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Femtosecond spectroscopy of excitation energy transfer and initial charge separation in the reaction center of the photosynthetic bacterium *Rhodopseudomonas viridis*

(primary donor photooxidation/bacteriochlorophyll/electron transfer/stimulated emission)

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ABSTRACT **Reaction centers from the photosynthetic bacterium *Rhodopseudomonas viridis* have been excited within the near-infrared absorption bands of the dimeric primary donor (P), of the "accessory" bacteriochlorophylls (B), and of the bacteriopheophytins (H) by using laser pulses of 150-fsec duration. The transfer of excitation energy between H, B, and P occurs in slightly less than 100 fsec and leads to the ultrafast formation of an excited state of P. This state is characterized by a broad absorption spectrum and exhibits stimulated emission. It decays in 2.8 ± 0.2 psec with the simultaneous oxidation of the primary donor and reduction of the bacteriopheophytin acceptor, which have been monitored at 545, 675, 815, 830, and 1310 nm. Although a transient bleaching relaxing in 400 ± 100 fsec is specifically observed upon excitation and observation in the 830-nm absorption band, we have found no indication that an accessory bacteriochlorophyll is involved as a resolvable intermediary acceptor in the primary electron transfer process.**

The initial separation and stabilization of electric charges, which constitute the key processes of photosynthesis, occur in a transmembrane chlorophyll–protein complex named the reaction center. Recently the organization of the prosthetic groups within the protein scaffold of the reaction center isolated from the photosynthetic bacterium *Rhodopseudomonas viridis (Rps. viridis)* has been solved to 3-Å resolution (1). The pigments exhibit an approximate *C-2* symmetry, with two closely interacting bacteriochlorophyll molecules forming a special pair (P). Two bacteriopheophytins (H_A and H_B) are located on either side of P, while two other bacteriochlorophylls (B_A and B_B) are arranged approximately in between H_A or H_B and P. The primary quinone electron acceptor (Q_A) lies at a greater distance on the "branch" occupied by the B_A and H_A molecules. This structural organization of the pigments suggests that the charge separation initially occurs between P and B_A and is followed by migration of the electron to H_A and then to Q_A. Indeed, using pulse-probe experiments on *Rps. viridis* reaction centers with 150-fsec pulses at 620 nm, a wavelength at which all four bacteriochlorophyll molecules absorb, Zinth *et al.* (2) have observed a transient absorption change, which they have attributed to the $P^+B_A^-$ state. Such a state has been proposed previously on the basis of picosecond spectroscopy on *Rhodopseudomonas sphaeroides* reaction centers (3). However, doubts have also been raised regarding the existence of the $P^+B_A^-$ state (4, 5).

In a recent femtosecond spectroscopy study of the initial charge separation in *Rps. sphaeroides* reaction centers with direct excitation of P at 850 nm (6), we have observed the generation in less than 100 fsec of an excited state of P (P^*) that decays directly to $P^+H_A^-$ in 2.8 ± 0.2 psec. We found no experimental evidence for a transient state $P^+B_A^-$. Investigating the same system but using 0.8-psec pulses at 610 nm for excitation, Woodbury *et al.* (7) have also proposed the same reaction scheme but reported a 4.1 ± 0.2-psec time constant for the initial charge separation. Furthermore, they observed a transient bleaching in the absorption band of B, which could in principle represent the state $P^+B_A^-$. However, they favored an alternative interpretation in which the transient bleaching is assigned to the initially excited B molecules before energy transfer to P occurs (within about 1.5 psec). Such an energy transfer step might explain, at least in part, the longer time constant for charge separation observed in ref. 7 as compared to ref. 6, because in the latter study P was directly excited by the 150-fsec pulse. A comparison of the kinetics of P^* formation upon excitation in B or in P should resolve this question, while observation at longer times should also allow the role of B in the electron transfer sequence to be better characterized.

