A theoretical explanation for quantum yield failure in bacterial photosynthetic reaction centers

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Abstract

A new theoretical model addresses the reduction in the quantum yield for primary charge separation in bacterial photosynthetic reaction centers (RCs) in an applied electric field. The electric field dependence of the internal conversion rate constant for the primary donor is proposed to act as a drain that competes with primary charge separation. The field dependence of the internal conversion process is based on experimental data that have shown that the excited state of the primary donor has a large polarizability suggesting that the excitonic basis of the primary donor is mixed with charge transfer (CT) basis states. The model provides analytic expressions for the electric field dependence of the primary charge separation rate constant, prompt and delayed fluorescence, and predicts an effect on the intersystem crossing rate constant. The model provides a mechanism for a reduction of the quantum yield and an explanation for the lack of a concomitant increase in either prompt or delayed fluorescence.

1. Introduction

The quantum yield for the primary charge separation step in the native bacterial photosynthetic reaction center (RC) is nearly unity [1]. Upon photoexcitation the primary donor transfers an electron to the primary acceptor within ≈ 3 ps at room temperature and about ≈ 1 ps at cryogenic temperature [2–6]. This remarkable efficiency appears to be due in large part to the specific electrostatic environment in the protein that surrounds the donor P, a bacteriochlorophyll dimer, and the acceptor H_A, a bacteriopheophytin. With the exception of the heterodimer mutant discussed below [7], multiple mutations or substitution of non-native acceptors in the H_A binding site are required to reduce the quantum yield for primary charge separation by greater than ≈ 10% [8–16]. There are two mechanisms proposed for primary charge separation, superexchange and a two-step process [16–23] that both involve the bacteriochlorophyll B_A. The two-step mechanism proposes

\[ \text{(1)} \ \ ^1P \rightarrow \ (2) \ \ P^+B_A \rightarrow \ (3) \ \ P^+H_A, \]

where
\( P^+B_\Lambda \) is a population in the density matrix [24–26]. In superexchange \( P^+B_\Lambda \) is a coherence in the density matrix that contributes strongly to the electronic coupling \( V_{\text{super}} = V_{12}V_{23}/E_{21} \) [26–29]. \( P^+H_\Lambda \) is the ultimate acceptor in either of the proposed mechanisms. Regardless of the identity of the primary acceptor there is general agreement that the dipolar state \( P^+H_\Lambda \) is formed with very high quantum yield within a few picoseconds at all temperatures down to 1.5 K. No synthetic model electron transfer system is able to mimic the high efficiency and low driving force of the primary charge separation step probably due to the fact that synthetic control over the solvent environment is missing [30,31].

An applied electric field can reduce the efficiency of the primary charge separation process in bacterial photosynthetic RCs [32–35]. The analogy between an applied electric field and the transmembrane potential suggests that electric fields may serve to regulate charge separation in photosynthesis [36]. However, a mechanism for the electric field effect on the primary charge separation step that explains all of the experimental data has not yet been advanced [37,38]. The reduction of the quantum yield results from a return to the ground state from either the \( 1P \) state, the \( P^+B_\Lambda \) intermediate state, or the \( P^+H_\Lambda \) primary charge separated state [34,35]. The measurements of the reduced quantum yield in an applied electric field are quite accurate since the experiment can be carried out by monitoring kinetics on the millisecond, nanosecond and picosecond time scales [32–35]. Experiments on all time scales give similar results and these comparisons have been used to deduce that the origin of the quantum yield reduction is to be found in the primary charge separation step. Measurements of the effect of an applied electric field on kinetics are more difficult, however, electric-field-modulated kinetics have been measured on the millisecond time scale for \( P^+Q_\Lambda \) charge recombination, [39,40], the microsecond time scale for \( 3P \) decay [41] and the picosecond time scale for the primary charge separation reaction [42–45].

The model for the effect of an applied electric field on the quantum yield derived in this paper is based on the competition between the intrinsic field dependence of the internal conversion rate of \( 1P \) and the primary charge separation step which could be either \( 1P \to P^+B_\Lambda \) or \( 1P \to P^+H_\Lambda \). We develop the hypothesis that the field dependence of \( 1P \) is a consequence of the mixing of charge transfer (CT) configurations, \( P^+_\Lambda P^-_B \) and \( P^+_B P^-_\Lambda \), which promotes an electric-field-induced acceleration of the non-radiative decay rate from the primary donor state [46]. The key hypothesis is that the sensitivity of the internal conversion rate to the electric field is a consequence of the large polarizability of the \( 1P \) exciton [47]. The polarizability of an excitonic state, in turn, is in large part due to the admixture of close lying intradimer CT states [48]. This simple model is consistent with all available experimental data on the quantum yield failure of primary charge separation as well as electric field-effect, kinetic, and energetic data on the primary charge separation process [42].

The theory explains the lack of a large electric field effect on either the prompt or delayed fluorescence [49]. The theory developed below uses the nomenclature of the RC, but applies to any model system of the photosynthetic RC or indeed any excitonic excited state that can serve as an electron donor.

