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Role of charge-transfer states in bacterial photosynthesis

(reaction center/ultrafast process/photon echo/excited-state coupling)

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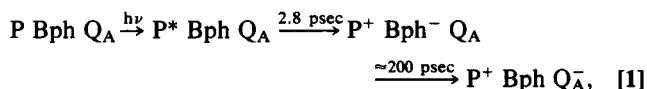
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ABSTRACT Photon echo, photon-echo excitation, and "hole-burning" data recorded in the 800-990 nm region of *Rhodobacter sphaeroides* R26 and *Rhodospseudomonas viridis* reaction centers are reported. The primary process in these reaction centers, following excitation, was found to occur in ≈ 25 fsec; the long-wavelength band of the primary electron donor (P) was largely homogeneously broadened. In accordance with our previous explanation of hole-burning and photon-echo measurements on *Rb. sphaeroides* [Meech, S. R., Hoff, A. J. & Wiersma, D. A. (1985) *Chem. Phys. Lett.* 121, 287-292], we interpret this as resulting from a dephasing of the excitation in P into a background of strongly coupled charge-transfer states. The previously reported picosecond lifetime of the excited P state is assigned to decay of these strongly mixed states. Further, a coupling between P and an adjacent bacteriochlorophyll was observed. The extent of this coupling and the role of charge-transfer states in the functioning of reaction centers is discussed.

The primary process in bacterial photosynthesis involves a rapid photoinduced charge separation that occurs in the reaction center (RC). Recently, the bacteriochlorophyll (Bchl) b-containing RC of *Rhodospseudomonas viridis* was crystallized and the spatial arrangement of the various pigments (1) was determined from x-ray data (2). Two of the Bchl molecules form a dimer (the "special pair"), next to which (≈ 11 Å away) are two more Bchl molecules, the accessory monomers. A further 11 Å away are the two bacteriopheophytin (Bph) molecules, to one of which a quinone is adjacent. The pigments are arranged in two chains converging at the dimer and exhibit an approximately 2-fold symmetry. These structural features correlate quite well with the bands observed in the room temperature optical spectra of RCs, although the origin of some of the additional spectral bands resolved at low temperature is still a matter of debate (3-6).

The kinetics of the extraordinarily efficient electron-transfer reactions that occur in the RCs have been the subject of several investigations (see, for example, refs. 7 and 8). Recent measurements with subpicosecond resolution have provided the reaction scheme (9, 10)



in which the photoexcited special pair (P*) rapidly transfers an electron to a Bph, which subsequently transfers an electron to a quinone. These rapid reactions are followed by slower steps (11) until P Bph Q_A is regenerated. Note that no reduction of the accessory Bchl monomers occurs, which is surprising in view of the configuration of the RC pigments.

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Also, only one Bph is reduced; the reaction is one-sided. We further note that in these transient absorption measurements, a stimulated emission, with a lifetime of 2.8 psec, was observed, which was assigned to the lifetime of the excited state of P. In the experiments reported here, the optical dephasing associated with the P transition is determined directly. We apply the accumulated photon echo (12) and the "hole-burning" (13) coherent optical techniques in an investigation of the spectroscopy and electron-transfer dynamics of *Rhodobacter sphaeroides* and *Rps. viridis*. We extend our previous measurements (14) of the ultrafast (tens of femtoseconds) relaxation of *Rb. sphaeroides* to the red edge of the P band, and we report data on the P band of *Rps. viridis*. The ultrafast decays observed are assigned to a dephasing of the initially excited dimer state into a strongly coupled underlying charge-transfer state. This is an extension of our earlier proposal (14) that a charge-separation reaction occurs within the Bchl dimer. The origin and role of charge-transfer states in the spectroscopy and functioning of photosynthetic RCs are discussed. Further, we report data, obtained from photon echo spectroscopy, that permits an experimental study of the interpigment coupling and an unambiguous assignment of the bands observed in the optical spectra.

EXPERIMENTAL METHODS

Optical Measurements. In both of the experiments employed in this study, T_2 , the optical dephasing time, was measured. In the case of a simple two-level system, T_2 is related to the population-relaxation time (lifetime) T_1 by

$$\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{1}{2T_1} \quad [2]$$

where T_2^* represents the pure dephasing contribution to T_2 . At low temperature, T_2^* processes, due to the coupling of the optical excitation to the environment (protein and glass medium), are negligible on a picosecond time scale. Consequently all measurements were made in liquid helium below the λ point (< 2 K). Thus, the remaining T_2^* processes are truly intra-aggregate (molecular) dynamical processes.

