Section 3
DEVELOPMENTS IN PICOSECOND RESEARCH

3.A Applications of the Jitter-Free Signal-Averaging Streak Camera

Introduction

The picosecond streak camera is an extremely versatile instrument for the detection of fluorescence. The photocathode element responds over a wide spectral range (~200 nm to 800 nm for S-20 response), it responds equally to either polarization of incident light, and it is not selective in terms of solid angle of incoming light. This degree of versatility is not matched by other methods of fluorescence detection with a few picosecond resolution such as the optical Kerr shutter,[1] or fluorescence upconversion.[2] These other techniques are, however, jitter-free.

We recently demonstrated a nearly jitter-free (2 ps) operation of a streak camera[3-6] using various high-power picosecond photoconductors. Since this first demonstration, we have proceeded to apply this system to a wide range of studies in solid-state physics, biophysics, and chemistry. We discuss here several recent results in these areas which illustrate the importance of signal averaging in picosecond fluorescence kinetics experiments.

Streak Camera

The jitter-free streak camera in its present form[5] (Fig. 14) uses a high-power picosecond photoconductive switch made of chromium-doped GaAs, a semi-insulating material.[7] When excited by a single laser pulse from an active-passive mode-locked Nd:YAG laser, the switch starts conducting and charges the deflection plate of a Photochron-II streak camera tube. A portion of the same optical pulse is frequency-doubled,

and used to excite a sample. Fluorescence is collected and imaged onto the photocathode through bandpass or cutoff filters. The streaked image is amplified in a four-stage magnetically-focused intensifier stage, and recorded with an optical multichannel analyzer image device (Princeton Applied Research Model OMA II).

