Two Dimensional Transient Absorption Spectroscopy Using a Streak camera for Detection and Singular Value Decomposition for Data Analysis.

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Abstract : A setup in which a streak camera is used to perform nanosecond time-resolved optical absorption spectroscopy is described. The system provides spectral and temporal information in a single measurement. The time resolution ranges from 2 nanoseconds to several milliseconds, making possible the study of many different processes that occur in molecular systems upon photo-excitation, *e.g.* singlet-to-triplet intersystem crossing or energy transfer. A simple analysis method for the spectro-temporally resolved absorption data is proposed. This method is based on principal components analysis through singular value decomposition (SVD).

I - INTRODUCTION

Currently time-resolved absorption techniques are mostly designed to provide either optimal information on the spectral features of the transient species or to record high resolution kinetic traces of the transient absorption at a certain wavelength. To obtain good resolution in both the time and the spectral dimensions either many spectra at different delay times or time traces at many wavelengths need to be measured.[1] Streak cameras allow for the simultaneous recording of spectral and temporal information.[2,3] In a typical streak tube, (spectrally dispersed) light is converted into photoelectrons by a linear photocathode. After acceleration, the resulting strip of electrons is temporally and spatially dispersed by applying a time-variant electrostatic potential perpendicular to it. When arriving at the phosphor screen at the end of the tube, the electrons will be distributed in two dimensions, generating the streak image.

As for optical spectroscopy, streak cameras have been used mainly for the study of excited state processes by the emission of the excited molecules, in *e.g.* dye solvation[4] and molecular reorganisation.[5] Recently also picosecond transient absorption has been realized with a streak camera by Ito *et al.*[6] Their setup uses a picosecond Nd:YAG laser pump source and an optically excited Xenon plasma tube

producing 50 ns (FWHM) pulses of white probe light. It has been used to study fast processes (50 ps - tens of nanoseconds) such as intersystem crossing in polymers[7] and fullerenes.[8] Picosecond single-wavelength transient absorption using streak camera techniques was done several years before this.[9-11]

Many processes in molecular photophysics and photochemistry occur in the nano- to microsecond domain. Simultaneous recording of reliable spectra and kinetics is valuable also for the study of such processes, especially when multiple species are involved. Combining relatively standard components like a nanosecond laser and a low-pressure xenon flashlamp with a commercial streak camera system, we have constructed a setup that can generate transient absorption images with time windows that range from a few nanoseconds to several milliseconds and cover a spectral range that extends from 300 to 900 nm. These images (or matrices) contain a wealth of information that is often very well suited for principal component analysis. We also present a simple recipe based on singular value decomposition for analysing the transients generated by some basic molecular photoprocesses.

II - RESULTS

A. Experimental setup

In the streak transient absorption (sTA) experiment, the molecules are excited by short (nanosecond) laser pulses (Coherent Infinity-XPO Laser with SHG option) of a chosen wavelength (420-710 nm (XPO), 220-350 nm (SHG), pulse duration ~2 ns, typical power used 0.5-2 mJ/pulse). The excitation light is manipulated using optics like cylindrical lenses (L, Figure 1) in order to have it illuminate the entire probe volume. For measuring the transient changes in the absorption spectrum of the sample as a result of the excitation, white probe light is needed with a duration equal or beyond that of the time window to be investigated. When the observation times are short (10 ns - 5 μs), we use an EG&G flashlamp (low pressure Xenon lamp, FX-1160 high power with FYD 1150 flashpack. max. energy 5J, power 20W) that generates 'white' light in flashes of approximately 5 μs. For larger time windows (10 μs - 25 ms) a continuous light source is used (450 W high pressure Xe lamp, Müller lamp housing LAX1450, power supply SVX1450). Filters (F1, Figure 1) may be employed to remove unwanted wavelengths from the probe light, or to optimize the spectral distribution of the light. The filters behind the sample (F2, Figure 1) are mainly intended to cut away scattered laser light and fluorescence.

