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POSSIBLE ROLE OF PROTEIN IN PHOTOSYNTHETIC ELECTRON TRANSFER

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Summary

Photosynthetic electron transfer is discussed from a theoretical viewpoint. Theoretical description of electron transfer including the effect of low-frequency mode of protein is first discussed briefly. Then typical electron transfers in the primary photosynthesis are discussed as examples for the comparison between the theory and experiments. Attention is focussed on the fact that the photosynthetic system organizes a variety of electron transfers in a systematic manner to achieve a very efficient energy conversion, and it is suggested that the protein environment plays an important role in controlling the rate of electron transfer and maximizing the efficiency of the primary reaction. We emphasize that not only the electronic but also vibrational interactions are important for the regulation of electron transfer. Some novel processes such as activationless and negative activation transfers are shown to be connected with the significance of vibrational factor.

Introduction

In the recent studies of photosynthesis, considerable experimental and theoretical efforts have been focussed on the primary electron transfer reaction. In the last two decades, various spectroscopic studies performed over a wide temperature range (from room temperature to liquid helium temperature) have elucidated the chemical and physical nature of this process.

Chance and coworkers extensively investigated the electron transfer between *c*-type cytochrome and the reaction center in various bacterial species, and noticed that many species continue their reactions even at cryogenic tempera-

Abbreviations: BChl, bacteriochlorophyll; BPh, bacteriopheophytin.

tures [1—4]. In the case of *Chromatium* [1—3], the rate of transfer was essentially independent of temperature in the low-temperature range, which is quite different from the ordinary reactions characterized by an Arrhenius-type temperature dependence. This finding was the first indication that quantum mechanical tunneling plays an important role in biological processes. Later, the similar observations were made for various processes in several photosynthetic and other organisms (see Refs. 5 and 6 for thorough review of tunneling in biology).

This interesting finding stimulated the theoretical investigation of electron transfer in photosynthesis. Hopfield [7] applied the Förster-Dexter theory of excitation transfer [8,9] to the problem of electron transfer, i.e., expressed the transfer rate by the convolution of the electron insertion and removal spectra, which are analogous to the photon absorption and emission spectra. In his formalism, the effect of temperature was introduced through the overlap of the line shape functions, and he was thus able to account for the non-Arrhenius temperature dependence in *Chromatium* [1—3]. Jortner [10] described electron transfer in terms of the non-adiabatic multiphonon formalism, which was an extension of the general treatment of electronic and vibrational relaxation phenomena [11—13]. The advantage of his formalism was that it permitted the inclusion of the effect of the low-frequency solvent (soft) vibrational mode as well as high-frequency molecular (quantum) mode. However, the effect of the soft mode was not considered explicitly in the case of *Chromatium*.

The role of low-frequency modes has recently been discussed by Kuznetsov et al. [14] who suggested that the electron should be strongly coupled to the continuous medium modes to explain the temperature-independent branch observed in *Chromatium*. In our earlier report [15], on the other hand, we considered the soft mode of protein as well as the quantum mode, assuming that the coupling of the protein mode is small for biological electron transfer in a protein environment, and noted some novel features which might be relevant to the biological processes.

In the present report, we discuss primary photosynthetic electron transfer, comparing the presently available data with the earlier theoretical results. Our main object is to understand how the photosynthetic system controls a variety of electron transfers characterized by a wide range of relaxation time (10^{-2}—10^{-11} s) and yet achieves a very efficient energy conversion. Emphasis is laid on the importance of the protein environment in controlling the transfer rates. It is suggested that not only the electronic but also vibrational interactions are essential for the regulation of electron transfer.

