Picosecond Streak Camera Performance in Studies of Exciplex Formation Dynamics

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Abstract. A crow-bar technique employing a light-activated silicon switch is described to overcome stray electron effects in streak cameras. The technique is applied in picosecond fluorescence studies of intramolecular charge transfer processes in a compound of the type $A\text{-}(CH_2)_3\text{-}D$ (A: anthracene, D: dimethylaniline) where the locally excited state and the exciplex state are shown to be formed sequentially.

In the last couple of years streak cameras have become an important tool in the investigation of ultrafast light signals [1–6], particularly in studies of photochemical reactions where energy, proton or charge transfer is taking place [6]. Among the streak camera problems, all of which are not yet solved satisfactorily in the different designs, are the limitations resulting from e.g. low dynamic range, poor sweep linearity, the difficult calibration procedure to obtain the flat field response, and the large sweep jitter. In the present work we wish to describe a phenomenon which has not been addressed previously in the literature: the influence of stray and secondary electrons on streak camera measurements of rising time functions of luminescence signals which exhibit a long decay time.

Streak cameras are generally not designed to cope with the task of measuring a short rise time followed by a long decay time and one encounters the following problem. The streak camera sweep time, covering the range of the rise time τ (rise) to be measured, has already ended when photoelectrons from the slowly decaying part of the time-dependent luminescence start to hit the "opposite" deflection plate and continue to do this until the luminescence has fully decayed. Stray and secondary electrons are produced and contaminate the original rise signal stored on the phosphor screen. We have studied the influence of stray electrons on streak camera measurements in connection with the investigation of the intramolecular

exciplex formation kinetics of a selected charge transfer system.

Experimental

In the photochemical system 1-(9-anthryl)-n-(p-N, N-dimethylaminophenyl) alkane, abbreviated as A–D, photoinduced intramolecular charge transfer processes between electron donor (D) and excited acceptor (Å) lead to the formation of exciplexes $^1(A^-\text{-}D^+)$ in the low polar solvent diethylether. The characteristic spectrum of the exciplex fluorescence, with maximum around 505 nm, is quite similar to the extensively studied intermolecular exciplex spectrum [7]. Equation (1) summarizes the relevant photochemical and photophysical events. It is expected that the states $^1\overset{*}{A}\text{-}D$ and $^1(A^-\text{-}D^+)$ are formed sequentially according to the reaction scheme

$$^1\overset{*}{A}\text{-}D \xrightarrow{k_c} {}^1(A^-\text{-}D^+)$$

$$k_f \downarrow h\nu_L \qquad\qquad k_f' \downarrow h\nu_E \tag{1}$$
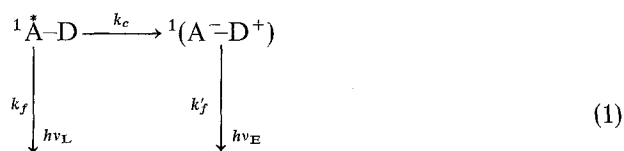
with the rate constants k_f and k_f' for the emissions $h\nu_L$ and $h\nu_E$. Figure 1 illustrates the spectral and time behavior of the fluorescence of the locally excited state
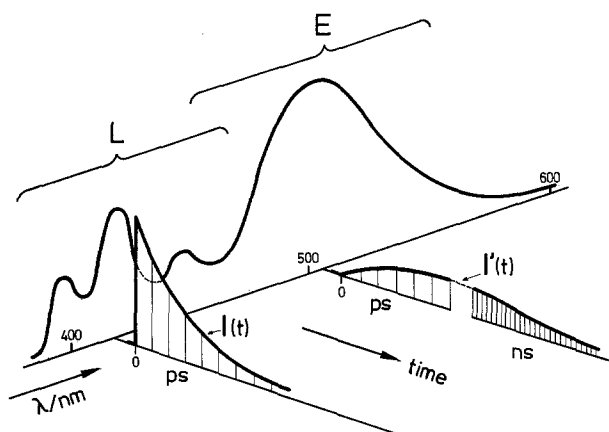
Fig. 1. Spectral and time behavior of the fluorescence of the locally excited state L, and the exciplex E

Fig. 2. Streak camera set-up with sample S, silicon switch Si, intensifier tubes CIT_1 and CIT_2, silicon-diode array camera DAC–OMA. The ps light pulses $P_{1,2,3}$ arrive with due delay in this order: P_1 (1064 nm, sweep trigger), P_2 (354 nm, sample excitation), P_3 (1064 nm, silicon switch trigger)