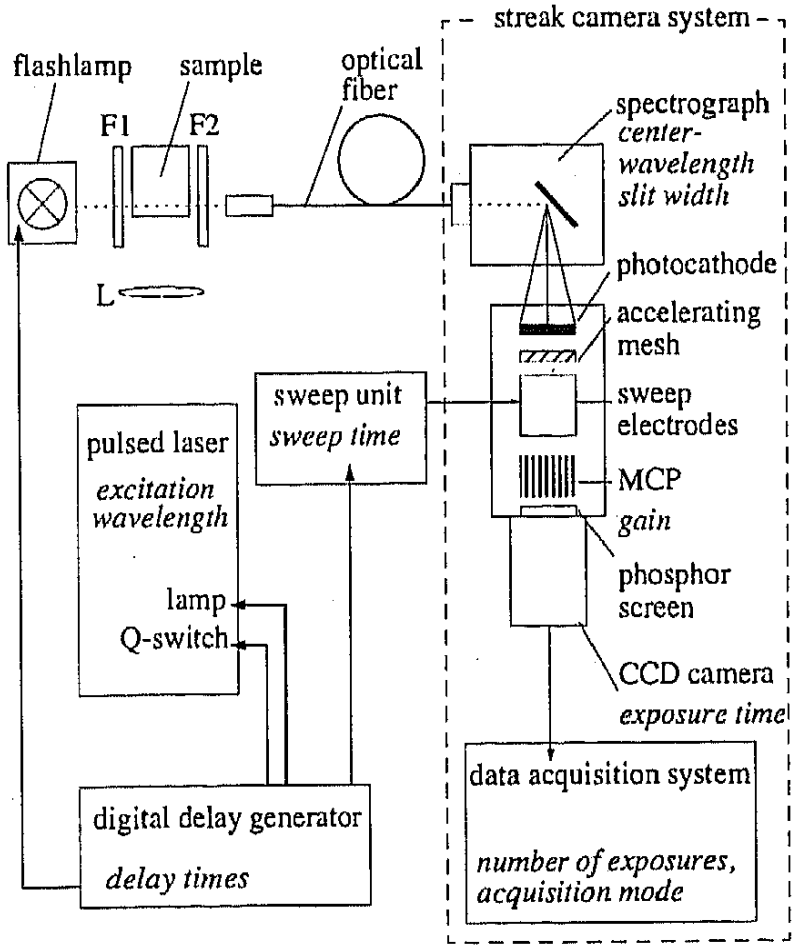

FIGURE 1. Setup for transient absorption spectroscopy using a streak camera. The experimental parameters that need attention are mentioned in *italics*.

The transmitted probe light enters a streak camera system through an optical fiber. In the streak camera system, the light is dispersed using a spectrograph (Chromex IS250), and then directed into the streak camera unit (Hamamatsu C5680-21). In the streak camera unit the photocathode converts the spectrally dispersed photons into electrons, that are accelerated by a positively charged mesh. They then enter the region between the sweep electrodes where the time resolution takes place. After receiving a trigger, the sweep unit (Hamamatsu M5677 Low-Speed Single-Sweep Unit) ramps the relative potential of the electrodes in a certain time. This *sweep time* can be chosen by the user, from 1 ns up until 25 ms giving a broad range of experimental time scales.

The electrons, which are now two-dimensionally distributed, may be amplified by the microchannel plate (MCP). This is usually necessary to obtain a detectable signal. After amplification (multiplication) the electrons hit a phosphor screen, generating an optical streak image. The streak system is capable of producing images at repetition rates of several kHz. In our setup, the repetition rate is limited by the flashlamp (10 Hz) or the laser (100 Hz).

Using exposure times in the order of seconds, several streak images are integrated in a digital CCD camera (Hamamatsu C4742-95) and subsequently

transferred to a workstation running the data acquisition software (Hamamatsu HPD-TA, version 3.0.2). The software sums up several exposures and carries out the necessary time and wavelength calibrations. When carrying out absorption measurements, it is not necessary to perform a shading correction[3] since the time-resolved absorption image is calculated from three individual images by

$$A(t,\lambda) = \log\left(\frac{I_0(t,\lambda) - D(t,\lambda)}{I(t,\lambda) - D(t,\lambda)}\right) \qquad \text{(Equation 1)}$$

and are the signal (pump and probe light) and reference (probe light only) images, respectively. is the background image (pump nor probe light). The software controls the recording of the three required images and finally computes the time-resolved absorption image. For highly fluorescent samples an additional fourth image (pump only) can be recorded to eliminate the effects of the fluorescence.