### 2. Methods

#### 2.1. The connection between the transition polarizability and excited state polarizability

An applied electric field, \( F \), induces mixing of exciton and charge transfer configurations of the excited state (either singlet or triplet) bacteriochlorophyll dimer \( 1^3P \).

\[
\langle 1^3P \rangle = \langle 1^3P_0 \rangle + \frac{\langle 1^3P_0 \rangle |H|^2(1^3P^-)}{E(1^3P_0) - E(1^3P^-)} |1^3(P^+P^-)\rangle,
\]

(1)

where \( H = -eF \) and \( \langle 1^3P_0 \rangle \) is the excited state (exciton) wave functions of either singlet or triplet \( P \) at zero field, respectively. Eq. (1) describes the mixing of the intradimer charge transfer basis states \( 1^3(P^+P^-) \) into the (excitonic) states of the
singlet or triplet manifold.\textsuperscript{2} The designation $^1(P^+P^-)$ assumes that both dipolar directions, $^1(P_A^+P_B^-)$ and $^1(P_B^+P_A^-)$, can contribute. The intradimer CT (CT or $P^+P^-$) configurations, $P_A^+P_B^-$ and $P_B^+P_A^-$ can also be described as a charge resonance basis: $CR_{\pm} = 1/\sqrt{2}(P_A^+P_B^- \pm P_B^+P_A^-)$.

The rate constant for internal conversion of the primary donor state $^1P_0$ to the ground state is affected by the addition of CT configurations $|P^+P^-\rangle$ into the excitonic state \[46]. In the triplet manifold an analogous expression exists for the intersystem crossing of $^3P_0$. At zero applied electric field, the intrinsic internal conversion rate or intersystem crossing rate constants are:

$$k_{ic,isc} = \frac{\hbar^2}{2\pi} \left\langle \frac{\partial}{\partial Q} \right| P \right\rangle^2$$ (2)

and

$$k_{CT} = \frac{\hbar^2}{2\pi} \left\langle \frac{\partial}{\partial Q} \right| P \right\rangle^2,$$ (3)

where $|P\rangle$ is the ground state wave function of the primary donor and $Q$ is the nuclear coordinate. Eq. (2) represents an internal conversion process from a pure exciton excited state of the dimer $P$. In principle, the internal conversion indicated by Eq. (2) involves vibronic coupling along nuclear coordinates identical to the internal conversion of a monomer and the rate constant is similar to that of a monomer. Eq. (3) represents a charge recombination process that occurs following intradimer charge separation. Because of the much larger effect of the $^1(P^+P^-)$ dipole on the excited state nuclear coordinates such a process involves a different vibronic coupling and the rate constant is significantly larger than for the internal conversion represented by Eq. (2) [46].

The electric-field-dependent rate constants for internal conversion, $k_{ic}(F)$ and intersystem crossing, $k_{isc}(F)$, can be expressed in terms of the transition polarizability $\alpha$ and hyperpolarizability $\beta$

$$k_{ic}(F) = k_{ic}(1 + \alpha F + \beta F^2),$$

$$k_{isc}(F) = k_{isc}(1 + \alpha' F + \beta' F^2),$$ (4)

where

$$A, A' = \frac{2e^{\langle 1,3P_0| \frac{\partial}{\partial Q} |1,3P_0^+P^-\rangle}}{E(1,3P_0^+P^-) - E(1,3P_0)},$$

$$B, B' = \left(\frac{e^{\langle 1,3P_0| \frac{\partial}{\partial Q} |1,3P_0^+P^-\rangle}}{E(1,3P_0^+P^-) - E(1,3P_0)}\right)^2,$$

$$\eta = \sqrt{\frac{k_{CT}}{k_{ic}}} = \left\langle \frac{1,3P_0^+P^-| \frac{\partial}{\partial Q} \right| P \right\rangle \left\langle 1,3P_0 \right| \frac{\partial}{\partial Q} | P \right\rangle.$$
bacteriochlorophyll monomer lifetime for non-radiative decay $k_e(0) \approx (2 \text{ ns})^{-1}$ is a reasonable value for a pure exciton state indicated by Eq. (2). The intrinsic lifetime for fluorescence decay of monomer bacteriochlorophyll has been estimated to be $\tau_0 \approx 4 \text{ ns}$ by hole-burning measurements [53]. However, the intrinsic lifetime may longer than the observed value, which is shortened by energy transfer to neighboring molecules (self-quenching).