Previous picosecond absorption spectroscopy studies on the reaction center of *Rps. viridis* (8, 9) have demonstrated that P^+ and H_A^- appear in less than 10 psec and less than 20 psec, respectively, while the subsequent electron transfer step to Q_A occurs in ≈200 psec. Although there are considerable analogies between the reaction centers of *Rps. sphaeroides* and *Rps. viridis* regarding the polypeptide primary sequence (10), the spectroscopy and organization of the pigments (11), and the electron transfer processes (12), one cannot exclude that subtle modifications in the arrangement of the chromophores lead to larger changes in the most primary energy transfer and electron transfer reactions. It is thus important to assess whether the differences in the initial electron transfer mechanisms and kinetics reported for *Rps. viridis* (2) and for *Rps. sphaeroides* (6, 7) can be rationalized in terms of differences in the experimental conditions used in these femtosecond spectroscopy studies or if these discrepancies come from a genuine difference between the two types of reaction centers.

In the present work, reaction centers of *Rps. viridis* have been excited at a variety of wavelengths (between 800 and 930 nm), and the photoinduced absorbance changes have been monitored in the 545- to 1310-nm spectral range with 100-fsec time resolution in order to investigate both the excitation energy transfer from the H and B molecules to P and the initial steps and kinetics of the electron transfer.

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Abbreviations: B, accessory reaction center bacteriochlorophyll (B_A or B_B); H, reaction center bacteriopheophytin (H_A or H_B); P, primary electron donor; Q_A, first quinone acceptor; Q_X, $S_2 \leftarrow S_0$ electronic transition of chlorophyllous pigments; Q_Y, $S_1 \leftarrow S_0$, electronic transition of chlorophyllous pigments.

MATERIALS AND METHODS

The femtosecond laser pump–probe setup has been described previously (6). For continuum amplification at 900 and 930 nm the dye LDS 867 (Exciton, Dayton, OH) has been used. At 930 nm the energy per pulse was 0.5 mJ·cm^{-2}. The full width at half-maximum of the pump pulses was 6 nm. At all the excitation and probe wavelengths the duration of the pulse was close to 150 fsec. Handling of the data and the fitting procedure of the kinetics of absorbance changes were carried out essentially as described in ref. 13.

Reaction centers from *Rps. viridis*, prepared according to ref. 11, were suspended in Tris·HCl buffer (20 mM, pH 8.0) containing 0.5% sodium cholate.

RESULTS

In the near infrared region the absorption spectrum of *Rps. viridis* reaction centers (Fig. 1*a*) shows the main $S_1 \leftarrow S_0 (Q_Y)$ absorption band of P around 960 nm and of the B molecules at ≈830 nm. The shoulder around 800 nm is assigned to the H molecules, whose $S_2 \leftarrow S_0 (Q_X)$ transitions absorb around 540 nm. The 600-nm band is due to the Q_X transitions of both the B and the P bacteriochlorophylls. In Fig. 1*b* the rise of the bleaching at 960 nm representing the disappearance of the ground state of P is shown after excitation of P (930 nm), of B (827 nm), or predominantly of H (803 nm). On a 2-psec time scale these three kinetics all present an instrument-limited risetime and are well fitted with a 150-fsec pulse duration, indicating an "instantaneous" bleaching—i.e., occurring in less than 100 fsec. Such an instantaneous rise has also been observed upon an excitation at 900, 854, 837, and 797 nm (data not shown).

When observed on extended time scales, the initial bleaching at 960 nm shows a small relaxation phase that becomes more pronounced toward the long-wavelength side of the 960-nm band (data not shown). At 1050 nm the asymptotic value of this apparent bleaching is zero (Fig. 2*a*) and a monoexponential time constant of 2.8 psec gives the best fit to the relaxation kinetics. Because this apparent bleaching is significantly larger than the absorbance at this wavelength, it has to be assigned to stimulated emission. The instantaneous rise followed by the 2.8-psec decay of the stimulated emission has been observed both for relatively high energy pulses at 803 nm causing the photooxidation of about 40% of the reaction centers (Fig. 2*a*) and for lower energy pulses (causing less than 10% photooxidation) at either 854 nm or 930 nm (data not shown).