B. Timing

The triggering of the three main components (pump, probe and detection) of the present system is done by a digital delay generator (DDG, EG&G DDG 9650, with options 95/97/99 installed) running at 10 Hz. When using continuous probe light, a repetition rate of 100 Hz can be attained, if the sample under study and the chosen sweeptime (< 10 ms) allow it. The laser in our setup is a Q-switched Nd^{3+} laser which needs two trigger pulses. The Q-switch is triggered by the negative slope of the trigger pulse, whereas the DDG only delivers jitter-free positive slopes. In our case this problem could be solved by combining two outputs of the DDG: the first controls the positive slope, the second the negative slope of the pulse. The time between reception of the trigger and the occurrence of a sweep in the streak camera depends on the time window. For time windows larger than 100 µs, the streak system needs to be triggered before the laser lamps (Table 1). For reasons explained later, the timing is arranged such that the laser pulse arrives after 10% of the streak sweep has been completed.

C. Experimental parameters

Most of the experimental parameters can be set from within the data acquisition software. The settings of the spectrograph and the sweep time of the streak camera need no further explanation, but some other parameters do.

CCD camera and image acquisition

The CCD chip is read out through an analog-to-digital converter with a resolution of 10 bits (0, 1, 2... 1023). Like with all CCDs, every time the chip is read out there is a constant background that is independent of the signal detected and the exposure time. Therefore, it is recommended that the CCD is read out as little as possible. Exposure times, however, should not be so long that the 10 bit dynamic

range is overloaded. With time-resolved absorption experiments, it is advisable to leave some 'headroom' to be able to deal with decreases in absorbance of the sample upon photoexcitation. When aligning the setup, it is convenient to take shorter exposure times (< 0.5 s) to ensure quick feedback.

TABLE 1. Typical insertion delay times of the various components (*i.e.* delay between the trigger and the start of the triggered event)

Triggered event		Insertion delay
flashlamp		5.6 μs[a]
laser[b]	lamps	0.27 ms
	Q-switch	483 ns
streak	20 ns	267 ns
	100 μs	110 μs
	25 ms	19.8 ms

a) flash reaches maximum energy,
b) the laser operates optimally when the delay between lamp trigger and Q-switch trigger is 0.27 ms

The software can acquire images in three ways, of which two are used. The so-called 'live mode', in which the signal on the CCD camera is visualized in real time, is used when aligning and optimizing the experimental settings. The 'analog integration mode' is active when performing measurements: several exposures are added together in the computer's memory (16 bits buffer). At least three of such recordings (I, I_0 and D) are needed for calculation of a time-resolved absorption streak image, which is controlled by the software. The photon counting mode is intrinsically not suited for transient absorption measurements because it relies on minimizing the detected signal to the single photon level and for transient absorption measurements the dynamic range of the detection system should be fully exploited.

Microchannel plate gain

When working with small time windows, amplification of the photoelectrons is necessary to obtain sufficient probe signal. Transient absorption spectroscopy is often concerned with small changes in intensities of the probing light, so the dynamic range of the detection should be used optimally. On the other hand, a high microchannel plate gain results in a worse noise figure (ratio between the signal-to-noise ratio of the output signal and that of the input signal) for the amplification process. If the probe signal is too noisy to produce acceptable transient absorption images, longer exposure times should be used, which also implies more pump-probe cycles.

III - DATA ANALYSIS

The Hamamatsu streak software calculates the transient absorption image. For data analysis the image is transferred to the Igor Pro data analysis package

(WaveMetrics, Inc., Lake Oswego, Oregon, USA). To this end a program was written to enable Igor Pro to read the binary data files generated by the Hamamatsu software.

A. Baseline correction

Since the spectro-temporal matrices for I_0 and I are not recorded simultaneously it is necessary to consider the effects of probe light intensity fluctuations (and spectral changes, which can be considered intensity fluctuations at certain wavelengths) between the determination of I_0 and I. If I_0 and I represent the signals generated using an ideally stable flash lamp, fluctuations in intensity are represented by the factors a and b (Equation 2). Note that A_{true} and $A_{measured}$ and all I's in fact represent spectro-temporal matrices, and a and b and $A_{baseline}$ might be scalars.

$$A_{measured} = \log\frac{aI_0}{bI} = \log\frac{I_0}{I} + \log\frac{a}{b} = A_{true} + A_{baseline} \qquad \text{(Equation 2)}$$

Provided that between measurement of I_0 and I the average lamp spectrum does not change and that the average lamp time profile does not change, the effect of the changes in probe light intensity show up as a 'baseline' that can simply be subtracted from the measured spectrum.