Theoretical

The theoretical method used here was described in detail earlier [10,15] and we quote only the final expression for the transfer rate:

$$W = \frac{2\pi}{\hbar^2 \omega_s} |J|^2 \exp[-\tfrac{1}{2}\sum_i^N \Delta_i^2(2\bar{v}_i + 1)] \times \prod_{i \neq s}^N \sum_{n_i=-\infty}^{\infty} \left(\frac{\bar{v}_i + 1}{\bar{v}_i}\right)^{n_i/2} I_{n_i}(\Delta_i^2 \sqrt{\bar{v}_i(\bar{v}_i + 1)})$$

$$\times \left(\frac{\bar{v}_s + 1}{\bar{v}_s}\right)^{P(n_1 \ldots n_N)/2} I_{P(n_1 \ldots n_N)}(\Delta_s^2 \sqrt{\bar{v}_s(\bar{v}_s + 1)}) \quad (1)$$

$$P(n_1 \ldots n_N) = (\Delta E - \sum_{i \neq s}^{N} n_i \hbar\omega_i)/\hbar\omega_s$$

$$\bar{v}_i = [\exp(\hbar\omega_i/kT) - 1]^{-1}$$

where W is the transition probability between two vibronic states, corresponding to the transfer of electron, J represents the electron exchange matrix element, Δ_i and ω_i are the dimensionless displacement factor and frequency of ith normal mode, respectively (ω_s is the lowest frequency of all the modes), I_n represents the modified Bessel function, and ΔE denotes the energy gap. Eqn. 1 is valid over the whole temperature range and includes the contributions from an arbitrary number of normal modes (both from low and high-frequency modes). The physical meaning of this expression was discussed in Ref. 15.

Quantum mode

Photosynthetic electron transfer is usually mediated by conjugated proteins such as cytochromes and reaction center complexes, which contain prosthetic groups such as metalloporphyrins and chlorophylls. These groups, which are expected to bear the high-frequency quantum mode, play essential roles in the electron transfer. Thus the quantum mode is a primary concern for the description of this process.

When only one quantum mode is concerned, the temperature dependence of transfer rate is essentially determined by two parameters; $S = 1/2\Delta^2$ and $P = \Delta E/\hbar\omega$, which represent the displacement energy and energy gap, respectively, in the unit of vibrational quantum. Fig. 1 shows the W vs. S relationship for several values of P. For each curve W takes maximum value at $S \approx P$. This corresponds to the situation where the initial and final potential surfaces intersect near the bottom of the initial surface, as shown in the energy diagram (Fig. 2). In this case, the temperature dependence of W (curve 2 of Fig. 3) shows no activation in the whole temperature range (even slightly negative activation is recognized).

On the other hand, the conditions $S > P$ and $S < P$ cause activation energy, resulting in the temperature-dependent transfer. Especially, when S becomes large, the temperature dependence is characterized by distinct two regions; in the high-temperature range it is characterized by the Arrhenius-type activation, whereas in the low-temperature range the rate is almost independent of temperature. The latter is due to the fact that the Frank-Condon overlap does not vanish even if the vibrational energy is frozen into a zero point energy level (tunneling effect). The electron transfer from the cytochrome to the reaction center in *Chromatium* was successfully explained by this 'strong' coupling mechanism [7,10].

It should be noted in Figs. 1 and 3 that the transfer rate is strongly dependent on the values of S and P. As will be discussed later, this strong dependence is important for the variation of transfer rate.