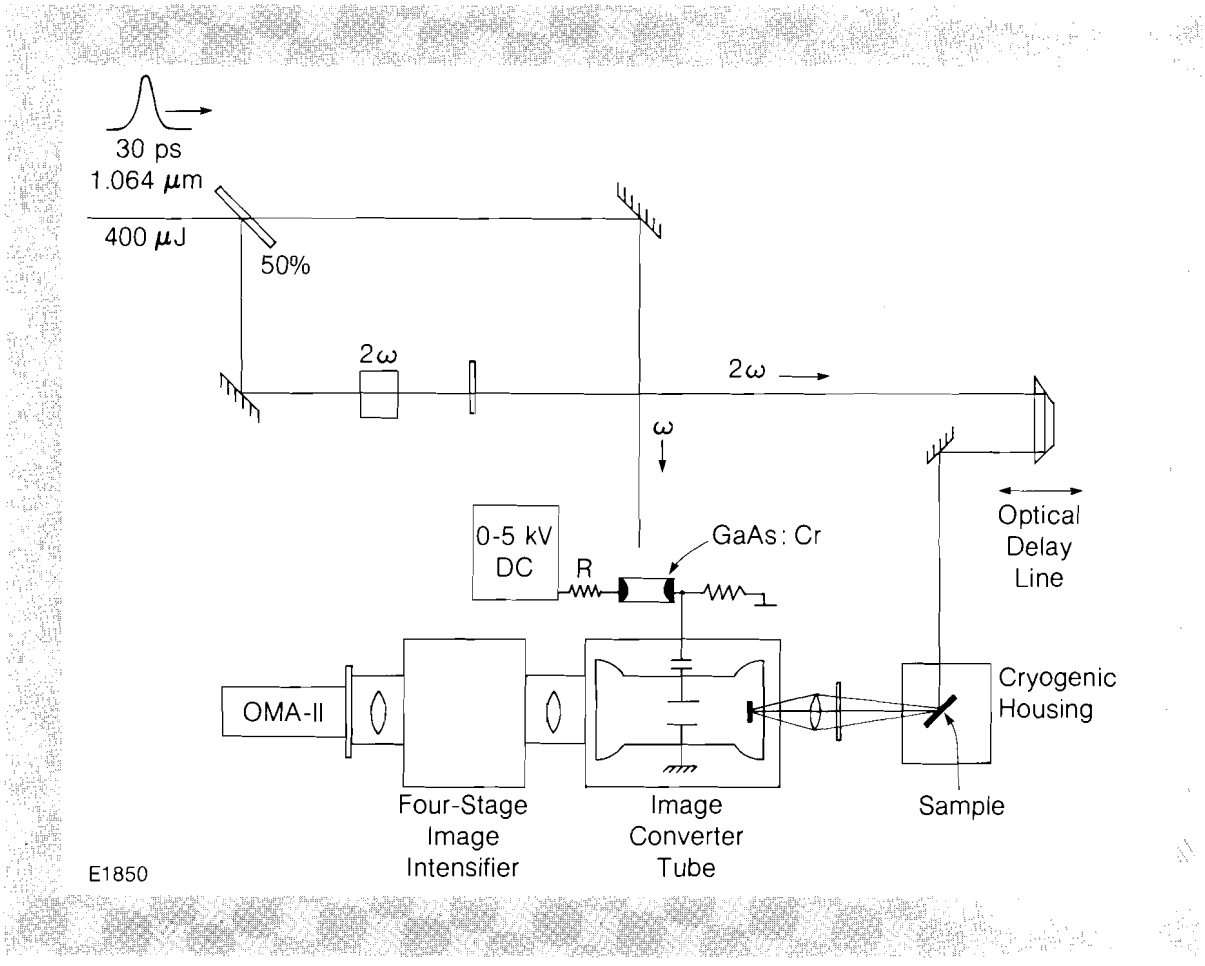

Fig. 14
Experimental configuration. A single pulse from an active-passive mode-locked Nd:YAG oscillator is directed upon a high-power picosecond semiconductor switch. The deflection plate is charged in ~1 ns in synchronization with the excitation pulse for the sample under study. The sweep speed is linearly proportional to the DC bias voltage applied to the switch.

The sweep speed is linearly proportional to the bias voltage applied to the switch, and there is no inherent time delay in the switching process. Sweep speeds of between 6 ps/mm and 50 ps/mm are obtained in this way.

In order to obtain 2 ps jitter, it is necessary for the laser system to satisfy several criteria: energy stability ± 15%, energy contrast ~ 10^5, and pulsewidth stability ± 5%. These are easily obtainable on a routine basis with an active-passive mode-locked laser,[8] but not with a passively mode-locked laser.

Since the switch operates in a linear photoconductive mode as opposed to an avalanche mode, it has a very long lifetime. We have used one switch for two years now, with no apparent deterioration.

We have also applied this technique to several other types of streak cameras with success: Electro-Photonics, Hadland, Thomson-CSF, and GEAR.[9]

Applications

Many luminescence phenomena in the area of solid-state physics exhibit decay times of up to several hundred microseconds. In the case of luminescence from amorphous semiconductors, decay times vary from nanoseconds to milliseconds. We have made the first measurement of luminescence from an amorphous semiconductor on the picosecond time scale in amorphous As_2S_3[10,11] (Fig. 15). In this experiment, the picosecond signal was extremely weak, such that a single shot at the highest detection system gain (10^7) was a statistical distribution of photoelectron events. After averaging up to 300 shots, it was possible to obtain a characteristic decay time (see insert). A strong temperature dependence of the decay rate was found by repeating this measurement at various temperatures. The interpretation of this data is given in detail in Ref. 11. In temperature cycling experiments, long-term stability is critical due to the slow thermal response time of sample holders.