Having found that due to probe light intensity fluctuations there is a baseline (or more correctly: a base-area) added to the transient absorption image, we devised a baseline subtraction that not only corrects for lamp intensity fluctuation, but also for small changes in the probe light's spectrum (which only arise when the lamp has been flashing for too short a period, so when it is still 'warming up'). In order for this procedure to work, one needs to make sure that the streak camera records before the transients are created. The laser pulse should arrive at 10-15% of the time window (see *e.g.* Figure 5). The region of the transient absorption image that contains the information of the time interval before arrival of the excitation pulse can be used to calculate a baseline. This is simply done by spectrally averaging over this time region. Finally this baseline can be subtracted in order to obtain a baseline corrected transient absorption image.

B. Singular value decomposition (SVD)

Spectral and kinetic data are usually extracted from streak images by selecting a region of the image and then averaging it spectrally or temporally. This has proved to be an adequate way to obtain the desired data. However, because of the extremely information rich datastream provided by streak images, a more information-efficient analysis can be applied advantageously. Since the streak images are discretized by the digital acquisition system, they are in fact matrices containing the summed-up spectra of a limited number of species whose concentrations change in time. Such data are ideally suited for principal components analysis (PCA) using singular value

decomposition (SVD). Without any *a priori* knowledge, PCA can give the number of components present in these data. We will now discuss very briefly SVD in relation to streak images. For a more detailed explanation the reader is referred to ref. 9.

Principles of SVD

Consider a set of m spectra each containing n data points. Each spectrum is the sum of the individual contributions of p components, whose concentrations change from spectrum to spectrum (*e.g.* as a result of excited state decay). The spectral responses of all components might be put in an $n \times p$ matrix **S**, so that each column consists of the characteristic responses (*e.g.* extinction coefficients) of one component at different wavelengths. The concentrations of the components in each of the spectra can be represented by a $p \times m$ matrix **C**, in which each column contains the concentrations of the components in a spectrum. Then, the set of spectra can be represented by $n \times m$ matrix **A**, the matrix product of **S** and **C** (Equation 3).

$$\mathbf{A} = \mathbf{SC} \qquad \text{(Equation 3)}$$

Each column of **A** contains the data points representing a spectrum consisting of the sum of the contributions of the individual components. (In absorption spectroscopy **S** would contain the extinction coefficients, and **C** the concentrations, so that A would yield the absorbances/optical densities).

Usually only **A** is known (since that is what is measured), whereas knowledge of **S** and **C** is desired, since these matrices contain information on the species present in the sample and their kinetics. Singular value decomposition, a technique originating from linear algebra, provides a way for determining the number of components that contribute to the set of spectra (or in this case a streak image) without *a priori* knowledge. In combination with a chemically acceptable model describing the concentrations of the species, even **S** and **C** can be reconstructed from the SVD matrices. SVD of the data is readily achieved by microcomputers running an appropriate computer program with an implemented SVD routine, such as the one described in Numerical Recipes in C[13]. We used Igor Pro for this purpose. Singular value decomposition can factorize *any* $n \times m$ matrix **A** into three matrices that satisfy Equation 4.

$$\mathbf{A} = \mathbf{UWV}^T \qquad \text{(Equation 4)}$$

U and **V** are orthonormal matrices of dimensions $n \times m$ and $m \times m$, respectively. **W** is an $m \times m$ square diagonal matrix, containing the *singular values*, w_{jj}, in descending order. Each of these values determines how much the corresponding columns of **U** and **V** contribute to the reconstruction of **A**. From the singular values one can determine the number of components contributing to the set of spectra. In the absence of noise, the number of independent components would equal the number of non zero singular values. However, all singular values in real-world data are non zero due to noise. In

most cases the magnitude of the singular values, combined with the evaluation of the shapes of the corresponding column vectors of **U** and **V** will provide enough information to find the number of components. If this is not the case, certain statistical tests can be applied to find the number of components.[12]

The insignificant components can be removed from the **U**, **W** and **V** matrices. In this case, **U** and $\mathbf{V}^T$ will end up having the same dimensions as the (still unknown) **S** and **C** matrices, respectively. It is obvious that **U**, **W** and **V** should contain the same information as **S** and **C**. In fact, if one inspects the column vectors of the 'shrunken' **U** and **V** matrices, one finds that they contain spectral and concentration information, respectively. However, these vectors are linear combinations of the physically meaningful vectors, and as a result they may look rather strange (*e.g.* contain negative concentrations).

