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STRUCTURE OF *RHODOPSEUDOMONAS VIRIDIS* REACTION CENTERS

ABSORPTION AND PHOTOSELECTION AT LOW TEMPERATURE

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The polarization excitation spectrum of *Rhodopseudomonas viridis* reaction centers is similar to those obtained with *Rps. sphaeroides* R-26 and 2-4-1 reaction centers. However, the absorption spectrum and photoinduced absorption changes are much better resolved, especially at low temperature, than in bacteriochlorophyll (BChl) *a*-containing reaction centers. This allows the separation of band shifts from bleaching in the light-induced difference spectra. In particular, the absorption band bleaching observed at 850 nm is shown to occur perpendicular to the 1000 nm long-wavelength band. This lends strong support to the assignment of the 850 nm band to the second excitonic component of the special pair. 'Voyeur' BChl absorption changes (presumably band shifts) upon photoformation of state $P^+Q_1^-$ are difficult to analyze quantitatively. The polarization values for these absorption changes are not easily reconcilable simply with absorption band shifts. We suggest that the relative orientation between the voyeur BChl transition moments and the long-wavelength transitions changes after charge separation. This reorientation may be responsible for the slow rate of back reaction between P^+ and Q_1^-. At 4.2 K two bands are apparent in the long-wavelength absorption band. We propose that this structure is due to a charge-transfer state between the special pair and B, the primary BChl acceptor. Finally, we show that the low extinction coefficient of the absorption band at 808 nm, and the appearance of the long-wavelength band (1300 nm) for the neutral BChl molecule left after photooxidation of one molecule of the special pair, can be explained in terms of quantum mechanics.

Introduction

The first photochemical event in purple bacterial photosynthesis occurs in a chromoprotein termed the reaction center in which four molecules of bacteriochlorophyll (BChl) and two molecules of bacteriopheophytin (BPh) are bound noncovalently [1]. After absorption of light by a special pair of BChl (P-870, P or $(BChl)_2$), an electron is transferred from the excited state $(BChl)_2^*$ to a BChl (B) absorbing at about 800 nm in less than 1 ps [2]. Subsequent electron transfer from this BChl to one of the two BPh (H) takes about 4 ps [3]. Under normal conditions, the electron then moves from the BPh to a quinone (Q_1) in 200 ps [4,5]. This photoinduced electron transfer occurs with a quantum yield of unity [6]. The origin of this extremely efficient light-induced charge separation and stabilization (a factor of 10^8 is measured between the rate constant of the forward and back

Abbreviations: BChl, bacteriochlorophyll, BPh, bacteriopheophytin.

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reactions of the state $(BChl)_2^+ Q_1^-$) is currently not understood. Some theoretical explanations have, however, been recently proposed [7]. Knowledge of both thermodynamic parameters and structural information is necessary for an adequate description of these photochemical processes.

In recent years, an angular relationship between the two BChl of the dimeric primary donor or (and) between the different transition moments of the reaction center chromophores has been obtained from photoselection [8–11] and magneto-photoselection [12,13] experiments and analysis of the ESR parameters of the P triplet state [14]. Completely different pictures of the arrangement of the BChl in the reaction center have, however, been proposed from photoselection studies [8,9,11]. The main controversy arises from the different attribution of the reaction center spectral components and the interpretation of the absorption changes occurring upon photooxidation of the special pair.

Shuvalov and co-workers [8,9] propose that the special pair presents a single band absorbing at 870 nm (BChl *a* reaction center) or 970 nm (BChl *b* reaction center). This implies, from excitonic coupling theory [15], that the Q_y transition moments of the two BChl of the special pair are parallel. Other absorption changes observed in the near infrared region are interpreted as band shifts of the two voyeur BChl and appearance of a monomer-like BChl absorption band [9]. In the alternative model of Vermeglio and Clayton [10,11,16–18] the special pair possesses two distinct excitonic components (870 and 805 nm for the BChl *a* reaction center, and 970 and 850 nm for the BChl *b* reaction center). It follows from excitonic coupling theory [15] that the Q_y transition moments of the BChl in the special pair are not parallel in the latter model.

Both models are, however, not easily reconciled with some features of the absorption spectrum of reaction centers:

(1) The half bandwidth of the long-wavelength dimer band is much greater than that expected from excitonic theory where it has to be narrower by a factor of $1/\sqrt{2}$ than monomeric BChl.