The accumulated three-pulse stimulated echo (A3PSE) is a simple and versatile method for the determination of optical T_2 values. The principles have been described in depth elsewhere (12). Here we merely reiterate that the crucial point in these experiments is that the optically excited transition should transfer some of its population to a long-lived bottleneck state. A frequency grating on the pumped transition, from which the echo is scattered, is thus generated (12). RCs are especially suitable, because the long-lived

Abbreviations: RC, reaction center; Bchl, bacteriochlorophyll; Bph, bacteriopheophytin; P⁽⁺⁾ and P⁽⁻⁾, special-pair positive and negative exciton states.

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charge-separated state is populated with near unit quantum efficiency.

For the experiments reported here, subpicosecond time resolution with near-IR radiation was required. The subpicosecond pulses were obtained from synchronously pumped dye lasers by the technique of active-passive mode locking (15, 16). For excitation in the P band of *Rps. viridis*, 1.5- to 2.0-psec pulses were obtained from an IR140 dye laser tandem-pumped (17) by a mode-locked styryl-9 laser.

Further improvements in time resolution were made by exploiting the fact that the radiation correlation time, not the pulse width, is the determining factor in coherent measurements like the A3PSE (18, 19). In these stochastic experiments, radiation with a correlation time of ≈ 150 fsec was employed.

The population-bottleneck hole-burning experiments were performed as described (14), by taking the difference transmission spectrum of the RC with narrow-band laser excitation on and off at various positions in the P absorption band. The exciting laser was modulated at a few hundred hertz and the (modulated) transmitted probe light was phase-sensitively detected by a silicon photodiode. The transmission measurements were made with a dispersed halogen lamp at 5-Å resolution (7 Å for the hole-burning experiments).

Sample Handling. RCs of *Rb. sphaeroides* R26 and *Rps. viridis* were prepared as in refs. 1 and 5 and were stored under liquid nitrogen. Dilution was made with glycerol/buffer (3:1, vol/vol) to give an OD < 0.4 at the excitation wavelength. Samples were cooled in a bath cryostat to 77 K before immersion in liquid helium.

RESULTS

Absorption Spectroscopy. The absorption spectra of RCs of *Rb. sphaeroides* and *Rps. viridis* are presented in Fig. 1. The bands at $11,200\text{ cm}^{-1}$ (*Rb. sphaeroides*) and $10,000\text{ cm}^{-1}$ (*Rps. viridis*) represent the transitions to the lower energy component of the excitonically coupled special pair, the $P^{(-)}$ state. These bands are very well separated [1260 cm^{-1} (*Rb. sphaeroides*) and 1800 cm^{-1} (*Rps. viridis*)] from the next transitions, which are mainly due to the accessory Bchl molecules, suggesting that these bands should represent an almost pure (uncoupled) transition (6, 20). However, neither of the $P \rightarrow P^{(-)}$ transitions can be well fit by a Gaussian

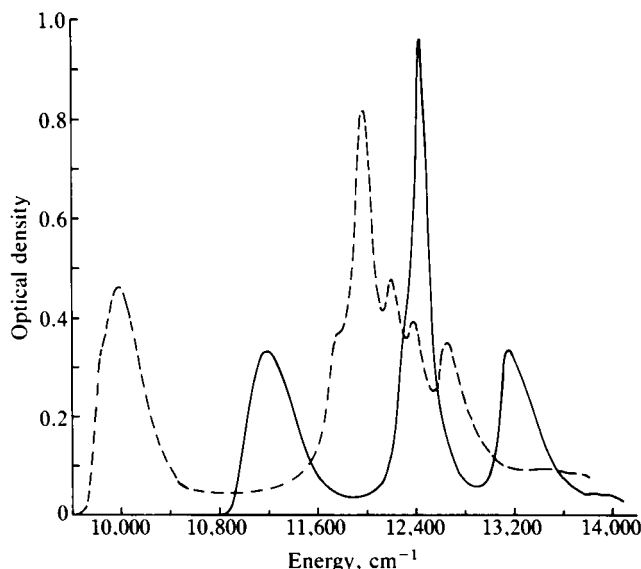


FIG. 1. Absorption spectra of *Rb. sphaeroides* (solid line) and *Rps. viridis* (broken line) RCs at 1.5 K. The peak at $12,200\text{ cm}^{-1}$ in *Rps. viridis* is due to an impurity.