The intrinsic rate constant for intradimer charge recombination, $k_{CT}$ (Eq. (3)) can also be estimated from experimental data. An example of the effect of mixing of the CT basis is found in the heterodimer mutant (BH200L in $Rb. \text{ capsulatus}$ and BH202L in $Rb. \text{ sphaeroides}$) where the internal conversion lifetime is 30 ps [48,54]. In the heterodimer mutant, one of the bacteriochlorophyll molecules of P is replaced by a bacteriopheophytin. Stark effect data indicate that the difference dipole moment of $\Delta \mu_A = 18 D/f$ in the excited state is consistent with a much greater degree of charge separation within $1P$ than found in wild type RCs. The degree of charge separation in a $P^-P^+$ CT basis state would be larger still, however, since the center-to-center distance between the magnesium atoms of the dimer is 7.7 Å corresponding to a dipole moment of $\Delta \mu_{CT} \approx 37 D$. As we have pointed out previously, the strong mixing of one of the intradimer CT configurations in this mutant results in a reduction in the quantum yield for primary charge separation to $\Phi_0 \approx 0.5$ and provides a model for the mechanism of quantum yield failure proposed here [54]. Thus, the estimated non-radiative decay in the heterodimer serves as a lower bound estimate for the zero-field rate constant $k_{CT} \approx (30 \text{ ps})^{-1}$. Based on these data and the fact that the non-radiative decay in the heterodimer is the lower limit for a pure CT process, we have assumed that $k_{CT} \approx (5 \text{ ps})^{-1}$ at zero field as the CT rate constant for charge recombination from a pure intradimer charge separated state. Based on the available data and above assumptions, it can be seen that $k_{CT}/k_e \approx (5 \text{ ps})^{-1} \approx (2 \text{ ns})^{-1} = 400$ and thus $e = \langle |P| \partial/\partial Q| \rangle (P^+P^-)/\langle |P_0| \partial/\partial Q|P_0\rangle \approx 20.4$

The difference polarizability obtained from electroabsorption experiments can be used to estimate other matrix elements [47]. The magnitude of the excited state dipole moment $1\mu$ is

$$\langle |P|e| \rangle = \langle |P_0|e| \rangle + 2eF$$

$$\times \frac{\langle |P_0|e| (P^+P^-) \rangle \langle (P^+P^-)|e|P_0 \rangle}{E(\langle |P^+P^-| \rangle - E(\langle P_0 \rangle)}$$

where the first term on the right-hand side represents the dipole moment in the absence of the admixture of CT states $1\mu_0$ and the second term represents the contribution from the excited state polarizability $\alpha_{excited}$. If we assume that the ground state polarizability is much smaller than the excited state polarizability, $\alpha_{ground} \ll \alpha_{excited}$, then Eq. (5) indicates that

$$\alpha_{excited} = 2e^2 \frac{\langle |P_0|e| (P^+P^-) \rangle \langle (P^+P^-)|e|P_0 \rangle}{E(\langle |P^+P^-| \rangle - E(\langle P_0 \rangle)}.$$  

Electroabsorption spectroscopy indicates $\alpha \approx 1000 \text{ Å}^3$ [47]. The polarizability, $\alpha'$ is related to the polarizability volume $\alpha$ by the relationship $\alpha'(D^2/\text{cm}^3) = 4\pi\epsilon_0\alpha(A^3)$ with the corresponding units in parentheses, so that $\alpha'(D^2/\text{cm}^3) \approx 2 \times 10^{-4}\alpha(A^3)$. Note that $\alpha'$ has the form $2T^2/\Delta E$ where $T$ is the transition dipole moment in Debye and $\Delta E$ refers to the energy difference be-

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3 The applied electric field $f_{app}$ is related to the internal field, $f$ by the equation $F = f_{app}$, where $f$ is the local field correction. The local field correction for a spherical cavity is $f = 3\epsilon/(2\epsilon + 1)$ for a medium with a dielectric constant of $\epsilon$ [67]. Thus, the correction is at most 1.5 and has been estimated to be around 1.1 under the conditions that most quantum yield failure data have been obtained [39]. The field used in Fig. 1, and all subsequent figures, is the internal field. Experimental dipoles such as $\Delta \mu_A$ are determined only to within a factor $f$ since only the applied field is determined in the experiment. The remaining dipoles discussed in the paper are calculated using distance data available from X-ray crystal structures of the RC.

4 The model will still account for the data if the $k_{CT}/k_e$ ratio is as small as 100, but not much below this value. A smaller $k_{CT}/k_e$ ratio requires greater field dependence in the transition polarizability and hyperpolarizability and hence smaller values of the energy gap between the $P_0$ and $P_{1A}$ CT configurations and the $1P$ exciton configuration at zero field (i.e. for $\Delta E = E(\langle P^+P^- \rangle)/E(\langle P_0 \rangle) < 500 \text{ cm}^{-1}$).
between the states in cm\(^{-1}\). For primary donor excited state \(a' \approx 0.2\), and if we estimate the energy difference \(\Delta E = E(1^1P^+\cdot P^-) - E(1^1P_0)\) \(\approx 500\) cm\(^{-1}\) then \(T = e\langle 1^1P_0|z|1^1P^+\cdot P^-\rangle \approx 7.5\) D.\(^4\) Using this analysis we can estimate \(A\) and \(B\) in terms the intrinsic internal conversion rate constant. For example, for a \(T = 7.5\) D transition dipole moment aligned in a field of \(F = 10^6\) V/cm the interaction energy is \(-T\cdot F \approx -125\) cm\(^{-1}\), thus

\[
T = \frac{e\langle 1^1P_0|z|1^1P^+\cdot P^-\rangle}{E(1^1P^+\cdot P^-) - E(1^1P_0)} \approx 0.25\ \text{(MV/cm)}^{-1}.
\]

(7)

Under these conditions \(k_{ic}(F) = k_{ic}(0)(1 + 10F + 25F^2)\) where \(F\) is in MV/cm. This simple model predicts a 36-fold increase in the internal conversion rate constant due to the admixture of a CT component in a field of 1 MV/cm for dipoles aligned along the axis of the applied electric field. Up to this point we have assumed a single CT configuration called \(P^+\cdot P^-\). However, the presence of two CT dipolar basis states is implied by the large polarizability. When two CT configurations, \(P^+_A P^-_B\) and \(P^+_B P^-_A\), are considered whose dipoles are equal in magnitude and opposite in direction, there will be two \(A\) terms and two \(B\) terms, \(A_+ = 5\) and \(B_+ = 6.25\), since the ratio \(T/\Delta E \approx 0.125\) (MV/cm\(^{-1}\)) in this case. Thus, the internal conversion rate constant can be written as \(k_{ic}(F) = k_{ic}(0)(1 + A_+ F + A_- F + B_+ F^2 + B_- F^2)\).