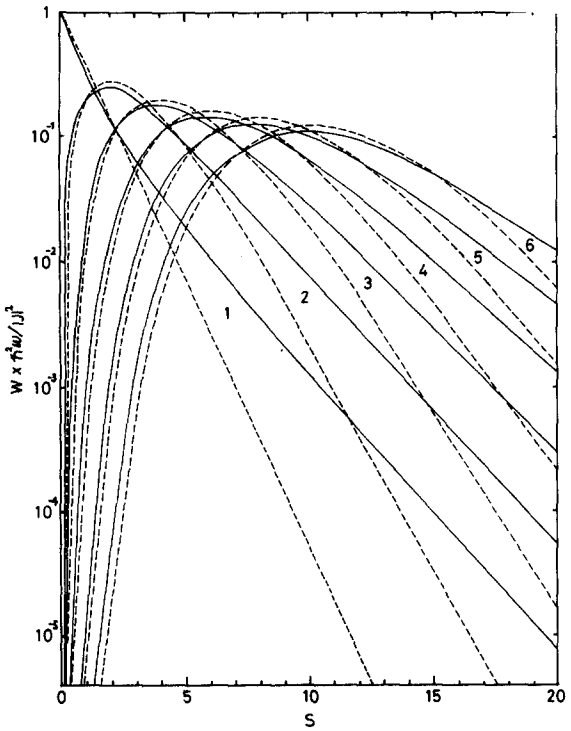


Fig. 1. P and S dependencies of transfer rate. 1, $P = 0$; 2, $P = 2$; 3, $P = 4$; 4, $P = 6$; 5, $P = 8$; 6, $P = 10$. ———, $kT/\hbar\omega = 0.486$ (high temperature); - - - - - -, $kT/\hbar\omega = 0.028$ (low temperature). When $\hbar\omega = 400$ cm^{-1}, these correspond to $T = 280$ K and 16 K, respectively.

Soft mode

According to the above simplified situation where only one kind of quantum mode is involved, the energy gap ΔE must be such that P will be an integer to ensure energy conservation during the transfer. However, this is an abnormal situation and it is usual to find a multitude of energy gaps as a result of couplings between the various modes. Low-frequency soft modes contribute to this phenomenon as in the case of electron transfers in solution where the modes of the surrounding solvent medium play a dominant role [16—19]. A similar situation is expected in biological electron transfers which frequently

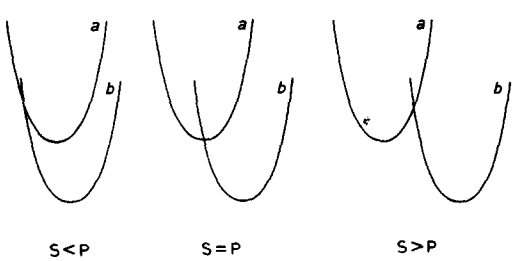
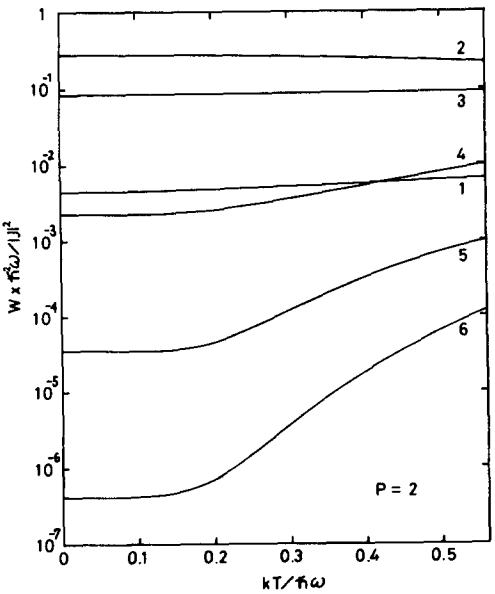


Fig. 2. Schematic energy diagrams of nuclear potential surfaces in three different situations. a and b, the initial and final surfaces, respectively.



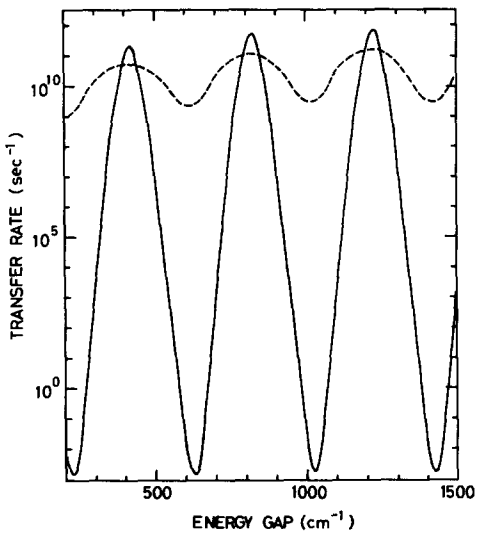


Fig. 3. Temperature dependencies of transfer rate for several values of S. 1, $S = 0.1$; 2, $S = 2$; 3, $S = 5$; 4, $S = 10$; S, $S = 15$; 6, $S = 20$.

