

SINGLET AND TRIPLET EXCITED- STATE ABSORPTION STUDIES BY TRANSIENT MEASUREMENT TECHNIQUES

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The singlet-triplet intersystem crossing rate, the absolute excited-state singlet-singlet absorption cross-section spectrum and the triplet-triplet absorption cross-section spectrum of the organic dye eosin Y were determined by transient measurement techniques. An active and passive mode-locked Nd:glass laser system (fundamental and second harmonic) and a XeCl excimer laser were applied.

The intersystem crossing of eosin Y solutions in methanol and water was studied by picosecond double-pulse transient absorption measurements (determination of quantum yields of triplet formation Φ_T) [1]. Two intense picosecond pulses (duration $\Delta t_{SH} \approx 5$ ps, wavelength $\lambda_{SH} = 527$ nm) separated by 10 ns were passed through the dye sample. The transmission of the second pulse is modified by the triplet level population caused by intersystem crossing from the S_1 -state which is populated by the first pump pulse. Additionally the fluorescence quantum yield Φ_F was measured with a spectrofluorimeter. The determined quantum yields are $\Phi_T \approx 0.8$ and $\Phi_F \approx 0.2$ for eosin Y in water, and $\Phi_T \approx 0.56$ and $\Phi_F \approx 0.44$ for eosin Y in methanol.

The absolute $S_1 \rightarrow S_n$ singlet absorption cross-section spectrum of eosin Y in methanol was determined by intense picosecond pump pulse excitation at $\lambda_{SH} = 527$ nm and picosecond light continuum SH probing in the wavelength range from 980 nm to 400 nm [2]. The spectral light continuum pulses were generated by passing Nd:glass laser pulses ($\lambda_{SH} = 1054$ nm) through a D₂O sample [3, 4]. The obtained singlet excited-state absorption cross-section spectrum $\sigma_{ex}(\lambda)$ and the ground-state absorption cross-section spectrum $\sigma_a(\lambda)$ are shown in Fig.1.

The absolute triplet-triplet absorption cross-section

spectrum of eosin Y in methanol at room temperature was determined in the wavelength region from 400 nm to 1000 nm [5]. The triplet state was populated by XeCl excimer laser excitation ($\lambda = 308$ nm, duration 10 ns) to a higher-lying singlet state and subsequent intersystem crossing. The triplet level population was determined by numerical simulation of the pump pulse absorption dynamics. The triplet-triplet absorption

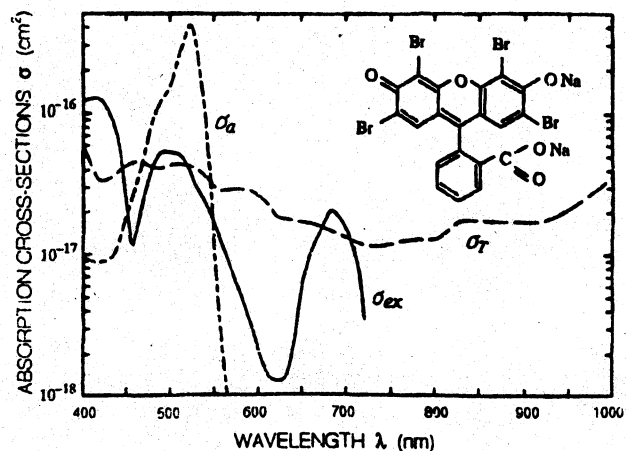


Fig. 1. Absorption cross-section spectra of eosin Y in methanol at room temperature. σ_a , ground-state absorption cross-section; σ_{ex} , S_1 -singlet excited-state absorption cross-section; σ_T , triplet-triplet absorption cross-section. The structural formula of eosin Y is included.

was probed with picosecond spectral light continua which were generated in a D₂O sample. For this purpose, the active and passive mode-locked Nd:glass laser was additionally Q-switched to achieve good synchronization to the excimer laser. The triplet-triplet absorption cross-section spectrum $\sigma_T(\lambda)$ is included in Fig. 1. The triplet level depopulation was studied by delayed picosecond light continuum probing. It varied from exponential decay with $\tau_p \approx 0.6 \mu\text{s}$ for air-saturated samples to nonexponential decay with an initial time constant $\tau_p \approx 24 \mu\text{s}$ for deaerated samples.

References

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