(inhomogeneously) or Lorentzian (homogeneously) broadened line shape. Further, both spectra exhibit fine structure, especially in the case of *Rps. viridis*. Such data could argue against the assignment of these transitions to a pure state. The widths of these transitions are, respectively, 450 (*Rb. sphaeroides*) and 410 cm^{-1} (*Rps. viridis*). In neither spectrum does the absorbance decrease to zero before the $12,400\text{ cm}^{-1}$ ($11,800\text{ cm}^{-1}$) transition. Both of these latter transitions exhibit broadening or structure on the low-energy side; the origin of this has been the subject of extensive investigations (3–6, 21). Our assignment, that this structure largely (but not exclusively) represents the intensity of the upper part of the special pair ($P^{(+)}$) transition, will be discussed below.

From the *Rps. viridis* absorption, it is evident that the 2-fold symmetry observed in the x-ray structure (2) is not carried through in the spectrum. In particular, the two Bph species absorb at significantly different energies ($12,980$ and $12,650\text{ cm}^{-1}$). However, in the spectrum of *Rb. sphaeroides* this behavior is much less apparent and is only reflected in the larger width of the Bph band (at $\approx 13,200\text{ cm}^{-1}$), relative to the (mainly) Bchl band ($12,460\text{ cm}^{-1}$). Such spectral asymmetry is presumably due to differing protein-pigment interactions.

Excitation in the $P^{(-)}$ Bands. In this section we present evidence that there exists an ultrafast (≈ 25 fsec) primary optically excited step in RCs. Fig. 2 A and B show the echo decay traces for excitation into the bulk of the $P^{(-)}$ bands. In both *Rb. sphaeroides* and *Rps. viridis* the decay time is less than the resolution of our instrument. Simulations showed that a decay is resolvable (i.e., as a significant asymmetry in the echo trace) for T_2 longer than half the autocorrelation width. Thus, upper limits for the $T_2 (= 2T_1)$ of *Rb. sphaeroides* and *Rps. viridis* are set at 700 and 900 fsec, respectively. Note, however, that in both cases the echoes are narrower than the observed autocorrelation widths. For *Rb. sphaeroides* a study of the wavelength dependence of the signal within the $P^{(-)}$ band was possible. Excitation between 855 and 913 nm (Fig. 2C) produced the same result; an unresolvably fast decay. This observation would seem to rule out an assignment of this ultrafast process to an extraordinarily rapid vibrational relaxation within $P^{(-)}$. With regard to this, a study of the Bchl monomer in a glass (14) produced a T_2 of ≈ 100 psec throughout the wavelength range 765–781 nm. This suggests that the oscillator strength is largely electronic in character. Similar results have been obtained for Bchl dimers in glasses (26). We conclude that the ultrafast decay in these RCs represents some electronic relaxation process.

As was noted above, the echo traces are narrower in time than the widths of the autocorrelations. This results from the fact that the pulses were not fully coherent, so that the echo width reflects the correlation time (inverse bandwidth) of the radiation. To exploit this phenomenon, stochastic echo measurements were made on *Rb. sphaeroides* at 880 nm. The laser was adjusted to give an output with a correlation time of 130 fsec. The resulting echo trace is shown in Fig. 2D. The trace is symmetrical, with a width of ≈ 150 fsec; again no decay is resolved. This result sets an upper limit for T_2 at ≈ 100 fsec.

