

## Uphill Energy Trapping by Reaction Center in Bacterial Photosynthesis. 2. Unistep Charge Separation, Virtually Mediated by Special Pair, by Photoexcitation in Place of Excitation Transfer from the Antenna System

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In photosynthesis of purple bacteria, excitation energy of bacteriochlorophylls in the core antenna LH1 is transferred to the excited state ( $P^*$ ) of the special pair (P) in the reaction center (RC). Subsequently, charge separation to the adjacent monomeric bacteriochlorophyll (B) occurs from  $P^*$ , producing  $P^+B^-$  as initial energy fixation in the RC. Although the absorption-peak energy of P is appreciably (by 200–430  $\text{cm}^{-1}$ ) higher than that of the lowest excited state  $LH1^*$  of LH1, these sequential events occur still at low temperatures for the energy trapping in *Rhodobacter sphaeroides*, while in *Rhodospseudomonas viridis*  $LH1^*$  is unistep converted to  $P^+B^-$  in the RC by the superexchange mechanism due to quantum-mechanical virtual mediation by  $P^*$  at low temperatures, as clarified in part 1 (Sumi, H. *J. Phys. Chem. B* 2002, 106, 13370). Such differences arise since in the free energy  $LH1^*$  is slightly (by  $\sim 50 \text{ cm}^{-1}$ ) higher than  $P^*$  in *Rb. sphaeroides*, while in *Rps. viridis*  $LH1^*$  is still considerably ( $\sim 150 \text{ cm}^{-1}$ ) lower than  $P^*$  in the free energy, after reorganization of the medium around  $P^*$ . An experiment is proposed to investigate unifiedly such differences, by photoexcitation of a single RC from either *Rb. sphaeroides* or *Rps. viridis*. When the photon energy  $E$  is higher than about the free energy  $E_0$  for  $P^*$ , the production rate of  $P^+B^-$ , measurable as the rate of absorption by the RC, will be nearly equal to that by  $P^*$ , measurable as its excitation spectrum, at all temperatures by the sequential mechanism. When  $E$  is considerably lower than  $E_0$ , the former will become much larger than the latter at low temperatures by the superexchange mechanism. The photoinduced production rate of  $P^+B^-$  mediated by  $P^*$  is given as an analytic formula bridging the two limits, for analyzing such observations expected.

### I. Introduction

In the primary process of photosynthesis, the solar energy is first harvested by the antenna system as electronic excitations of pigments therein. The excitation energies are transferred among pigments toward the reaction center (RC) and trapped by it. The RC is a transmembrane protein–pigment complex, whose three-dimensional structure was clarified first for photosynthetic purple non-sulfur bacteria in 1984.<sup>1</sup> The excitation energy trapped by the RC is fixed initially as an electrochemical energy in a state of a pigment pair charge separated against the transmembrane electrostatic-potential gradient in the RC. The RC is enclosed by the core antenna LH1 in purple bacteria, and it is surrounded by a peripheral antenna system composed of LH2s and LH3s.<sup>2</sup> They are also a transmembrane protein–pigment complex, whose three-dimensional structure was clarified for LH2 in 1995,<sup>2</sup> and for LH3 in 2001.<sup>3</sup>

Pigments immersed in the RC constitute two strands which are in the 2-fold rotational symmetry. Pigments in both LH2 and LH3 are arranged to form a beautiful ring with the 9- or 8-fold rotational symmetry depending on species. It was shown also for purple bacteria that pigments in LH1 are arranged to form a ring with the much higher (16-fold) rotational symmetry.<sup>4</sup> It seems, however, that LH1 has a complete ring structure only when it is reconstituted from detergent-solubilized protein complexes.<sup>5</sup> It has been shown, in fact, as an image of electron microscopy, that LH1 enclosing the RC in an intact membrane has a C-shaped open structure with a cut of about one-fourth of the whole ring.<sup>6</sup> Very recently, X-ray structure determination

was reported for the LH1–RC complex that LH1 with an oval shape fitting roughly the outer rim of the RC inside has an open break on the short oval axis.<sup>7</sup> Such a break in the structure of LH1 plays an important role in giving an appreciable value to the coupling for excitation-energy trapping by the RC from LH1 in their complex<sup>8</sup> as well as giving a hole for quinone exchange.

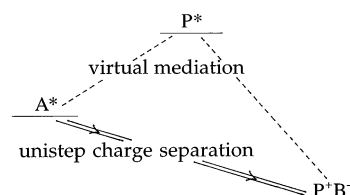
The present work is devoted to proposing an experiment for investigating this energy trapping process by the RC, by means of direct photoexcitation of the RC in place of excitation transfer from LH1.<sup>9</sup> Since the experiment reflects the specific features in the excitation-energy trapping by the RC from LH1, let us begin with briefly surveying them below, before explaining the experiment. The excitation-energy trapping by the RC is a crucial process, being rate-limiting in the whole primary events of photosynthesis which range from solar-energy harvesting by the antenna system through initial energy fixation in the RC.<sup>10,11</sup> It begins with excitation transfer from the core antenna to the (so-called) special pair (P) of bacteriochlorophylls in bacterial photosynthesis (alternatively, to that of chlorophylls in higher plants and algae) in the RC.<sup>1,2</sup> As the initial energy fixation, the excitation of P is very rapidly converted to a state of charge separation along only one of the pigment strands within the RC by transferring an electron to the primary acceptor, that is bacteriopheophytin (H) in purple bacteria. The distance between P and H is so large ( $\sim 17 \text{ \AA}$ ) that the electron transfer from P to H is mediated stepwise by a pigment (B) located between.<sup>12</sup> Accordingly, the initial charge-separated state produced in the RC is  $P^+B^-$ , and it is produced  $\sim 3 \text{ ps}$  after excitation of P in purple bacteria, where B is a bacteriochlorophyll monomer. Unless otherwise noted hereafter, the present work explicitly

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treats purple bacteria, since both structural and kinetic data have most been accumulated for them, where the core antenna is LH1 mentioned above.

Excitations of antenna pigments are transferred from LH3 to LH2 and from LH2 to LH1 toward the RC in purple bacteria. Their excitation energies are arranged in such a way that they decrease from LH3 toward LH2 and from LH2 toward LH1.<sup>2,13</sup> This situation is called the funnel structure, along which an electronic excitation flows down toward its central sink. Excitation energies thus collected into the core antenna LH1 are trapped by the special pair P in the RC. Curiously, however, the excitation energies rise from LH1 to P at the last step of the excitation-energy flow.<sup>10</sup> Such a situation has been described in terms of red pigments in the core antenna. The uphill excitation-energy difference  $\Delta E$  amounts to  $\sim 200\text{ cm}^{-1}$  in *Rhodobacter (Rb.) sphaeroides* in purple non-sulfur bacteria, i.e., to a value comparable to the thermal energy of  $\sim 210\text{ cm}^{-1}$  at room temperature.<sup>14</sup> In *Rhodospseudomonas (Rps.) viridis* therein,  $\Delta E$  is considerably larger than the thermal energy, amounting to  $\sim 350\text{--}400\text{ cm}^{-1}$ .<sup>15</sup> Amounting to  $\sim 430\text{ cm}^{-1}$ ,  $\Delta E$  becomes much larger than the thermal energy in a recently isolated species of purple sulfur bacteria, provisionally called strain 970.<sup>16</sup> Nevertheless, the time constant for excitation-energy trapping from LH1 by the RC is nearly uniform among these species at room temperature, with magnitudes of about several dozens of picoseconds.<sup>16,17</sup> The fact that the excitation-energy trapping by the RC takes place via uphill energy transfer to  $P^*$  in the RC from the red pigments in the core antenna has been known widely in photosynthesis<sup>14</sup> also in higher plants and algae<sup>18</sup> as well as in other photosynthetic bacteria<sup>7,15b,17a,19</sup> with nearly the same magnitudes of its time constant. But both the origin and the meaning of such uniformity in the time constant has not well been rationalized.<sup>16,18a,19b,f</sup>

