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Spectro-Streak Picosecond Studies of Intramolecular Charge-Transfer Fluorescence

H. Staerk,[1] A. Wiessner,[1] and W. Kühnle[1]

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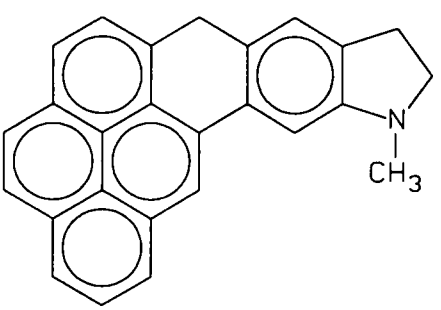
A spectro-streak photometer, an instrument for simultaneously measuring fluorescence intensity, time, and wavelength, $I(t, \lambda)$, with a single picosecond excitation pulse, has been constructed. Two typical and currently highly topical examples of measurements are discussed. (1) the temporal development of the fluorescence form the intramolecular charge-transfer (ICT) state of the rigid aromatic compound 4,5-(1′-methylindolino)-3,4-naphthanthracene is studied in the protic solvent hexanol. (2) Propyl chain-linked pyrene/*N,N*-dimethylaniline is used as the model compound to study conformational changes associated with the transition from a contact ion pair to a sandwich exciplex.

KEY WORDS: Spectro-streak photometer; picosecond excitation; intramolecular charge transfer.

INTRODUCTION AND EXPERIMENTAL

Conventional streak camera apparatuses measure fluorescence time functions at fixed wavelengths. In many photophysical and photochemical kinetic studies, such as solvent relaxation, exciplex formation, electron, proton, or energy transfer, conformational changes, excimer formation, and ionization reactions, however, fluorescence emission must be measured simultaneously as a function of time *and* wavelength. Global analysis is required to determine kinetic rate constants and thermodynamic properties related to these processes.

In the present contribution, we used a single-shot spectro-streak apparatus (Fig. 1). Its design details and the necessary signal correction procedures are described elsewhere [1]. Characteristics are the combination of a compact grating objective, i.e., a small grating spectrometer with spheric holographic grating (replacing the conventional lens objective), and a commercial streak camera (Hamamatsu Type 1370-01, 2-ps resolution), allowing simultaneous intensity/wavelength/time measurements: The streak camera output provides an $I(t,\lambda)$ histogram making dynamic chromatic fluorescence shifts directly visible after only one excitation event. This advantage is obtained, however, at the expense of time resolution, which is determined by the parameters of the grating; e.g., a grating with 133 lines/mm results in a time delay (between the marginal defracted first-order rays) of 14 ps at a 65-mm and 6.7 ps at a 30-mm grating illumination diameter [1].



Scheme I

Fluorescence light from the laser-excited sample is relayed by two achromats to the input pinhole of the grating objective. The image of the dispersed spectrum in the output focal plane is a thin line focused sharply

[1] Max-Planck-Institut für biophysikalische Chemie, Abteilung Spektroskopie und Photochemische Kinetik, Am Fassberg, D-37077 Göttingen, Germany.

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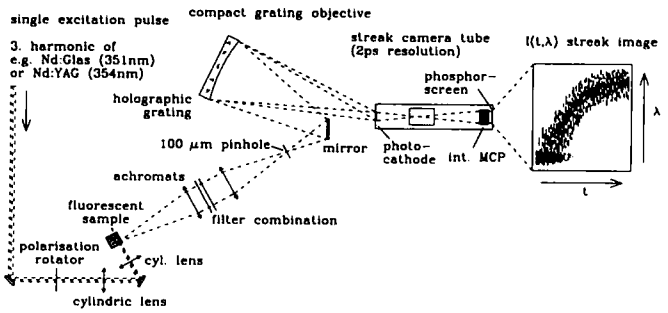


Fig. 1. Scheme of the spectro-streak apparatus. Fluorescence from the excited sample is projected onto the pinhole diaphragm of the grating objective in front of the streak camera. The streak pattern on the phosphor screen of the streak tube is approximately 8 mm (λ) × 11 mm (*t*). The streak image is detected and evaluated by a video system (not shown) comprising an external microchannel plate (MCP) amplifier, a CCD camera, and a PC.