Fig. 4. Energy gap dependencies of transfer rate at low ($T = 20$ K, ———) and high ($T = 300$ K, - - - - - -) temperatures. The value of electronic matrix element (J) is taken to be 10 cm^{-1}. Coupling strength (S_q) and frequency (ω_q) of quantum mode are 4 and 400 cm^{-1}, respectively. Similarly, $S_s = 1$ and $\hbar\omega_s = 10$ cm^{-1} for soft mode.

occur in a protein matrix where conformational changes may be coupled to the electron transfer processes. If the coupling of protein mode is not very strong, it has been shown [15] that the rate of electron transfer has an oscillatory dependence on the value of the energy gap. The temperature dependence of the transfer rate can then assume different forms according to the energy gap (Fig. 5) with even negative temperature coefficients being possible (curve 1, Fig. 5).

When a variety of modes are considered, interference among the quantum modes or among the soft modes tends to smear out the oscillatory energy gap dependence [15]. Incorporation of the semicontinuous frequency band which may be caused by the dispersion of the medium enhances this effect [14], so that in many situations the temperature dependence due to the excitation and de-excitation of soft modes should only be apparent to a diminished extent.

Nevertheless, as will be shown later, some experimental data seem to reflect the direct involvement of soft mode. It is possible that for the electron transfer in the protein environment the number of good accepting modes of protein is limited, or the frequency (band) of protein mode is well separated from that of quantum mode. For example, some collective modes of protein have been observed in the frequency range from 10 to 200 cm^{-1} [20,21]. If some of these modes are active for the electron transfer, we may expect to observe their direct effect on the transfer rate.

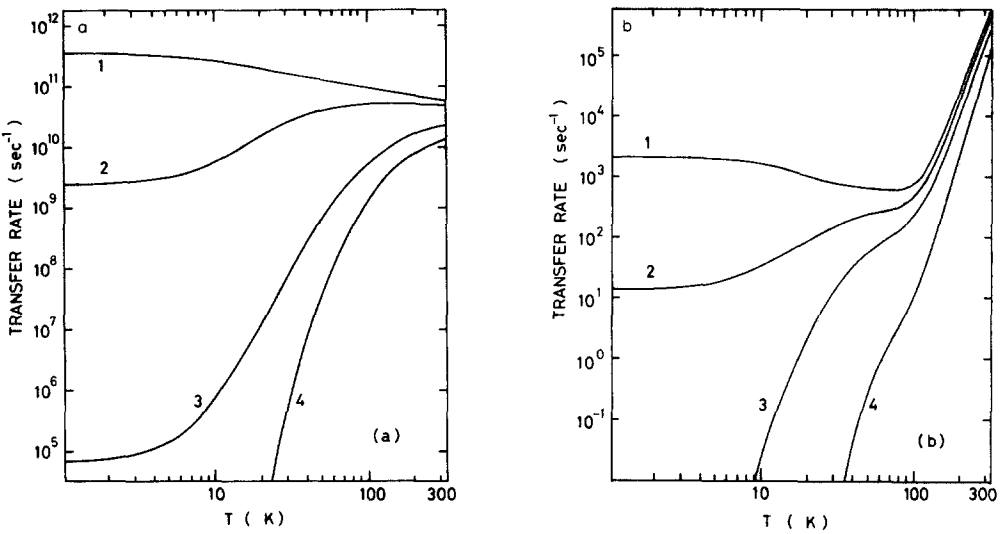


Fig. 5. Temperature dependencies of transfer for various energy gaps. (a) $S_q = 4$, $J = 10$ cm^{-1}. 1, $\Delta E = 400$ cm^{-1}; 2, $\Delta E = 450$ cm^{-1}; 3, $\Delta E = 500$ cm^{-1}; 4, $\Delta E = 300$ cm^{-1}. (b) $S_q = 20$, $J = 1$ cm^{-1}. 1, $\Delta E = 400$ cm^{-1}; 2, $\Delta E = 450$ cm^{-1}; 3, $\Delta E = 350$ cm^{-1}; 4, $\Delta E = 300$ cm^{-1}. Soft mode parameters and $\hbar\omega_q$ are the same as in Fig. 4 for both cases.

