

Femtosecond energy transfer in the physical steps of photosynthesis

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Experiments with a time resolution of 10^{-13} s have been carried out on the transfer of an electron and of excitation energy at the reaction centers for bacterial photosynthesis. The energy migration rate depends strongly on the intensity of the exciting light pulse.

The reaction centers in which the energy of photons is converted into the energy of separated charges in the course of photosynthesis are exceedingly interesting physical entities.¹ The base of a bacterial reaction center consists of six porphyrine molecules, which, as recent x-ray structural studies have shown,² are strongly bound by protein α spirals. The distances between pigments (~ 10 – 15 Å) are comparable to the dimensions of the tetrapyrrole rings, and their relative positions in the reaction center are strictly fixed. In order to reach an understanding of the physics of the functioning of such systems, it is of fundamental importance to study the primary processes of the transfer of energy and charge between the components of the reaction center—processes which occur on a picosecond or femtosecond time scale.^{1,3}

The spectrum of the bacterial reaction center studied, *Rhodospseudomonas* sphere, has three main absorption bands in the region 700–900 nm. The most intense band, near 800 nm, is attributed to bacteriochlorophyll (*B*) molecules; the band at 750 nm is attributed to bacteriopheophytin (*H*) molecules; and the band at 870 nm is attributed to bacteriochlorophyll molecules forming a dimer (*P*).¹ When the various pigments of a reaction center are excited, the energy is known to migrate rapidly to the *P*. The excitation of *P*, which is the primary electron donor, serves in turn as the starting point for the charge-separation process.¹ In the present letter we are reporting the first study at a time resolution of 10^{-13} s of the migration of excitation energy from the *B* to the *P*. For this purpose, we use a subpicosecond laser spectrometer and the technique described in Refs. 3 and 4 to record the kinetics of the time evolution of the difference spectra of the radiation centers. The sample is excited by a 300-fs laser pulse at the wavelength of 620 nm, at which it basically absorbs the *P*. The absorption cross section of the *B* is smaller by a factor of about three, while the *H* essentially does not absorb at all at this wavelength.

Figure 1 shows the kinetics found near the maxima of the absorption bands of the radiation centers: $P(\Delta A_{875})$, $B(\Delta A_{795})$, and $H(\Delta A_{755})$. The time $t = 0$ corresponds to the passage of the peak of the exciting pulse through the sample. The kinetics of ΔA_{875} reflects the excitation of the *P* as a result of both the direct absorption of light by the dimer and the migration of energy from the B^* to the *P*. The $\Delta A_{755}(t)$ dependence also demonstrates the excitation of the *P* (the front of the curve) and the subsequent transfer of an electron from the excited dimer P^* to *H* (the decay of the curve). The

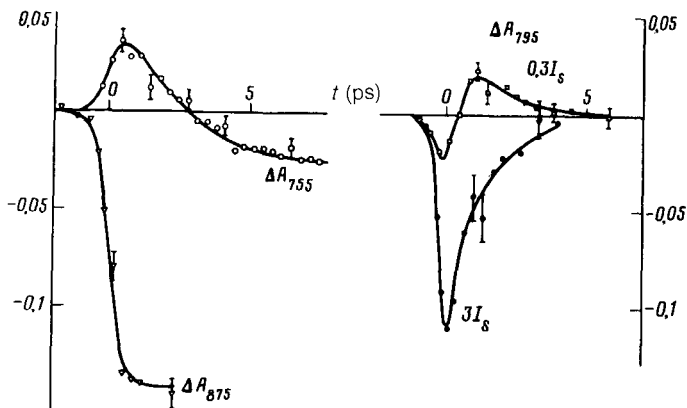


FIG. 1.

charge-transfer process is not visible in the ΔA_{875} kinetics, since the P^* and the radical cation P^+ have identical absorption cross sections in this region.

The most interesting result is the ΔA_{795} kinetics, recorded near the peak of the B absorption band. The initial part of the kinetics corresponds to three fast processes that occur simultaneously. In accordance with the magnitudes of the absorption cross sections at 620 nm, the P is excited in about 75% of the reaction centers that absorb light, with the consequence that an absorption appears (ΔA increases) in the difference spectrum. In the other 25% of the reaction centers, the B is excited, causing a fading of the absorption (a decrease in ΔA). The resultant effect of the two processes is a fading at the beginning of the kinetics. The rapid replacement of the fading by an absorption in the time interval 0–0.5 ps reflects a migration of excitation energy from the B^* to the P , while the subsequent decay of the absorption reflects a transfer of an electron from the P^* to the H . A mathematical analysis of the kinetic curves shows that the experimental data correspond best to a time of 150 ± 100 fs for the migration of energy from the B^* to the P and to a time of 2.5 ± 0.1 ps for the transfer of an electron from the P^* to the H .

The results reported here were obtained at exciting-pulse energies well below that which would saturate the absorption of the P at 620 nm, I_S ($\sim 0.3I_S$).

When the energy of the exciting pulse is increased to $3I_S$, two components—the P and the B —are excited in most of the reaction centers. Under these conditions, the relaxation of the excitation B^* slows down substantially to a scale time of 1.7 ± 0.1 ps.

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