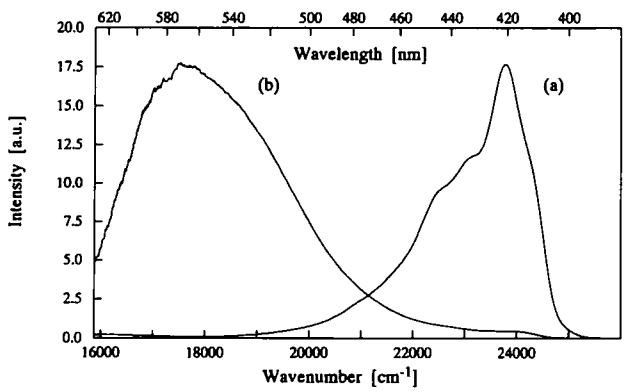
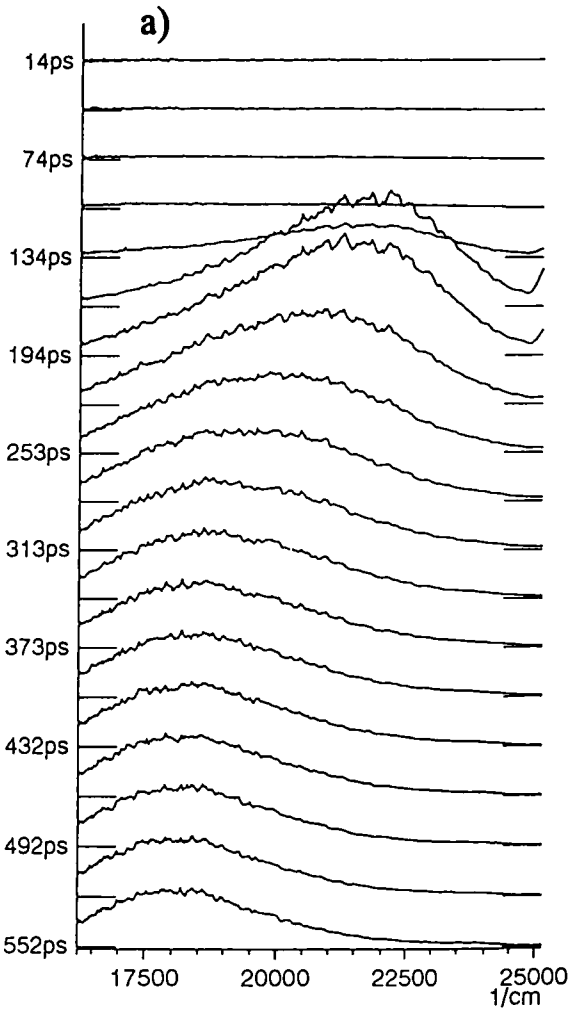


Fig. 2. Photostationary fluorescence spectra (uncorrected) of the compound shown in Scheme I: (a) in *n*-hexane; (b) in *n*-hexanol.

on the photocathode, which is deposited on the inside of the glass envelope of the streak tube. The streak tube incorporates a microchannel plate amplifier (int. MCP) which intensifies the photoelectron beam current before it reaches the phosphor screen. An external microchannel plate (ext. MCP), a CCD-camera (Photometrics STAR 1 with 384 × 576 pixels), and an IBM-compatible computer complete the spectro-streak apparatus (the latter three components are not shown in Fig. 1). Sample excitation in our setup is accomplished with a single pulse from a Nd:glass laser (7-ps half-width) or a Nd:YAG laser (28-ps half-width).

The signals from the two-dimensional CCD-detector array do not reproduce the spectral and time-dependent intensity distribution emanating from the fluorescing sample correctly. The reasons for this are the (generally)



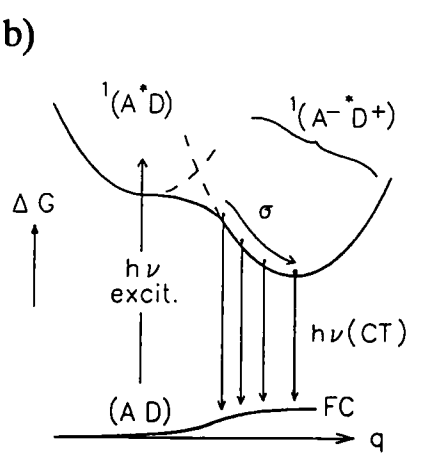
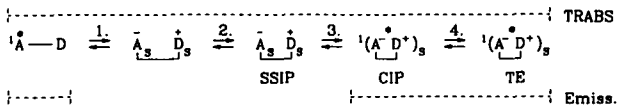


Fig. 3. (a) The temporal development of the charge-transfer emission maximum $\tilde{\nu}_{max}(t)$ (Stokes shift) of the compound shown in Scheme I in *n*-hexanol. The correlation function $C(t) = [\tilde{\nu}_e - \tilde{\nu}_{max}(t)]/(\tilde{\nu}_e - \tilde{\nu}_0)$ yields a relaxation time of about 140 ps. (b) Qualitative energy scheme, ΔG vs configuration/reaction coordinate q, indicating the spectroscopic consequences of the solvation process σ.