In ref 8 which is called part 1 hereafter, the present author clarified theoretically that at room temperature, the excitation-energy trapping by the RC in both *Rb. sphaeroides* and *Rps. viridis* proceeds by the ordinary-sequential mechanism, where formation of the charge separated state  $P^+B^-$  from  $P^*$  follows excitation transfer to P from the lowest excited state LH1\* of the core antenna LH1 after thermalization of phonons at  $P^*$ . Such a feature is accomplished by utilization of the thermal energy at room temperature in combination with a large width of the absorption peak of  $P^*$ . In fact, its half-width at half-maximum amounts to  $\sim 380\text{ cm}^{-1}$  at room temperature, being comparable to the uphill excitation-energy difference  $\Delta E$  from LH1\* to  $P^*$  even in *Rps. viridis*. This width is mainly caused by interaction with vibrations of the protein medium around  $P^*$ . Because of this interaction, the energy of  $P^*$  relaxes after its photoexcitation due to reorganization of the surrounding medium. The reorganization energy amounts to  $\sim 250\text{ cm}^{-1}$ ,<sup>20</sup> and the energy of  $P^*$  thus relaxed gives its free energy. As a result,  $P^*$  becomes lower in the free energy than LH1\* slightly by  $\sim 50\text{ cm}^{-1}$  in *Rb. sphaeroides*,<sup>8</sup> while in *Rps. viridis*,  $P^*$  is still higher than LH1\* appreciably by  $\sim 150\text{ cm}^{-1}$ .<sup>10</sup> Reflecting this situation in the free energy, the excitation-energy trapping proceeds practically by the ordinary-sequential mechanism even at liquid-helium temperature in *Rb. sphaeroides*, with a magnitude of the rate constant similar to that observed at room temperature. In *Rps. viridis*, on the other hand, real excitation transfer from LH1\* to  $P^*$  in the ordinary-sequential mechanism becomes very difficult at such low temperatures. In *Rps. viridis*, therefore, the uphill excitation-energy trapping by the RC at low temperatures proceeds by the superexchange mechanism where LH1\* in the core antenna is unistep converted into the



**Figure 1.** Unistep charge separation to  $P^+B^-$ , via virtual mediation at the excited state  $P^*$  of the special pair P in the reaction center (RC), from the lowest excited state  $A^*$  of the core antenna in the uphill excitation-energy trapping by the RC in *Rps. viridis* at low temperatures.

charge-separated state  $P^+B^-$  in the RC through the quantum-mechanical virtual mediation by  $P^*$ , without its real formation. This situation can be illustrated as Figure 1. At 6 K, the excitation-energy trapping in *Rps. viridis* was observed to take place with a rate constant  $(1.3\text{ ns})^{-1}$ ,<sup>16b</sup> which is only  $\sim 0.04$  times as small as its room-temperature value. That value of the rate constant at 6 K is astronomically (at least  $10^{14}$  times) larger than the value expected from the ordinary-sequential mechanism.<sup>8</sup>

Such a difference in the excitation-energy trapping between *Rb. sphaeroides* and *Rps. viridis* arises only from the free-energy difference  $\Delta G$  from LH1\* to  $P^*$  such as  $\Delta G = -50\text{ cm}^{-1}$  for *Rb. sphaeroides* while  $\Delta G = +150\text{ cm}^{-1}$  for *Rps. viridis*. The free-energy difference between  $P^*$  and the charge-separated state  $P^+B^-$  within the RC might also be different between *Rb. sphaeroides* and *Rps. viridis*. This part of the difference between them, if it exists, does not play an important role in the difference in the excitation-energy trapping between them, since  $P^+B^-$  is lower than  $P^*$  and hence the charge separation from  $P^*$  to  $P^+B^-$  is much faster than the excitation transfer from LH1\* to  $P^*$  in both of them. In the first simplification, therefore, the difference in the excitation-energy trapping between *Rb. sphaeroides* and *Rps. viridis* can be regarded as caused by the difference in the energy position of the initial state  $A^*$  in Figure 1 between them.

Now, we have come to a point where the experiment proposed in the present work can be explained. The excited state  $P^*$  of P can more conveniently be produced by photoexcitation of the RC than by excitation transfer from LH1 in the natural system.<sup>9</sup> In the photoexcitation, moreover, the energy position of the initial state  $A^*$  in Figure 1 corresponds to the photon energy, and it can easily be varied artificially. We expect, accordingly, that the difference in the excitation-energy trapping between *Rb. sphaeroides* and *Rps. viridis* could be investigated in a unified fashion by photoexcitation of a single RC, in place of excitation transfer from LH1 in the natural system, where the RC can be obtained from either *Rb. sphaeroides* or *Rps. viridis*. When the photon energy  $E$  is comparable to or larger than the free energy  $E_0$  for  $P^*$  in the RC, the trapping of the photon by the RC will proceed in the same way as the trapping of the excitation energy from LH1 in *Rb. sphaeroides*, that is, by the ordinary sequential mechanism at all temperatures. When  $E$  is considerably lower than  $E_0$ , it will proceed in the same way as that from *Rps. viridis*, that is, by the superexchange mechanism, at least at low temperatures. The present work will show the above-mentioned expectations in the experiment by explicit calculations as theoretical predictions, together with an analytic formula for describing them.

Let us describe the experiment more practically. When the ordinary-sequential mechanism takes place, a photon is absorbed by P, and subsequently charge separation takes place from  $P^*$  to  $P^+B^-$  after thermalization of phonons at  $P^*$ . The decay of  $P^*$  to  $P^+B^-$  is much faster than other decay processes of  $P^*$

including radiative ones. Accordingly, the rate for photoinduced production of the charge-separated state, giving the rate of optical absorption by the RC, will be nearly equal to that by  $P^*$ , since there exists no pigment, other than  $P^*$ , absorbing in the energy region of  $P^*$  in the RC. When the superexchange mechanism takes place, on the other hand, the charge-separated state  $P^+B^-$  is unistep produced by photoexcitation of the RC without real production of  $P^*$ , similarly to the situation in Figure 1. Although its rate still gives that of optical absorption by the RC, it will be much larger than that by  $P^*$ , which can be measured as the excitation spectrum of  $P^*$ . These alternatives will be realized when the photon energy is higher or lower than about the free energy  $E_0$  for  $P^*$ , respectively. Consequently, the absorption spectrum of the RC, to be more exact, the excitation spectrum for production of the charge-separated state therein, will be greatly enhanced from the excitation spectrum of P in its low-energy-tail region. Such an enhancement may manifest itself also as a peak in the absorption spectrum of the RC at low temperatures when the charge-separated state as the final state of optical absorption is low enough.

The present work gives as an analytic formula the rate constant for photon trapping by formation of the charge-separated state  $P^+B^-$  in the RC. The photon trapping is really mediated by  $P^*$  in the sequential mechanism, but virtually in the superexchange mechanism. These two alternatives are realized in mutually opposite limits, and in general cases between them, the photon trapping by the RC can be regarded as a single process with a definite rate constant.<sup>21</sup> The analytic formula gives this rate constant of general cases. It will therefore be conveniently utilized for analyzing the data of the rate constant in the experiment proposed here. The temperature dependence of the rate constant given by the formula will be similar to that investigated in part 1,<sup>8</sup> which treats trapping of the excitation energy from the core antenna LH1, although the excitation energy treated therein was restricted to its natural value found in LH1 from either *Rb. sphaeroides* or *Rps. viridis*. In the present work, alternatively, the  $E$  dependence of the rate constant will be given at several fixed values of the temperature.

The plan of the present work is as follows. The next section describes the theoretical framework in which the rate constant for trapping of a photon by formation of the charge-separated state in the RC is calculated, although the explicit analytic formula of the rate constant is shown in the Appendix. Calculated results and related discussions are given in section III. The final section is devoted to summarization.

## II. Framework for Calculating the Optical Absorption by Charge Separation Mediated by $P^*$

The mechanism of the photon trapping by charge separation mediated by  $P^*$  in the RC will change from the ordinary-sequential to the superexchange with a decrease in the photon energy  $E$  at low temperatures. To describe the whole  $E$  dependence of the rate constant in such a situation, we must stand on a unified treatment between the ordinary-sequential and the superexchange mediation at the intermediate state, where P is excited in the present problem. Such a treatment has been presented by Sumi and Kakitani,<sup>21</sup> giving an analytic formula of the rate constant for electron transfer mediated by a midway molecule in the primary process of photosynthesis. Their theory was employed in part 1<sup>8</sup> with modifications appropriate for describing excitation transfer followed by charge separation in the process of the excitation-energy trapping. For the present purpose, further modification is needed for treating photoexcitation of P followed by charge separation in the process of the photon trapping by the RC.