(2) The extinction coefficient of the new absorption band attributed in both models [9,14, 19,20] to a monomer-like BChl molecule upon photooxidation of one of the BChl dimers is much smaller than expected. Moreover, in the model of Vermeglio and Clayton, this absorption band is predicted to absorb around 918 nm for *Rhodopseudomonas viridis* reaction centers instead of 808 nm as observed [19,20].

In the present report, the absorption spectrum together with the light-induced difference spectra of state $P^+ Q_1^-$ and PH^- were recorded at 4.2 K for *Rps. viridis* reaction centers to allow a better attribution of the different absorption components. Photoselection experiments were done at different temperatures to discriminate between absorption band shifts and bleaching. These photoselection experiments were performed under conditions of high polarization values [11] in contrast to the previous report of Shuvalov and Asadov [9] for the same species.

Materials and Methods

Rps. viridis reaction centers were prepared as described by Clayton and Clayton [21].

Photoselection experiments were performed essentially as described in Ref. 11. A monochromator (Jobin Yvon H_{20} IR) was placed between the sample and the detector to prevent scattered exciting light reaching the latter. Both excitation and analysis beams were linearly polarized before reaching the sample. Upon excitation with vertically polarized light, absorbance changes detected with either vertical (ΔA_V) or horizontal (ΔA_H) polarization of the analyzing beam were measured.

Results

Absorption spectrum and difference spectrum of state PH^- at helium temperature for Rps. viridis reaction centers

The helium-temperature absorption spectrum of *Rps. viridis* reaction centers (Fig. 1A, full line) presents similar but better resolved spectral forms than those observed at higher temperature (77 K) [20]. Seven absorption bands (b) or shoulders (s) are observed: around 788 nm (b), 810 nm (b), 820 nm (b), 833 nm (b), 850 nm (s), 996 nm (b) and 1010 nm (s). For certain preparations of reaction centers the 820 nm band was not apparent (see Fig. 3A). Its amplitude compared to other reaction

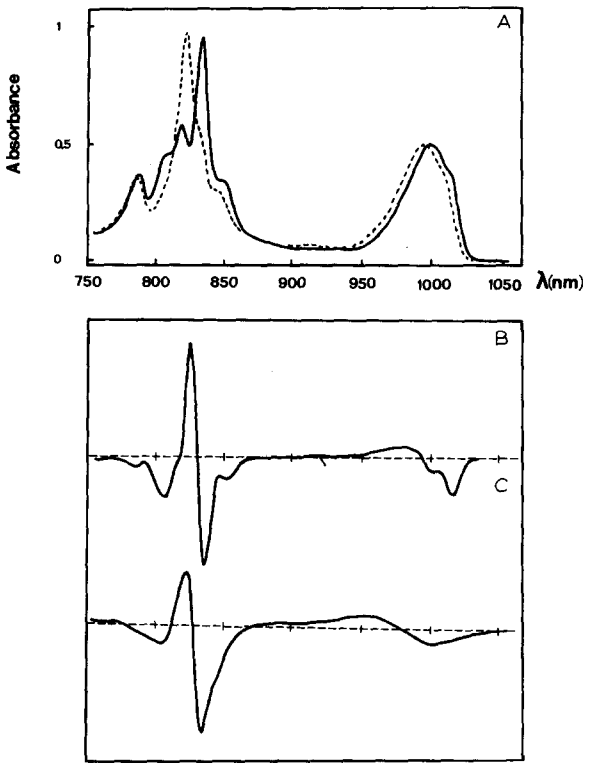

Fig. 1. (A) Absorption spectrum, recorded with a Cary 17 spectrophotometer, of *Rps. viridis* reaction centers suspended in 0.1%, lauryldimethylamine *N*-oxide, 10 mM Tris-HCl buffer (pH 7), 30% glycerol (v/v) in the presence of a few grains of dithionite. (———) Spectrum recorded at 4.2 K after dark adaptation (5 min) at room temperature (state PIQ^-). (- - - - - -) Spectrum recorded at 4.2 K after strong side illumination at this temperature (state PI^-Q^-). (B) Difference spectrum obtained by subtraction of the two spectra shown in A (temperature 4.2 K). (C) Same as B but the sample temperature was 180 K.

center absorption bands varies from preparation to preparation, therefore, we believe that it is partly due to a contaminant. The shoulder at 1010 nm observed on the long-wavelength absorption band has not been reported previously. It is only observable at very low temperature. We shall return to its attribution in the Discussion.

