

Resonant picosecond spectroscopy of the physical stages of photosynthesis with the aid of tunable lasers

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The kinetics of the charge-separation process in molecular complexes of the reaction centers has been investigated for the first time by the methods of resonant picosecond spectroscopy. A picosecond spectrometer is described in which both the excitation of the investigated molecules and the registration of the photo-induced spectral changes were effected with the aid of tunable parametric picosecond lasers with well-controlled temporal and spatial characteristics. The quantum yield of the photoexcitation was measured at various wavelengths. The picosecond kinetics of the process was determined. Some new applications of picosecond spectroscopy are discussed.

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1. The purpose of the present article is to report the results of an experimental study in which the primary separation of charges in molecular complexes of photosynthesis reaction centers (RC) were first attempted by using resonant picosecond spectroscopy methods using frequency-tunable exciting and probing picosecond lasers. Under conditions of direct picosecond resonant excitation of a photoactive RC into an absorption band having a maximum at 870 nsec, the picosecond and nanosecond kinetics of the absorption changes has been determined in the absorption regions $\lambda_1=870$ nm of the electron donor molecules and $\lambda_2=765$ nm of the electron acceptor molecules. The quantum yield of the charge-separation process, measured for the first time under conditions of resonant picosecond excitation, was not less than 80% and turned out to exceed by almost one order of magnitude the quantum yield of the excitation at 530 nm.

2. The investigation of the primary photophysical stages of the energy transformation in molecular RC complexes is one of the principal fields of application of laser picosecond spectroscopy (PS).^[1] Prior to the advent of picosecond lasers, the data on the kinetics of the indicated processes were obtained by indirect methods.^[2,3] Direct measurements of the characteristic times using picosecond lasers were initiated in 1972.^[4] Now possibilities of investigating the physical energy-conversion processes in RC is uncovered by resonant PS,^[5] wherein the excitation and the probing are effected by tunable-frequency lasers (in the earlier studies, the excitation was usually carried out only at $\lambda=530$ nm), and the intensity can be varied in a wide range. In the present study this procedure was used to investigate molecular RC complexes.

3. A block diagram of the experimental setup is shown in Fig. 1. We used a two-channel picosecond spectrometer with independent tuning and control of the emission parameters in each channel. The driving generator was a monopulse AlYG:Nd³⁺ picosecond laser. The pulse duration was 45 psec, the pulse energy 10 mJ, and the pulse repetition frequency could reach 25 Hz. The tunable sources were two-stage super-radiant picosecond parametric light generators (PPLG) using KDP crystals (tuning range 800–1700 nm) or LiNbO₃ (range 660–2700 nm). The product of the pulse duration τ by the spectral width $\Delta\nu$ was $\tau\Delta\nu=2$ for the KDP generator and $\tau\Delta\nu=4$

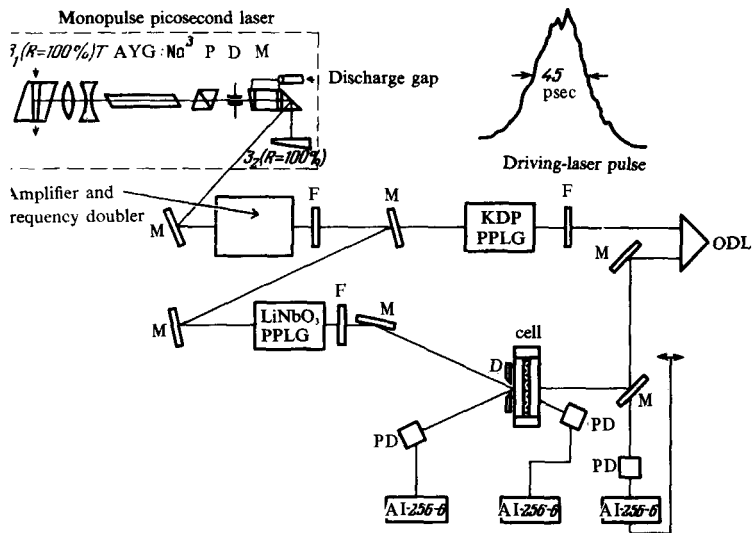


FIG. 1. Block diagram of picosecond spectrometer. Driving generator—picosecond monopulse AYG:Nd^{3+} laser. Picosecond parametric light generators (PPLG) using KDP crystals (frequency tuning range 800–1700 nm) are used in the excitation channel, and PPLG with LiNbO_3 (tuning range 600–2700 nm) are used in the probing channel. The recording part consists of an automatic optical-delay lines and three AI-256-6 multichannel pulse-height analyzers.