The theory by Sumi and Kakitani was originally presented to rationalize the temperature dependence<sup>22</sup> of electron transfer from  $P^*$  to bacteriopheophytin mediated by the accessory monomeric bacteriochlorophyll B within the RC of purple bacteria. In the natural system, this process has been attributed to the sequential process where the initial charge-separated state  $P^+B^-$  is really formed in the course of the mediation,<sup>12</sup> as mentioned earlier. This situation arises mainly because the energy position of the intermediate state is lower than the initial state  $P^*$  by about several hundred wavenumbers in the organism of wild type. In the artificial system, therefore, even if the energy of the intermediate state is raised only by about several hundred wavenumbers, the mediation easily becomes superexchange at low temperatures,<sup>21</sup> in agreement with observation. Similarly, also the ordinary-sequential mediation at  $P^*$  in the excitation-energy trapping from LH1\* to  $P^+B^-$  in *Rb. sphaeroides* has been expected to easily become superexchange at low temperatures even if the energy of  $P^*$  is raised artificially only by about several hundred wavenumbers, as described theoretically in part 1.<sup>8</sup>

In general cases between the ordinary-sequential and the superexchange mechanisms, the process of the photon trapping by charge separation mediated by  $P^*$  in the RC is described as a single process with a definite rate constant in a situation similar to those in the theory by Sumi and Kakitani and in part 1.<sup>8</sup> The initial state in photoexcitation of the RC is written as  $|d\rangle$  with the same notation as used in part 1,<sup>8</sup> to make the adaptation of the formulation in part 1<sup>8</sup> straightforward. Let us consider that in this state a photon with energy  $E$  is present with both the special pair P and the monomeric bacteriochlorophyll B kept in their neutral ground states in the RC. Both the intermediate and the final states are respectively written as

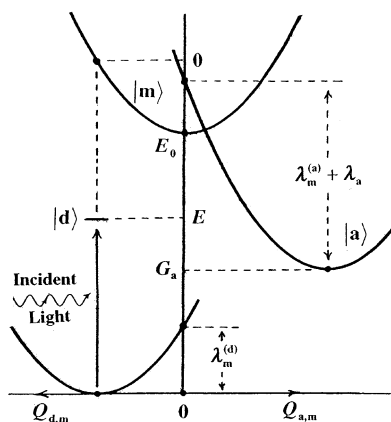
$$|m\rangle \text{ for } P^*B, \text{ and } |a\rangle \text{ for } P^+B^- \quad (2.1)$$

They are the same as in the formulation of part 1.<sup>8</sup> The matrix element for electronic coupling between  $|d\rangle$  and  $|m\rangle$  is written as  $J_{md}$  with the same notation as used in part 1.<sup>8</sup> Since  $J_{md}$  induces photoexcitation of P, the square of  $J_{md}$  is proportional to both the oscillator strength of P and the light intensity. The matrix element for electronic coupling between  $|m\rangle$  and  $|a\rangle$ , written as  $J_{am}$ , induces electron transfer from  $P^*$  to B. The direct electronic coupling ( $J_{ad}$ ) between  $|d\rangle$  and  $|a\rangle$  can be neglected,<sup>23</sup> similar to the situation in both part 1<sup>8</sup> and ref 21.

In part 1,<sup>8</sup>  $|d\rangle$  described the electronic excited state LH1\* of the core antenna LH1, with both P and B in the electronic ground state. In this case, when  $|d\rangle$  is seen from the intermediate state  $|m\rangle$  with the surrounding medium relaxed after excitation transfer from  $|d\rangle$ , the surrounding medium around LH1 was regarded as reorganized by an energy  $\lambda_d$  while that around P by an energy  $\lambda_m^{(d)}$ . These reorganizations were simplified in such a way that phonons participating in the reorganization around LH1 did not participate in the reorganization around P and vice versa since LH1 and P are sufficiently apart from one another. In the present problem of the photon trapping by the RC, we have no antenna system such as LH1, and  $\lambda_d$  should vanish although  $\lambda_m^{(d)}$  should not vanish, with the same meaning as before.

After formation of the charge-separated state  $P^+B^-$  from  $P^*B$ , the medium around  $P^+$  and  $B^-$  is regarded as reorganized by an energy  $\lambda_m^{(a)}$  and  $\lambda_a$ , respectively, as in part 1.<sup>8</sup> Phonons participating in the reorganization around  $P^+$  are regarded as not participating in the reorganization around  $B^-$  and vice versa, as also in part 1.<sup>8</sup> Accordingly, the total reorganization energy





**Figure 2.** Adiabatic potential for the final state  $|a\rangle$  with the free energy  $G_a$  and the energy of reorganization  $\lambda_m^{(a)} + \lambda_a$  in the direction of a coordinate  $Q_{a,m}$  from the bottom of the adiabatic potential for the intermediate state  $|m\rangle$  with the free energy  $E_0$ , and the adiabatic potential for the initial state  $|d\rangle$  containing the incident photon with energy  $E$  and the reorganization energy  $\lambda_m^{(d)}$  along a coordinate  $Q_{d,m}$ . Here,  $E_0$  is located at  $-\lambda_m^{(d)}$  with the origin of the energy axis taken at the absorption peak of  $|m\rangle$ , and  $Q_{a,m}$  and  $Q_{d,m}$  are in general neither perpendicular nor parallel to one another in the multidimensional phonon-coordinate space.

in association with the formation of the charge-separated state  $P^+B^-$  in  $|a\rangle$  from  $P^*B$  in  $|m\rangle$  is given by  $\lambda_m^{(a)} + \lambda_a$ . The free energy for  $|a\rangle$  thus relaxed is written as  $\Delta G_{a,m}$  seen from that for  $|m\rangle$  in the medium around  $P^*$  relaxed after photoexcitation of  $P$ , also as in part 1.<sup>8</sup>

In part 1,<sup>8</sup> the free energy for  $|m\rangle$  in the medium relaxed after excitation transfer to  $P$  from  $LH1^*$  was regarded as higher by  $\Delta G_m$  than that for  $|d\rangle$  in the medium relaxed before the excitation transfer. In the present problem without  $LH1^*$  but a photon with energy  $E$  in  $|d\rangle$ ,  $\Delta G_m$  in part 1 corresponds to  $-\lambda_m^{(d)} - E$  with the origin of energy put at the absorption peak of  $P$ , since the free energy for  $|m\rangle$  written as  $E_0$  in section I is given by  $E_0 = -\lambda_m^{(d)}$  in this energy scale. The free energy for  $|a\rangle$  is written as  $G_a$ , which is equal to  $-\lambda_m^{(d)} + \Delta G_{a,m}$  in this energy scale. As in Figure 2, it is intelligible to locate such energies as  $E_0 (= -\lambda_m^{(d)})$ ,  $\lambda_m^{(a)} + \lambda_a$ ,  $G_a$  and  $E$  in the phonon-coordinate diagram showing a typical arrangement of adiabatic potentials for electronic states  $|d\rangle$ ,  $|m\rangle$  and  $|a\rangle$  along the coordinates  $Q_{d,m}$  and  $Q_{a,m}$  for reorganization of the medium after electronic transition to  $|d\rangle$  and  $|a\rangle$ , respectively, from  $|m\rangle$ . Here,  $Q_{d,m}$  and  $Q_{a,m}$  are in general neither perpendicular nor parallel to one another in the multidimensional phonon-coordinate space.

When these replacements mentioned above and  $\lambda_d = 0$  are applied to the formulation in part 1,<sup>8</sup> the analytic formula of the rate,  $k_{a,d}$ , for production of the charge-separated state  $P^+B^-$  in the RC under photoexcitation at energy  $E$  is given in the same form of an integral as eq 2.12 in part 1

$$k_{a,d} = \int_0^\infty F(\tau) d\tau \quad (2.2)$$

where  $F(\tau)$  is a positive function shown in Appendix (eq A1 with eq A2). This  $k_{a,d}$  can also be regarded as giving the rate of optical absorption by the RC, as noted in the previous section.

In discrimination of whether the mediation at  $|m\rangle$  in production of  $|a\rangle$  from  $|d\rangle$  is ordinary-sequential or superexchange, a decisive role is played by the dephasing-thermalization time  $\tau_m$  of phonons at  $|m\rangle$ .<sup>21</sup> Here,  $1/\tau_m$  can be estimated by the average width in frequency dispersion of phonons participating in the reorganization  $\lambda_m^{(d)}$  around  $P$ .<sup>21,24</sup> The integration variable  $\tau$  on

the right-hand side of eq 2.2 physically represents time spent at  $|m\rangle$  after a quantum-mechanical virtual transition to  $|m\rangle$  from  $|d\rangle$  at  $\tau = 0$ . At time  $\tau \gg \tau_m$ , the reorganization of the medium around  $P$  at  $|m\rangle$  has almost been completed. As shown in ref 21b, the lowest limit of this time can be estimated at

$$\bar{\tau}_m \approx 1.52\tau_m \quad (2.3)$$

Accordingly, it is convenient to divide the  $\tau$  integration on the right-hand side of eq 2.2 into contributions before and after  $\bar{\tau}_m$ . As shown in ref 21b, this division leads us to

$$k_{a,d} \approx \int_0^{\bar{\tau}_m} F(\tau) d\tau + k_{a,d}^{(OS)} P_m \quad (2.4)$$

where  $P_m$  represents the survival probability of an electronic excitation at  $P^*$  until after  $\bar{\tau}_m$ , given explicitly in Appendix (eq A16 with eqs A13 and A14), and  $k_{a,d}^{(OS)}$  represents the rate for production of  $|a\rangle$  from  $|d\rangle$  mediated by  $|m\rangle$  in the ordinary-sequential mechanism.