In a previous work [17], we proposed from the analysis of the linear dichroism of absorbance changes measured on oriented whole cells for state PH^- that the spectral form absorbing around 850 nm was involved in the light-induced difference spectrum. Because the 850 nm spectral form is clearly resolved from the main 833 nm absorption band at helium temperature (Figs. 1A, full line, and 3A), it is possible to check this hypothesis by recording the light-induced difference spectrum of this state at that temperature. After strong illumination at 4.2 K of the reaction center suspension in the presence of dithionite (photoconversion to state PH^-), the oscillatory strength of the 850 nm band is diminished (Fig. 1A, dotted line). This is clearly shown in the light minus dark difference spectrum (Fig. 1B). Three other observations can be made from this low-temperature difference spectrum:

(a) The BPh molecule involved in state PH^- absorbs around 810 nm as shown by the net through at this wavelength (Fig. 1B).

(b) The 833 nm absorption band shifts to 822 nm.

(c) The shape of the light minus dark difference spectrum in the long-wavelength region (950–1050 nm) clearly reveals the composite structure of the long-wavelength absorption. For comparison, the spectrum of state PH^- recorded at 180 K, where such features are not revealed because of the higher temperature, is also shown (Fig. 1C).

Polarization excitation spectrum of Rps. viridis reaction centers at 4.2 K

Fig. 2 shows the absorption changes occurring at 970 nm for both vertical (ΔA_V) and horizontal (ΔA_H) polarization of the analyzing beam, induced by excitation of an isotropic suspension of *Rps. viridis* reaction centers with 1000 nm vertically polarized light. The temperature of the sample was 4.2 K. The polarization value $P = (\Delta A_V -$

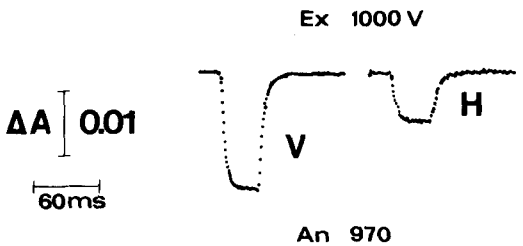

Fig. 2. Kinetics of absorbance changes induced in *Rps. viridis* reaction centers at 4.2 K by 1000 nm vertically polarized light. The analyzing beam was set at 970 nm and was polarized either vertically (V) or horizontally (H).

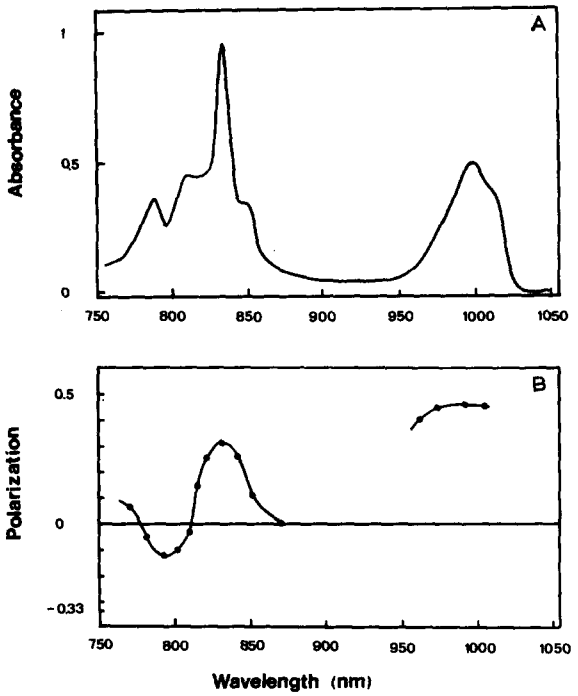

Fig. 3. (A) Absorption spectrum of *Rps. viridis* reaction centers recorded at 4.2 K with a Cary 17 spectrophotometer. (B) Polarization excitation spectrum of the bleaching observed at 970 nm. The polarization values were calculated from data similar to those shown in Fig. 2 but for different excitation wavelength.

$\Delta A_H)/(\Delta A_V + \Delta A_H)$ is equal to $+0.46$, in agreement with values reported for *Rps. sphaeroides* reaction centers [10,11], and with the value obtained for the rapidly decaying component for *Rps. viridis* reaction centers [9]. Our polarization value ($P = +0.46$) is significant higher than that measured by Shuvalov and Asadov [9] for the total absorption changes. This difference is due to our experimental conditions where the amount of reaction centers back reacting with a slow rate was minimized by blocking electron transfer between primary and secondary electron acceptors by addition of 4 mM *o*-phenanthroline [11].

