

# Measurement of electron and energy transfer rates in physical stages of photosynthesis with subpicosecond time resolution

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The kinetics of the transfer of excitation energy and charge in the molecular complexes of photosynthetic reaction centers is measured with a resolution of better than  $10^{-12}$  sec for the first time ever. The measurements were made with an apparatus incorporating a dye laser with pulses shorter than  $10^{-12}$  sec. on the basis of the data obtained. The distance between donor and acceptor sites is estimated.

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1. The transfer of electronic excitation energy in condensed media is of fundamental importance for photosynthesis, one of the principle problems of bioenergetics. The primary stage in the transformation of the photon energies of solar radiation into the energy of separated charges occurs in so-called reaction centers.<sup>1</sup> A reaction center consists of a series of chromophoric molecules having characteristic absorption bands and definite positions with respect to one another. The physical problem of studying the primary stages of photosynthesis is to establish the sequences and rates of energy and charge migration and to elucidate the relative positions of the chromophores in a reaction center. Present-day methods of picosecond spectroscopy make it possible to measure the excitation and charge transfer rates directly all the way down to  $10^{-12}$  sec. It has been established<sup>2</sup> by these methods that when one of the chromophores (bacteriopheophytin--BP) is excited, the migration of the excitation energy from BP to the primary electron donor (the dimer bacteriochlorophyll  $P_{870}$ ) and the transfer of the electron from the excited donor  $P_{870}^*$  to the primary acceptor occurs in less than 10 psec.

In this letter we report a measurement of the rate constants of these processes with a time resolution of better than  $10^{-12}$  sec. It is shown that the migration of the excitation energy to  $P_{870}$  occurs in  $1.5 \pm 0.5$  psec, while the transfer of an electron from  $P_{870}$  to the primary acceptor takes  $7 \pm 1$  psec. On the basis of the theory of Ferster and Galanin, the distance between the chromophores BP and  $P_{870}$  is estimated to be  $12 \pm 1$  Å.

2. A block diagram of the apparatus is shown in Fig. 1. It is a double-beam picosecond spectrometer with a laser source of exciting and probing pulses. The master oscillator is a CW dye laser with passive mode locking.<sup>3</sup> It employs a free-flowing stream of a mixture of the dyes rhodamine 6G (the active medium) and DODCI (a saturable absorber) in ethylene glycol. A CW argon laser is used as the pump. The laser radiates a continuous sequence of pulses with energies of  $\sim 10^{-10}$  J each at 7.8

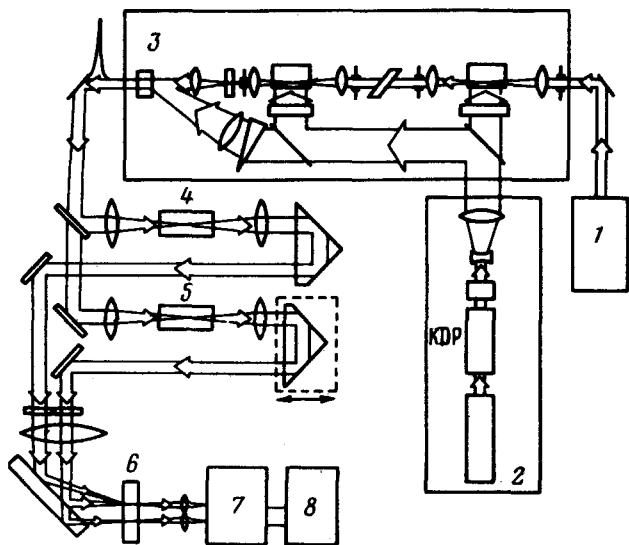


FIG. 1. Block diagram of subpicosecond double-beam absorption spectrometer: 1—master oscillator (dye laser with passive mode locking), 2—garnet laser with second-harmonic converter used to pump the amplifier stages, 3—three-stage amplifier of single subpicosecond pulse based on the dye rhodamine B, 4—cell containing cyclohexane for obtaining  $\lambda = 718$  nm, 5— $H_2O$  cell for obtaining continuous spectrum, 6—sample, 7—monochromator, 8—recording and data processing system (the dashed encloses a delay line).

nsec intervals. The pulse duration was determined by measuring the profile of the autocorrelation function of the radiation and was found to be 0.4 nsec. The duration depended on how precisely the resonator was tuned and could be increased to 0.8 psec. A detailed description of the laser and the experimental procedures is given in Ref. 4. It should be stressed that in a laser of this kind the temporal parameters of the pulse are stable over the course of several hours.