The rate constant  $k_{a,d}^{(OS)}$  is given by

$$k_{a,d}^{(OS)} = k_{a,m} k_{m,d} / (\gamma + k_{a,m}) \quad (2.5)$$

where  $k_{m,d}$  and  $k_{a,m}$  represent respectively the rate for optical absorption to  $|m\rangle$  from  $|d\rangle$  and the rate constant for transition to  $|a\rangle$  from  $|m\rangle$ , while  $\gamma$  represents the rate of intramolecular decay of  $|m\rangle$ , including the radiative one.<sup>25</sup> Here,  $k_{a,m}$  describing the rate constant of charge separation from  $P^*B$  to  $P^+B^-$  has a magnitude on the order of  $(1 \text{ ps})^{-1}$  in purple bacteria<sup>12,22</sup> and is much larger than  $\gamma$  under usual intensities of exciting lasers, as noted in the previous section. Therefore,  $\gamma$  can practically be neglected in eq 2.5, and we see that  $k_{a,d}^{(OS)}$  actually gives the rate  $k_{m,d}$  of optical absorption by  $P$  as a function of the exciting photon energy  $E$ , as

$$k_{a,d}^{(OS)} \approx k_{m,d} \quad (2.5')$$

The first term on the right-hand side of eq 2.4 represents contributions to  $k_{a,d}$  in the time region before  $\bar{\tau}_m$  while phonons at  $|m\rangle$  are not thermalized yet. Taking place in this time region are not only the charge separation to  $|a\rangle$  unistep from  $|d\rangle$  but also the hot sequential charge separation. In the former, charge separation to  $|a\rangle$  from  $|m\rangle$  takes place before loss of phase memories among phonons at  $|m\rangle$  after a virtual transition to  $|m\rangle$  from  $|d\rangle$  at time  $\tau = 0$ . In the latter, it takes place after loss of phase memories among phonons at  $|m\rangle$  but during energetic thermalization of phonons therein after the transition to  $|m\rangle$  from  $|d\rangle$  at  $\tau = 0$ . In reality, however, it has been known<sup>24</sup> and also explicitly shown in ref 21b that such dephasing and thermalization of phonons take place simultaneously with the same time constant  $\tau_m$ . Therefore, contributions from the former and the latter cannot unambiguously be separated except in a special case. For example, the usual formula for the rate constant  $k_{a,d}^{(SX)}$  in the superexchange mechanism for the charge separation to  $|a\rangle$  unistep from  $|d\rangle$ , given by eq 3.7 in ref 21b, can analytically be cast into eq 5.31 therein in the semiclassical approximation for phonons. As shown in ref 21b, in fact, even this formula contains partially also contributions from the latter, that is, the hot sequential charge separation at  $\tau = 0$  in the present problem.<sup>26</sup>

In the situation mentioned above, it is possible only to introduce the degree of ordinary sequentiality,  $D_{OS}$ , as in ref 21b. Considering  $F(\tau) > 0$  on the right-hand side of eq 2.4 for the rate constant  $k_{a,d}$ , it is given by the proportionality of the

second term therein as

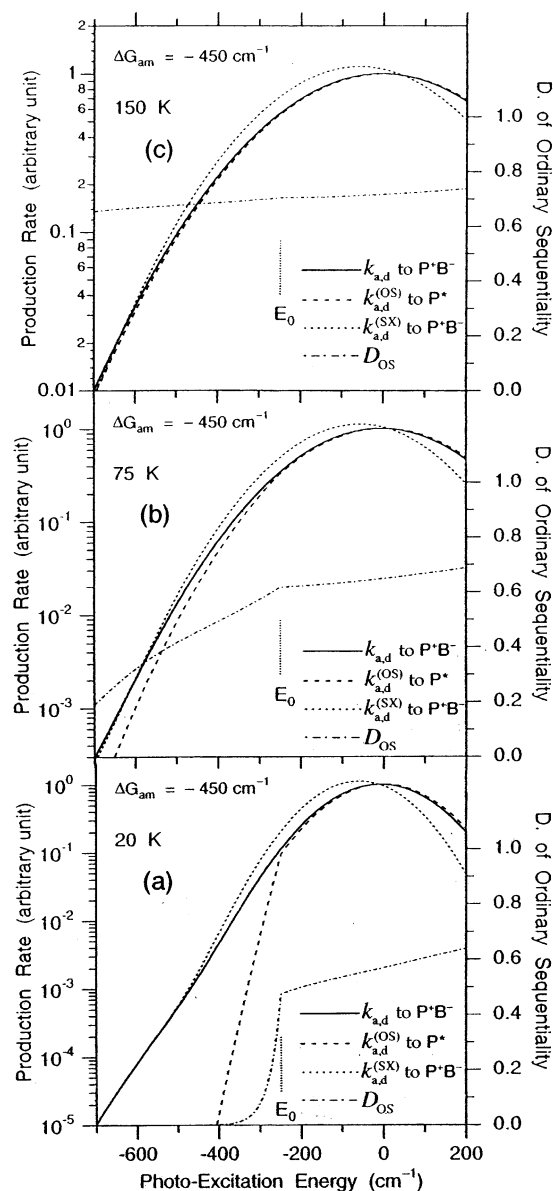
$$D_{OS} = (k_{a,d}^{(OS)}/k_{a,d}) P_m, \quad \text{with } 0 < D_{OS} < 1 \quad (2.6)$$

Charge separation to  $|a\rangle$  from  $|d\rangle$  mediated by  $|m\rangle$  proceeds by the ordinary-sequential mechanism when  $1 - D_{OS} \ll 1$ . For  $D_{OS} \ll 1$ , on the other hand, the charge separation proceeds by the superexchange mechanism when  $D_{OS} \ll 0.1$ , and subsequently the hot sequential charge separation also contributes when  $D_{OS}$  is on the order of 0.1.

### III. Unistep Charge Separation Sensitized by the Low-Energy-Tail Photoexcitation of P

Numerical calculation was performed for the RC from *Rb. sphaeroides*, where excitation transfer from the core antenna LH1 and the subsequent charge separation proceed practically by the ordinary-sequential mechanism even at low temperatures. As mentioned in the previous sections, the photon-energy dependence of the rate constant  $k_{a,d}$  of eq 2.2 thus obtained will essentially be unchanged even if the calculation was performed for the RC from *Rps. viridis* where in excitation-energy transfer from LH1, the mechanism of the charge separation changes from the ordinary-sequential to the superexchange with a decrease in temperature. Parameters for the calculation set in part 1<sup>8</sup> were used also here, especially as  $\lambda_m^{(d)} = 250 \text{ cm}^{-1}$ . The free energy for  $|a\rangle$  has been known to be  $\sim 450 \text{ cm}^{-1}$  lower than that for  $|m\rangle$  in *Rb. sphaeroides*.<sup>12</sup> This situation was set as  $\Delta G_{am} = -450 \text{ cm}^{-1}$  in the calculation, as the free energy for  $|a\rangle$  relative to  $|m\rangle$ . Since the origin of the energy axis is put at the absorption peak of the special pair P in the calculation, as in Figure 2, the free energy for  $|m\rangle$  written as  $E_0 (= -\lambda_m^{(d)})$  is located at  $-250 \text{ cm}^{-1}$ , and that for  $|a\rangle$  written as  $G_a (= E_0 + \Delta G_{am})$  is located at  $-700 \text{ cm}^{-1}$ . When  $E < E_0 (= -250 \text{ cm}^{-1})$ , the photon energy  $E$  is not sufficient to directly excite the special pair P without additional energy supply from thermal phonons, but is sufficient to directly produce the charge separated state  $P^+B^-$  without it as long as  $E > G_a (= -700 \text{ cm}^{-1})$ , as also understood in Figure 2.