Polarization values of the absorption changes detected at 1000 nm, calculated from experiments similar to those of Fig. 2, are plotted in Fig. 3B for different excitation wavelengths.

Polarization of light-induced absorption changes of state $P^+Q_I^-$ upon excitation within the 1000 nm absorption band at different temperatures

Because each reaction center's chromophores give different (absorption band shift, bleaching, etc.) or even no contribution to the total light-induced absorption difference spectrum, additional information will be provided by the analysis of the polarization values of the absorbance changes occurring at different wavelengths.

Light-induced absorption changes occurring at 160 K upon excitation of a suspension of reaction centers are plotted in Fig. 4A. Both analysis and excitation beams were unpolarized. Fig. 4B shows the absorption changes occurring either parallel ($\Delta A_{\parallel} = 2\Delta A_V - \Delta A_H$) or perpendicular ($\Delta A_{\perp} = 3\Delta A_H - \Delta A_V$) to the 1000 nm absorption. These difference spectra are calculated [11] from the experimental values of the absorption changes ΔA_V and ΔA_H, measured for the two polarizations (vertical and horizontal) of the analyzing beam

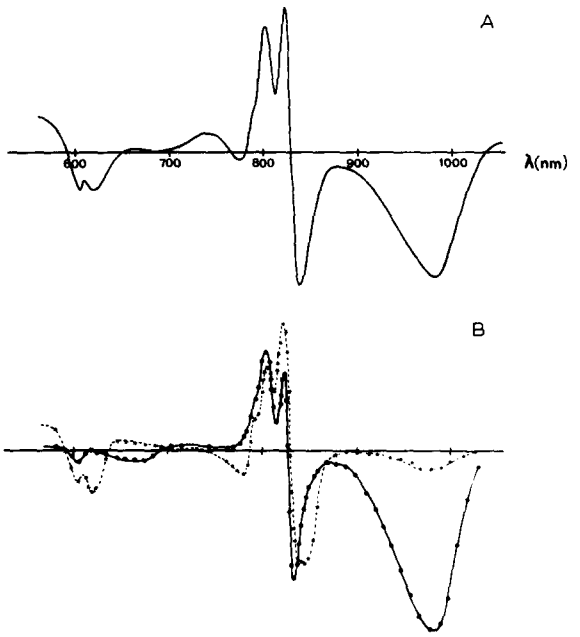

Fig. 4. (Upper) Difference spectrum observed for state P^+Q^-, at 160 K, with unpolarized light in the excitation and detection. (Lower) Difference spectra induced by 970 nm vertically polarized light occurring either parallel ($\Delta A_{\parallel}$, ●———●) or perpendicular ($\Delta A_{\perp}$, ★------★) to the excited transition calculated from the experimental values ΔA_V and ΔA_H. Temperature 160 K.