The interaction energy of the field with a CT dipole \(A_U = -\Delta \mu_{CT} \cdot F = -|\Delta \mu_{CT}| |F| \cos \theta\) requires averaging over all of the orientations in an isotropic sample, i.e. over the limits of integration of angle \(\theta\) from 0 to \(\pi\). For purely quadratic terms this is not necessary since the field dependence is symmetric about \(\theta = \pi/2\). For the internal conversion process \(k_{ic}(F)\) we assume the equivalence of \(P^+_A P^-_B\) and \(P^+_B P^-_A\) dipoles even though symmetry breaking occurs in RC due to protein contributions. Under this assumption there are dipoles in each direction, and with appropriate change in normalization, even for the linear term, the value of the integral from 0 to \(\pi/2\) is equal to the value of the integral from \(\pi/2\) to \(\pi\). This is equivalent to considering only one hemisphere of the isotropic distribution because of the dipole symmetry. Comparisons showing the effect of this assumption are given in the following. Specifically, we compare two cases:

- **case I** \(\frac{1}{2} \int_0^\pi \sin \theta d\theta = \frac{1}{2} \int_0^1 \text{d}x\),

- **case II** \(\frac{1}{2} \int_0^{\pi/2} \sin \theta d\theta = \frac{1}{2} \int_0^1 \text{d}x\).

The derivations in the present study have been carried out for case II. Very similar analytic formulae are also obtained for case I. The models show that for the quantum yield \(\Phi_{et}(F)\), prompt fluorescence \(\Phi_f(F)\) and delayed fluorescence \(\Phi_d(F)\) yields both models give the correct qualitative trends for the data. However, the model that assumes that both \(P^+_A P^-_B\) configurations contribute (i.e. integration from 0 to \(\pi/2\)) gives the best quantitative agreement with the data. To apply this model we use case II with the assumption that \(A_+\) and \(A_-\) contribute symmetrically to the orientation average. This type of consideration is the same as that for the dipole moment induced by an applied field interacting with a polarizable molecule. The induced dipole moment is always aligned along the field. For exactly the same reason the model suggests that \(k_{ic}(F)\) will increase due to mixing of CT terms for all orientational subpopulations in an isotropic sample. The model connects the transition polarizability \(A\) to the excited state polarizability \(z_{excited}\), which both give rise to bidirectional field effects. Consistent with this interpretation we ignore the \(\pm\) subscripts in the formulae and treat \(k_{ic}(F)\) as indicated above in Eq. (4).

In previous work we have used a cumulant expansion for electric-field-dependent rate constants [40,55]. In this study we use a polynomial that is justified on physical grounds by the perturbation theory result. Eq. (4) provides the field dependence of the non-radiative rate in terms of the transition polarizability \(A\) and the transition hyperpolarizability \(B\). In general, a polynomial model for the rate constant has the disadvantage that the rate constant can become negative for certain parameter values. However, \(k_{ic}\) and \(k_{ec}\) can only become negative when \(\Delta z\) is negative, and furthermore only when \([E(1^1P_0) - E(1^1P^+\cdot P^-)]] < -e\langle 1^1P_0|z|1^1P^+\cdot P^-\rangle\eta F\).
3. Results and discussion

3.1. The electric field effect on the primary charge separation rate

Marcus theory provides a useful model to represent the field dependence of the primary charge separation reaction that is in competition with internal conversion and radiative decay. The field dependent rate constant for primary charge separation is

$$ k_{\text{et}}(F) = \frac{V^2}{\sqrt{4\pi\lambda kT}} \exp \left\{ -\frac{(\lambda + \Delta G_{\text{et}} - \Delta \mu_{\text{et}} \cdot F)^2}{4\lambda kT} \right\}, $$

