Tetrahedron Vol. 45, No. 15, pp. 4683 to 4692, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00
Maxwell Pergamon Macmillan plc

PICOSECOND LASER PHOTOLYSIS STUDIES ON DIMER MODEL SYSTEMS IN RELATION TO PHOTOSYNTHETIC CHARGE SEPARATION PROCESSES

Noboru Mataga,* Hiroshi Yao and Tadashi Okada
Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan

(*Received in USA* 14 *December* 1988)

Abstract

In relation to the photoinduced charge separation in the special pair of photosynthetic reaction center, solvation induced intramolecular electron transfer in the excited state of composite system with identical halves have been investigated with picosecond spectroscopy in the case of 1,2-dianthrylethanes. The energy gap dependences of charge separation and charge recombination in these systems are demonstrated and compared with those of hybrid dimer model of metal porphyrins, porphyrin-quinone systems and various aromatic donor-acceptor systems. The significance of these results in the understanding of efficient charge separation in biological reaction center is discussed.

INTRODUCTION

In relation to the mechanisms of photoinduced electron transfer (ET) and charge separation (CS) processes in biological photosynthetic reaction center (RC), investigations on porphyrin-electron acceptor model systems have been made quite extensively.[1] On the other hand, result of the X-ray analysis on the bacterial photosynthetic RC[2] shows two-fold symmetric arrangement of chromophores with the special pair (SP) of bacteriochlorophylls at center, where the photoinduced ET starts leading to a series of redox processes. In the SP, two bacteriochlorophyll chromophores interact weakly and the first CS process seems to take place at SP, leading from a pair of symmetric neutral chromophores to a cation-anion pair.[3]

Therefore, the first step of CS in the photoexcited RC is a symmetry breaking process due to ET in the SP with identical halves, which might be induced by some environmental effect in proteins on which the chromophores are held. In this respect, it will be an important problem to examine the photoinduced CS in model systems with identical halves. However, contrary to the case of the intramolecular exciplex systems where donor and acceptor are combined with spacers or directly by single bond and photoinduced intramolecular CS takes place easily,[4] clear-cut examples of the systems with identical halves combined by spacer or directly by single bond are quite scarce.

An example is 9,9'-bianthryl (BA) which undergoes solvation-induced symmetry breaking due to the photoinduced intramolecular CS.[5] This system has a special conformation where two anthracene planes are perpendicular to each other due to the steric repulsion. This special structure keeps the electronic interaction between the two chromophores moderately weak, which prevents the formation of symmetrical excimer-like state overcoming the driving force of symmetry breaking by solvation. However, recent picosecond laser photolysis and accurate time resolved transient absorption spectral measurements show that the photoinduced CS of BA in polar solvent is not complete but a little delocalization interaction between cation and anion pair or some admixture of neutral excited state into the intramolecular electron transfer state should be taken into consideration.[6] This seems to be a reasonable result because two chromophores are directly combined by single bond even if this planes are perpendicular to each other in the equilibrium configuration in the ground state.

Another example with identical halves combined by spacer, which seems to undergo solvation induced intramolecular CS in the excited state are 1,2-dianthrylethanes[7] and [2.2](1,3)pyrenophane(metapyrenophane).[8] According to our previous fluorescence studies, these compounds show an enhancement of intramolecular excimer formation with increase of solvent polarity.[7,8] This result seems to indicate the solvation induced intramolecular CS in polar solvents, which accelerates a slight conformation change leading to the excimer formation. Therefore, these systems with identical halves combined by saturated carbon-carbon bonds will be also very interesting as models for the photoinduced CS in the SP of photosynthetic RC. Actually, we have observed directly by picosecond time-resolved transient absorption spectral measurements formation of intramolecular electron transfer (ET) state in the case of 1,2-dianthrylethanes (1,2-di(1-anthryl)ethane(1,2-D(1-A)E) and 1,2-di(9-anthryl)ethane (1,2-D(9-A)E)) dissolved in polar solvents.

In the following, results of this investigation will be reported and mechanisms of the photoinduced CS and recombination of the ET state of 1,2-dianthrylethanes will be discussed in comparison with those of various aromatic electron donor-acceptor pair,[4,9] porphyrin-quinone systems[1a-e,g-i] and some metal porphyrin dimer model compounds.[1f,j] We discuss here mainly the results of 1,2-D(1-A)E in polar solvents.

EXPERIMENTAL

Picosecond time-resolved transient absorption spectra and fluorescence rise and decay curves were measured by means of a mode-locked Nd^{3+}:YAG laser photolysis system.[10] 1,2-D(1-A)E and 1,2-D(9-A)E were the same sample as used before.[7] 1-Methylanthracene (1-MA) was sublimed before use and 9-methylanthracene (9-MA) was recrystallized from ethanol. Spectrograde n-hexane, ethylacetate, acetone and acetonitrile were used without purification. Sample solutions of ca. 10^{-4} M for the measurement were deoxygenated by freeze-pump-thaw cycles or by flushing with nitrogen gas.