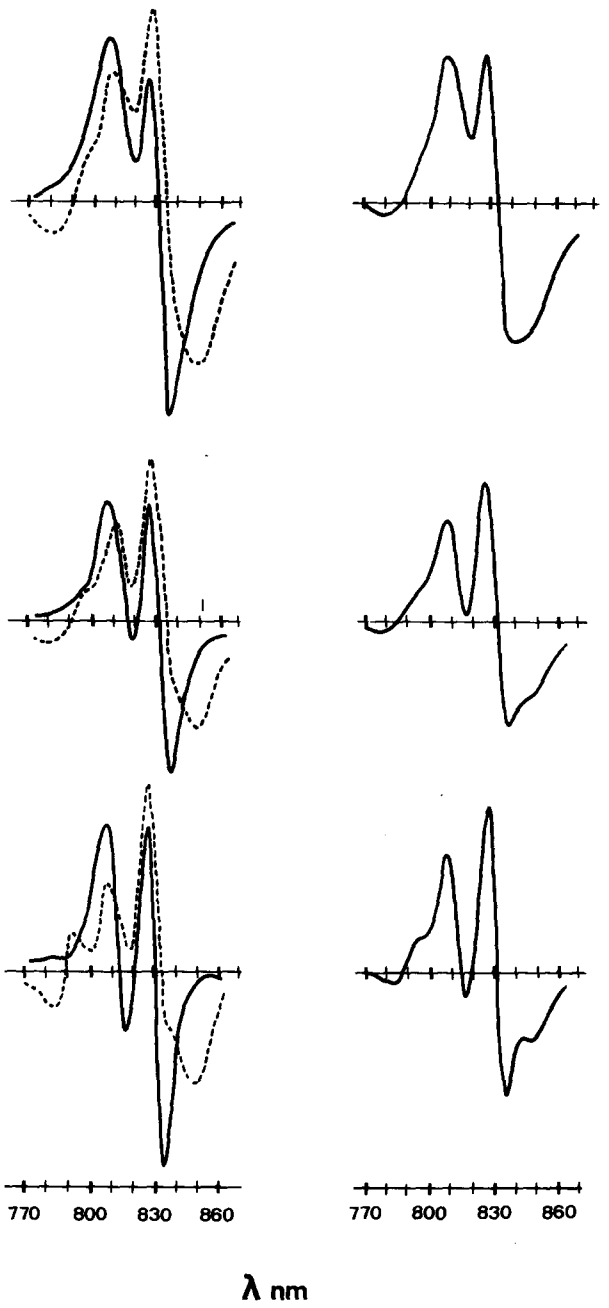

Fig. 5. (Left) Difference spectra induced by 1000 nm vertically polarized light occurring either parallel ($\Delta A_{\parallel}$, ———) or perpendicular ($\Delta A_{\perp}$, - - - - - -) to the excited transition (1000 nm), recorded at three temperatures 160 (upper), 77 (center) and 4.2 (lower). (Right) Difference spectra obtained with unpolarized light (detection and excitation) for the same three temperatures.

upon excitation with 1000 nm vertically polarized light.

To appreciate the contribution of bleaching and absorption band shifts in the 780–870 nm region, similar experiments were repeated at different temperatures. The results are summarized in Fig. 5 for 160, 77 and 4.2 K. From each temperature the polarization value of the bleaching measured at 970 nm upon excitation at 1000 nm was 0.45 ± 0.02.

Discussion

Attributions of absorption bands and interpretations of light-induced difference spectra are of prime importance in the analysis of photoselection experiments. But before discussing in detail these assignments, we can notice the similarity of the shape of the polarization excitation spectrum reported for *Rps. sphaeroides* 2-4-1 and R-26 reaction centers [11] and that depicted in Fig. 3B for the *Rps. viridis* reaction centers: high values of the polarization ($P = +0.45$) for the long-wavelength absorption band, and the BChl molecules absorbing at shorter wavelength (802 nm *Rps. sphaeroides* reaction center and 833 nm *Rps. viridis* reaction center) ($P = +0.33$) and a negative value in the BPh Q_y absorption region ($P = -0.13$). This emphasizes the structural similarity between BChl *a*- and BChl *b*-containing reaction centers, giving a more general purpose to our discussion [20].

The helium-temperature absorption spectrum of *Rps. viridis* reaction centers reveals six intrinsic bands or shoulders (see Fig. 1A and 3A) at 788, 810, 833, 850, 996 and 1010 nm. We will not discuss the attribution of the 820 nm band (Fig. 1A), since it is not clear at the present time if this component is an intrinsic part of the reaction center.

From the clear absorption decrease observed at 810 nm in the light minus dark difference spectrum of state PH^- recorded at 4.2 K (Fig. 1B), we deduce that the BPh molecule involved in that state absorbs at this wavelength. Because of its wavelength position, the 788 nm band can be attributed to the Q_y transition of the second BPh molecule of the reaction center. We propose that both voyeur BChl absorb at 833 nm rather than 833 and 850 nm, as suggested by Shuvalov and

Asadov [9]. This bring us to the interpretation of the shoulder at 850 nm in the absorption spectrum (Figs. 1A and 3A). It has been proposed from the shape of the oxidized minus reduced difference spectrum of *Rps. viridis* reaction centers at 77 K [20] and from linear dichroism spectra of oriented *Rps. viridis* cells at room temperature [17] that the 850 nm shoulder is one of the two excitonic transition moments of the special pair (the other one absorbing around 1000 nm). This assignment implies, according to the theory of Kasha et al. [15], that these two bands are mutually perpendicular and that both will bleach upon disruption of the special pair by photooxidation of one of the BChl molecules. The behavior of the absorption decrease at 850 nm (Fig. 5) as a function of temperature is characteristic of a bleaching rather than an absorption band shift. Moreover, this 850 nm bleaching occurs mainly in a direction perpendicular to the 1000 nm band as shown by the photoselection experiments depicted in Fig. 5. This result, i.e., 850 nm bleaching perpendicular to the 1000 nm band, is strong support for the attribution of the 850 and 1000 nm bands to the two excitonic components of the special pair.