The dephasing-thermalization time of phonons,  $\tau_m$ , at  $|m\rangle$  can be estimated by the inverse of the average width in frequency dispersion of phonons interacting with an electron,<sup>21,24</sup> as mentioned in the previous section. The average energy quantum of such phonons is denoted by  $\hbar\bar{\omega}$ . In both the antenna system and the RC, pigments are encompassed in proteins. It has been observed that vibrations of a protein nearly uniformly have average energies of several dozens of  $\text{cm}^{-1}$ , extending to  $\sim 100 \text{ cm}^{-1}$ .<sup>20,27</sup> In both part 1<sup>8</sup> and ref 21b, therefore, as a typical example  $\hbar\bar{\omega}$  was taken at  $50 \text{ cm}^{-1}$ , and  $\tau_m$  at 0.3 ps, which corresponds to an average width of  $\sim 100 \text{ cm}^{-1}$  in phonon-energy dispersion. This value of  $\tau_m$  was adopted also in the present work. Such a rapid thermalization of protein distortions in the time region of 0.3 ps has in fact been observed in association with electron transfer in a blue-copper protein, plastocyanin, by direct time-domain measurements (such as  $\sim 0.36 \text{ ps}$  in this case).<sup>28</sup> Such a value of  $\tau_m$  is also consistent with observations, by time-resolved stimulated<sup>29a,b</sup> and spontaneous emission<sup>29c</sup> from  $P^*$  in the RC from *Rb. sphaeroides* and *Rhodobacter capsulatus*, that vibrational quantum beats last until  $\sim 2 \text{ ps}$  with a half-decay time a little smaller than  $\sim 0.5 \text{ ps}$  after photoexcitation of P at low temperatures. In fact, these observations have reasonably been reproduced by a calculation<sup>30</sup> which takes into account the phonon-energy dispersion with the average width of  $\sim 100 \text{ cm}^{-1}$ .



**Figure 3.** Optical absorption spectrum of the reaction center (RC) due to production of the charge-separated state  $P^+B^-$  therein shown by the solid line ( $k_{a,d}$ ), the spectrum for photoinduced production of the excited-state  $P^*$  of the special pair P in the RC shown by the dashed line ( $k_{a,d}^{(OS)}$ ), and that for photoinduced unistep production of  $P^+B^-$  in the superexchange mechanism shown by the dotted line ( $k_{a,d}^{(SX)}$ ), predicted for the RC from *Rb. sphaeroides* at 20 K in part a, 75 K in part b, and 150 K in part c. The degree of ordinary sequentiality ( $D_{OS}$ ) is shown by the dash-dot line with a scale on the right ordinate.

Shown by the solid lines in Figure 3 are the  $E$  dependence of the rate  $k_{a,d}$  for production of the charge-separated state  $P^+B^-$  in the RC under photoexcitation at energy  $E$  at 20 K in part a, 75 K in part b, and 150 K in part c. The scale on the ordinate is arbitrary. The dashed lines therein show that of the corresponding rate  $k_{a,d}^{(OS)}$  in the ordinary-sequential mechanism by the same scale as for the solid lines. As noted in the previous section,  $k_{a,d}^{(OS)}$  can be regarded as equal to the rate for production of the excited state  $P^*$  of the special pair in the RC under photoexcitation at energy  $E$ . Let us first see the energy region of  $E > E_0$ . In this region,  $k_{a,d}$  shown by the solid lines are nearly equal to  $k_{a,d}^{(OS)}$  by the dashed lines at all temperatures. This means that production of the charge-separated state  $P^+B^-$  can practically be regarded as ordinary sequential, mediated by real

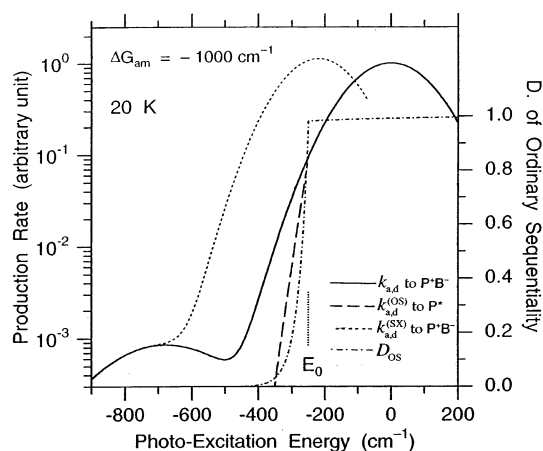
formation of the intermediate state  $P^+B$  in this  $E$  region even at 20 K. The degree of ordinary sequentiality  $D_{OS}$ , represented by the dash-dot lines in Figure 3, however, is not very close to 1.0, for example at  $E = E_0$ ,  $\sim 0.6$  at 20 K in part a, although it increases to  $\sim 0.7$  at 150 K in part c. This means that  $k_{a,d}$  in this region of  $E > E_0$  contains a non-negligible contribution of hot sequential charge separation occurring during reorganization of the medium around P after formation of  $P^*$  by photoexcitation at energy  $E$ , although  $k_{a,d} \approx k_{a,d}^{(OS)}$  apparently.

In *Rb. sphaeroides*, absorption by the lowest excited-state LH1\* of the core antenna LH1 peaks at an energy  $\sim 200$   $\text{cm}^{-1}$  lower than that by the special pair P in the RC.<sup>14</sup> This situation corresponds to  $E \approx -200$   $\text{cm}^{-1}$  in the present case of direct photoexcitation of the RC, since LH1\* associates with little reorganization of the surrounding medium.<sup>31</sup> The temperature dependence of  $D_{OS}$  in the case of excitation transfer from LH1\* in *Rb. sphaeroides* was shown in Figure 3 of part 1.<sup>8</sup> It agrees with that obtained in the present work on a line of  $E \approx -200$   $\text{cm}^{-1}$  in Figure 3.

In the energy region of  $E < E_0$ , on the other hand,  $k_{a,d}$  becomes deviating from  $k_{a,d}^{(OS)}$  depending on temperature. At 20 K in part a,  $k_{a,d}^{(OS)}$  represented by the dashed line decreases very rapidly, reflecting that P in the RC cannot be photoexcited without assistance of simultaneous absorption of thermal phonons which are rarely present at 20 K. In contrast,  $k_{a,d}$  represented by the solid line does not decrease as rapidly as  $k_{a,d}^{(OS)}$ , approaching the dotted line which represents the  $E$  dependence of the rate  $k_{a,d}^{(SX)}$  for unistep production of the charge-separated state  $P^+B^-$  in the superexchange mechanism. Reflecting this situation, the degree of ordinary sequentiality  $D_{OS}$  represented by the dash-dot line becomes very rapidly much smaller than unity in part a. We see, therefore, that in the energy region considerably lower than  $E_0$  at temperatures as low as 20 K the charge-separated state  $P^+B^-$  is unistep produced in the RC by photoexcitation without real excitation of the special pair P in the superexchange mechanism.

The deviation of  $k_{a,d}$  from  $k_{a,d}^{(OS)}$  in the energy region of  $E < E_0$  becomes much smaller at 75 K in part b and even smaller at 150 K in part c than at 20 K in part a. Reflecting such a change, the degree of ordinary sequentiality  $D_{OS}$  becomes considerably larger than 0.1 even in the energy region of  $E < E_0$ . At 150 K in part c,  $k_{a,d}$  becomes nearly equal to  $k_{a,d}^{(OS)}$  in the entire energy region. Correspondingly,  $1 - D_{OS}$  becomes  $\sim 0.3$ , much smaller than unity in the entire energy region. We can estimate that, above about 100 K,<sup>8</sup> the uphill energy trapping by the special pair P into the charge separated state  $P^+B^-$  in the RC becomes governed by the ordinary-sequential mechanism with real production of P in the entire energy region of  $E$  on the abscissa of Figure 3.

When  $E \approx E_0 - 150$   $\text{cm}^{-1}$  ( $= -400$   $\text{cm}^{-1}$ ) at 20 K in part a,  $k_{a,d}$  becomes several hundreds times as large as  $k_{a,d}^{(OS)}$ . This  $E$  value corresponds to that at the lowest excited state LH1\* of the core antenna LH1 in *Rps. viridis*,<sup>8</sup> since the excitation energy for LH1\* is  $\sim 350$ – $400$   $\text{cm}^{-1}$  lower than the absorption-peak energy of the special pair in the RC.<sup>15</sup> We have, thus, predicted that even if the RC is from *Rb. sphaeroides*, photon-energy trapping by it will become superexchange, as seen in *Rps. viridis* at 6 K,<sup>8</sup> as the RC is shined at an energy  $E$  lower than  $E_0$ , which is  $\sim 250$   $\text{cm}^{-1}$  below the absorption-peak energy of P. It is interesting that the LH1–RC complex in the natural system from *Rb. sphaeroides*, corresponding to  $E \approx -200$   $\text{cm}^{-1}$ , has been organized in the transition region between the ordinary-



**Figure 4.** Optical absorption spectrum of the reaction center (RC) due to production of the charge-separated state  $P^+B^-$  therein shown by the solid line ( $k_{a,d}$ ), the spectrum for photoinduced production of the excited state  $P^*$  of the special pair P in the RC shown by the dashed line ( $k_{a,d}^{(OS)}$ ) and that for photoinduced unistep production of  $P^+B^-$  in the superexchange mechanism shown by the dotted line ( $k_{a,d}^{(SX)}$ ), predicted for the RC from *Rb. sphaeroides* at 20 K when the free energy  $\Delta G_{am}$  for  $P^+B^-$  relative to  $P^*$  is artificially changed to  $-1000$   $\text{cm}^{-1}$  from its wild-system value of  $-450$   $\text{cm}^{-1}$ . The degree of ordinary sequentiality ( $D_{OS}$ ) is shown by the dash-dot line with a scale on the right ordinate.

sequential and the superexchange mechanisms, but on the side of the former in trapping of excitation energies from LH1 by the RC.