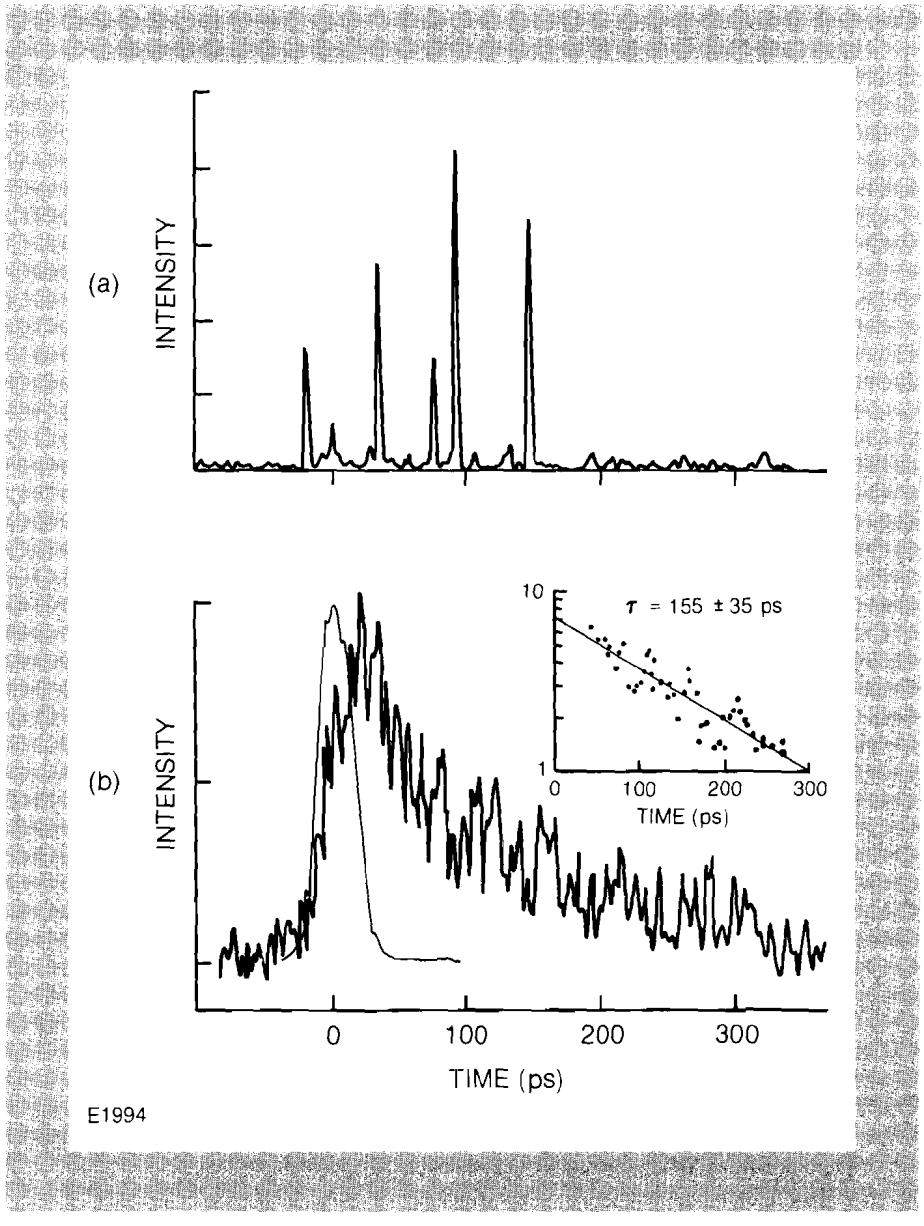

Fig. 15
Averaging of very weak signals. Shown are (a) one and (b) 300 shots of luminescence of amorphous As_2S_3 under excitation by a 30 μJ pulse at 532 nm. Despite the extremely weak signal, signal-averaging allows a determination of the decay time (inset). Also shown are 30 shots of the scattered excitation pulse at t = 0.

In other studies in this area, we have investigated fluorescence kinetics of cis- and trans-polyacetylene,[12] and vibrational relaxation of molecular ions, color centers and heavy metal ions in alkali-halide crystals.[13]

We have measured the fluorescence kinetics of biosystems at relatively high excitation levels ($\sim 10^{18}$ photons/cm^2) in order to study the process of exciton annihilation. In a recent experiment,[14] we have measured the fluorescence of Photosystem-I[15] particles under excitation by the second harmonic (532 nm) pulse (Fig. 16) from a Nd^{+3}:YAG laser. We have obtained a good analytical fit to the data assuming a simple bimolecular recombination rate. The calculated curve is the solution to:

$$\dot{N} = -\frac{N}{\tau} - \gamma N^2 + \sigma I N_o \qquad (2)$$

where N is the number density of excited species, τ is the ordinary decay time, γ is the bimolecular recombination constant, σ is the absorption cross section, I is the pump intensity, and N_o is the ground state density, assumed constant. This fit suggests that a simple biomolecular recombination kinetic model is appropriate in this complex system over a large intensity range. By averaging 100 shots we obtained a sufficiently high signal-to-noise ratio to make a determination of γ to within $\pm$ 10%. The value of γ in a system is related to the topology and accurate