The interpretation of the absorbance changes occurring in state $P^+Q_1^-$ is quite complex (Figs. 4 and 5), in particular in the 780–870 nm region. From the temperature dependence of these changes we propose different contributions:

(a) Between 780 and 800 nm band shift of the 788 nm BPh molecule;

(b) Appearance around 808 nm of a monomer-like BChl molecule [9,17,19,20] and possibly band shift of the 810 nm BPh molecule;

(c) The absorbance changes between 815 and 840 nm can be described by band shifts in opposite directions to the two voyeur BChl molecules or by a band shift to shorter wavelength and narrowing of the bandwidth of the 833 nm transitions.

(d) Bleaching around 850 nm of the excitonic transitions of the special pair. Confident with the above interpretations of the light-induced absorption changes in state $P^+Q_1^-$, we can go further into our analysis of the photoselection experiments (Figs. 4 and 5). The absorbance changes occurring either parallel or perpendicular to the long-wavelength absorption band (1000 nm) have been calculated [11] (Fig. 5) from photoselection experiments similar to those reported in Fig. 4. Between 780 nm and 800 nm the BPh Q_y bandshift appears uniquely in the perpendicular difference spectrum (Fig. 5), in agreement with previous results obtained with the BChl *a* reaction center [8,11] and with the negative value of the polarization measured in this region of the excitation spectrum (Fig. 3B). As already pointed out, the bleaching around 850 nm occurs mainly in the perpendicular difference spectrum (Fig. 5). More difficult to analyze are the absorption changes observed between 815 and 840 nm. The difference spectra, in particular in the perpendicular direction, are not conservative (the areas above and below the baseline are not equal). This can be explained only if one supposes different orientation between the 833 nm transitions and the long-wavelength band before and after charge separation. Two nonexclusive hypotheses can account for this change of orientation:

(1) The 833 nm BChl(s) molecular framework moves in the reaction center complex;

(2) The electronic transition Q_y of these molecules occurs in a different direction in the molecular framework due to a reorganization of the π-electron cloud.

This photoinduced movement or reorganization of the π-electron cloud of the 833 nm BChl molecule(s), one of which at least is involved in electron transfer from P to Q_1, may be an excellent way to prevent wasteful back reactions. However, a more quantitative analysis of the absorption changes is necessary to prove definitively these hypotheses. This will require photoselection experiments with excitation at different wavelengths and deconvolution of absorbance changes.

Our interpretation of the absorption spectrum of *Rps. viridis* reaction center, in particular the assignments of the 850 and 1000 nm bands to the two excitonic components of the special pair, poses some problems, however. As already pointed out in the Introduction, in the excitonic coupling theory [15] (even if one does not accept the idea of an allowed transition at 850 nm), the bandwidth of the 1000 nm band has to be narrower by a factor of $1/\sqrt{2}$ than the monomeric one. The opposite is observed: the 1000 nm band is about twice as broad as expected. To explain this discrepancy we have already proposed some hypothe-

ses [11]. This broadening could be due to:

(1) Heterogeneity: for each reaction center, the special pair can have different configuration states in equilibrium.

(2) Dependence of the resonance interaction between the two BChl on their vibrational mode [22].

(3) Existence of several electronic transitions under the 1000 nm band.

The appearance of a shoulder in the 1000 nm band in the absorption spectrum recorded at 4.2 K (Figs. 1A and 3A) favors the last hypothesis. Two experiments show that this shoulder is an intrinsic absorption band of the complex and is not due to undissociated antennae or two different populations of reaction center.

(1) The same structure is observed in the bleaching of the long-wavelength band measured at 4.2 K in state $P^+Q_1^-$ for both isolated reaction centers [23] and untreated chromatophores (data not shown).

(2) Upon photoconversion to state PH^- at 4.2 K (Fig. 1B), both bands (the shoulder at 1010 nm and the mean band at 996 nm) are affected.

The fact that the polarization ratio is constant within the long-wavelength band (Fig. 3) and that the circular dichroism spectrum [9] does not present an S-shaped signal in this wavelength region suggests the following assignments:

One of these energy levels is the first excited singlet state of the special pair.