(8)

where $V$ is the electronic coupling, $\lambda$ is the reorganization energy, $\Delta G_{\text{et}}$ is the free energy for electron transfer and $\Delta \mu_{\text{et}}$ is the dipole for the electron transfer process. For simplicity in the orientation averaging we have assumed that $\Delta \mu_{\text{et}}$ and $\Delta \mu_{\text{CT}}$ are roughly collinear. The justification for this is that the angle for either $P^+H^+_A$ or $P^+B^-_A$ difference dipole moment with $^1P$ transition moment is not more than $10^\circ$ from the value for $\Delta \mu_A$ measured for the absorption electrochromism of the $P \rightarrow ^1P$ transition [56]. We further assume that the dipolar and polarizability terms that give rise to $\Delta \mu_{\text{et}}$ are the very $P^+P^-$ configurations that result in $\Delta \mu_{\text{CT}}$, hence $\Delta \mu_A = \Delta \mu_{\text{CT}}$. The orientation of $\Delta \mu_{\text{CT}}$ is nearly aligned with $\Delta \mu_{\text{et}}$ for one of the $P^+P^-$ states and very nearly opposing $\Delta \mu_{\text{et}}$ for the other. In other words, the angle between these dipoles is assumed to be either 0 or $\pi$ for the $P^+_A P^-_B$ and $P^+_B P^-_A$ states, respectively, in the orientation averaging in this study. Assuming that $\lambda = -\Delta G_{\text{et}}$ and that the effect of an applied electric field on $k_{\text{et}}(F)$ is small we expand the rate constant in powers of the field and keep only the first two terms:

$$ k_{\text{et}}(F) = k_{\text{et}}(0)(1 + CF^2x^2), \quad C = -\frac{\Delta \mu_{\text{et}}^2}{2\lambda kT}, \quad x = \cos \theta, $$

(9)

where $k_{\text{et}}(0)$ signifies the rate constant at zero applied electric field $k_{\text{et}}(F = 0)$. Assuming an isotropic sample, the angle $\theta$ is the angle between the applied electric field and the molecular difference dipole moment $\Delta \mu_{\text{et}}$ for the electron transfer reaction, $\Delta \mu_{\text{et}} = \mu(P^+I^-) - \mu(^1P)$. This model is only valid when $\Delta \mu_{\text{et}}F$ is less than $\sqrt{(2kT)}$ and therefore, the Marcus theory model is applicable near room temperature i.e. $kT = 200$ cm$^{-1}$ at 300 K.

We can consider the two possible primary acceptors. If the bacteriopheophytin $H_A$ is the primary acceptor and $P^+H^+_A$ is formed directly we estimate $\lambda = 2000$ cm$^{-1}$ (0.25 eV) and $\Delta \mu_{\text{et}} \approx 50$ D. If the bacteriochlorophyll $B^-_A$ is the primary acceptor and $P^+B^-_A$ is formed directly we estimate $\lambda = 1200$ cm$^{-1}$ (0.15 eV) and $\Delta \mu_{\text{et}} \approx 30$ D. In either case we obtain a value of $C \approx -0.8(MV/cm)^{-1}$. These values of $\lambda$ are in reasonable agreement with literature analyses [57]. As stated in the introduction, regardless of the mechanism for the primary charge separation step the model gives roughly the same predicted reduction in rate constant. The following calculations reveal that competition between $k_{\text{et}}(F)$ and $k_{\text{ic}}(F)$ can simultaneously account for all of the observed electric field effect data using analytical formulae.

The first observed effect to be tested is the very small change in rate constant for primary charge separation in an applied field observed both in transient absorption studies [42,44] and time-resolved fluorescence experiments [43,45]. The orientation-averaged change in the excited state population of $^1P$ is

$$ \Delta S(0, t) = S_0 \exp\{-k_{\text{et}}t\}, $$

$$ \Delta S(F, t) = S_0 \int_0^1 \exp\{-k_{\text{et}}(F)x\} dx $$

$$ = S_0 \int_0^1 \exp\{-k_{\text{et}}(1 + CF^2x^2)t\} dx $$

$$ = S_0 \frac{\text{erf}(F \sqrt{Ck_{\text{et}}t})}{2F \sqrt{Ck_{\text{et}}t}} \exp\{-k_{\text{et}}t\}, $$

$$ \Delta \Delta S(F, t) = S_0 \left( \frac{\text{erf}(F \sqrt{Ck_{\text{et}}t})}{2F \sqrt{Ck_{\text{et}}t}} - 1 \right) \exp\{-k_{\text{et}}t\}, $$

(10)
where \text{erf}(x) is the error function [58].\(^5\) Here \(\Delta S(F, t)\) is the normalized difference decay defined in previous reports on electric field effects on a variety of CT reactions in the bacterial photosynthetic RC. \(S_0\) is proportional to the population of \(^1P\) following photoexcitation. Eq. (10) can represent a transient absorption measurement, \(S = A\) or a fluorescence upconversion measurement, \(S = \text{FL}\) of the excited state population. A plot of the estimated effect of an applied field of \(F = 1\) MV/cm on the kinetics of \(^1P\) decay is shown in Fig. 1.\(^3\) The exponential decay shown in Fig. 1 assumes \(k_{et} = 10^{12}\) s\(^{-1}\) as an order of magnitude estimate for the zero-field primary charge separation rate constant. The positive sign of \(S_0\) and \(\Delta S(0, t)\) are intended to represent a fluorescence upconversion measurement \(\Delta\text{FL}(0, t)\). Of course, the magnitude of \(\text{FL}_0\) in a fluorescence upconversion experiment is also affected by the quantum yield for prompt fluorescence in the field (see below). A combined model that simultaneously includes both effects on kinetics and fluorescence quantum yield is not analytic. However, such a model is not required to account for the data. The form of the difference decay, \(\Delta\text{FL}(F, t)\) agrees with observed fluorescence upconversion data in an applied electric field [45].