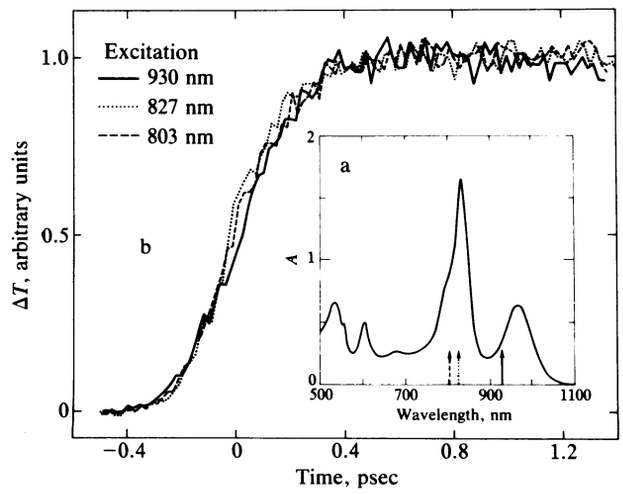

FIG. 1. (*a*) Room temperature absorption spectrum of the reaction centers from *Rps. viridis* used for the kinetic measurements (light path, 0.1 cm). (*b*) Kinetics of induced transmission at 960 nm upon excitation of the reaction centers at 930, 827, and 803 nm. The curves are normalized in amplitude and the respective zero-delay positions have been placed at the inflection point of the rise.

Fig. 2*b* shows the induced absorption increase at 1310 nm after excitation at 803 nm. The 1310-nm absorption band has been assigned at equilibrium to P^+ (8, 14). The kinetics is biphasic with an instantaneous contribution and a 2.8-psec component. More precisely, the best fit corresponds to the sum of two species with different absorption coefficients; the first species appears instantaneously and populates, in 2.8 psec, the second one, whose lifetime is much larger than the time domain investigated. Fig. 2*c* depicts the induced absorption at 675 nm, which has been attributed to the formation of H_A^- (14). Within our experimental uncertainty this kinetics is identical to the one measured at 1310 nm. The formation of H_A^- in the states $P^+H_A^-$ and PH_A^- is accompanied by a bleaching of the Q_X band of H_A at 545 nm. Fig. 2*d* shows the measurement at 545 nm after excitation at 854 nm. It reveals a biphasic response with an initial instantaneous absorption increase followed by a recovery phase that leads to an induced bleaching with a formation time of 2.8 psec. After an instantaneous absorbance rise, the blue shift of the 830-nm band occurring upon $P^+H_A^-$ formation (measured at 815 and 830 nm following excitation at 930 nm) appears with a 2.8-psec time constant (Fig. 2 *e* and *f*). There is no evidence for an appreciable transient bleaching in the 100-fsec to 3-psec time domain.

When both the excitation and observation wavelengths are within the 830-nm band, rather complex kinetics are observed (Fig. 3). In Fig. 3 *a–c*, which shows the signals observed at 850 nm upon excitation at 827 nm with pulses of increasing energy, the three kinetic traces have been fitted with two exponentials: an instantaneous bleaching recovering with a 400-fsec time constant and a slower bleaching that develops with a 2.8-psec time constant. The amplitude of the fast transient bleaching exhibits an approximately linear dependence versus the energy of the pump pulse when the latter is decreased (Fig. 3*a*) or increased (Fig. 3*c*) by a factor of 4 from the normal intensity used (Fig. 3*b*), with which about 20% of the reaction centers are photooxidized. In contrast, the amplitude of the 2.8-psec phase of bleaching appears less linear, especially at the highest intensity used, with which a saturation effect is observed. Such saturation of photochemistry has been previously reported for *Rps. sphaeroides* reaction centers excited with pulses of 10- or 25-psec duration (15, 16). At least for the high excitation energies, the kinetics of relaxation of the transient bleaching cannot be fitted with a 100-fsec time constant, as demonstrated in Fig. 3*d*. Upon detection at 832 nm, the kinetics are very dependent upon the excitation wavelength: when the excitation is at 854 nm, no fast transient bleaching is observed, while a kinetic trace identical to that shown in Fig. 3*d* is found upon excitation at 803 nm. On the other hand, when both the excitation (803 nm) and the detection (810 nm) are located predominantly in H, a fast transient bleaching is observed, the decay of which can be fitted with a 100-fsec time constant (data not shown).