We can confidently assert that the observed traces are photon-echo phenomena, since the signal [which was very large, as is predicted (12) for an efficiently populated, long-lived bottleneck state] exhibited the proper dependence on excitation intensity and modulation rate (12). Spurious bottleneck effects, such as excited-state absorption or coherent coupling artifacts, can be ruled out as contributing to these transients, because at some wavelengths no signal is observed, even though the bottleneck is efficiently populated (see below). Consequently, we conclude that these photon-echo traces result from some ultrafast relaxation in the RC

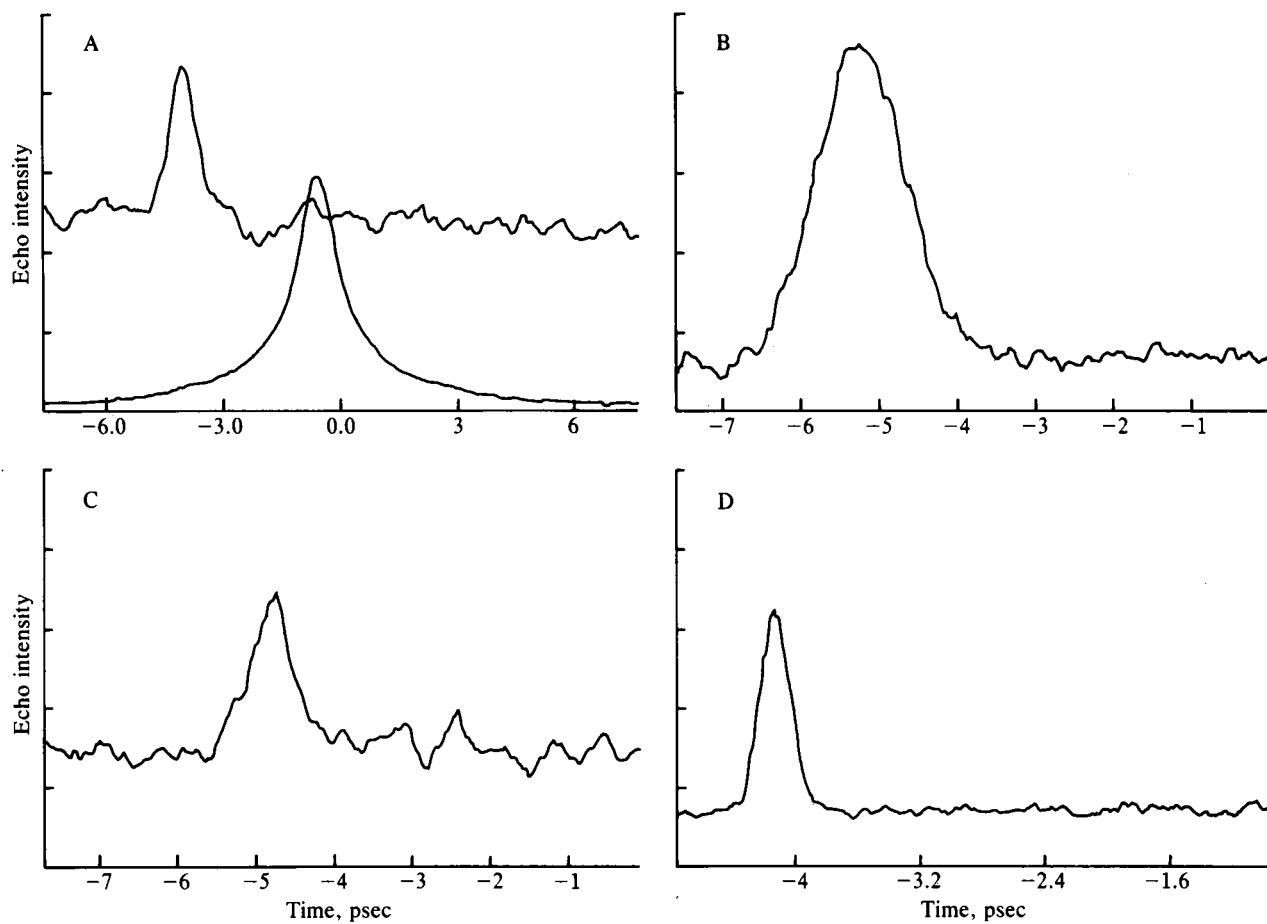


FIG. 2. (A) Echo decay (upper) and laser autocorrelation (lower) traces for *Rb. sphaeroides* at 865 nm. Offset is due to a neutral density filter in one of the beams. (B) Echo decay of *Rps. viridis* at 990 nm. (C) Coherent echo decay of *Rb. sphaeroides* at 913 nm. (D) Stochastic echo trace for *Rb. sphaeroides* at 880 nm. All traces were recorded with $<100 \mu\text{W}$ of laser power. Spot size, 0.01 mm^2 .