It is interesting, then, to investigate an artificially modified system in which the free energy for the charge separated state  $P^+B^-$  is lowered from its natural value of  $\Delta G_{am} = -450$   $\text{cm}^{-1}$  by about several hundred wavenumbers. As a typical example, in Figure 4,  $\Delta G_{am}$  was changed to  $-1000$   $\text{cm}^{-1}$  with other parameters fixed unchanged at 20 K. In the energy region of  $E > E_0$ , the solid line of  $k_{a,d}$  for producing the charge-separated state  $P^+B^-$  by photoexcitation merges completely into the dashed line of  $k_{a,d}^{(OS)}$  for exciting the special pair P, obeying the ordinary-sequential mechanism. In fact, the dash-dot line for the degree of ordinary sequentiality  $D_{OS}$  is very close to unity in this energy region. In the energy region of  $E < E_0$ , on the other hand,  $D_{OS}$  rapidly decreases to approach zero, meaning that production of the charge-separated state  $P^+B^-$  by photoexcitation changes so rapidly as to proceed by the superexchange mechanism with virtual mediation by the special-pair excitation. We note in Figure 4 that this unistep production of  $P^+B^-$  by photoexcitation manifests itself as an absorption peak when the energy of the charge-separated state,  $\Delta G_{am}$ , is as low as  $-1000$   $\text{cm}^{-1}$  from the intermediate state  $P^*$ . It should also be noted that production of such a peak in the absorption spectrum does not arise from the usual photoinduced charge-separation mechanism, which is due to a direct photoinduced electronic coupling between PB and  $P^+B^-$  mentioned in ref 23.

Physical parameters including the threshold energy  $E_0$  in Figure 2 have an inhomogeneous broadening. Even in this case, the superexchange mechanism in the photon trapping by the RC should still be observed, for example, at  $E = E_0 - 150$   $\text{cm}^{-1}$ , since it has really been observed in the excitation-energy trapping from the core antenna in the natural system of *Rps. viridis*.

#### IV. Summary

The present work is a continuation from part 1 (ref 8), which theoretically investigated the temperature dependence of the rate constant for uphill trapping by the RC of excitation energies



from the lowest excited state LH1\* of the core antenna LH1 in purple bacterium *Rb. sphaeroides* and *Rps. viridis*. The present work is devoted to proposing an experiment for investigating the uphill excitation-energy trapping from a different section by its dependence on the initial energy, which is given by the energy of LH1\* in the natural system. The energy has been fixed at a definite value in the natural system, at  $\sim 200\text{ cm}^{-1}$  in *Rb. sphaeroides*<sup>14</sup> and  $\sim 350\text{--}400\text{ cm}^{-1}$  in *Rps. viridis*<sup>15</sup> lower than the absorption-peak energy of the special pair P in the RC. To vary the energy, a stripped RC without LH1 associated<sup>9</sup> is directly photoexcited by a photon with varying energies, in place of excitation-energy transfer from LH1\* in the natural system. Such an RC obtained from either *Rb. sphaeroides* or *Rps. viridis* is acceptable in this experiment, and the data expected to be obtained by this experiment will essentially be the same between the two cases, although the mechanism of the uphill excitation-energy trapping by the RC from LH1\* is quite different between *Rb. sphaeroides* and *Rps. viridis* at low temperatures as clarified in part 1.<sup>8</sup> This experiment will, therefore, enable us to investigate the difference between *Rb. sphaeroides* and *Rps. viridis* in the uphill energy trapping by the RC in a unified fashion.

In the experiment proposed in the present work, the energy of LH1\* and the photon energy  $E$  can be regarded as equal to each other, since LH1\* is not associated with appreciable reorganization of the surrounding medium,<sup>31</sup> as so is the photon. In this experiment, the energy  $E$  is trapped by the RC, very rapidly inducing a state  $P^+B^-$  of initial charge separation between P and the accessory monomeric bacteriochlorophyll B in the RC. Measured in this experiment is, therefore, the  $E$  dependence of the rate for formation of the  $P^+B^-$  state in the RC. The rate can easily be measured as that of optical absorption by the RC, since formation of the charge-separated state in the RC is mediated by the excited-state  $P^*$  of the special pair P, and there exist no pigments in the protein–pigment complex of the RC absorbing in the same energy region as  $P^*$ , which is the lowest among excited states of pigments in the RC.

The free energy  $E_0$  for  $P^*$  is  $\sim 250\text{ cm}^{-1}$  lower than its absorption-peak energy, by an amount of energy for reorganization of the medium in association with the excitation or deexcitation of  $P$ ,<sup>20</sup> as seen in Figure 2. The free energy for LH1\* is slightly (by  $\sim 50\text{ cm}^{-1}$ ) higher than that  $E_0$  in *Rb. sphaeroides*,<sup>8</sup> while in *Rps. viridis* it is considerably lower (by  $\sim 150\text{ cm}^{-1}$ ) than  $E_0$ .<sup>10</sup> The experiment proposed in the present work will observe the following. When the photon energy  $E$  is higher than  $E_0$  at all temperatures, the absorption spectrum of the RC will be nearly equal to the excitation spectrum of P, which can be measured by a pump–probe experiment. Above  $\sim 100\text{ K}$ , this will occur in the whole  $E$  region in Figure 3 where  $E_0$  was taken at  $-250\text{ cm}^{-1}$  with the absorption-peak energy of P taken as the zero of energy. As  $E$  decreases from  $E_0$ , on the other hand, the former will deviate from the latter, becoming several hundreds times as large as the latter at  $E \approx E_0 - 150\text{ cm}^{-1}$  ( $\approx -400\text{ cm}^{-1}$ ) at  $20\text{ K}$ , as shown in Figure 3a. This energy of  $E \approx -400\text{ cm}^{-1}$  corresponds to the energy of LH1\* in *Rps. viridis*, where the observed value<sup>15b</sup> of the rate for excitation-energy trapping by the RC from the core antenna at  $6\text{ K}$  is astronomically (at least  $10^{14}$  times) larger than the value expected from the  $P^*$  absorption, as noted in part 1.<sup>8</sup> At this energy, the excitation-energy trapping at low temperatures occurs by the superexchange mechanism in Figure 1 where LH1\* is unistep converted to the charge-separated state in the RC without real formation of  $P^*$  since mediation at the intermediate state  $P^*B$  takes place as a quantum-mechanical

virtual process. In contrast to this mechanism, when  $E > E_0$  at all temperatures, or when the temperature is above  $\sim 100\text{ K}$  irrespective of  $E$ , the excitation-energy trapping proceeds practically by the ordinary-sequential mechanism where the charge separation to  $P^+B^-$  in the RC follows the excitation transfer to  $P^*B$  from LH1\* after thermalization of phonons in the intermediate state  $P^*B$ . This is the case in *Rb. sphaeroides* corresponding to  $E \approx -200\text{ cm}^{-1}$ .

In the superexchange mechanism for unistep charge separation into  $P^+B^-$  from the photon by means of quantum-mechanical virtual mediation by  $P^*$ , an electron in the LUMO (lowest unoccupied molecular orbital) of P is transferred to B. It is different from the usual photoinduced charge separation in which an electron in the HOMO (highest occupied molecular orbital) of P is directly transferred to B by photon absorption without mediation at  $P^*$ .<sup>23</sup>

The present work has thus predicted that a crossover in the mechanism of energy trapping by the RC from the ordinary-sequential to the superexchange mechanism can be investigated in its absorption spectrum by sweeping the photon energy from higher to lower than  $E_0$  in a single system at low temperatures. The crossover will be realized for the RC not only from *Rps. viridis* but also from *Rb. sphaeroides* where energy trapping from the core antenna in the natural system proceeds always by the ordinary-sequential mechanism in the whole temperature range. At about the liquid-nitrogen temperature, the above-mentioned enhancement of the absorption spectrum of the RC over the excitation spectrum of P for  $E < E_0$  becomes weak, as shown in Figure 3b for  $75\text{ K}$ . It will become virtually negligible at  $150\text{ K}$ , as shown in Figure 3c.