DISCUSSION

Excitation Energy Transfer to the Special Pair. The identical kinetics of the bleaching of the band of P at 960 nm observed upon excitation either directly in P at 930 nm or at several wavelengths within the B or H absorption bands (Fig. 1*b* and *Results*) demonstrate that the transfer of excitation energy from the B and H molecules to the special pair occurs in less than 100 fsec. This ultrafast process of energy transfer, which to our knowledge constitutes the fastest direct measurement reported so far in a biological system, implies a very close proximity of the chromophores, as is indeed observed in the

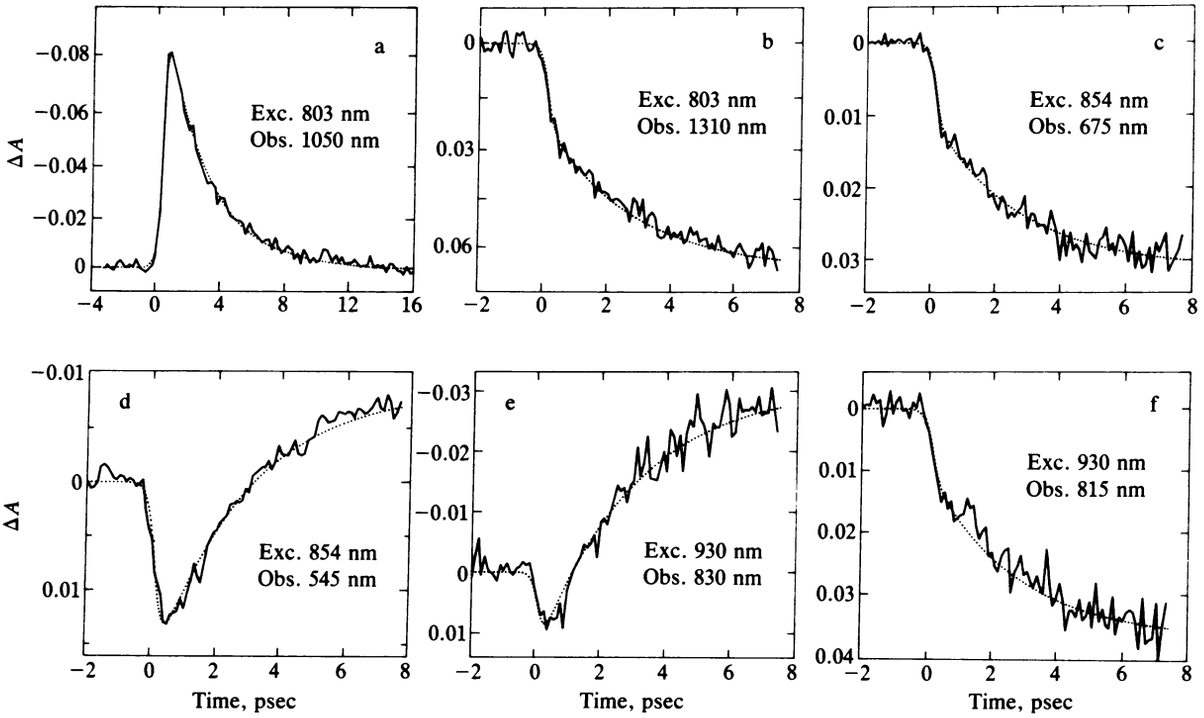

FIG. 2. (*a*) Kinetics of stimulated emission at 1050 nm. The relaxation phase is best fitted (·····) with a single exponential decay of 2.8 psec. Exc., excitation; Obs, observation. (*b–f*) Different kinetics at the indicated wavelengths demonstrating an instantaneous induced absorption relaxing in 2.8 psec superimposed upon an absorption increase (*b, c, f*) or decrease (*d, e*) developing with a 2.8-psec time constant. The asymptotic values for the kinetics *b–f* have been determined on a full scale of 20 psec.

molecular model of the reaction center of *Rps. viridis* (1). Although in this system the distances and relative orientations between the various pigments are now well characterized, the precise assignment of the various transitions underlying the 830-nm band and the degree of electronic coupling of the chromophores is still debated (11, 17, 18). The resolution of four distinct absorption bands at very low temperature in the 830-nm spectral range (11) should permit a more precise characterization of the kinetics of energy transfer amongst the various spectral components. However, to conclude which mechanism of energy transfer is dominant in this system, Förster or electron exchange, it would be necessary to know other parameters such as the overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor as well as the precise orbital overlaps.