The other level, singlet also, can be photoexcited only if it is energetically coupled to the first excited singlet state. Such a level can be a charge-transfer state. In other terms, the energy coupling between the first excited singlet state and a charge-transfer state gives rise to two distinct transitions. The light absorption probability of the special pair P is spread equally over these two levels, leading to a broadening of the $P \rightarrow P^*$ transition. Coupling between electron and nucleus motions can be different for the first excited state P* and for the charge-transfer state, causing a supplementary broadening.

Such a charge-transfer state can exist for the special pair itself ($BChl^+BChl^-$) or, as proposed by Shuvalov and Parson [24], between the special pair P and B, a BChl molecule initial acceptor of an electron from P*. Consistent with the later proposition is the rapid electron-transfer rate (within 1 ps) between P and B [25]. The energy difference between the first excited singlet state P* and the singlet ionized state $^1(P^+B^-)$ has been estimated to be 0.025 eV by Shuvalov and Parson [24]. From the difference in wavelength position of the two transitions resolved in the 1000 nm absorption band, i.e., 995 and 1010 nm, we can estimate the energy difference between these two levels to be equal to 0.0185 eV. This value is smaller than that obtained by Shuvalov and Parson [24]. However, the state $^1(P^+B^-)$ considered by these authors is in the nucleus equilibrium configuration, when in the case of absorption the state P^+B^- has to be considered in the nucleus equilibrium configuration of the ground state. Furthermore, from the qualitative formula of Hopfield [25] we can estimate an edge-to-edge distance between P and B of 3.5 Å. A similar value (3.1 Å) has been estimated by Shuvalov and Parson [24] from the difference in energy between the $^1(P^+B^-)$ and $^3(P^+B^-)$ states.

A second problem concerns the attribution of the band appearing at 808 nm to a monomeric BChl upon photooxidation of one molecule of the special pair P [9,18–20]. The oscillatory strength of this 808 nm band is much smaller than expected (i.e., equivalent to one BChl molecule absorption band). Moreover, this band does not appear between the 850 and 1000 nm bands, specifically at 918 nm, as predicted by the model of Vermeglio and Clayton [10,16,17]. These anomalies can be explained if one considers the effects of the unpaired electron of $BChl^+$ on the other BChl. The first one is the ordinary electrochromic effect that induces a shift of the monomer absorption band. But there is also a quantum effect which is described in more detail in the Appendix. Because of the presence of the unpaired electron with spin 1/2, a mixing of the BChl singlet and triplet excited state arises. Thus, when the monomer of BChl has only one allowed transition from the ground state S_0 to the first singlet excited state S_1, the transition to the first triplet excited state T_1 being forbidden, the oxidized special pair ($BChl^+$ BChl) has two allowed transitions to the states S_1' and T_1' which both have some singlet character. As compared to S_1, the excitation energy of S_1' is higher and the corresponding oscillation strength

is smaller. On the other hand, a second absorption band must appear in the infrared region. This second band corresponds to a transition to T_1'. A similar explanation has been proposed by Shuvalov and Parson [24] to account for the long-wavelength (1300 nm) band appearing in oxidized reaction centers. The amplitude of this effect depends on two parameters W and W'. They are, respectively, equal to half of the singlet-triplet splitting of the two species (BChl BChl)* (special pair excited) and ($BChl^+$ $BChl^-$) (biradical). When W and W' are comparable two bands are expected. This is very likely the case for the special pair, since one observes too small an absorption band at 808 nm and an extra absorption band around 1300 nm. The difference of energy between these two transitions (0.58 eV) is compatible with Eqn. A.2 of the Appendix if one assumes that W' is about 0.3 eV. It must be noted that this value is also in agreement with the large shift toward the infrared observed for the 'true' absorption band of the monomer (918 nm) as compared to the voyeur BChl (833 nm). Such a large value of W' implies that the two BChl molecules of the special pair are in strong interaction. Applying the same formula as that of Shuvalov and Parson [24] which gives the edge-to-edge distance r between the interacting molecules of a biradical as a function of the singlet-triplet splitting W', one obtains $r = 2.8$ Å. Furthermore, one can expect, because of the value of W', that the singlet excited states of the special pair have some charge-transfer character which facilitates the electron donation to B.

The quantum effect of the unpaired electron can also occur for the voyeur BChl molecules and especially for B which must be located near the special pair (between 3 and 4 Å) (Ref. 24, and this paper). According to Shuvalov and Parson [24], in the case of the pair P^+B, W' is again rather large and equal to 0.18 eV. Introducing this value into Eqn. A.3 of the Appendix one can predict a decrease of about 10% of the oscillatory strength of the B absorption band in state P^+B. This may explain in part the asymmetric and complex shape of the absorption band shifts around 833 nm (see Fig. 5).