RESULTS AND DISCUSSIONS

1. Picosecond time-resolved transient absorption and fluorescence measurements on 1,2-dianthrylethanes

1.A. 1,2-D(1-A)E.

As examples of time-resolved transient absorption spectra of 1,2-D(1-A)E, those in n-hexane, ethylacetate and acetonitrile are shown in Figs. 1, 2 and 3, respectively. In Fig. 4a, $S_n \leftarrow S_1$ absorption spectrum of 1-MA in n-hexane (at the delay time of 100 ps) and those of 1-MA anion and 1-MA cation in acetonitrile are indicated for the purpose of comparison with the spectra in Figs. 1-3, where 1-MA anion and cation radicals are produced by photoinduced electron transfer from N,N-dimethylaniline to excited 1-MA and from excited 1-MA to p-dicyanobenzene.

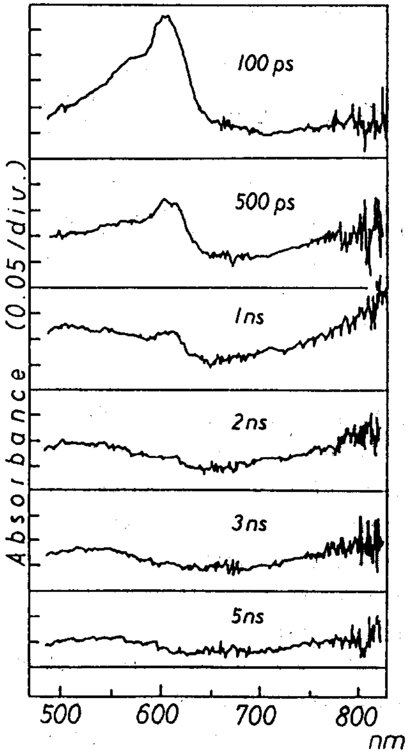

Fig. 1. Picosecond time-resolved transient absorption spectra of 1,2-D(1-A)E in n-hexane.

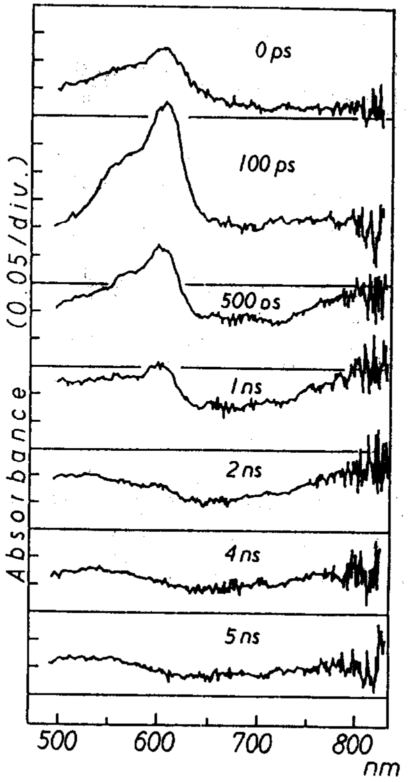

Fig. 2. Picosecond time-resolved transient absorption spectra of 1,2-D(1-A)E in ethylacetate.

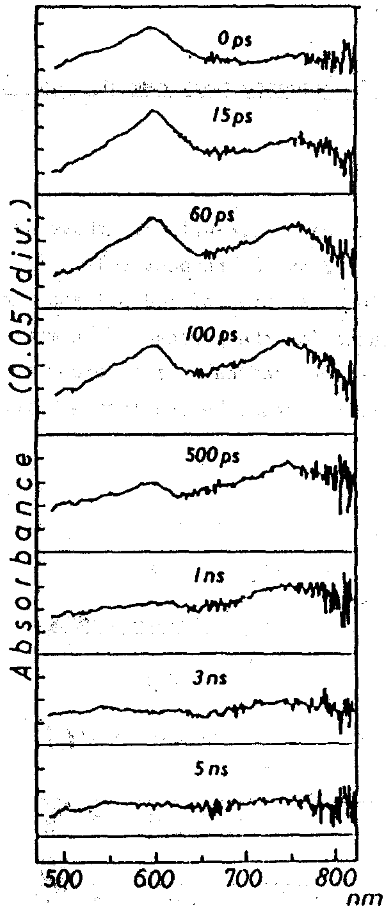

Fig. 3. Picosecond time-resolved transient absorption spectra of 1,2-D(1-A)E in acetonitrile.