Transient absorption measurements of the excited state population often measure the decay of stimulated emission of \(^1P\) at 920 nm. The signal is a negative \(\Delta A\) in this case and the traces shown in Fig. 1 would need to be multiplied by \(-1\) to model the negative sign of \(\Delta A(0, t)\) in that experiment. The modest predicted effect is consistent studies that monitor the rate of appearance of \(P^+H_A^-\) at 665 nm [42]. Because of the quantum yield reduction \(\Delta\Phi\) for \(P^+H_A^-\) acceptor is smaller in the applied field than at zero field. The long-time baselines are not the same on the picosecond time scale and this effect is not treated in the model in Eq. (10), which is proportional to the \(^1P\) excited state population. Although the reduction of the quantum yield for \(P^+H_A^-\) complicates quantitative determination, it is clear that the electric field effect on \(k_{et}\) rate constant is small. Other transient absorption studies utilizing an applied field have shown no measurable change in the decay kinetics [44].

\(^5\) In the analytic expressions we use the following tabulated functions.

The error function is

\[
\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-w^2} \, dw.
\]

The gamma function is

\[
\Gamma(x) = \int_1^\infty \frac{e^{-t}}{t} \, dt.
\]

The hyperbolic arctangent is

\[
\text{arctanh}(x) = \frac{1}{2}(\ln(x + 1) - \ln(1 - x)).
\]
\[ \Phi_{el}(F) = \frac{k_{et}(F)}{k_t + k_{ic}(F) + k_{el}(F)}, \]

\[ \langle \Phi_{el}(F) \rangle = \frac{\int_0^1 \left[ k_{et}(1 + CF^2 x^2) \right] }{\left\{ k_t + k_{ic}(1 + AFx + BF^2 x^2) + k_{et}(1 + CF^2 x^2) \right\} dx} \]

\[ = k_{et} \frac{2 \Omega + N \ln(\Psi) - 4 \Omega P^2}{2 \Omega \Omega^2 F^2}, \]

\[ M = \frac{2k_{et}CF - k_{ic}(A + 2BF)}{\Pi}, \]

\[ N = \frac{k_{ic}A}{\Pi}, \]

\[ \Omega = \text{arctanh}(M) + \text{arctanh}(N), \]

\[ \Pi = \{ 4k_t k_{et} C - 4k_t k_{ic} B + 4k_{et} C \]

\[ + k_{ic} (A^2 - 4B) + 4k_{ic} k_{et} (C - B) \}^{1/2}, \]

\[ \vartheta = k_{et} - k_{ic} B, \]

\[ P = \left( B k_{ic} / C + k_t \right) \vartheta + k_{ic} (C k_{et} - B k_t) + k_{ic} (A^2 / 2 - B), \]

\[ \Psi = \frac{\vartheta F^2 - k_t - k_{et} - k_{ic} (1 + AF + BF^2) }{k_t + k_{et} + k_{ic}}, \]

(11)

where \text{arctanh} is the hyperbolic arctangent [58].

The constants \( A \) and \( B \) are associated with \( k_{ic}(F) \) in Eq. (4) and the constant \( C \) is associated the \( k_{et}(F) \) in Eq. (9). Inserting the values \( k_t = 10^8 \text{ s}^{-1} \) and \( k_{ic} = 10^{10} \text{ s}^{-1} \) we obtain the calculated curve for the reduction in quantum yield shown in Fig. 2. This calculated reduction is close to the experimental values [32–35]. The model can account for both a small effect on \( k_{et} \) and a large effect on \( \Phi_{el} \) in an applied field.

3.2. Implications for observed prompt and delayed fluorescence in an applied electric field

The electric field dependence of the fluorescence is mathematically equivalent to the above expression for the quantum yield for primary charge separation with the intrinsic fluorescence rate constant \( k_t \) replacing \( k_{et}(F) \) in the numerator:

\[ \Phi_t(F) = \frac{k_t}{k_t + k_{ic}(F) + k_{et}(F)}, \]

\[ \langle \Phi_t(F) \rangle = \int_0^1 \frac{k_t}{k_t + k_{ic}(1 + AFx + BF^2 x^2) + k_{et}(1 + CF^2 x^2)} dx \]

\[ = k_t \Omega \frac{2 \Omega + N \ln(\Psi) - 4 \Omega P^2}{2 \Omega \Omega^2 F^2}, \]

(12)