Several picosecond measurements on *Rps. sphaeroides* reaction centers have been previously interpreted in terms of finite energy transfer steps among the various pigments. For example, Moskowitz and Malley (15) have estimated a time constant of ≈10 psec for the energy transfer from H to P, while Akhmanov *et al.* (16) have proposed values that are one order of magnitude shorter. More recently, Woodbury *et al.* (7) have also proposed an energy transfer step occurring within about 1.5 psec between the B molecules and P in order to explain a transient bleaching of the 800-nm band of B observed upon excitation at 610 nm. The <100-fsec transfer between H or B and P in *Rps. viridis* determined in the present study is thus significantly shorter than the values or upper limits previously proposed. These faster kinetics observed here cannot be due to a difference in the bacterial species used, as we have also observed ultrafast energy transfer to P in *Rps. sphaeroides* upon excitation in the H and B molecules at 760 nm and at 800 nm, respectively (19).

The Initial $P^+H_A^-$ Charge Separation. The instantaneous absorbance increase observed at a variety of wavelengths (Fig. 2 *b–f*) is assigned to an excited state of P, called P^* for simplification (6, 7). This state could correspond to a quantum mechanical mixture of the pure electronically excited state and of an internal charge transfer state $P^{\pm}$ within the

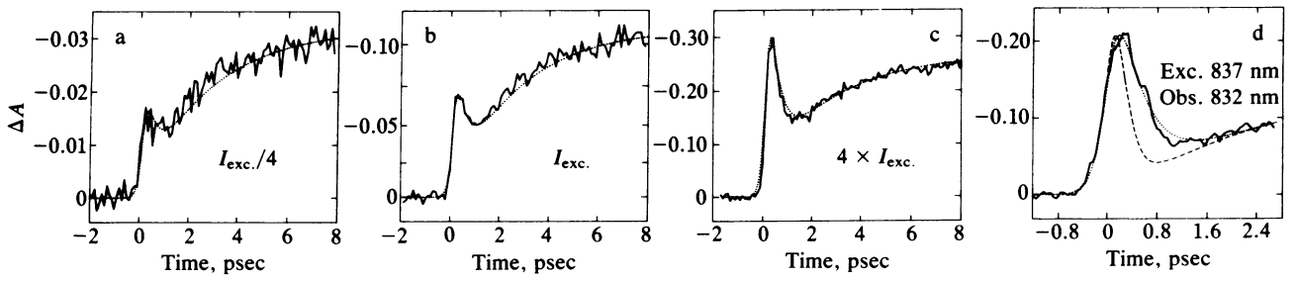

FIG. 3. (*a–c*) Kinetics of induced bleaching observed at 850 nm upon excitation at 827 nm. The intensity of the excitation, $I_{exc.}$, has been varied over a factor of 16, demonstrating the change of shape due to the saturation of the formation of the state $P^+H_A^-$ (2.8-psec rise component). The fast transient bleaching, whose amplitude is linear with excitation, is best fitted (·····) with a 400-fsec relaxation time. (*d*) Kinetics of induced bleaching observed at 832 nm upon excitation at 837 nm. In addition to the 2.8-psec phase of bleaching the fits include a fast transient bleaching that decays with a 400-fsec (·····) or a 100-fsec (---) time constant. Exc., excitation; Obs., observation.

dimer making up P. Alternatively, P^* might correspond to a charge transfer state $P^{\pm}$ generated from the electronically excited state. These interpretations are consistent with recent reports from photochemical hole-burning experiments (20, 21), which are interpreted as indicating an ultrafast (15- to 25-fsec) relaxation of the initial singlet excited state of P. The stimulated emission observed within the long-wavelength band of P is assigned to the state P^* (6, 7) and its kinetics of decay can be best measured at 1050 nm, which represents an isosbestic point for the $P - P^+$ transition (Fig. 2*a*). An instantaneous rise followed by a monoexponential 2.8-psec decay has been observed at 1050 nm upon excitation with pulses of various wavelengths and energies (see *Results*). Thus, provided the fast transient bleachings discussed in the following section are taken into account, the decay of P^* and the generation of the ionized species can be monitored upon excitation either directly in P or within the 830-nm band.