Scheme II

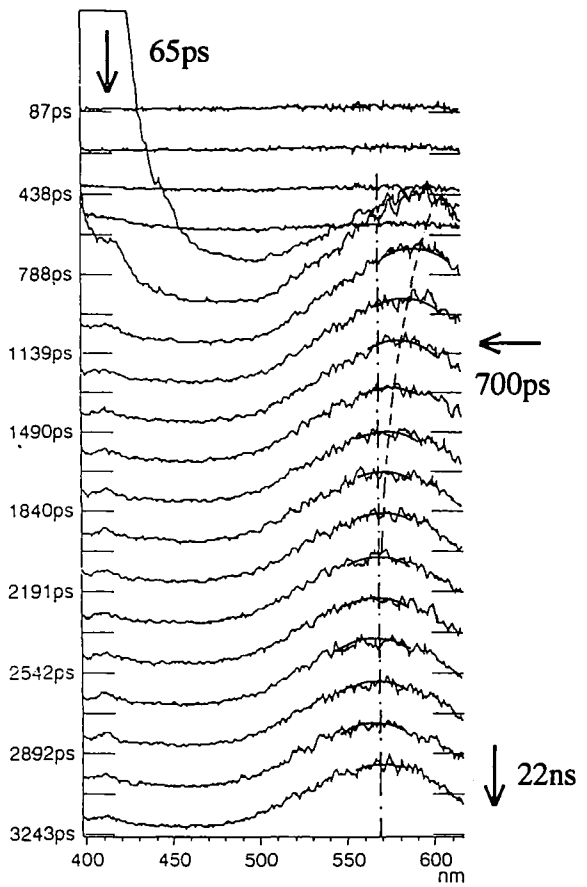


Fig. 4. Anti-Stokes shift of charge-transfer emission of 1-Py–$(CH_2)_3$–DMA in acetonitrile shown on an λ scale (the relaxation time of 700 ps was evaluated from a $\tilde{\nu}$ plot).

nonlinear time sweeps of streak cameras, the geometric image distortion of streak tubes, and the varying sensitivity and transfer efficiency in the different signal-converting optoelectronic elements. Therefore, to take full advantage of the spectro-streak camera in quantitative fluorescence studies, signals from the CCD detector transferred to the computer must be corrected. The different correction and calibration functions must be obtained in the following sequence: (i) *time calibration* and *sweep nonlinearity correction* of the streak camera, (ii) *shading correction* (amplitude correction) of the streak camera and detector combination, (iii) *geometric distortion correction* of the streak tube, (iv) *wavelength calibration* of the grating objective, (v) *spectral intensity correction* with the grating objective in front of the streak camera photocathode, and (vi) *dispersion correction.* Quantitative calibration and correction procedures have been developed and are described in detail in Ref. 1; they are carried out conveniently and rapidly with a personal computer.

RESULTS AND DISCUSSION

The time evolution of the solvatochromic Stokes - and anti-Stokes shift, respectively, of the charge transfer fluorescence bands of two compounds has been studied. Excitation was accomplished with a 28-ps (FWHM) third-harmonic Nd:YAG laser pulse at 354 nm.

Example 1. The rigid aromatic compound 4,5-(1′-methylindolino)-3,4-naphthanthracene (Scheme I) shows solvent-dependent characteristic fluorescence bands (Fig. 2). In polar solvents (e.g., alcohols or acetonitrile) fast adiabatic intramolecular charge transfer in the excited state takes place. The fluorescence kinetics are determined by the completion of solvent relaxation around the charge-transfer dipoles. Decay and rise time functions are thus strongly influenced by the decrease in the emission frequency (transition from the charge-transfer state to the Franck–Condon ground state) during the solvation process (see Fig. 3b). In hexanol the dynamic *Stokes-shift* i.e. the relaxation of the CT-emission maximum towards the equilibrium position, takes place in about 140 ps (Fig. 3a) [2].

Example 2. An intramolecular radical ion pair reaction which proceeds according to the "harpooning" mechanism, i.e., a multistep process where electron transfer is followed by the association of the radical ions, assisted by their Coulombic attraction, can lead to an emissive exciplex (see Scheme II). The final step in such a reaction from the contact ion pair (CIP) to a possible sandwich exciplex (tight exciplex; TE) is probably accompanied by a loss of entropy and by a change in the CT dipole moment ($\mu_{CIP} > \mu_{TE}$). Figure 4 shows spectro-streak measurements which display the dynamics of the *anti-Stokes* relaxation of the CT band of 1-Py–$(CH_2)_3$–DMA (pyrene linked to *N,N*-dimethylaniline) in the solvent acetonitrile. The above conclusions are additionally supported by picosecond transient absorption (TRABS) experiments [3,4] which provide kinetic and spectral data of all intermediate species as designated in Scheme II.

Lifetimes of *emissive* species (indicated by "Emiss." in Scheme II) are as follows: primary excited state, 65 ps; and exciplex, 22 ns. The anti-Stokes relaxation takes place in about 700 ps (±25%), as evaluated from a $\tilde{\nu}$ plot.

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