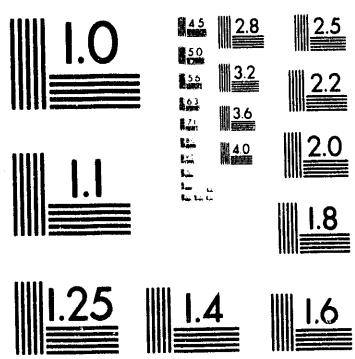
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Femtosecond Transient Absorption Studies Of The Light Harvesting Chl a/b Protein Complex Of Photosystem II In Higher Plants

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Excitation energy transfer processes in the main antenna complex of photosystem II have been studied. The intensity dependent results are discussed with emphasis on the interaction of exciton migration and exciton-exciton annihilation processes.

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Introduction

The first steps of the primary reactions in photosynthesis are the generation of electronically excited states (excitons) by light absorption within pigment protein complexes referred to as light harvesting antenna complexes and rapid exciton migration to the photoactive pigments embedded into the reaction center complex where the transformation into electrochemical free energy takes place. In green algae and higher plants the light harvesting Chl a/b complex associated with Photosystem II (LHC II) serves as the main antenna complex. Previous studies in the red absorption band of LHC II have shown that excitation energy transfer occurs in the ps- (transient absorption /1/) and the sub-ps- (fluorescence upconversion /2/) time scale, as well. In addition to limited time resolution the interpretation of the different transfer times measured with transient absorption technique is complicated by exciton-exciton annihilation processes. Even at low photon densities previous work could not exclude the possibility that the kinetic curves were affected by annihilation processes.
In this communication we present intensity dependent transient absorption measurements with fs-time resolution in isolated LHC II preparations to address the problem of the interaction of ultrafast exciton migration and exciton-exciton annihilation.

Experimental

The isolation of the light harvesting Chl a/b complexes has been described earlier /3/. The transient absorption data were obtained using a double beam, fs-dye laser system described in detail previously /4/. The samples have been excited with 100 fs-pulses, at 585nm and a 1kHz repetition rate. A white continuum generated in fused silica was used as the probe light. The suspensions of LHC II proteins exhibited about 0.2 A at 585nm.

Results

Fig.1 shows the time dependence of the transient absorption in LHC II measured at a probe wavelength of 680nm for different excitation intensities. The kinetic curves are characterized by a negative absorption change which is due to photobleaching/ stimulated emission. The intensity dependence of the maximum amplitude of the curves is nonlinear. The results of the fitting analysis can be summarized as follows: (a) For all intensities used in our experiments ΔA shows biexponential rise with time constants of τ_{R1}=200-400fs and τ_{R2}=8-12ps, respectively. (b) At an excitation intensity of $7 \cdot 10^{13}$ photons$\cdot$cm$^2\cdot$pulse^{-1} the bleaching decays with a time constant of $\tau_{D1} \geq 2$ns. This is in agreement with fluorescence decay measurements performed at low excitation conditions /5/. (c) At higher photon densities a shorter decay constant of τ_{D2}=20-30ps has to be added to fit the experimental data.

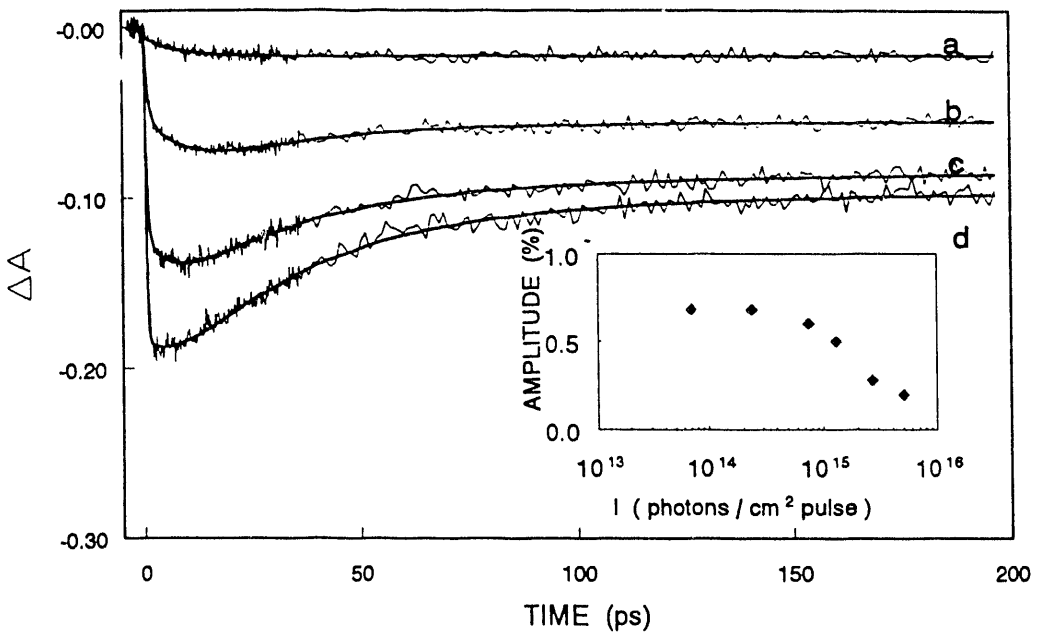

Fig.1 Transient absorption in LHC II at a probe wavelength of 680nm for different excitation intensities: (a)$7 \cdot 10^{13}$, (b) $7.5 \cdot 10^{14}$, (c) $2.7 \cdot 10^{15}$ and (d) $5 \cdot 10^{15}$ photons·cm^{-2}·pulse^{-1}. Insert: Relative amplitude of the rise time τ_{R2} as a function of excitation intensity.