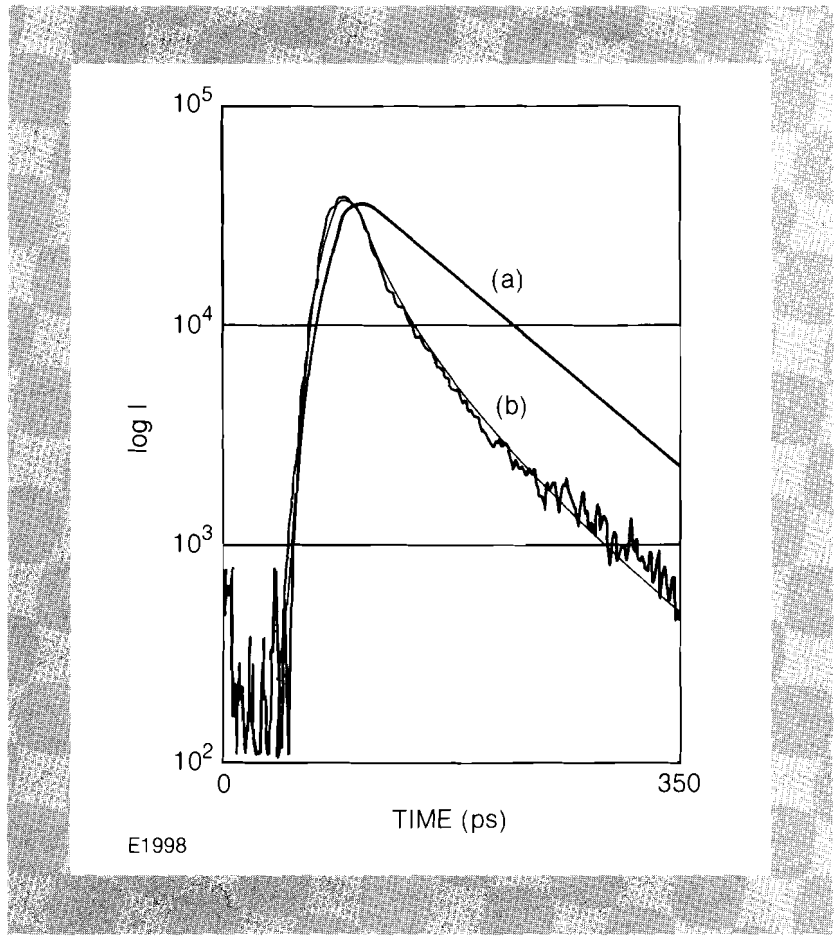

Fig. 16
Detailed curve fitting. Fluorescence of Photosystem-I particles under excitation at 532 nm. 100 shots of fluorescence are accumulated.
a) the solution to Eq. (2) asuming $\gamma = 0$ and $\tau = 80$ ps (the fluorescence decay time
b) the solution to Eq. (2) assuming a simple bimolecular recombination
The fit is extremely sensitive to the value of γ used, and its value can be determined to within 10% by this method.

measurements of γ in many systems may provide additional insight into the role of excitons in biological systems.