Photosynthetic electron transfer

Electron transport in the primary photosynthesis has been extensively investigated by many researchers (see Refs. 42 and 43 for recent review) and much useful information obtained. In bacteria, excitation of the reaction center leads to the formation of a state P^F in which a complex (P) containing a dimer of bacteriochlorophyll (BChl) is oxidized and an intermediate electron carrier (I) which contains bacteriopheophytin (BPh) is reduced. This initial charge separation proceeds with a half-time of about 10 ps [27]. The electron carrier I is reoxidized in a process whose half-time is about 150 ps by donating its electron to a quinone-iron complex (QFe) which in turn is oxidized by another quinone. The oxidized form of P is reduced by a *c*-type cytochrome. If QFe is reduced before the excitation of the reaction center, the transient state P^F decays with a half-time of 10 ns by the back electron transfer from I^- to P^+, or via the triplet state at low temperatures [26]. The primary photochemistry is more complex in plants and algae where two kinds of photosystems are involved.

A summary is given in Table I of the results of various studies of the temperature dependence of photosynthetic electron transfer reactions. While the information is considerable interest, it is not sufficiently detailed to permit the estimation of the parameters relevant to our analysis, except for one particular case. That exception concerns the cytochrome-reaction center redox processes in *Chromatium* for which detailed temperature experiments [2,3,46] and relevant theoretical calculations [7,10,29] have been performed. Accordingly, our discussion below of four typical electron transfer processes will in the main be theoretical but non-quantitative in nature.

TABLE I

TEMPERATURE DEPENDENCE OF ELECTRON TRANSFER PROCESS

Process	Material	Temperature dependence	Reference
RC photooxidation	*Rps. spheroides*	1K → 300K (same spectral change and quantum yield) 4K → 300K (quantum yield approx. 1)	22,23 25,26
$P * I \rightarrow P^+I^-$	*Chromatium* (RC) *Rps. viridis* (RC)	120K → 300K ($\tau_{1/2} \leqslant 10$ ps)	27
	Rps. spheroides (RC)	4.2K → 300K ($\tau_{1/2} \leqslant 10$ ps)	28
$P^+I^-Q^-Fe \rightarrow PIQ^-Fe$	*Rps. spheroides* (RC)	25K ($\tau_{1/2} \approx 20$ ns); 200 K (approx. 10 ns)	26,30
$P^+I^-QFe \rightarrow P^+IQ^-Fe$	*Rps. spheroides* (RC)	4.2K → 300K ($\tau_{1/2} \approx 150$ ps)	28
$IQ^-Fe \rightarrow I^-QFe$	*Rhs. rubrum*	29K ($\tau_{1/2}$ = 15—20 ms) ↘ 240K (approx. 35 ms) ↗	33
	Rps. spheroides (RC and whole cell)	1.5K → 80K ($\tau_{1/2} \approx 18$ ms)	44
	Rps. spheroides (RC and chromatophore)	→ 150K ($\tau_{1/2} \approx 20$ ms) ↘ 300K (approx. 70 ms)	35
	Rhs. rubrum (chromatophore and and subchromatophore)	4K ($\tau_{1/2} \approx 15$ ms) ↘ 300K (approx. 100 ms)	34
	Rps. spheroides (RC)	170K ($\tau_{1/2} \approx 25$ ms) ↘ 230K → 300K (approx. 90 ms)	36
	Rps. spheroides (RC)	90K → 200K ($\tau_{1/2} \approx 20$ ms) ↘ 270K → 300K (approx. 180 ms)	37
	E. shaposhnikovii	120K → 260K ($\tau_{1/2} \approx 35$ ms)	45
Cyt *c* $P^+ \rightarrow$ Cyt c^+ P	*Chromatium*	80K → 300K	1
	Chromatium (LP)	oxidizable >50K	39
	Chromatium (HP)	oxidation stops <160K	
	Rhs. rubrum (HP)	oxidation stops <243K	
	Rhs. spheroides	— ($\tau_{1/2}$ at 77K) — 8 μs (at 330K)	4
	Rps. capsulata	— 20—40 μs	
	Rps. gelatinosa	10—20 μs 0.5—0.8 μs	
	Rhodosporomonas sp. NW	2—6 μs 0.3—0.6 μs	
	Rps. palustris	8—12 ms <2 μs	
	T. floridana	400—800 μs <2 μs	
	Chromatium (LP)	4K → 120K ($\tau_{1/2}$ = 2 ms) ↗ 300K (<2 μs)	2,3
	Chromatium (LP) (subchromatophore)	77K → 120K ($\tau_{1/2}$ = 2.5 ms) ↗ 295K (approx. 1 μs)	46
	Rhodasporomonas sp. NW	77K → 150K ($\tau_{1/2}$ = 4 μs) ↗ 300K (approx. 0.5 μs)	47