The similarity of the kinetics of the absorbance changes at 1310 nm (Fig. 2*b*) and at 675 nm (Fig. 2*c*) demonstrates that P is oxidized simultaneously to the reduction of H_A with a time constant of 2.8 psec, which also corresponds to the decay of P^*. This is confirmed by the 2.8-psec phase of the kinetics of the absorbance decrease at 545 nm (Fig. 2*d*) and the same kinetics for the blue shift of the 830-nm band (Fig. 2 *e* and *f*). The involvement of a transient state such as $P^+B_A^-$ in the electron transfer pathway between P^* and $P^+H_A^-$ should manifest itself as a transient bleaching in the absorption band of B around 830 nm. Thus, the absorbance increase observed in the 830-nm band upon excitation at 930 nm (Fig. 2 *e* and *f*) excludes the participation of B_A as a distinct intermediary electron acceptor operating in the 100-fsec to 2.8-psec time range—i.e., between the appearance of P^* and the reduction of H_A.

Fast Transient Bleaching Associated with Excitation and Detection Within the 830-nm Band. Fast transient bleachings can be expected before the excited species H^* or B^* transfer their excitation energy to P. However, while we know from Fig. 1*b* that this transfer should not take more than 100 fsec, it is also clear (Fig. 3 *b–d*) that some of the transient bleaching of B^* decays more slowly than this. If we assume that only one relaxation is involved, the best fit gives a 400-fsec decay time, which cannot correspond to the decay of the main precursor of the P^* state (Fig. 1*b*). Thus, we have to conclude that at least two parallel processes are occurring. These observations suggest that most of the states B^*P decay to BP^* in a time $\tau_1 < 100$ fsec, while a small fraction of B^* enters a competitive channel and relaxes back in one or more steps to the ground state of B in a time $\tau_2 \approx 500$ fsec. Although the signal-to-noise ratio in Fig. 1*b* does not allow us to exclude that about 10% of P^* is generated in ≈500 fsec, we note that a quantum yield of P^+ formation $r = 0.93$ has been reported for *Rps. sphaeroides* reaction centers excited at 800 nm in the band of B, compared to a yield of essentially 1.0 when P is excited directly (22). Using 800-nm excitation, we have observed the same transient bleaching in *Rps. sphaeroides* (19) as reported here for *Rps. viridis* reaction centers. This decreased yield compared to that observed upon direct excitation of P could correspond to the small loss of B^* described in our scheme provided $\tau_1/\tau_2 = 1 - r$. The fast transient bleaching would then include the contributions (*i*) of a small fraction of the B^* population relaxing to the B ground state in about 500 fsec and (*ii*) of most of the B^* states transferring to P in ≈50 fsec.§ Due to the fact that the kinetics are measured with pulses longer than this characteristic time, the maximum amplitude of the ≈50-fsec contribution is attenuated by roughly a factor of 6, while the 500-fsec component is almost not affected. With 5–10% of B^* participating in the 500-fsec kinetics, this would lead to an apparent bleaching of 20–25% of the absorption of B. However, taking into account the absorption cross-sections at 850 and 960 nm for the states P (Fig. 1*a*) and P^+ (9, 23), the amplitude of the fast transient bleaching at 850 nm (Fig. 3 *a–c*) can be estimated at ≈30% of the absorption of the fraction of excited reaction centers at this wavelength. Thus, even without considering a probable component of absorption from P at 850 nm (11, 23), it seems very likely that the transient signal also includes a contribution of stimulated emission from B^*. This effect also would explain the absence of a fast transient bleaching upon excitation at 854 nm and observation at 830 nm (see *Results*), while a large transient bleaching is observed upon the almost symmetrical condition of excitation at 827 nm and observation at 850 nm (Fig. 3 *a–c*).

