Transient Absorption Spectroscopy Using a Streak Camera for Detection and Singular Value Decomposition for Data Analysis.

Koeberg, M.; Werts, M.H.V.; van Ramesdonk, H.J.; Verhoeven, J.W.

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Mattijs Koeberg, Martinus H.V. Werts,
Hendrik J. van Ramesdonk and
Jan W. Verhoeven
Laboratory of Organic Chemistry,
University of Amsterdam

Transient absorption spectroscopy is an indispensable tool for the identification and study of excited state species. Usually the focus is either on the time domain or on the transient spectrum, [1] but by making use of a streak camera spectral data and kinetics can be recorded simultaneously which is very valuable for the study of photoprocesses, especially when multiple species are involved. Combining relatively standard components like a nanosecond laser (Infinity, Coherent, pulse duration ~2 ns FWHM), a low-pressure xenon flashlamp (or a Müller 450 W low pressure Xe continuous light source for observation times longer than 5 μs), a Chromex IS250 spectrograph and the C5680-21 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. [2] These images contain a wealth of information that is often very well suited for principal component analysis using a simple recipe based on singular value decomposition.
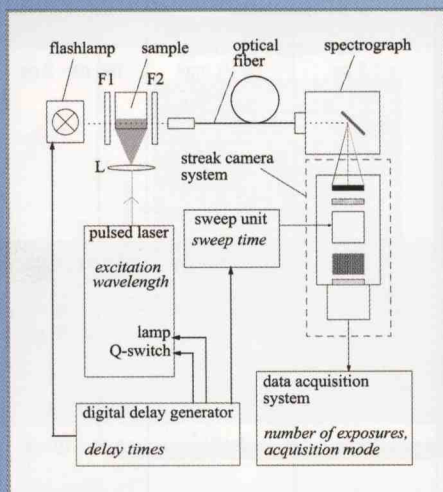

Figure 1

Using exposure times in the order of seconds, several streak images are integrated in the C4742-95 digital CCD camera and subsequently transferred to a workstation running the HPD-TA data acquisition software. The repetition rate in the current setup is limited by the flashlamp (10 Hz) or the laser (100 Hz). The time-resolved absorption image is cal-

culated from three individual images: The signal (pump and probe light), reference (probe light only) and background image (pump nor probe light). The software controls the recording of the three required images and finally computes the absorption image. For highly fluorescent samples an additional fourth image (pump only) can be recorded to eliminate the effects of the fluorescence. A typical experiment runs 30 exposures for each image.

Due to probe light fluctuations during an experiment a non-zero baseline (or base area) can be present. Correction for this is conveniently done by averaging the area in the streak image before the laser pulse and
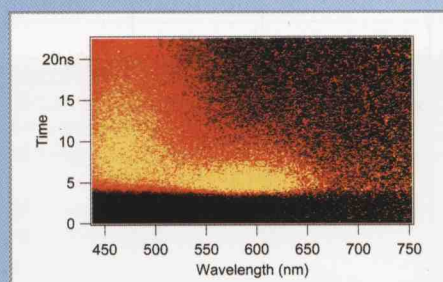

Figure 2

substracting this from the rest of the image. In our photophysical studies of photoactive organic and organometallic molecular systems photoinduced electron transfer as well as singlet and triplet energy transfer processes are of key importance. Observation of precursor states of the excited states of interest can e.g. be important to clarify competing singlet and triplet routes. In Figure 2 a transient absorption image is shown of an electron donating chromophore of the N,N-dimethyl-aniline type frequently used in electron transfer systems. From this image it is already clear that after laser excitation at least two, spectrally overlapping, species are present. Tentatively these species are attributed to the S1 and T1 excited states of the N,N-dimethyl-aniline chromophore.

Analysis is possible by horizontal or vertical integration of (parts of) the image to obtain spectral and time traces. By employing singular value decomposition (SVD), however, the high data content of a streak image is more effectively used. Singular value decomposition, a technique originating from linear algebra, provides a way for determining the number of components that contribute to the the streak image without a priori knowledge. In combination with a chemically acceptable model describing the temporal behaviour of the concentrations of the species, spectra and kinetics of the individual species may be retrieved from the SVD matrices using a procedure known as 'target transformation'. [3]

In Figure 3 the result of the SVD analysis of

the image in Figure 2 and subsequent reconstruction are shown. Apart from the 'pure' spectra of the singlet and triplet species also the kinetic parameters of the intersystem crossing process are obtained.

These results show that transient absorption spectroscopy using a streak camera is a flexible technique, especially in combination with an analysis technique based on singular value decomposition where the possibility to determine the number of components in the transient absorption image and their simultaneous spectroscopic and temporal identification provides a powerful tool for the study of excited state species. Currently we also employ this technique to study energy transfer in lanthanide complexes [4,5] as well as photoprocesses in the solid state, using the diffuse reflectance method.

References:
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[4] S.I. Klink, L. Grave, D.N. Reinhoudt, F.C.J.M. van Veggel, M.H.V. Werts, F.A.J. Geurts, J.W. Hofstraat, Journal of Physical Chemistry A 104, p.5457 (2000)
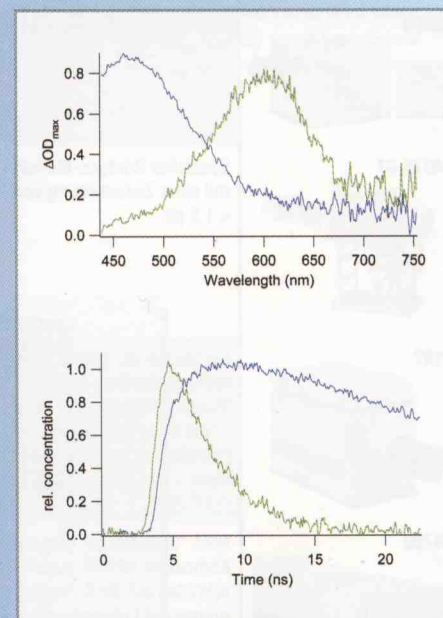[5] M.H.V. Werts, Thesis, University of Amsterdam, in preparation

Figure 3