L, and the exciplex fluorescence E. The expected time functions, corresponding to the simplified reaction scheme (1) are

$$I = I_0 \exp(-t/\tau_L),\qquad (2)$$

$$I' = I_0'[\exp(-t/\tau_E) - \exp(-t/\tau_L)].\qquad (3)$$

The relevant features of the modified streak camera set-up are shown schematically in Fig. 2. The camera, manufactured by General Engineering and Applied Research, Inc. (GEAR), utilizes a proximity-focussed, or planar, streak tube based upon a design developed at the Los Alamos Scientific Laboratory, and manufactured by ITT. We incorporated a laser-triggered silicon switch close to the photo cathode (S 20 on quartz) of the streak camera to switch-off the photocurrent immediately after the rising part of the exciplex fluorescence signal has passed the photo-cathode. We use a frequency tripled (354 nm) picosecond laser pulse (25 ps) from a mode-locked Nd^{3+}/YAG laser (Quantel) to excite the sample. The streak camera monitors the fluorescence intensity time profile of the sample (S) placed in front of an adjustable precision slit. The function of the silicon switch (Si) [8, 9] which is made of intrinsic silicon (Wacker Chemie) and is used here to crow-bar the photo-cathode positioned in front of the proximity focussed channel plate, is also indicated in Fig. 2. The silicon slab (2 mm long, 1 mm wide, 0.5 mm thick) which has been machined with great care, to withstand high voltages, is incorporated in a coaxial HV–HN structure. It can hold a voltage pulse of 8 kV lasting 15 µs. When a laser pulse of 1.064 µm wavelength and 10 µJ of energy is incident on the silicon slab, electron-hole pairs are formed throughout the bulk of the semiconductor, thereby increasing its conductivity by many orders of magnitude. Because of the extremely fast switch-off time
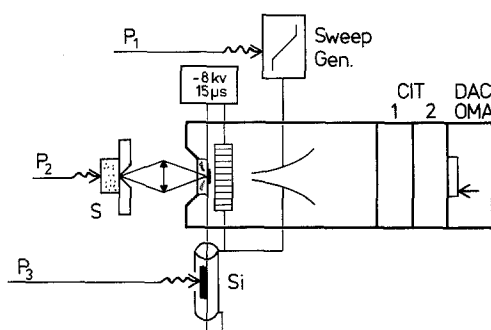
function and the unavoidable impedance mismatch (Si · switch, line and pulser) one has to accept some damped oscillations which, however, are tolerable.

The streak image is intensified by two channel plate intensifier tubes (CIT_1, ITT; CIT_2, Proxitronic) and finally detected by a silicon-diode array camera (DAC–OMA, B&M Spektronik) or a SIT vidicon. The use of SIT-vidicon-OMA systems has been critically examined elsewhere [10]. Signals from the DAC–OMA have been computer corrected, first with the flat-field function of the apparatus, and second with the sweep-time function obtained by Fabry-Perot etalon calibration.

Results and Discussion

Figure 3a–d exhibit streak camera signals of the fluorescence of the locally excited state (L) and exciplex (E) of compound A–D in diethylether after excitation with a uv pulse of 25 ps duration. This demonstrates the tremendous distorting influence of the stray electron signal when the silicon switch is not employed. Figure 3a shows the exponential decay of the locally excited state fluorescence measured through an interference filter at 408 nm. It has a lifetime of $\tau_L = 470 \pm 50$ ps. Figure 3b is the signal of the exciplex fluorescence at wavelengths > 550 nm which rises as $[1 - \exp(-t/470 \text{ ps})]$. The streak camera has been operated with the Si switch blanking applied. The exciplex formation time was thus found to be the same as the locally excited state decay time. If there was no blanking of the photoelectrons after the rising part of the exciplex signal has passed, the photoelectrons originating from the long-lasting exciplex fluorescence decay ($\tau_2 = 173$ ns) would contaminate the originally stored rise signal. This is seen in Fig. 3c. The correct signal with the rise time $\tau_L = 470$ ps has been swamped
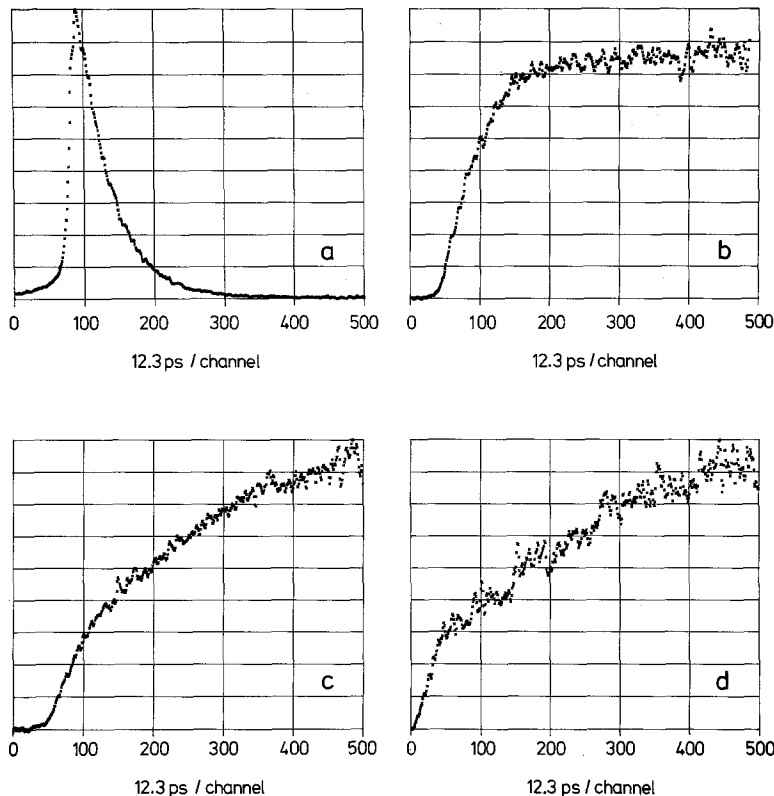
12.3 ps / channel   12.3 ps / channel