An alternative to the competitive channel scheme discussed above would be a situation in which a small fraction (≈10%) of photooxidized reaction centers is present. However, this interpretation can be ruled out in view of the observation of this transient relaxing in ≈400 fsec even when the redox state of the reaction centers is strongly modified by chemical oxidation ($P^+H_AQ_A$), chemical reduction ($PH_AQ_A^-$), and photochemical reduction ($PH_A^-Q_A^-$). This striking observation (unpublished data) can be rationalized with our model, which primarily involves excited states of B and not of P or H. Furthermore the ultrafast energy transfer $B^*P \rightarrow BP^*$ offers a plausible explanation of the different intensity dependence of the two phases seen in Fig. 3 *a–c* if the decreasing yield of photochemistry observed at high intensity is due to the absorption of 830-nm light by reaction centers that have already entered the state BP^* during the pulse.

As already mentioned, the fast transient bleaching of B^* relaxing in ≈400 fsec has been detected in both *Rps. viridis* and *Rps. sphaeroides* reaction centers (19). It is thus justified to ascribe the transient bleaching around 800 nm reported upon excitation of *Rps. sphaeroides* reaction centers at 610 nm with 0.7- to 0.8-psec pulses (7, 24) to the same effect as discussed here. In both types of reaction centers the 600-nm region corresponds to the Q_X transitions of the four bacteriochlorophylls. A bleaching of the Q_Y transitions of the B molecules should thus be accompanied by a corresponding bleaching of their Q_X transitions. This constitutes in our view the simplest interpretation of the fast transient bleaching at 620 nm reported by Zinth *et al.* (2) for *Rps. viridis*.

CONCLUSIONS

Using a pulse–probe technique featuring a 100-fsec resolution and tunability of the excitation in the near-infrared, we have investigated the excitation energy transfer and the initial charge separation occurring in the reaction center of the photosynthetic bacterium *Rps. viridis*. Energy transfer from H to B and then to P, occurring on an ultrafast time scale, leads to the formation of the state P^* in slightly less than 100 fsec. This state, characterized by a broad absorption spectrum, is capable of stimulated emission and decays in 2.8 ± 0.2 psec with formation of the radical pair $P^+H_A^-$. Upon direct excitation of P at 930 nm no fast transient bleaching is observed around 830 nm, thus excluding any significant contribution of the state $P^+B_A^-$ as a spectrally or kinetically resolvable intermediate. This conclusion contradicts the reaction scheme recently proposed by Zinth *et al.* (2).

Upon excitation in the H or B absorption bands the initial charge separation also proceeds from the state P* and its kinetics is unaffected when the excitation energy is varied by more than one order of magnitude. However, under these conditions, a large transient bleaching recovering in 400 ± 100 fsec is detected in the spectral range 830–850 nm and

§The limits for the latter time constant are estimated from a model involving the branching ratio described above, which gives a lower limit of 35 fsec, and from our experimental time resolution, which gives an upper limit of 100 fsec.

could be mistakenly interpreted as a transient state such as $P^+B_A^-$. The magnitude and spectral characteristics of this transient bleaching, as well as the observation that it is essentially unaffected when the redox state of P, Q_A, and H_A is altered, lead us to propose that it is due to the combination of a fast (≈50 fsec) component of energy transfer $B^*P \rightarrow BP^*$ that affects most of the B molecules and of a slower (≈500-fsec) relaxation to the ground state that affects a much smaller fraction of B^*, both components probably being enhanced by stimulated emission. Additional information on a possible difference in the involvement of B_A and B_B in this process as well as on the kinetics of energy transfer from H_A or H_B to B and P might be obtained by kinetic measurements at low temperature.

An analogous fast transient bleaching has also been observed around 800 nm in the reaction center from *Rps. sphaeroides*. More generally, the excitation energy transfer among H, B, and P as well as the characteristics of the initial charge separation (kinetics, nature of the ionized species involved) appear identical in the reaction centers of *Rps. sphaeroides* (6, 19) and of *Rps. viridis*. These conclusions thus further strengthen the proposal (11) that the geometrical organization of the chromophores is essentially the same in the reaction center of these two organisms.

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