Table I summarizes our assignments for the near-infrared absorption bands of *Rps. viridis* reaction centers at 4.2 K. These assignments are essentially the same as those proposed by Thornber et al. [20] except for the 810 nm band attributed by these authors to a voyeur BChl Q_y transition.

TABLE I

Absorption band (nm)		Assignments
P	P^+	
≈788	≈790	BPh *b* Q_y transition
	808	Transition, with singlet character of the monomer in the photooxidized special pair
810		BPh *b* Q_y transition, involved in H^-
833	830	Two voyeur BChl
850	bleached	Excitonic component of the special pair
996	bleached	Excitonic component of the special pair, split by the coupling with a charge transfer state
1010		
	1300	Transition, with triplet character of the monomer in the photooxidized special pair

Appendix

Let us consider the pair $[B_1^+ \; B_2]$ where B_1^+ is a BChl radical cation and B_2 a BChl molecule. In order to analyze in a very simple way the optical properties of such a pair, we only consider three energy levels described by one-electron orbital functions:

(i) the orbital of the unpaired electron of B_1^+ : a_1 or $\tilde{a}_1$ according to the spin projection is $M_S = 1/2$ or $M_S = -1/2$;

(ii) the upper filled orbital of the ground state of B_2: a_2 or $\tilde{a}_2$ ($M_S = 1/2$ or $-1/2$);

(iii) the lowest vacant orbital of the ground state of B_2: b_2 or $\tilde{b}_2$. We start from a ground state where $M_S = 1/2$ for the radical B_1^+. When there is only one allowed transition for the free molecule B_2, two excited states of the pair can be reached under the action of light. One can specify these states by the two basis wave functions ψ_1 and ψ_2:

$$\psi_1 = \frac{1}{\sqrt{2}}\left(a_1 a_2 \tilde{b}_2 - a_1 \tilde{a}_2 b_2\right)$$

$$\psi_2 = \frac{1}{\sqrt{6}}\left(a_1 a_2 \tilde{b}_2 + a_1 \tilde{a}_2 b_2 - 2\tilde{a}_1 a_2 b_2\right)$$

The first function has a singlet character for B_2 and the second a triplet one. The matrix elements of the Hamiltonian are:

$$\mathcal{H}_{11} = E + \frac{W' - W''}{2} + V$$

$$\mathcal{H}_{22} = E - 2(W - W'') + \frac{3(W' - W'')}{2} + V \qquad \text{(A.1)}$$

$$\mathcal{H}_{12} = \mathcal{H}_{21} = \frac{\sqrt{3}}{2}(W' - W'')$$

Where E is the excitation energy of the first singlet state of B_2 in the presence of B_1 instead of B_1^+, V the classical electrical effect of the positive charge on B_2 and W, W' and W'' the exchange integrals between the orbitals a_2b_2, a_1b_2 and a_1a_2, respectively. Consequently, W, W' and W'' are half of the difference between the singlet and triplet states of the following species: B_2 excited, biradical pair $B_1^+ B_2^-$ and biradical pair $B_1^+ B_2^+$.

For a BChl molecule $W = 0.2$ according to Ref. 24 or 0.29 according to Seely [26]. Very likely, in the case of a reaction center W'' is small, since the interactions between BChl molecules in the ground state are relatively small [1]. In contrast, W' may be large. This is the case, for instance, for the biradical (P^+B^-) where $W' = 0.18$ [24].

According to Eqn. A.1, when W'' is negligible, the excitation energies of the two resulting transitions are:

$$E_1 = E + (W' - W) + (W^2 - WW' + W'^2)^{1/2} + V \qquad \text{(A.2)}$$

$$E_2 = E + (W' - W) - (W^2 - WW' + W'^2)^{1/2} + V$$

with the oscillatory strength:

$$f_1 = f_0\left(1/2 + \frac{2W - W'}{2(E_1 - E_2)}\right) \quad f_2 = f_0(1 - f_1)$$

where f_0 is the oscillatory strength of the allowed transition to the first singlet state for molecule B_2.

For instance, if $W \simeq W'$:

$$E_1 = E + W + V$$

$$E_2 = E - W + V \qquad \text{(A.3)}$$

$$f_1 = \tfrac{3}{4} f_0 \quad f_2 = \tfrac{1}{4} f_0$$

Of course this treatment is a first approximation which must be used cautiously for accurate quantitative calculations.

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