In purple bacteria, the free energy  $G_a$  for the charge-separated state  $P^+B^-$  in Figure 2 is located at  $\sim 450\text{ cm}^{-1}$  lower than  $E_0$ .<sup>12</sup> If it can artificially be lowered by several hundred wavenumbers, the unistep charge separation with quantum-mechanical virtual mediation by  $P^*$  in the photon field will manifest itself as a peak in the low-energy tail of the absorption peak of P, as shown explicitly in Figure 4 where  $G_a$  was lowered to  $1000\text{ cm}^{-1}$  below  $E_0$ .

Theoretically, the present work calculated the rate for production of the charge-separated state  $P^+B^-$  from the initial state PB in the field of photons with energy  $E$  by mediation at the intermediate state of  $P^*B$  in the RC. The rate can be interpreted as that for optical absorption by the RC, since  $P^*B$  surely decays to  $P^+B^-$  with a rate much larger than the radiative as well as nonradiative decay of  $P^*B$  to PB in the present system. The ordinary-sequential and the superexchange mediation at the intermediate state are located at mutually opposite limits. In general cases between them, such an electronic transition mediated by an intermediate state can be described as a single process with a definite rate constant.<sup>21</sup> In the present work, an analytic formula for the rate constant was given as eq 2.2 (with eq A1 in the Appendix). This formula will be powerful in analyzing the absorption spectrum of the RC in the energy region of the  $P^*$  absorption for clarifying the uphill excitation-energy trapping by  $P^*$  into the charge-separated state in the RC. Experimentally, the  $E$  dependence of the rate constant has an advantage over its temperature dependence investigated in part 1,<sup>8</sup> since we do not have to worry about the unknown temperature dependence of physical parameters such as reorganization energies and free energies appearing in Figure 2. The uphill excitation-energy trapping by the RC is characterized by the red pigments in the core antenna. Their presence has been known widely also in higher plants and algae<sup>18</sup> as well as in other photosynthetic bacteria<sup>7,15b,17a,19</sup> with nearly uniform

magnitudes of the rate constant for the uphill excitation-energy trapping by the RC. But both the origin and the meaning of such uniformity in the rate constant has not well been rationalized.<sup>16,18a,19b,f</sup> The analytic formula for the rate constant given in the present work as well as in part 1<sup>8</sup> will powerfully be utilized in clarifying such problems.

### Appendix: Analytic Formula for Function $F(\tau)$ in Eqs 2.2 and 2.4

As shown in part 1<sup>8</sup> and also in ref 21,  $F(\tau)$  in eqs 2.2 and 2.3 is composed of two parts

$$F(\tau) = f(\tau) \exp[-\int_0^\tau C_m(t) dt], \quad (A1)$$

where both  $f(\tau)$  and  $C_m(t)$  are given as analytic functions, shown below, in the semiclassical approximation for phonons contributing to the reorganization energies. First, applying  $\Delta G_m = -(E + \lambda_m^{(d)})$  and  $\lambda_d = 0$  to  $f(\tau)$  given in Appendix D of part 1,<sup>8</sup> we get

$$f(\tau) \approx \left( \frac{J_{am} J_{md}}{\hbar} \right)^2 \frac{2\pi \exp(-S_a)}{[(D_a^2 + D_m^{(a)2})D_m^{(d)2} - D_m(\tau)^4] \sum_{n=0}^{\infty} \frac{S_a^2}{n!}} \times \exp\left( -\frac{(n\hbar\omega_a + E_{am}(\tau) - E)^2/2}{D_a^2 + D_m^{(a)2} + D_m^{(d)2} - 2D_m(\tau)^2} - y^2 \right) \mathcal{R}[\text{erf}(x + iy)] \quad (A2)$$

with

$$x = \left( 2 \frac{(D_a^2 + D_m^{(a)2})D_m^{(d)2} - D_m(\tau)^4}{D_a^2 + D_m^{(a)2} + D_m^{(d)2} - 2D_m(\tau)^2} \right)^{1/2} \frac{\tau}{\hbar}, \quad (A3)$$

$$y = [D_m^{(d)2} - D_m(\tau)^2][n\hbar\omega_a + E_{am}(\tau)] + [D_a^2 + D_m^{(a)2} - D_m(\tau)^2]E \left/ \left\{ 2[(D_a^2 + D_m^{(a)2})D_m^{(d)2} - D_m(\tau)^4][D_a^2 + D_m^{(a)2} + D_m^{(d)2} - 2D_m(\tau)^2] \right\}^{1/2} \right., \quad (A4)$$

and

$$E_{am}(\tau) = \Delta G_{am} + \lambda_a + \lambda_m^{(a)} - 2\lambda_m(\tau), \quad (A5)$$

where  $\mathcal{R}[\text{erf}(x + iy)]$  represents taking the real part of the error function of a complex argument  $z = x + iy$  defined by<sup>21b,32</sup>

$$\text{erf}(z) = (2/\sqrt{\pi}) \int_0^z \exp(-t^2) dt$$

$\lambda_m^{(a)} + \lambda_a$  in eq A5 represents the energy of reorganization of the medium, along the coordinate  $Q_{a,m}$  in Figure 2, in association with charge-separation transition from  $|m\rangle$  to  $|a\rangle$ . Individually,  $\lambda_m^{(a)}$  and  $\lambda_a$  represent energies of reorganization of the medium around P and B in association with oxidation of (i.e., electron removal from)  $P^*$  to  $P^+$  and reduction of (i.e., electron insertion to) B into  $B^-$  in the RC, respectively. Similarly, along the coordinate  $Q_{d,m}$  in Figure 2, the energy of reorganization of the medium around P in association with its deexcitation to P or its excitation to  $P^*$  is represented by  $\lambda_m^{(d)}$ . Interaction of an electron with distortions of the surrounding medium brings about not only its reorganization but also (both thermal and quantum-mechanical) fluctuations in the energy of the electron. The average squared amplitude of the fluctuations are expressed as

$D_m^{(d)2}$ ,  $D_m^{(a)2}$ , and  $D_a^2$ , accompanied by the reorganization energies  $\lambda_m^{(d)}$ ,  $\lambda_m^{(a)}$ , and  $\lambda_a$ , respectively. They are related as

$$D_m^{(d)2} = 2k_B T' \lambda_m^{(d)}, \quad D_m^{(a)2} = 2k_B T' \lambda_m^{(a)}, \quad \text{and} \quad D_a^2 = 2k_B T' \lambda_a, \quad (A6)$$

in the semiclassical approximation, by an effective temperature  $T'$  of phonons participating in the reorganization of the medium. It is determined in such a way that  $k_B T'$  gives the average squared amplitude of (both thermal and quantum-mechanical) fluctuations of distortions in the medium.<sup>21b,33</sup> When  $\hbar\bar{\omega}$  represents the average energy quantum of such phonons,  $k_B T'$  can be approximated by

$$k_B T' = \frac{1}{2} \hbar\bar{\omega} \coth\left(\frac{1}{2} \hbar\bar{\omega}/k_B T\right) \quad (A7)$$

At high and low temperatures,  $k_B T'$  approaches, respectively

$$k_B T' \approx \begin{cases} k_B T, & \text{for } k_B T \gg \hbar\bar{\omega} \\ \frac{1}{2} \hbar\bar{\omega}, & \text{for } k_B T \ll \hbar\bar{\omega} \end{cases} \quad (A8)$$

This equation means that at high temperatures  $k_B T'$  approaches the average energy  $k_B T$  of a single oscillator determined by the equipartition law of energy in classical mechanics, while at low temperatures it approaches the quantum-mechanical energy of zero-point vibrations,  $\hbar\bar{\omega}/2$ , of the single oscillator with angular frequency  $\bar{\omega}$ .

In part 1,<sup>8</sup> the energy of reorganization of the medium around P in association with oxidation of (i.e., electron removal from) P into  $P^+$  was written as  $\lambda_m^{(a)} + \lambda_m^{(d)} - 2\lambda_m$ , and it is accompanied by fluctuations in the energy difference between P and  $P^+$ . When the average squared amplitude of the fluctuations is written as  $D_m^{(a)2} + D_m^{(d)2} - 2D_m^2$ , in the semiclassical approximation the last term therein is related to  $\lambda_m$  by

$$D_m^2 = 2k_B T' \lambda_m \quad (A9)$$

similar to eq A6, with an expediency that  $D_m^2$  is negative when  $\lambda_m$  is negative.