A single pulse from the sequence was amplified in a three-stage amplifier based on rhodamine B. The amplifier stages were pumped by the second harmonic of a Q-switched garnet laser. The overall gain for a weak signal reached  $10^9$ – $10^{10}$ . To prevent self-excitation and to lower the background level we used spatial and spectral filters and a saturable absorber. The amplified pulse energy reached 1 mJ at a pulse-repetition frequency of 1 Hz. After amplification, the beam was split into two beams, one of which was directed into a continuum-generating channel (picosecond continuum in a cell containing  $H_2O$ ) and served as the probing pulse, while the second was directed into a cell containing cyclohexane for frequency conversion by stimulated Raman scattering (SRS). The resulting pulse had a wavelength of 718 nm and was used to excite the pigments of the reaction center. With the aid of delay lines it was possible to follow the changes in the absorption spectra after excitation. The recording and data-processing system included a mini-computer (15VSM-5), which averaged the data and partially controlled the operation of the spectrometer.

3. The shape of a pulse can change under amplification and frequency conversion.

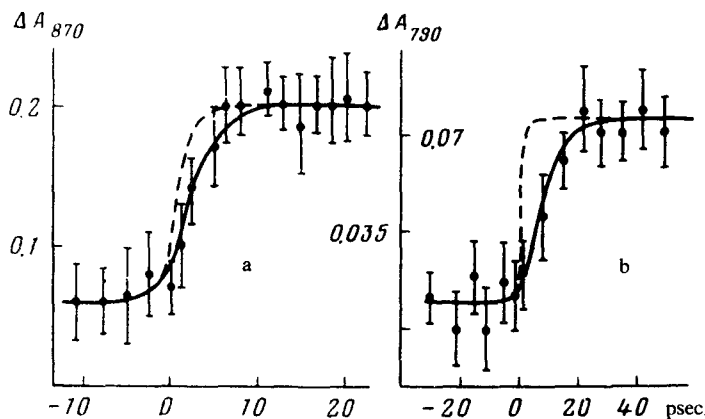


FIG. 2. Kinetics of photo-induced changes in the absorption of the reaction centers at 870 nm (a) and at 790 nm (b) for excitation at 718 nm. The optical path length of the cell was 0.2 cm and the intensity of the exciting radiation was  $10^{15}$  photons/cm<sup>2</sup>. The kinetic curves calculated for  $K_M^{-1} = 1.5$  psec and  $K_e^{-1} = 7$  psec are shown by the solid lines. The dashed line gives the kinetic curves calculated for instantaneous response.

Analysis of the time-resolved spectroscopic measurements shows that knowledge of the correlation function of the radiation is sufficient. We therefore measured the profile of the correlation function of the SRS radiation at 718 nm and that of the continuum at the same wavelength. On the basis of these measurements we calculated the instantaneous response of the spectrometer (the dashed curve of Fig. 2).

The points in Figs. 2a and 2b are the experimental data. Figure 2a shows the changes in the absorption at 870 nm after excitation in the absorption band of BP at 718 nm. The kinetics ( $-\Delta A_{870}$ ) reflects the transition of  $P_{870}$  to an excited state  $P_{870}^*$  as a result of the migration of energy from BP\*. The kinetics of the removal of an electron  $P_{870}^*$  with the formation of a cation-radical  $P_{870}^{+\cdot}$  is much smaller than the extinction of  $P_{870}$ . It is known, however, that the formation of  $P_{870}^{+\cdot}$  is accompanied by the appearance of absorption bands at 790 and 1240 nm.<sup>2</sup> We therefore took measurements of the absorption at 790 nm, which does reflect the process of electron removal from  $P_{870}^*$  (Fig. 2b).

4. The kinetic behavior given by the solid curves in Figs. 2a and 2b was calculated under the assumption that the interaction of the picosecond pulse with the ensemble of reaction centers is incoherent, that the energy migration and electron transfer are irreversible, and the  $P_{870}$  is the immediate acceptor of the excitation energy of BP\*. These curves correspond to a time constant of  $K_M^{-1} = 1.5$  psec for the transfer of excitation energy and  $K_e^{-1} = 7$  psec for the removal of the electron. Because  $K_M$  is much smaller than the vibrational relaxation constant, one can use Ferster-Galanin theory<sup>5</sup> in the calculations and, knowing  $K_M$ , estimate the distance between  $P_{870}$  and BP. For this purpose it was assumed that the 810 nm absorption band of the reaction centers is the second electronic transition of the dimer  $P_{870}$ . The calculation gives  $12 \pm 1 \text{ \AA}$  for the distance between  $P_{870}$  and BP.

5. We have made the first demonstration of the possibility of directly measuring the rates of excitation and charge transfer with subpicosecond time resolution. This possibility was realized thanks to the high reproducibility of the shape and duration of the subpicosecond pulses used in the spectrometer.

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<sup>4</sup>Yu. A. Matveets and V. A. Semchishen, *Kvant. Elektron.* **6**, 848 (1979) [*Sov. J. Quant. Electron.* **9**, 503 (1979)].

<sup>5</sup>V. M. Agranovich and M. D. Galanin, *Transfer of Electronic Excitation Energy in Condensed Media* [in Russian], Nauka, Moscow, 1978.