The solution to this problem is to take linear combinations of these vectors such that these comply with a certain chemical model. In order to do so, it is possible to perform a rotation on the **U** or the **V** matrix using a p x p rotation matrix **T**. This matrix should satisfy $\mathbf{T}\mathbf{T}^{-1} = \mathbf{1}$. Since both and should reconstruct the original **A** matrix, we can relate **U**, **W** and **V** to **S** and **C** (Equation 5).

$$\mathbf{SC} = \mathbf{UTT}^{-1}\mathbf{WV}^T \qquad \text{(Equation 5)}$$

It is possible to find a matrix **T** such that

$$\mathbf{S} = \mathbf{UT} \qquad \text{(Equation 6)}$$

Then,

$$\mathbf{C} = \mathbf{T}^{-1}\mathbf{WV}^T \qquad \text{(Equation 7)}$$

Obviously, it is also possible to start the reconstruction by finding a matrix that transforms $\mathbf{V}^T$ into **C** and then use its inverse to reconstruct the associated spectra.

One should bear in mind that SVD is a purely mathematical method for determining the number of independent vectors in a matrix. As a result, chemically different species that have either equal spectra or equal kinetics will show up as one component. Another remark that should be made is that SVD is in principle not suited for components whose spectra shift and/or broaden in time.

Reconstruction

We now present a simple recipe for finding a matrix **T** that converts the vectors $\mathbf{V}^T$ into concentration vectors that fit a certain kinetic model. **T** is found by minimizing the difference between the trial concentration vectors and the model. The scheme is depicted in Figure 2. The model concentration vectors are determined by a set of parameters, p_i. Using the Nelder-Mead Simplex algorithm,[13] all the elements of

T and all p_i's are optimized. This can be done simultaneously, but usually it is wise to start with keeping the initially guessed model parameters at fixed values.

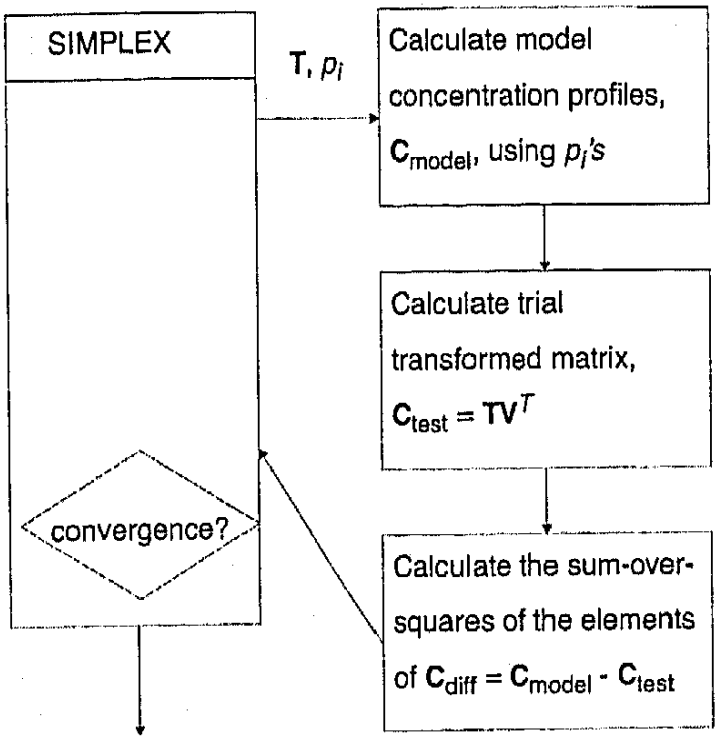

FIGURE 2. Simplified flowchart of the recipe for finding transformation matrix **T** and the parameters p_i that yield a concentration matrix and a chemical model that are consistent. Using the well-known Simplex minimization algorithm (shown here as a 'black box') the matrix elements of **T** and the model parameters p_i are varied so as to minimize the difference between the reconstructed concentration vector and the model.

One component data

It is often the case that time-resolved absorption spectroscopy is applied to only one species in solution. Although SVD at first looks superfluous in such a situation, it is in fact very useful. One can prove that one is really looking at one component. After having performed the SVD, finding the 1x1 **T** matrix is a trivial task. We prefer to choose it such that at "t = 0" (the maximum of the excitation pulse) the concentration vector has a value of 1. The reconstructed spectrum then represents the optical densities at the time that maximum absorbance is achieved. The reconstructed temporal and spectral vectors will have been extracted from the data without averaging, and a lot of noise will have disappeared into the components with insignificant singular values.