$\lambda_m$  in eq A9 arises from correlation between phonon modes participating in the reorganization of the medium around P along the coordinate  $Q_{d,m}$  in Figure 2 in association with deexcitation of  $P^*$  into P and those along the coordinate  $Q_{a,m}$  in Figure 2 in association with oxidation of  $P^*$  into  $P^+$ . Since the energies of reorganization of the medium around P by these modes are  $\lambda_m^{(d)}$  and  $\lambda_m^{(a)}$ , respectively,  $\lambda_m$  can be written as

$$\lambda_m = g(\lambda_m^{(a)} \lambda_m^{(d)})^{1/2}, \quad (A10)$$

where  $g$  represents the direction cosine between the two directions along the coordinates  $Q_{d,m}$  and  $Q_{a,m}$  in the multidimensional phonon-coordinate space. The absolute value of  $g$  is smaller than unity, ensured by Schwarz's inequality. Therefore,  $\lambda_m^{(a)} + \lambda_m^{(d)} - 2\lambda_m$  is positive, irrespective of the sign of  $\lambda_m$ . In general,  $g$  does not vanish, reflecting that the two directions are not perpendicular to each other, i.e., that phonon modes participating in these two directions are made of vibrations in the same medium around P and overlap with each other.

By using the dephasing-thermalization time  $\tau_m$  among phonons participating in the reorganization of the medium around P at  $|m\rangle$ , we can approximate  $\lambda_m(\tau)$  in eq A5 by<sup>21</sup>

$$\lambda_m(\tau) = \lambda_m \exp(-\tau^2/\tau_m^2) \quad (A11)$$



$D_m(\tau)^2$  in eqs A2–A4 is related to this  $\lambda_m(\tau)$  in the same form as eq A9, resulting in

$$D_m(\tau)^2 = D_m^2 \exp(-\tau^2/\tau_m^2) \quad (\text{A12})$$

Here,  $1/\tau_m$  can be estimated by the average width in frequency dispersion of such phonons around P. Reorganizing motions of the medium around P associated with deexcitation of P\* and those associated with its oxidation correlate with energy  $\lambda_m$ . As a result of this correlation, time evolution in the former induces that in the latter, described by the  $\tau$  dependence of  $\lambda_m(\tau)$ . Such an evolution of correlation between the reorganizing motions is accompanied by a time-dependent broadening correlation  $D_m(\tau)^2$  given by eq A12. Both  $\lambda_m(\tau)$  and  $D_m(\tau)^2$  decay to zero in the limit of  $\tau \gg \tau_m$ , starting from  $\lambda_m$  and  $D_m^2$ , respectively, at time  $\tau = 0$ .

It has been taken into account in eq A2 that an electron interacts at  $|a\rangle$  not only with distortions in the medium around B, contributing to the reorganization energy  $\lambda_a$ , but also with intramolecular phonons of a large energy quantum  $\hbar\omega_a$ , with a reorganization energy  $S_a\hbar\omega_a$ . In this situation, the reorganization energy  $\lambda_a$  has been called the outersphere component while that  $S_a\hbar\omega_a$  the innersphere component with  $S_a$  called the Huang–Rhys factor.<sup>33</sup> In the analytic formula in eq A2, phonons contributing to the outersphere reorganization by energies  $\lambda_m^{(d)}$ ,  $\lambda_m^{(a)}$ , and  $\lambda_a$  are treated in the semiclassical approximation.

Let  $k_{a,m}(t)$  represent the rate constant for hot decay of an electronic excitation at  $|m\rangle$  to  $|a\rangle$  at time  $t$  ( $>0$ ) during thermalization of phonons under the condition that  $|m\rangle$  is produced by photoexcitation from  $|d\rangle$  at time  $t = 0$ . With this  $k_{a,m}(t)$ , we can give  $C_m(t)$  in eq A1 as

$$C_m(t) = \gamma + k_{a,m}(t) \quad (\text{A13})$$

where  $\gamma$  represents the rate of intramolecular decay of P\* at  $|m\rangle$ . In the semiclassical approximation for phonons contributing to the outersphere reorganization,  $k_{a,m}(t)$  is given by

$$k_{a,m}(t) = \frac{J_{am}^2}{\hbar} \left( \frac{2\pi}{D_a^2 + D_m^{(a)2}} \right)^{1/2} e^{-S_a} \sum_{n=0}^{\infty} \frac{S_a^n}{n!} \times \exp\left(-\frac{[n\hbar\omega_a + E_{am}(t)]^2}{2(D_a^2 + D_m^{(a)2})}\right) \quad (\text{A14})$$

Energy  $E_{am}(t)$  in eq A14 approaches  $\Delta G_{am} + \lambda_a + \lambda_m^{(a)}$  from eq A5 when  $t \gg \tau_m$ . In this limit,  $k_{a,m}(t)$  approaches the rate constant  $k_{a,m}$  for an electronic transition from  $|m\rangle$  to  $|a\rangle$  after thermalization of phonons at  $|m\rangle$ . The rate  $k_{m,d}$  for an electronic transition from  $|d\rangle$  to  $|m\rangle$  in the field of photons with energy  $E$  is given in the semiclassical approximation for phonons by<sup>33</sup>

$$k_{m,d} = [\sqrt{2\pi}J_{md}^2/(\hbar D_m^{(d)})] \exp[-E^2/(2D_m^{(d)2})] \quad (\text{A15})$$

This equation is appropriate for  $E > E_0$ , where  $E_0$  represents the free energy for  $|m\rangle$ , given by  $-\lambda_m^{(d)}$  in the present energy scale. When  $E$  is replaced by  $E + 2\lambda_m^{(d)}$ , the right-hand side of eq A15 gives the rate for inverse transition from  $|m\rangle$  to  $|d\rangle$ , written as  $k_{d,m}$ . They should be related to each other by the principle of detailed balance,  $k_{m,d} \exp(-\beta E) = k_{d,m} \exp(-\beta E_0)$  with  $\beta = 1/(k_B T)$ . When  $E < E_0$ , the semiclassical approximation for phonons is more appropriate for  $k_{d,m}$  than for  $k_{m,d}$ . Therefore,  $k_{m,d}$  for  $E < E_0$  should be given by

$$k_{m,d} = \frac{\sqrt{2\pi}J_{md}^2}{\hbar D_m^{(d)}} \exp\left(-\frac{(E + 2\lambda_m^{(d)})^2}{2D_m^{(d)2}} + \frac{E + \lambda_m^{(d)}}{k_B T}\right) \quad (\text{A15}')$$

By  $k_{a,m}$  and  $k_{m,d}$  obtained above, we get the rate constant  $k_{a,d}^{(OS)}$  of eq 2.5 in the ordinary-sequential mechanism. The degree of ordinary sequentiality  $D_{OS}$  of eq 2.6 can be obtained by calculating the survival probability  $P_m$  of an electronic excitation at P until time  $\bar{\tau}_m$  by

$$P_m = \exp\left[-\int_0^{\bar{\tau}_m} C_m(t) dt\right], \quad \text{with } \bar{\tau}_m \approx 1.52\tau_m \quad (\text{A16})$$

Since  $\gamma$  in eq A13 can practically be neglected in comparison with  $k_{a,m}$ , as noted in the text, we get eq 2.5' for  $k_{a,d}^{(OS)}$ . Since  $J_{md}^2$  is proportional to the intensity of light incident to the RC, it is convenient to calculate both  $k_{a,d}$  of eq 2.2 and  $k_{m,d}$  of eq A15 or eq A15', giving  $k_{a,d}^{(OS)}$ , as dimensionless quantities. For this purpose, the preexponential factor in the expression of  $k_{m,d}$  in eq A15 was taken as a unit for showing these rates with a dimension of inverse time on the ordinates of the figures in the text. In quantities actually necessary for their calculation, we set as  $\lambda_m^{(d)} = 250 \text{ cm}^{-1}$ ,  $\Delta G_{am} = -450 \text{ cm}^{-1}$ ,  $\hbar\omega = 50 \text{ cm}^{-1}$ , and  $\tau_m = 0.3 \text{ ps}$ , as mentioned in the text. Let us set the Huang–Rhys factor  $S_a$  to be vanishingly small, as in part 1.<sup>8</sup> Also as adopted in part 1,<sup>8</sup> values of other quantities were set as  $\lambda_m^{(a)} = 250 \text{ cm}^{-1}$ ,  $\lambda_a = 350 \text{ cm}^{-1}$ , and  $g = 0.7$ . These values can be used for the wild system of both *Rb. sphaeroides* and *Rps. viridis*. Since the value of  $J_{am}$  is slightly different between them as shown in ref 21b, it was taken as  $J_{am} = 24 \text{ cm}^{-1}$  appropriate for *Rb. sphaeroides* in the figures shown in the text.

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