted by an HP 7210A digital plotter for more leisurely and complicated analyses.

(c) Time Resolution of the Detection System

The time resolution of any image tube streak camera is ultimately limited by the spread of the initial velocities of the photoelectrons, which arises close to the photocathode where the electrons are moving slowly. The distribution of photoelectron transit times through the image tube has a half-width\(^1\)

\[ \Delta t_D = m \Delta u/eE \]

where \( \Delta u \) is the half-width of the initial electron velocity distribution, and \( E \) is the strength of the extraction field; \( e \) and \( m \) are the electron charge and mass respectively. The larger the electric field strength near the photocathode, the smaller the transit-time spread. For a particular photocathode, the half-width of the initial electron velocity distribution depends on the wavelength of the incident light, being smaller close to the long-wavelength cut-off of the photocathode. In the Photochron II ICT, a field strength of 18 kV/cm near the photocathode enables a time resolution of \( \leq 2 \) ps over the whole spectral range of the photocathode, and sub-picosecond time resolution at wavelengths close to the photocathode cut-off. For example, for a S20 photocathode, \( \Delta u = 1.3 \times 10^5 \text{ m s}^{-1} \) at 0.53 \( \mu \text{m} \), giving \( \Delta t_D = 0.73 \) ps.

To calculate the total instrumental resolution of the streak camera, one must also consider the contribution to the time resolution due to the finite dynamic spatial resolution of the ICT phosphor, \( \Delta t_S \). Provided that the slit width is smaller than the spatial resolution, \( \Delta t_S \) is given by

\[ \Delta t_S = 1/10^3 Vx \]

where \( V \) is the deflection speed (ms\(^{-1}\)) and \( x \) is the spatial resolution (line pairs/mm). A dynamic resolution of 10 line pairs/mm and a streak speed of \( 8 \times 10^7 \text{ ms}^{-1} \) (the fastest sweep speed of our camera) give \( \Delta t_S = 1.25 \) ps.

For Gaussian shaped pulses, the measured pulse half-width \( \Delta t_m \) is given by

\[ \Delta t_m = (\Delta t_S^2 + \Delta t_D^2 + \Delta t_p^2)^{1/2} \]

where \( \Delta t_p \) is the laser pulse half-width.

However, the use of multichannel detection allows for a more direct method of deconvoluting the instrumental response from the measured pulsewidth. The
response of the ICT–IIT–OMA combination to a δ-pulse can be obtained to a very good approximation by measuring the image produced by a single laser pulse on a sweep speed where the dynamic spatial resolution, $\Delta r_s \gg \Delta r_p$. The instrumental response and the pulse recorded on a fast sweep speed can then be deconvoluted by standard methods. This method does not take $\Delta r_p$ into account, but as the calculation above shows, in the Photochron II tube, the photoelectron transit-time dispersion is insignificant for pulses $\geq 2$ ps.

On the fastest sweep speeds a slight curvature of the streak image can be seen (Fig. 5). This is caused by photoelectrons originating from the ends of the slit having slightly different transit times than photoelectrons originating from the centre of the slit. Thus time resolution will be lost if the streak image is integrated over the whole length of the slit. This is only a problem when time resolution of $< 5$ ps is required, and in this case the two-dimensional option of the OMA (see Section 3a) can be used to scan only the centre portion of the slit image, at the cost of reduced sensitivity.

Taking all the above factors into account, the time resolution of the streak camera/OMA combination at the fastest streak speed (c. 1 ps per channel) is 4–5 ps.

A loss in time resolution can also be introduced external to the streak camera. For example, in fluorescence measurements the finite size of the fluorescent image can lead to a loss in time resolution. Normally we use a right-angle geometry for excitation and collection of fluorescence to minimize the effect of scattered light. In a 1-cm cell, if the absorbance is low, a time dispersion of c. 40 ps (water solvent, increasing with solvent refractive index) will be introduced if fluorescence is collected along the whole length of the cell. With a ‘straight through' geometry, only the (small) difference in phase velocity between exciting and fluorescent light need be considered.

(d) Accuracy of Fluorescence Decay Measurements

The ability to measure fluorescence lifetimes with the streak camera depends on:

1. The linearity of the response of the streak camera/OMA to variations in light intensity.
2. The accuracy of the time base calibration.
3. The linearity of the streak deflection ramp.
4. Reproducibility of the streak velocity.
5. The signal-to-noise ratio of the observed fluorescence decay.

The response of the SC/OMA to light intensity has been found to be linear to within $\pm 5\%$ (cf. Section 3b). The time bases can be calibrated very accurately by means of a multiple-reflection delay line in which a single laser pulse is split into a series of sub-pulses of accurately known separation. This delay line was also used to check the linearity and reproducibility of the streak deflection ramp. The streak speeds shows a shot-to-shot variation of c. $\pm 3\%$ with a much smaller deviation from linearity.

When using the whole mode-locked pulse train for excitation, we have observed a distortion of the fluorescence decay for the faster sweep speeds. This distortion is caused by an intensity-dependent ‘hump' of roughly constant shape and position on the sweep. A similar hump is also obtained when a millisecond flash-lamp is used as a light source, even when the camera is not streaked. The most likely explanation is that some of the electrons leaving the photocathode before and after the sweep,
Instead of being stopped by the baffles in the ICT, are scattered and eventually arrive at the phosphor. The intensity of the hump produced by these stray electrons depends on the total amount of light entering the streak camera, but not on its temporal properties. By selecting a single pulse from the mode-locked train, the number of photoelectrons which the ICT baffles are required to trap can be reduced severely—to essentially zero if the whole fluorescence decay is on the ICT phosphor. Using single pulse excitation, we are able to obtain accurate and reproducible fluorescence decays, with no detectable distortion from the 'hump'.