where \( \Omega \) and \( \Pi \) are defined above in Eq. (11). The major difference between Eqs. (11) and (12) is that the fluorescence rate constant \( k_t \) is assumed to be independent of the applied electric field. Thus, the integrals are slightly less cumbersome than those above for the quantum yield of the primary charge separation process. Inserting the values for \( k_t, k_{ic}, k_{et}, A, B \) and \( C \) into the integrated value of the above equation we find the \( \Phi_t(F = 1 \text{ MV/cm}) \approx 1.4 \Phi_t(F = 0) \) in agreement with experiment. The calculated result for the normalized difference in steady-state fluorescence reported as \( \Delta \Phi/\Phi(0) = \left( \Phi(F) - \Phi(0) \right) / \Phi(0) \) is roughly 0.4 as found in experimental studies [59].
Delayed fluorescence is calculated based on the equilibrium between the radical pair state and the \(^1\)P emitting state. The delayed fluorescence yield is given by
\[
\langle \Phi_d(F) \rangle = \int_0^1 \Phi_t(F) \exp \left\{ \frac{(\Delta G_{e\text{t}} - \Delta \mu_{e\text{t}} F \xi)}{kT} \right\} \ dx,
\]
(13)
where \(x = \cos \theta\) and \(\Phi_t(F)\) is the prompt fluorescence yield given above. This expression can be evaluated analytically as given by the formula below:
\[
\langle \Phi_d(F) \rangle = \frac{k_i \exp\{\Delta G_{e\text{t}} + \zeta_-(x)\}}{2\Sigma F} \left( I(Y_+) + e^{-2\Sigma F} I(Y_-) \right)
\]
\[
+ I(\zeta_+) - e^{-2\Sigma F} I(\zeta_-),
\]
\[
\Sigma = \left\{ k_{ic}^2 A^2 - 4C(k_i k_{ec} + k_{ic}^2 + k_{ic} k_{et}) \right. 
\]
\[
- 4B(k_i k_{ec} + k_{ic}^2 + k_{ic} k_{et}) \right\}^{1/2},
\]
\[
\zeta_\pm = (k_{ic} A \pm \Sigma) \Xi,
\]
\[
(14)
\]
where \(I(x)\) is the gamma function \([58]\). Although the delayed fluorescence increases exponentially with applied field, the effect of the quantum yield term is to reduce \(\Phi_d\) by two orders of magnitude compared to that expected in the absence of quantum yield failure. For example, in a field of 1 MV/cm the relative delayed fluorescence yield \(\Phi_d(F)/\Phi_d(0)\) is calculated to be 14 with a quantum yield failure process instead of \(6 \times 10^4\) without it. The reduction in the delayed fluorescence yield by \(10^4\) relative to the anticipated value arises from a rapid drain that returns that population that has a smaller driving force, \(- \Delta G_{et}\) to the ground state by a non-radiative decay pathway. The population of RCs that has the greatest field-dependent reduction in \(- \Delta G_{et}\) also has the largest field effect on the non-radiative rate because we have assumed that the difference dipoles for \(\Delta \mu_A\) and \(\Delta \mu_{et}\) are roughly collinear (see Fig. 3).

In a steady-state experiment it is difficult to separate the prompt from the delayed fluorescence. However, using time-resolved fluorescence techniques it has proven possible to obtain separate estimates of the effect of an applied electric field on the prompt and delayed fluorescence. Two methods have been applied to the problem, time correlated single photon counting (TCSPC) and fluorescence upconversion. TCSPC experiments with 50 ps resolution have measured the electric field-induced change in the prompt and delayed emission from RCs of \(Rb.\ sphaeroides\) at 80 K \([43]\). These data were fitted to five lifetimes, including 2, \(~100, \sim 300, \sim 800,\) and \(~6000\) ps. No field effect on the fluorescence quantum yield of the fastest two components was observed, however the quantum yield for the 300 ps component doubled and the quantum yield for the 800 ps component increased by a factor of 5. This result is consistent with the electric field-induced changes obtained in steady-state fluorescence measurements \([49,60]\). Much higher time resolution was obtained using femtosecond fluorescence upconversion \([45]\). In these experiments, applied fields of up to 1 MV/cm were obtained for \(Q\)-depleted \(Rb.\ sphaeroides\) at 85 K. Measurements were made out to about 100 ps with \(<150\) fs resolution. With this time resolution a small increase in the fluorescence quantum yield was observed at the earliest times (i.e. less than 1 ps), in
contrast to the result obtained by TCSPC. In addition, an increase in the quantum yield of about a factor of 2 was observed for delayed fluorescence, from about 10 to 100 ps. The increase in the integrated fluorescence (from 0 to 100 ps) agrees well with previous steady-state measurements, about 40% at the fields obtained [43,59–61].

The unusual result from the upconversion TCSPC and steady-state fluorescence electric-field-effect experiments, is the lack of a larger change in the fluorescence, either prompt or delayed. The reduction in quantum yield implies either that the applied field should be large enough to modulate (i.e. slow down) the primary CT rate by orders of magnitude unless a competing pathway to the ground state exists. All available experimental data indicate that the electric field effect on $k_{et}$.

Delayed fluorescence resulting from $P^+I^-/C_0$ recombination to form $^1P$ would be expected to increase exponentially in the field due to a shifted equilibrium

$$\exp\left(\frac{\Delta G_{et} - \Delta \mu_{et} F}{kT}\right).$$

Instead, the field effect on the delayed fluorescence at more than five times the lifetime of prompt fluorescence is less than 1% of $I(0)$, the zero-field fluorescence at $t=0$ [45]. These kinetic effects suggest a competing pathway must exist. The model presented here points to a fast drain of $^1P$ population that leads to a large reduction in the overall quantum yield. The dramatic reduction in delayed fluorescence predicted by the model for $k_{et}(F)$ provides a consistent explanation for the experimental data [43,45,49, 60,61].