Multi-component data

For two component data that obey a relatively simple kinetic scheme (*e.g.* transformation of one species into an other), the aforementioned recipe works very well. Three component data are usually not so easily reconstructed, since the transformation matrix then already holds nine elements that need optimization. Moreover, additional degrees of freedom are provided by the parameters p_i that are used in the model. Reconstruction of the temporal and spectral vectors for such systems requires advanced statistical methods to remove any ambiguity, and lies not within the scope of this discussion. The reader is referred to.[14-16]

A. One component data: transient excited states in luminescent lanthanide complexes

Lanthanide ions have special luminescence characteristics, such as a long excited state lifetime and narrow emission bands. This luminescence is exploited in television screens and fluorescent tubes (Tb^{3+}-doped phosphors for green, Eu^{3+} for red), lasers (*e.g.* Nd^{3+}:YAG), optical amplifiers (Er^{3+}-doped fibers), and fluoroimmunoassays. However, it is difficult to excite the photoluminescence of these ions because direct excitation is an almost forbidden process. The trick that circumvents this excitation bottle-neck is to use an organic chromophore, the "antenna", to absorb the light, and then have this antenna transfer the absorbed energy to the lanthanide ion.[17] An important question in the study of such antenna-lanthanide complexes is how fast the energy transfer takes place, and what intermediate excited states are involved. Time-resolved absorption spectroscopy using the streak camera is able to both identify the intermediate state, and to tell about its fate, in a single measurement.

Recently we found that Michler's ketone (4,4'-bis(N,N-dimethylamino)benzophenone, Mk) forms complexes with various lanthanide FOD chelates (Eu(fod)3, Gd(fod)3, Yb(fod)3 etc., fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione).[18] In toluene, these Mk-LnFOD complexes have an absorption band at 414 nm that extends towards the red beyond 450 nm. Moreover, for Eu^{3+} and Yb^{3+}, these complexes show sensitized lanthanide luminescence upon excitation in this band. In the Gd^{3+} complex no energy transfer can take place because of the lack of accepting energy levels in the Gd^{3+} ion. Therefore only antenna triplet states are generated upon photoexcitation in Mk-GdFOD. Solutions of the complexes were excited using 440 nm pulses from the laser (0.5 mJ/pulse) and probed using the microsecond flashlamp.

The absorption spectrum of the triplet state of Mk-GdFOD was observed in a μs sTA experiment. SVD indicates one component, of which the spectrum and kinetics are reconstructed using the method described above. The spectrum is broad, and has a maximum around 690 nm. The triplet state of Mk-GdFOD is long lived (estimated approx. 8 μs). The transient spectrum of Mk-YbFOD implies that the same triplet state is involved in the photosensitisation of Yb^{3+}. With a time-constant of 100

ns the triplet is deactivated, probably by energy transfer to Yb^{3+}. Mk-EuFOD has a very short-lived intermediate state, that seems also to be the triplet state.