↗, →, ↘, the rate of reaction is increasing, constant and decreasing, respectively, with increasing temperature. LP and HP represent low-potential and high-potential cytochromes, respectively. RC, reaction center complex.

Activationless electron transfer

The photooxidation of the reaction center in bacteria occurs at very low temperatures, down to 1 K [22,23]. The quantum yield has been estimated to be 1.02 ± 0.04 for *Rhodopseudomonas spheroides* [24], and is independent of temperature in the range 4—300 K [25,26]. Furthermore, it was shown recently that the electron transfers from P to I and I to QFe are independent of temperature throughout the temperature range from 4.2 to 300 K [27,28]. This activationless behavior of the primary photooxidation implies the situation where the coupling strength S and the energy gap parameter P are close each other, as inferred by above authors [28]. As shown before (see Figs. 1 and 3), this condition corresponds to a maximum transfer rate. Thus the activationless behavior may be closely connected with the ultrafast transfer, e.g., even if the electronic matrix element (J) is as small as 10 cm^{-1}, the rate of transfer can have a value of 10^{11} s^{-1}.

It should be pointed out, however, that the temperature dependence is expected to be quite small for most values of P, when S is relatively small (weak electron-phonon coupling). For example, according to Fig. 1, the transfer is almost activationless for $P \geqslant 2$ and $S \leqslant 10$. Furthermore, the incorporation of soft modes can extend the temperature region where zero activation energy can be observed and so temperature independency alone is not conclusive evidence for the condition $S \approx P$. But this condition is quite likely to be satisfied in the case of the reaction center since it can produce an ultrafast process without utilizing strong electronic overlap which usually requires specific restrictions for the relative position of the molecules.

Slow back electron transfer

In contrast with the rapid forward reactions, the back reactions are generally much slower. The electron transfer from I^- to P^+ is characterized by a half-time of 10 ns at room temperature [26,30]. The remarkable difference between the forward and back reaction rates appears to be crucial for an efficient primary photooxidation, and can be contrasted with the similar process in solution where the two rates are similar in magnitude [31]. A possible explanation for this difference has been discussed recently [29,31].

In principle, the difference will come from two contributions; electronic [31] and vibrational factors. In the former case, the relative positions of the donor and acceptor molecules (i.e. BChl and BPh) within the reaction center complex is of special importance, since the electronic overlap between these molecules is essential. In the latter case, the important parameters are the energy gap (or P) and the rearrangement energy (or S). Since the value of P for the forward reaction will be much less than the value for the back reaction it is possible to have $S \approx P$ for the forward reaction and $S < P$ for the back reaction. Thus the rate of the back reaction will be considerably reduced as can be seen in Fig. 1. For example, when $S = 2$, increase of P from 2 to 10 reduced the rate by a factor of 10^3. However, this argument becomes invalid if the value of S is relatively large (greater than or equal to 5) (in the case of cytochrome-reaction center reaction S was estimated to be 20 [10]) and it is not certain whether this factor alone is responsible for the roughly thousand fold difference in the rates.