In other applications in biophysics, we have made measurements of the excitation intensity dependence of chlorophyll a/b protein fluorescence,[16] anisotropy decay time constants of Tryptophan in various environments,[17] the temperature dependence of purple membrane fluorescence lifetime,[18] the energy transfer rate in spinach chloroplasts,[19] and the fluorescence decay of hematoporphyrin derivative.[20]

The jitter-free streak camera, coupled to the OMA-II—which has the capability to do multi-track scanning—is a powerful tool to probe depolarization of fluorescence. Depolarization is measured experimentally by measuring the intensities of fluorescent components, $I_{\perp}(t)$ and $I_{||}(t)$, polarized perpendicular to and parallel to the excitation polarization, respectively. The ratio of these components formed by

$$R(t) = \frac{I_{||} - I_{\perp}}{I_{||} + 2I_{\perp}} \tag{3}$$

is of interest and is very sensitive to noise in the component signals. In Fig. 17, we show one result of measurement of fluorescence depolarization of Rhodamine-6G in water.[21] An average of 50 shots were fired in order to obtain an adequate signal-to-noise ratio for a detailed study of the dependence of the decay time as a function of solvent viscosity and ionic strength.[21] Data for $I_{\perp}$ and $I_{||}$ were simultaneously accumulated in separate files. In some cases, we averaged signals from up to 200 shots in order to measure the decay constant to within 5%. Decay times as short as 10 ps may be measured with this technique.

In other applications, we have measured fluorescence decay of Phthalazine in various solvents[22] and fluorescence kinetics of molecular monolayers on solid surfaces.

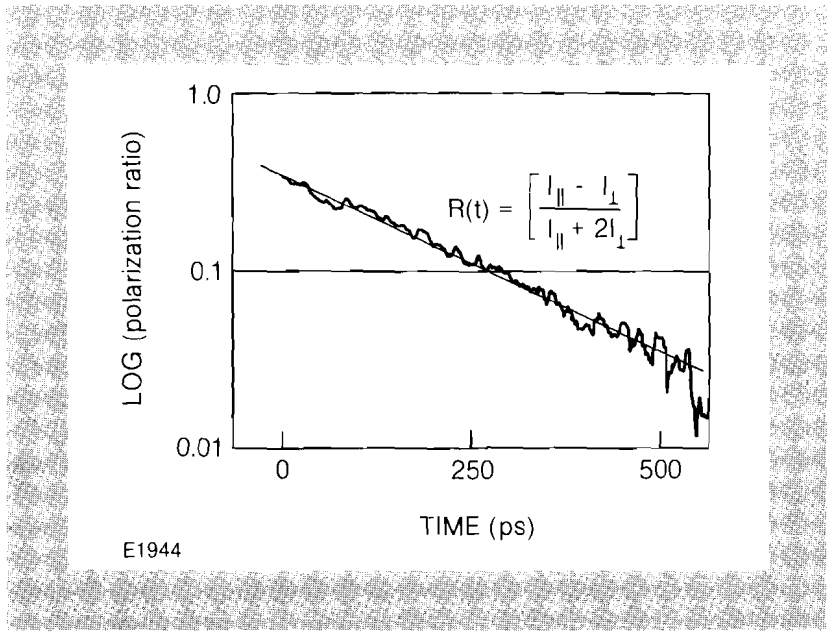

Fig. 17
Measurement of fluorescence depolarization. Fluorescence anisotropy decay of Rhodamine-6G in water. The anisotropy parameter R(t) is calculated from 50 shot averages of $I_{\perp}$ and $I_{||}$. The high signal-to-noise ratio of these data allow for a determination of the value of the anisotropy decay time to within 5%. Decay times as short as 10 ps can be measured with this method.

Conclusion

The signal-averaging capability of the jitter-free streak camera makes it a powerful diagnostic in picosecond fluorescence kinetics experiments. By averaging 50 shots, one has access to ± 0.5 ps timing stability.[5,13] The system is capable of performing both high-power excitation experiments ($\sim$GW/cm^2) and low-excitation intensity experiments (10^{12} photons/cm^2). In the case of long fluorescence lifetimes, high sensitivity is needed to record picosecond time-scale information. The high stability of the system makes possible extended studies where only one parameter is changed, such as temperature, excitation intensity, collection wavelength, or detector polarization.

The use of the DC-biased photoconductive switch operated at room temperature results in a simple system to operate which avoids the timing drift and inherent jitter which are characteristic of other sweep driver systems. This permits the simple accumulation of many successive (laser-initiated) events resulting in a dramatic increase in the precision of measurement. With the versatility of the streak camera coupled to the jitter-free feature, one has a powerful diagnostic for picosecond fluorescence kinetics studies.

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