or LiNbO_3 . The exciting pulse (whose intensity was varied in the range 10^{13} – 10^{16} photons/cm²) changed the absorption in the cell with the RC; the probing pulse was made congruent with the exciting one (particular attention was paid to uniformity of the exciting field in the overlap region of the beams). The absorption was measured at various time delays, exciting-pulse intensities, and polarizations. A use of data-accumulation scheme with the aid of high-speed pulse-height analyzers has made it possible to vary the absorption with accuracy to within 1–2%. The time resolution of the apparatus was ~ 20 nsec.

4. The experimental data are shown in Figs. 2 and 3. Figure 2 shows the kinetics of the photo-induced changes in the absorption by the electron donor molecules in the RC (at $\lambda_1=870$ nm) and in the electron acceptor molecule region (at $\lambda_2=765$ nm), following resonant excitation into the 870 nm band. We note the presence of a picosecond component in the relaxation of the RC

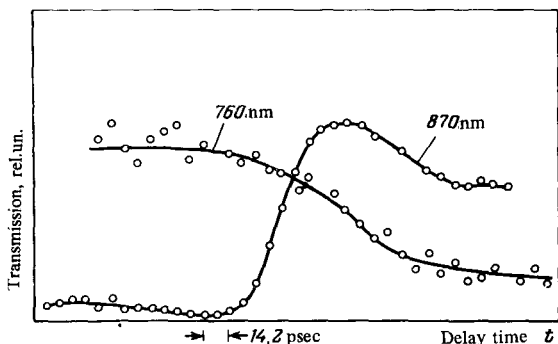


FIG. 2. Kinetics of photo-induced changes of absorption of the molecular complexes of reaction centers at $\lambda_1=870$ nm and $\lambda_2=765$ nm following resonant excitation at 870 nm. The intensity of the exciting radiation is 5×10^{15} photons/cm².

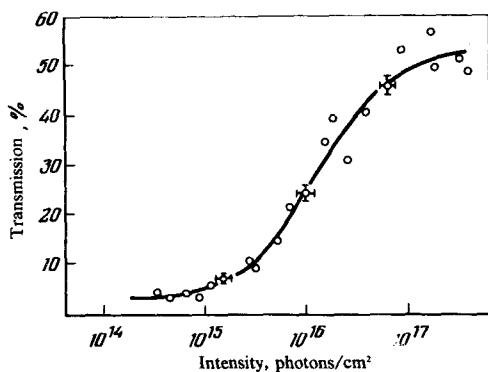


FIG. 3. Dependence of the photoresistance of reaction centers on the intensity of the exciting radiation at 870 nm. The bleaching was also registered at 870 nm.

absorption. Figure 3 shows plots of the RC photoemission at 870 nm as functions of the excitation intensity, for an exciting wave $\lambda_{\text{exc}}=870$ nm. These data make it possible to determine the quantum yield Q of the photoexcitation. The use of the data shown in Fig. 3 yields for $\lambda_{\text{exc}}=870$ nm a value $Q=70-90\%$. At $\lambda_{\text{exc}}=530$ nm the quantum yield is much less; $Q \leq 10\%$. The statistical error was determined by the accuracy of the absorption measurement. The systematic errors in the measurement of the energy of the picosecond pulses can reach 50% according to the data of [11]

5. The fast picosecond component of the bleaching at 870 nm should be attributed to the presence in certain RC of light-gathering antenna molecules that take part in the absorption. The duration of this component increases when the RC are chemically oxidized. An interesting feature of the investigated RC is the relatively slow kinetics of the relaxation of the darkening at $\lambda_2=765$ nm. The obtained data allow us to state that in time shorter than 50–100 psec the losses of optical energy to physical processes not connected with charge separation do not exceed 50%.

6. Resonant picosecond spectroscopy with frequency-controlled PPLG is an effective method of investigating fast processes wherein light energy is transformed in molecules. The possibility of recording small absorption changes yields for primary photosynthesis processes information that is not distorted by nonlinear effects.

Probing with a tunable picosecond laser offers, in our opinion, definite advantages over the picosecond-continuum technique, since it excludes the fluctuations of the probing radiation.

We note in conclusion that the described procedure, with probing from excited states, can replace to a considerable degree the laborious luminescence technique, as has already been done for simpler molecules.^[6]

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