Let us consider the possible role of the protein mode in controlling the transfer rate. As discussed previously, the soft mode may play a sensitive role in determining the transfer rate and its temperature dependence under certain conditions, i.e., the transfer rate and temperature dependency may be sensitively affected by the values of energy gap and rearrangement energy. In the case of electron transfer in solution, various surrounding medium (phonon) modes will promote rapid reactions [31], and the drastic variations of transfer rate due to soft mode will not be expected. In a protein environment, however, the number of such modes for accelerating electron transfer may be limited. It is interesting that the state P-I^- survives for 20 min at 200 K [32]. This remarkable stability suggests that the reaction center protein prevents interaction between prosthetic groups and the medium. Thus, for example, if the situation for the back reaction is such that the number of vibrational quanta distributed to the protein mode and the coupling strength of protein mode are mismatched, the transfer rate will be considerably reduced.

In summary, we suppose that the reaction center protein prevents a wasteful energy loss due to the back reaction, by controlling the distribution of vibrational energy. However, more research is necessary to determine whether the electronic or vibrational factor is dominant in controlling the transfer rate.

Negative activation

As can be seen in Table I, the back electron transfer from Q^-Fe to the BChl-BPh complex shows the negative activation, i.e. the transfer rate decreases with increasing temperature. Furthermore, the detailed temperature behavior seems to depend on species and the method of preparation: in *Rhodospirillium rubrum* the transfer rate shows the temperature dependence down to quite low temperature [33,34], while in *Rps. spheroides* the rate is temperature independent below about 150 K [35—37].

These peculiar types of temperature behavior have been explained in two ways; (1) the geometry of molecular association changes with temperature (molecular distance increases with increasing temperature) [35,38], or (2) there is another competitive route for electron transfer with different activation energy, so that the temperature dependence of back reaction apparently decreases with increasing temperature [33,35]. Hsi and Bolton [35] estimated that there was a change of 2 Å in the distance between the reaction center complex and acceptor, which explained the change in half-time from 20 to 70 ms as the temperature rose from 150 to 300 K. It is not obvious that such a large change in distance could occur at such low temperatures where molecular association should be quite rigid. Furthermore, if such geometrical changes are involved, they should also affect the kinetics of forward electron transfer (i.e. from I^- to QFe) in the similar way but there is no sign of a negative activation for this process in *Rps. spheroides* [28].

On the other hand, we have already pointed out [15] that these phenomena could be caused by the vibrational factor under certain condition (Fig. 5). In particular, the negative activation observed at very low temperatures seems to reflect the direct effect of the protein mode. An interesting consequence of the negative activation due to soft mode is that it may apparently lower the activation energy caused by quantum mode.

Cytochrome-reaction center reaction

The low-temperature electron transfer from cytochrome *c* to the reaction center was first recognized in the sulfur bacterium *Chromatium* [1], and its temperature dependence has been extensively investigated both experimentally [2,3] and theoretically [7,10]. Later, the low-temperature experiments for various bacterial species [4,39] revealed the species variation in the temperature behavior of cytochrome oxidation (see Table I). In some species, low-temperature (less than or equal to 77 K) reactions proceed at rates too low to measure. It is now recognized that the variation of temperature behavior is partly associated with the existence of two kinds of *c*-type cytochromes with different redox potentials [40].

From a theoretical viewpoint, the variation can be caused by either electronic or vibrational factors, as already pointed out. It is quite likely that the variation in the absolute rate is caused by the former [4], however, the variation in the temperature dependence due to this factor is expected to be small unless J has strong temperature dependence. On the other hand, the vibrational factor should be mainly responsible for the temperature dependence.

While quantum modes have been shown to play an important role in the temperature dependence [7,10], we have shown that the incorporation of soft modes may cause further temperature dependences via the protein environment. For example, in some situations where soft modes are involved the rate will be considerably diminished at low temperature (Fig. 5). Thus we suppose that the various temperature behaviors observed in different species may be partly attributed to the variability of protein soft mode. Unfortunately, the present knowledge of the temperature dependence of cytochrome oxidation is insufficient to make a definite conclusion. It will be quite interesting to investigate the detailed temperature dependence in various bacterial species, which will afford valuable informations about the molecular environment in which the electron transfer occurs.