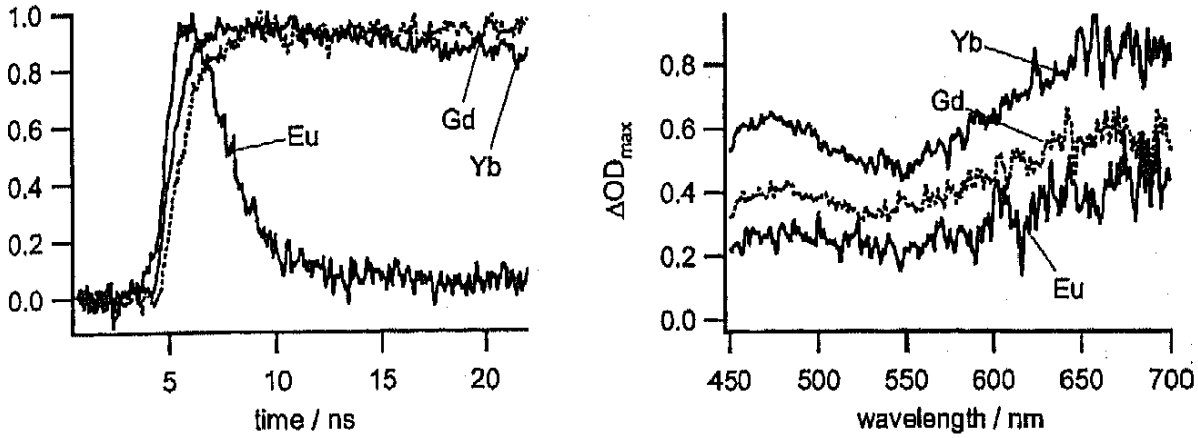

FIGURE 3. Nanosecond time-resolved absorption spectroscopy of Mk-LnFOD complexes: traces obtained by reconstruction of the first component of the SVD output. All other components only contained noise. The data are normalized such that the concentration curve is 1 in its maximum. As a result the spectra represent the optical density at this maximum.

We can "zoom in" on this short-lived transient by using the 20 ns streak time window. In Figure 3 the Mk-EuFOD triplet state can be readily identified. Its kinetics follow that of the laserpulse, so that we may assume the energy transfer process to be faster than 1 ns.

These results show the flexibility of the streak transient absorption setup, and its power to monitor the spectra and kinetics of excited states at the same time. The time-resolution of the detection is much better than that of 'conventional' gated CCD camera systems.

B. Two component data: singlet-to-triplet intersystem crossing in an electron donor model compound

In the study of inter- and intra-molecular photoinduced electron transfer it is important to know the photophysical properties of the individual electron donor and acceptor chromophores because they determine the fate of the excitation energy in the actual donor-acceptor system. The rate of singlet-to-triplet intersystem crossing in the excited chromophore can, *e.g.* determine the initial spin state of the charge separated state, as indicated in Figure 4.

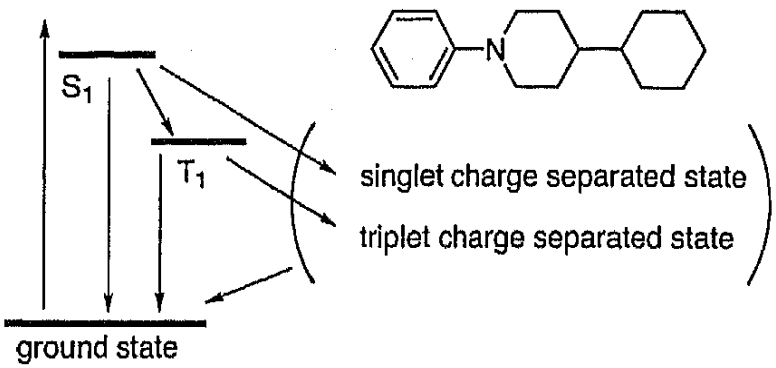

FIGURE 4. The structure of the studied system D1 (top) and an energy diagram of the possible involved states in the separate donor chromophore and, between brackets, of a donor-acceptor system derived from it.