4. Applications

The applications of the system we have described to several photophysical and photochemical problems will be the subject of succeeding papers of this series; however, it is appropriate here to describe our measurements of the laser pulsewidth and shape, as an example of the measurements which are possible with our apparatus and to characterize a fundamental parameter of the system, the width of the pulses used for excitation.

When investigating the temporal properties of single picosecond pulses, it is usually unnecessary to select a single pulse from the pulse train. With streak camera detection, our temporal measurements are limited by photocathode sensitivity (S20) and glass camera lenses to a study of the second harmonic; Fig. 4 shows a plot of a portion of the second harmonic pulse train, recorded when we used a slow streak camera sweep speed (c. 200 ps/channel). The signal-to-background ratio is better than 500:1, indicating an absence of any satellite pulses of measurable intensity.

![Fig. 6. Single pulses showing the pulse asymmetry.](image)

(a) 2.3 silicate glass; (b) LHG-5 phosphate glass. Both pulses have a FWHM of 7.0 ± 0.5 ps after deconvoluting the instrumental response function.

At the faster streak camera sweep speeds, the details of the single pulse can be studied; Fig. 6 shows two separate pulses recorded at the fastest streak speed (1 ps/channel). The approximate laser pulse half-width $\Delta \tau_p$ can be calculated from the measured pulse half-width $\Delta \tau_m$ by means of the relationship

$$\Delta \tau_p^2 = \Delta \tau_m^2 - \Delta \tau_s^2 - \Delta \tau_D^2$$

where $\Delta \tau_s$ and $\Delta \tau_D$ have already been defined (Section 3c). This equation is exact for Gaussian pulses. If one assumes a camera resolution $\Delta \tau_s$ of 5 ps and a transit-time dispersion $\Delta \tau_D$ of 0.75 ps, the approximate widths of these pulses are 7.5 and 6.5 ps. These values are consistent with the results obtained by Bradley and Sibbett;12 their results predict pulsewidths of 7–8 ps for a thick dye cell. Bradley et al.26 found

a pulsewidth of 5–6 ps from t.p.f. measurements with a thick dye cell, and commented that overall pulse train reproducibility was less with a thick non-contacted dye cell than with a thin contacted cell.

Fig. 7. Semi-log plot of a single pulse. The falling edge is approximately exponential with a decay time of c. 4 ps.

Table 4. Summary of spectral and temporal characteristics of single pulses from mode-locked Nd : phosphate glass and Nd : silicate glass oscillators

<table>
<thead>
<tr>
<th></th>
<th>Phosphate glass</th>
<th>Silicate glass</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fundamental</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>spectral band centre (nm)</td>
<td>1054</td>
<td>1062</td>
</tr>
<tr>
<td>spectral bandwidth (cm⁻¹)</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td><strong>Second harmonic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>temporal pulsewidth (ps)</td>
<td>6.5 ± 1</td>
<td>6.5 ± 1</td>
</tr>
<tr>
<td>spectral band centre (nm)</td>
<td>526.8</td>
<td>530</td>
</tr>
<tr>
<td>spectral bandwidth (cm⁻¹)</td>
<td>46 ± 5</td>
<td>c. 40</td>
</tr>
<tr>
<td><strong>Third harmonic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>spectral band centre (nm)</td>
<td>351.4</td>
<td>354</td>
</tr>
<tr>
<td>spectral bandwidth (cm⁻¹)</td>
<td>22 ± 2</td>
<td>—</td>
</tr>
<tr>
<td><strong>Fourth harmonic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>spectral band centre (nm)</td>
<td>263.4</td>
<td>265</td>
</tr>
<tr>
<td>spectral bandwidth (cm⁻¹)</td>
<td>15 ± 2</td>
<td>15</td>
</tr>
</tbody>
</table>

^ From ref. 22.

The second pulse in Fig. 6 has also been plotted on a semi-logarithmic scale and is shown in Fig. 7. Both are clearly asymmetric, with a more rapidly rising leading edge; the falling edge is roughly exponential with a decay time of c. 5 ps. Von der Linde²⁷ has shown that the 0.53 μm pulses from a silicate glass oscillator, measured by a method based on stimulated Raman scattering, are also asymmetric in the same sense. We believe that this is the first time that pulse asymmetry has been observed by direct linear measurement. Previous measurements of the pulse shape have produced conflicting results. Treacy²⁸ and Shelton and Shen²⁹ have reported asymmetry in the opposite sense, while Auston has discerned no pulse asymmetry.

or only occasional asymmetry. These earlier studies all relied on indirect methods for determining pulse shape. In fact, a pulse shape of the form shown in Figs 6 and 7 is expected because of the finite excited state lifetime of the mode-locking dye, since the leading edge of the pulse is more strongly absorbed than the falling edge, which interacts with the already partly bleached dye. The decay time for the falling edge of the pulse (c. 4 ps) is thought to be closely related to the recovery time of the saturable absorber. For Eastman 9860 dye, recovery times of 9 ps and 6 ps have been reported.

These results refer to picosecond pulses produced by neodymium silicate glasses. A detailed study of the temporal and spectral properties of pulses produced by the new neodymium phosphate glass reveals essentially identical characteristics; the properties of the two types of laser glass are compared in Table 4.

Application of the system we have described here to measurement of phenomena as diverse as exciton migration in crystals, rotational diffusion in fluids, solvent effects on dye fluorescence lifetimes, dynamics of stimulated emission will be described in other papers.

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