which occurs on a time scale much shorter than the reduction of Bph. In an attempt to put a number to this decay time, population hole-burning experiments (13) were performed. In these frequency-domain coherent optical experiments, use is made of the fact that an exciting laser field affects only those molecules whose homogeneous line shapes overlap with the laser spectral bandwidth. By using laser radiation with a bandwidth much smaller than the homogeneous width of an

optical transition one can sometimes, under suitable conditions, burn a "hole" of twice the homogeneous width in an inhomogeneously broadened transition. When pure dephasing processes are negligible, as is the case in RCs at low temperature, the hole width is only determined by population-relaxation processes, and one measures T_1 . In the experiment, the laser bandwidth was adjusted to give a 2-Å spectral width at 980 nm. The very surprising result obtained

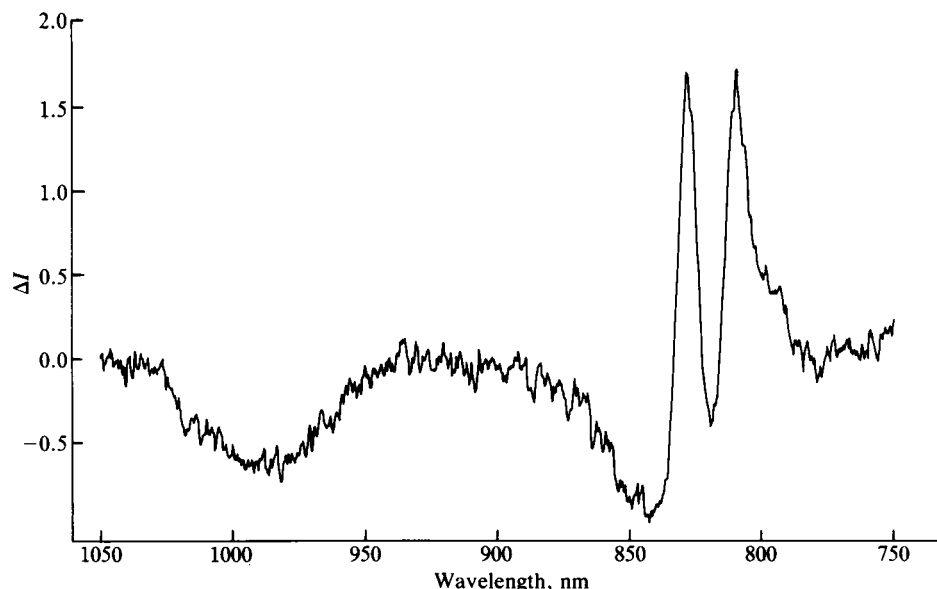


FIG. 3. Hole-burning spectrum for *Rps. viridis*, recorded with 0.4 mW of laser power at 980 nm. Spot size, 2 mm^2 . ΔI , the change in intensity, is given in arbitrary units.

(Fig. 3) is that essentially the entire $P^{(-)}$ band of *Rps. viridis* is homogeneously broadened. The same result was obtained for *Rb. sphaeroides* (14, 22). This demonstrates that the primary relaxation step following absorption of a photon by the $P^{(-)}$ state of an RC occurs in ≈ 25 fsec. The nature of this relaxation process is discussed below. It is noteworthy that the same hole-burning spectrum is obtained for narrow-band excitation in the wavelength range 980–830 nm.

Photon-Echo Excitation Spectroscopy. In these experiments we recorded the integrated echo intensity as a function of the laser wavelength, at constant laser fluence. The rationale for this is as follows. If the laser is resonant with any state that has a component of P (that is, P itself, states wholly induced by mixing with P, or states with a strong admixture of P), then an echo will be generated. However, if the resonance is with a state that does not carry any of the P oscillator strength, an echo cannot be generated, even though the bottleneck state can still be populated.

An illustration of this effect arises from the hole-burning data. For excitation at $12,150\text{ cm}^{-1}$, it was observed that the hole spectrum was about as intense as at $11,860\text{ cm}^{-1}$, whereas the echo signal was decreased by a factor of 10. This is explained as follows. If radiation is absorbed by a state other than P, that state will rapidly transfer its energy to P and will itself return to the ground state. Consequently, no grating is formed on the pumped transition, so no echo is observed, but the bottleneck is, of course, still populated with unit quantum efficiency, so the hole spectrum may be recorded.