### 3.3. Implications for experiments that monitor intersystem crossing yield

The magnitude of dipoles and the relative values of matrix elements $\langle P^+P^-|\partial/\partial Q|P \rangle$ and $\langle 0|\partial/\partial Q|P \rangle$ are likely very similar in the triplet manifold. The magnitude of the energy gap $E[^3P] - E[^3P^+P^-]$ is likely somewhat larger than for $^1P$ internal conversion. However, the effect of an applied field on the rate constant is substantial even in the triplet manifold [41]. In fact, the model advanced predicts a new effect, electric field enhancement of the $^3P$ intersystem crossing rate due to the addition of CT basis states to the wave function.

For example, if the energy gap is $E[^3P] - E[^3P^+P^-] \approx 2000$ cm$^{-1}$ for the same transition moment $T \approx 7.5$ D used above, then the magnitude of $A' \approx 2.5$ cm/MV and $B' \approx 1.5$ (cm/MV)$^2$.

For the parameter values above the linear term in $k_{isc}(F) = k_{isc}(0) [1 + A'F + B'F^2]$ dominates and this will lead to a significant slowing in the rate for orientations of the $P^+P^-$ dipole that are aligned with the externally applied field. The presence of two CT configurations, $P^+_A^+P_B^-$ and $P^+_BP_A^-$ eliminates the effect of the linear term that would lead to field-dependent rate decreases for orientational subpopulations that oppose the field direction. As above we apply case II by integrating only over one half of the distribution (i.e. from 0 to $\pi/2$) as shown in Eq. (15). The resulting

**Fig. 4.** The effect an applied field on the intersystem crossing rate $^3P \rightarrow P$ is shown. The upper panel shows the exponential decay at zero applied field (thick line) and the accelerated decay at five values of the internal field, $F = 0.2, 0.4, 0.6, 0.8$ and 1.0 MV/cm. The low panel shows the predicted normalized difference decay $\Delta S(F,t) - \Delta S(0,t)/\Delta S(0,0)$ for $^3P$ decay at the same internal fields. The decays were calculated using a value of $k_{isc} = 10^4$ s$^{-1}$. The form of the difference decays is in agreement with experiment [41].
orientation average electric field dependent decay rate is:

\[
\Delta S(F, t) = S_0 \int_0^1 \exp \left\{ -k_{\text{isc}} (1 + A' F x + B' F^2 x^2) \right\} dx
\]

\[
= S_0 \sqrt{\pi} \exp \left\{ -Z_+ Z_- \right\} \left( \text{erf} \{ Z_+ \} + \text{erf} \{ Z_- \} \right),
\]

\[
Z_{\pm} = \left( F \pm \frac{A'}{2B'} \right) \sqrt{B' k_{\text{isc}} t}.
\]

(15)

As above in Eq. (10) the designation \( S_0 \) is proportional to the population of \( ^3P \) following preparation of that state by photoexcitation and spin evolution [62–64]. The electric field effect can be monitored either by observing field-dependent changes in the absorbance of the P band at 860 nm, \( S \equiv A \) [64,65] or phosphorescence, although the latter experiment is not recommended owing to its extreme difficulty [66]. Eq. (15) predicts difference decays shown in Fig. 4 at room temperature. These are of the correct magnitude compared to experimental data on the electric field effect on \( ^3P \) decay [41].

4. Conclusion

The mechanism for the reduction in the quantum yield for the primary charge separation reaction in bacterial RCs is attributed to the large electric field dependence of the internal conversion rate constant, brought about by the intrinsic CT character of the special pair. A connection between the excited state polarizability and the transition polarizability for the CT basis states of the primary donor excited state was noted and used to obtain an electric-field-dependent rate constant for internal conversion. The magnitude of the field dependence is calculated based on constraints imposed by the available experimental data. Although neither the energy gap \( \Delta E \) between the \( ^1P \) exciton state and \( P^+ P^- \) CT states nor the transition moment between these states \( T \) is known, the excited state polarizability defines the magnitude of \( z_{\text{excited}} = 2T^2/\Delta E \) based on experiment. Moreover, the weak optical coupling and strong mixing of CT basis states into \( ^1P_0 \) due to the dielectric asymmetry of the RC suggest that both \( T \) and \( \Delta E \) are small. The ratio of intrinsic exciton and CT internal conversion are estimated to give a ratio \( \eta = \sqrt{(k_{\text{CT}}/k_{\text{isc}})} \approx 20 \). Using these values, a significant electric field dependence for the internal conversion rate is predicted. Marcus theory was used to obtain the field dependence for the primary charge separation rate constant. The predicted field dependence is small in agreement with experimental results.

The competition between these two field dependent quantities gives rise to a remarkably simple model that reproduces all of the observed electric field effects associated with the quantum yield reduction in bacterial RCs in an applied electric field. To obtain this simplicity we have abandoned the use of the cumulant expansion as the mathematical form for the field dependent rate constant. Although this approach has the peril that the rate constant can become negative, in practice the parameter values obtained from the experimental data on the RC do not give any negative rate constants. The analytical form of the field effect on the primary charge separation rate, prompt and delayed fluorescence as well as the \( ^3P \) decay rate have been calculated to demonstrate the applicability of the model. The applicability of quantum yield failure to other types of RCs such as those of photosystems I and II of plants is still an area for active investigation [36].

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References