Ke et al. [41] investigated the oxidation of mammalian cytochrome *c* by the reaction center from *Rps. spheroides*, and observed an efficient electron transfer with a half-time of 25 μs. The temperature dependence of this process yielded an activation energy of 12 kcal/mol in the physiological temperature range, but the reaction was uncoupled below freezing temperature. This relatively large activation energy and the inability of reaction at low temperature indicate the vibrational mismatching in this system. Furthermore, it may also mean that the protein structure of the cytochrome-reaction center system in vivo provides an environment in which the reaction proceeds with a low activation energy; thus implying the role of soft mode in reducing the activation energy.

Conclusion and Discussion

The unusually efficient energy conversion in the primary reactions of photosynthesis is one of the most striking aspects in the overall photosynthetic process. This remarkable property seems to be closely connected with the fact that the photosynthetic system utilizes a variety of electron transfers which are characterized by a wide range of relaxation times (10^{-2}—10^{-11} s), and

arranges them in a very systematic manner to avoid wasteful energy losses. This led us to propose that the protein environment, unlike the situation in a solution, is important for the efficient operation of photosynthesis and, in particular, it is important in controlling the irreversibility of electron transfers and minimizing the energy dissipation due to back reactions.

For the initial photooxidation in the reaction center complex, it was suggested that the vibrational factor plays an important role in regulating the transfer rate; i.e. the ultrafast electron transfer from P to I would be realized by the activationless condition $P \approx S$, and the relatively slow back transfer from I^- to P^+ would be associated with the mismatching of the energy gap and rearrangement energy. Furthermore, the latter process indicated the possibility that the protein soft mode regulates the rate by controlling the distribution of vibrational quanta during the transfer. In the case of electron transfer from cytochrome *c* to reaction center, we supposed that the diversified temperature behaviors observed in various species might be partly associated with the variability of the protein mode, in addition to the contribution from the quantum mode.

As noted in the preceding section, the presence of many modes (or a continuous phonon mode) tends to smear out the vibrational structure due to the excitation or de-excitiation of the soft mode [14,15], and so the explicit effect of soft mode may not be observed. However, we have noticed the possibility that the number of accepting modes available for the electron transfer may be limited, since the chromophore molecules are embedded in the special protein structure which may serve as an insulator from the surrounding continuum. Even when the dispersion effect is considered, we may expect to find a quantum effect due to the soft mode as long as the frequency band is well separated from the frequency of quantum mode. In the protein environment, therefore, we may expect the oscillatory energy gap dependence of the transfer rate, which is analogous to the vibrational structure observed in the absorption spectrum.

In this situation, the direct effect of the protein mode will be revealed in the temperature dependence of transfer rate. The negative activation phenomenon observed in the back electron transfer from Q^-Fe to P^+-I complex at low temperatures appears to be an example which reflects the involvement of protein mode. However, the presently available temperature data are still insufficient to estimate how the protein mode is coupled to the electron. A detailed model for the role of protein must await further experimental studies. Especially, detailed temperature experiments for various species would provide useful informations for this problem.

In the present investigation we have neglected the temperature dependence of the electronic matrix element J, which may depend on temperature through the structural parameters such as molecular distance and orientation between acceptor and donor. At present we cannot estimate how much modification is introduced by these factors because of our lack of knowledge about the specific interactions among the complex molecular structure. In general, however, we might expect that the variation of molecular structure with temperature is quite small (especially at low temperatures) unless any cooperative structural changes (phase changes) are involved.

The theoretical method used here was based on the non-adiabatic transition between two vibronic states. The assumption of non-adiabatic transfer will be justified even when the ultrafast electron transfer in reaction center is concerned, since the large rate constant $10^{11}\ s^{-1}$ observed experimentally, is expected theoretically even if the value of J is as much as 10 cm^{-1} (see Fig. 5a). We suppose that in the reaction center complex the activationless condition $S \approx P$ makes the ultrafast process possible without utilizing strong electronic interaction.

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