The assignment of the peak observed at $11,750\text{ cm}^{-1}$ in the low-temperature spectrum of *Rps. viridis* has been the subject of much debate (3–6). It has been variously assigned to the $P^{(+)}$ state or to one of the accessory Bchl monomers. It is quite clear from Fig. 4 that this peak carries a large amount of P (presumably $P^{(+)}$) oscillator strength. However, the echo signal extends throughout the complex band structure found between 860 and 830 nm. This could be interpreted as resulting from a contribution due to a pure $P^{(+)}$ transition plus a contribution from mixing between Bchl and $P^{(+)}$. There may also be other states (see below) underlying this band, which could also give rise to an echo signal. Such a complex coupling scheme makes any attempt to assign absorption bands to localized transitions a somewhat fruitless task, a conclusion already implicit in the calculation of Knapp and coworkers (6, 20).

The coupling scheme is perhaps better illustrated by the data taken for *Rb. sphaeroides* (Fig. 4B). The asymmetric transition at $12,640\text{ cm}^{-1}$ has been assigned as containing the absorption of the $P^{(+)}$ state and both accessory Bchl molecules. However, the echo excitation spectrum clearly exhibits a double-peaked profile (this behavior is also discernible in Fig. 4A). The first peak coincides with the shoulder in the absorption spectrum, but the second is isoenergetic with the maximal absorbance, which is usually assigned to the Bchl. Fig. 4B, then, represents an experimental manifestation of a coupling between P and at least one of the accessory Bchl molecules. (Note that there is significant oscillator strength at $12,680\text{ cm}^{-1}$, although the echo intensity is negligible.) Such couplings can have important implications for the mechanism of the electron-transfer reactions within RCs.

DISCUSSION

Our data show that interstate and -pigment coupling plays an important role in the spectroscopy of RCs. It is most likely that the same mechanism underlies the observed ultrafast optical dynamics after direct excitation of the $P^{(-)}$ state. Therefore, we interpret the first step in the electron-transfer process as a decay of the initially excited wave packet, comprising the Frenkel-dimer state, into molecular eigenstates formed by mixing of the Frenkel-dimer state with the intradimer charge-transfer state. This process takes place in