In Fig.2 typical transient absorption kinetics in LHC II at a probe wavelength of 650nm are shown. In contrast to the kinetic curve at 680nm in Fig.1, the most striking feature is a very fast bleaching recovery followed by excited state absorption (ESA) that decays with a time constant ≥1ns. From triexponential fitting of the data lifetimes of τ_1=100-200fs, τ_2=1-2ps and τ_3=8-10ps have been obtained.

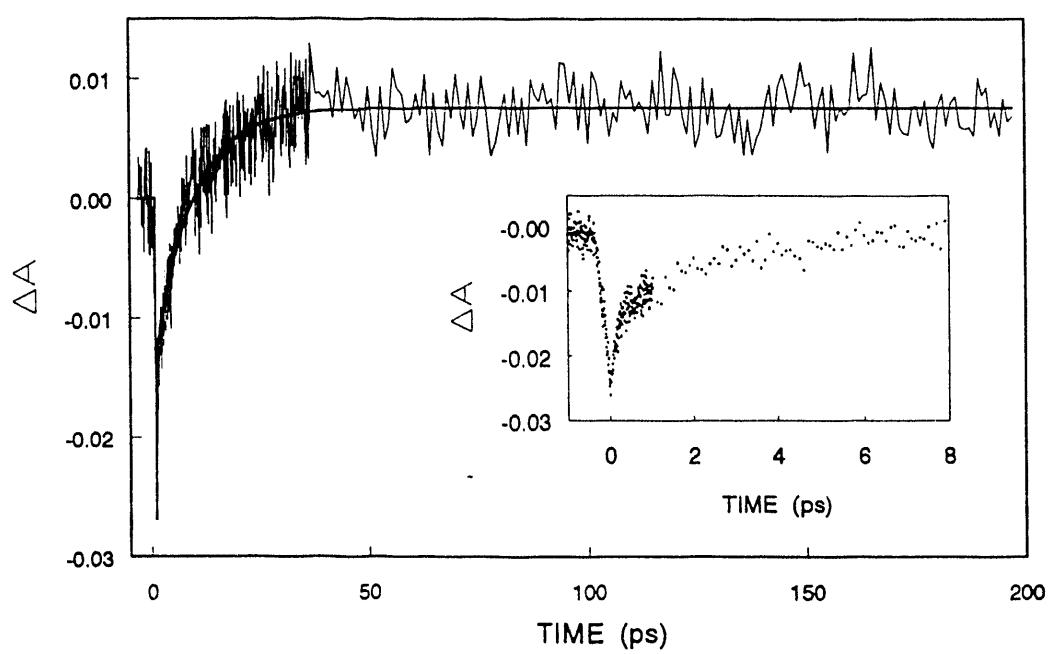

Fig.2 Transient absorption of LHC II at a probe wavelength of 650nm and an excitation intensity of $5 \cdot 10^{15}$ photons·cm^{-2} ·pulse^{-1}

Discussion

The experimental results presented in this study provide new information on the ultrafast pumped transient absorption behavior in LHC II suspensions and the influence of intensity dependent annihilation effects on these kinetics. In the red part of the absorption spectrum of this antenna complex Chl a as well as Chl b absorb. At an excitation wavelength of 585nm both chromophores have similar absorption cross sections. The measurements performed at two different probe wavelengths give the opportunity to study the exciton migration dynamics in spectral regions where either Chl a (680nm) or Chl b (650nm) dominate the absorption of LHC II.

680nm

For a probe wavelength of 680nm the measured kinetic curves show a pronounced intensity dependence (Fig.1). A biphasic rise (τ_{R1}=200-400fs, τ_{R2}=8-12ps) has been observed. τ_{R1} closely resembles to the time for the energy transfer from Chl b to Chl a (250fs) obtained from fluorescence upconversion /2/. τ_{R2} is shorter by a factor of two compared to results from earlier transient absorption data /1/, but is in good agreement with a fluorescence rise time of 13ps measured in single photon counting experiments /5/. Since the decay time τ_{D2} was not observed at lowest intensities used in our experiments, we assume that this decay constant is due to exciton-exciton annihilation. Therefore, the smaller relative amplitude of τ_{R2} at higher photon densities (see insert in Fig.1) is interpreted as the result of an increasing amount of annihilation processes characterized by τ_{D2}.

650nm

In the transient absorption curves measured at 650nm no pump intensity dependence of the kinetics was observed for excitation intensities used in our experiments. Furthermore, the amplitude of the bleaching showed a linear intensity behavior. We assume that these results are due to a very fast exciton transfer from Chl b to Chl a. This interpretation is supported by the experimental observation that the bleaching at 650nm decays very fast (see insert in Fig.2). Therefore we conclude that mainly Chl a molecules participate in the annihilation processes.

The fitting analysis yields three lifetimes (τ_1=100-200fs, τ_2=1-2ps and τ_3=8-10ps). τ_1 is slightly shorter than the fast rise time at 680nm, which is assigned to the exciton transfer between Chl b/Chl a. The intermediate time constant resembles the 2-6ps lifetime reported in previous absorption measurements /1/. The latter (longest) time is identical to the slower rise time constant at 680nm. Both lifetimes τ_2 and τ_3 may therefore characterize additional exciton transfer processes connected with spectral shifting.

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