12.3 ps / channel   12.3 ps / channel

Fig. 3a–d. Streak camera signals from intramolecular charge transfer system A–D in diethylether. (a) $^1\overset{*}{A}$–D fluorescence decays exponentially with $\tau_1 = 470 \pm 50$ ps at 408 nm. (b) Exciplex fluorescence of $^1(A^--D^+)$ rises as $[1-\exp(-t/470\,\text{ps})]$ at >550 nm when Si switch blanking is applied. (Plateau: 1750 counts.) (c) Si switch blanking not applied. Signal comprises exciplex rise signal plus stray electron signal. (Maximum: 3500 counts.) (d) Fluorescence signal is delayed to fall outside the sweep time range (right side). Si switch blanking not applied. Streak camera signal is entirely due to stray electrons. (Maximum: 1750 counts)

b + d = c → 1750 counts + 1780 counts ≈ 3500 counts

by stray electrons and is lost in a signal with an apparent rise time of more than 2 ns.

In a final experiment we delayed the excitation pulse several nanoseconds such that the exciplex fluorescence fell (to the right) well outside the sweep time range. The streak camera signal was entirely due to stray electrons, as can be seen in Fig. 3d. A zero offset of about 150 counts is subtracted in Fig. 3c and d.

It was furthermore found that the sum of the maximum counts of Fig. 3b and d reached approximately the maximum count number of Fig. 3c, (b + d = c: 1750 counts + 1780 counts ≈ 3500 counts), indicating a superposition of signals from useful photoelectrons and stray photoelectrons on the streak camera phosphor screen. The stray electron signal with its apparent "rise time" is in a trivial way wavelength-dependent, namely in as far as the intensity of exciplex emission depends on wavelength, see $I'(t, \lambda)$ in Fig. 1. We suggest that these findings demand a careful reinvestigation of the exciplex formation dynamics in systems where a wavelength dependence was found and interpreted as evidence for two distinct ground-state conformers [11]. We believe that stray electron effects of the kind described above seem to be a problem which is generally present in all commercially available streak cameras to a greater or lesser extent, dependent on design features. The smaller the ratio of sweep time to

full duration of the luminescence signal, the larger is the effect which has to be expected.

It is very instructive in estimating the signal intensity to be anticipated in studies of the formation kinetics of exciplexes with streak cameras to consider some quantitative relations. In spite of the fact that the photochemical system selected exhibits a relatively large quantum yield for the exciplex emission, $\phi_E = 0.18$, it is not easy to achieve a reasonable signal to noise ratio in these measurements. In less favorable cases measurements are even impossible. The exciplex quantum yield can be expressed, cf. (1), as

$$\phi_E = \phi_c k'_f \int_0^\infty dt\, E(t), \tag{4}$$

$$E(t) = \exp(-t/\tau_E) - \exp(-t/\tau_L), \tag{5}$$

$$\phi_c = k_c \tau_L. \tag{6}$$

In the example chosen, the decay time of the exciplex, measured with nanosecond methods (single photon counting), is $\tau_E = 173$ ns, and the decay time of the locally excited state as well as the rise time of the exciplex is $\tau_L = 470$ ps. From the exciplex quanta emitted into the collecting angle of the streak camera input optics, only the fraction τ_L/τ_E is available during the time τ_L to measure the exciplex rise time. There are

far fewer photons per ps in the exciplex emission than in the locally excited state emission in the case of A–D in diethylether, although the quantum efficiencies at first glance seem to indicate the opposite, $\phi_L/\phi_E = 0.04/0.018$ [12].

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