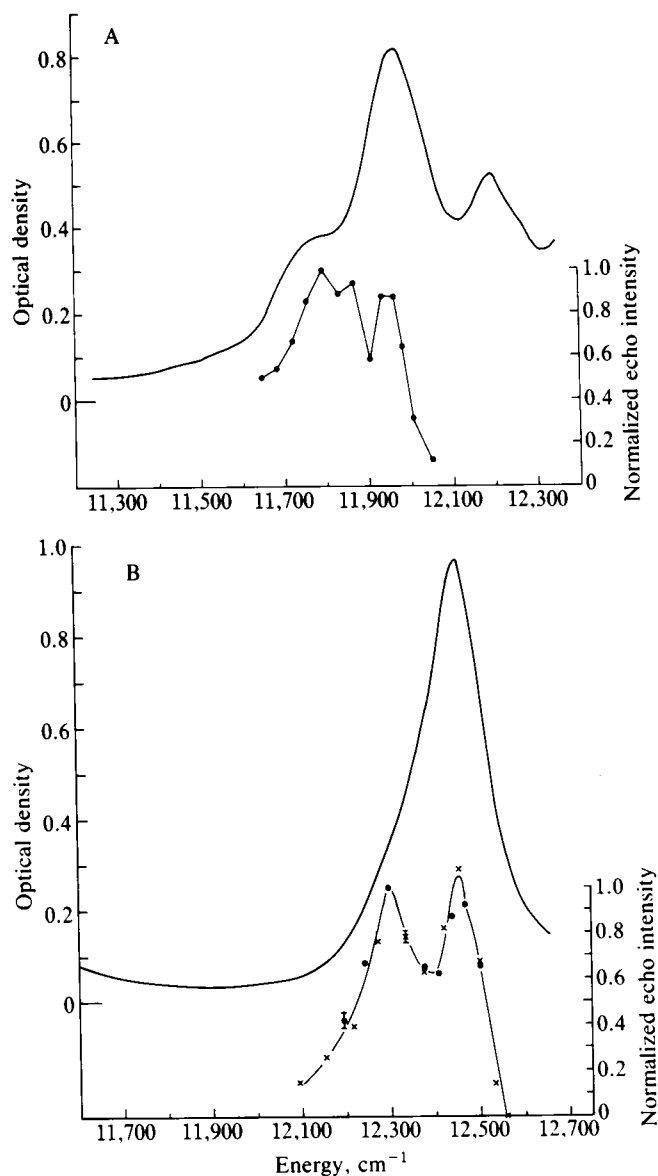


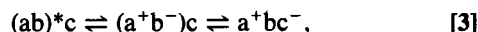
FIG. 4. Echo excitation spectra of *Rps. viridis* (A) and *Rb. sphaeroides* (B) with 50 (×) and 100 (●) μW of incident power. Error bars are for three traces at constant power. The absorption spectra are expansions of those in Fig. 1; the samples used were 3-fold more dilute.

≈ 25 fsec. These molecular eigenstates then relax on a picosecond time scale by transfer of an electron to a nearby Bph. It is this latter process that is monitored in the decay of the stimulated emission of these RCs (9, 10). This model, invoking strong mixing between an intra- and intermolecular excitation explains nicely, as noted by Warshel (23), the presence of a dimer in an efficient photosynthesis system; for conventional electron-transfer models, a monomer would do as well. The proposition of a charge-transfer state within P requires that the dimer exists in an asymmetric protein environment. The existence of a charge-transfer state is consistent with the measurement of a very large Stark effect reported by De Leeuw *et al.* (24).

It is also necessary to admit the possibility of other charge-transfer states among the RC pigments. In particular, a charge-transfer state between P and (one of) the adjacent accessory Bchl molecules is possible. Such a charge-transfer state could provide an efficient mechanism for the coupling between P and Bchl revealed in the echo excitation spectra (Fig. 4). Such a mechanism is appealing because it provides

a role for the accessory Bchl species in bacterial photosynthesis.

Thus, the mechanism we propose for the primary step in bacterial photosynthesis is that immediately after excitation of $P^{(-)}$, the wave packet formed develops into a large number of molecular eigenstates which have mixed intramolecular and interpigment charge-transfer character. The charge-transfer character is mainly localized at the dimer but also contains a contribution from at least one of the accessory Bchl molecules. This may be summarized in the simple coupling scheme



where *a* and *b* represent the special-pair Bchl molecules and *c* represents an accessory Bchl. Such a change in the nature of the excited state could be most effective in preventing such undesirable back reactions as reverse energy transfer from *P* to the antennae system and reverse electron transfer from Bph to *P* (see ref. 23).

Such charge-transfer states have very high permanent dipole moments and are thus likely to have a strong interaction with their environment. Thus, for a fuller understanding of RC reactions, more detailed information about the protein matrix is required.

We note two points that are relevant to some other measurements of RC spectroscopy and dynamics. First, the model outlined above does not necessarily imply a substantial bleaching of the Bchl transition. The involvement of an accessory Bchl in a charge-transfer state would indeed imply some spectroscopic manifestation, but this could be quite subtle. Second, the 860–830 nm region of the hole-burning spectrum (Fig. 3) can include effects due to decoupling of *P* (converted to P^+) from the accessory Bchl molecules, as well as those due to the often noted electrochromic shift (25). These should be accounted for in a quantitative simulation of these spectra.

Conclusions. Direct measurements of the dephasing rate and intramolecular coupling in RCs can best be explained by invoking the following mechanism for primary charge separation in bacterial photosynthesis: the excitation of the $P^{(-)}$ state is rapidly followed by a charge separation on the dimer and a delocalization of the excitation over a coupled *P*-Bchl pair. The presence of a dimer in an asymmetric protein environment provides the possibility for an intramolecular charge-transfer state, which in turn leads to a "one-sided" electron-transfer reaction. The observed coupling between *P* and Bchl provides a route for the efficient transfer of an electron to Bph. However, the relative time scales involved in the electron-transfer reactions [25 fsec and 2.8 psec (9)] suggest that this coupling need not be very large. To place the proposed mechanism on a more quantitative level, conventional spectroscopy, photon-echo excitation spectra, and

Stark effect measurements of (photo)chemically modified RCs will be required, as well as more detailed structural data.

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