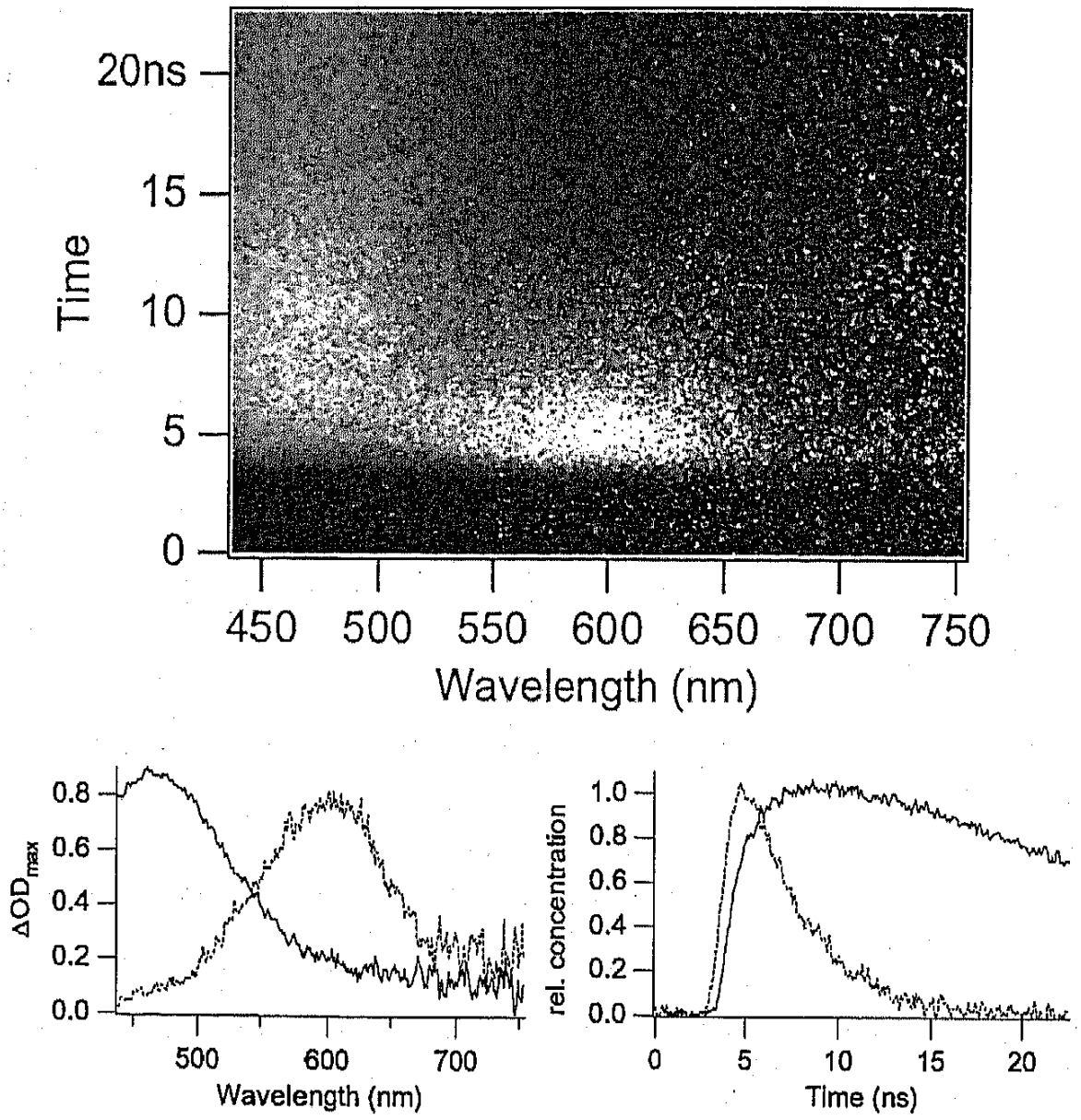

FIGURE 5. Time resolved absorption spectra and time traces of D1 in a benzene solution after excitation at 300 nm. Original streak image (top) and reconstructed spectra (left) and concentration profiles (right) of the singlet (----) and triplet (——) state.

The model system D1 shown in Figure 4 is a di-alkyl-aniline with a hydrocarbon skeleton, to which electron accepting chromophores can be attached.[19] This chromophore has been used extensively in our group and by others as an electron donating group in donor-bridge-acceptor systems.

In the streak transient absorption image of D1 in a benzene solution two species can be discerned (Figure 5). The absorption at 470 nm is due to triplet-triplet absorption of D1. This spectrum is well documented. To the red of this absorption a slightly weaker absorption is observed at 600 nm. The lifetime of this species is 33 ns which corresponds to the lifetime of the excited singlet state, determined earlier with time resolved fluorescence spectroscopy. Furthermore it is seen that the triplet state is formed with the same time-constant as the decay of the singlet state.
This experiment shows that two spectrally overlapping species can be separated by performing SVD and subsequent reconstruction of the major components (in this case two), at the same time producing the 'pure' concentration profiles.

V. CONCLUDING REMARKS

We have shown a method to obtain simultaneous time and spectral resolution in an optical transient absorption experiment using a streak camera and a tunable solid-state laser. The nanosecond to millisecond time resolution and the spectral range of 300 to 900 nm render this setup very useful for the study of many excited state processes. Two examples were given. The obtained spectro-temporal matrices can readily be analysed using the simple scheme based on singular value decomposition, provided the kinetic model is not too complicated. In any case, SVD will provide information on the number of components that make up the sTA data.

The current signal-to-noise ratio is not as good as for either single-wavelength or gated CCD transient absorption data. The big advantage of streak camera-based transient absorption spectroscopy, however, is that it provides reliable kinetic and spectral information at the same time. In the near future Hamamatsu Photonics will implement the possibility into the TA software to automatically average several sTA images. This will yield the higher signal-to-noise ratios that are needed for the detection of weakly absorbing transient species or when working with weak probe light.

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