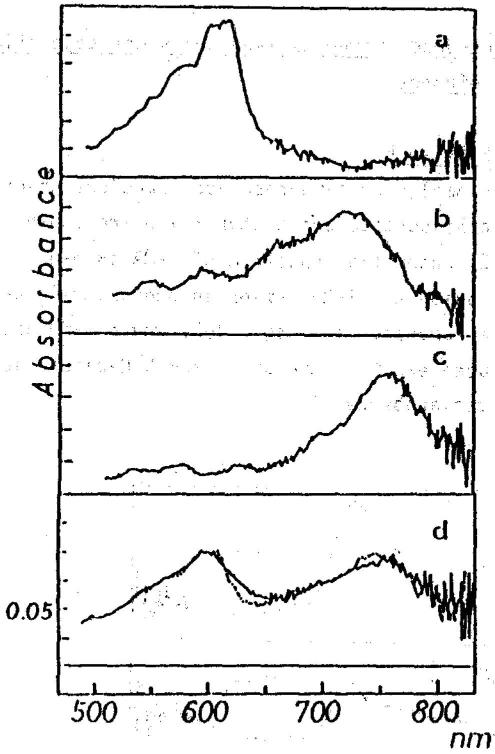

Fig. 4. a. $S_n \leftarrow S_1$ absorption spectrum of 1-MA in n-hexane. b. Absorption spectrum of 1-MA anion radical in acetonitrile. c. Absorption spectrum of 1-MA cation radical in acetonitrile. d. Simulation of the observed transient absorption spectrum (——) of 1,2-D(1-A)E in acetonitrile at 60 ps by superposition of the spectra in a. b. and c. with least squares method (·····).

The absorption spectrum in Fig. 1 at 100 ps is very similar to $S_n \leftarrow S_1$ spectrum of 1-MA indicated in Fig. 4a. With increase of delay time, the spectrum changes to a very broad one due to intramolecular excimer state. We have measured the decay time (τ_d(LE)) of fluorescence from locally excited (LE) state and rise time(τ_r(Ex)) of excimer fluorescence and have confirmed that τ_d(LE)$\sim\tau_r$(Ex)$\sim$450 ps, which are in an approximate agreement with the time constant of the change of transient absorption spectrum from $S_n \leftarrow S_1$ to the broad excimer band as shown in Fig. 1. At 500 ps$\sim$1 ns delay times, a remarkable enhancement of absorbance in the region longer than 750 nm is observed while this absorbance has decayed almost completely at 5 ns. We have confirmed that the excimer fluorescence shows two component decay with ca. 1$\sim$2 ns and 30$\sim$40 ns decay times in various solvents examined. In n-hexane, the decay times have been observed to be ca. 2 ns and 35 ns, respectively. The transient absorption in the wavelength region longer than 750 nm may be assigned to the short-lived excimer and the absorption observed at 5 ns may be due to the long-lived one. These two kinds of excimers seem to have different conformations and the long-lived one may have a more symmetrically overlapping structure. In any way, the excimer state is formed from the LE excited state by intramolecular diffusional rearrangement of anthracene chromophores in n-hexane solution

In ethylacetate solution, a large amount of excimer exists already at 100 ps as we can see from Fig. 2. With increase of delay time, rise and decay of the short-lived excimer showing characteristic absorption in the wavelength region longer than 750 nm can be observed. The rise of this excimer absorption is in accordance approximately with the decay of the absorption similar to the $S_n \leftarrow S_1$ band of 1-MA, which is in agreement with the fact that the decay time of the LE fluorescence is approximately the same as the rise time of the excimer fluorescence ($\sim$700 ps). Therefore, the short-lived excimer seems to be produced by intramolecular diffusional rearrangement of the chromophores and the slower formation process compared with the case of n-hexane solution may be due to higher viscosity of ethylacetate.

In acetone solution, we have observed more enhanced rapid excimer formation and also a slight indication of the intramolecular ion pair formation. Moreover, as it is discussed in the following, we have observed clearly very raid formation of a large amount of intramolecular ion pair in acetonitrile solution (Fig. 3). These results suggest strongly that the enhancement of the rapid excimer formation in ethylacetate and acetone compared with *n*-hexane solution is due to the photoinduced rapid intramolecular CS followed by a small conformation change leading to the excimer formation. This rapid intramolecular CS will take place immediately after excitation in the system where two chromophores are close to each other already in the ground state (cis or gauch form, for example). The slower excimer formation process in ethylacetate and acetone may be due to the intramolecular diffusional rearrangements of the chromophores which are more distant from each other (trans or gauch form) as discussed already. Whether intramolecular CS plays some role in the course of this slow excimer formation is not very clear at the present stage of investigation. In any way, the most important observation in the present work is the rapid photoinduced CS between the identical chromophores as discussed below in the case of acetonitrile solution.

In Fig. 3, a characteristic broad absorption band around 740 nm can be observed immediately after excitation in addition to the absorption band similar to the 1-MA $S_n \leftarrow S_1$ band. The observed spectrum at 60 ps, for example, can be approximately reproduced by the superposition of the $S_n \leftarrow S_1$ band of 1-MA and absorption bands of 1-MA anion and cation radicals as shown in Fig. 4d. The results in Fig. 3 and Fig. 4d indicate that very rapid photoinduced CS takes place within a few 10 ps. This rapid CS seems to occur in the system with two chromophores placed closely in the ground state as discussed already. In acetonitrile solution, strong solvation of the intramolecular ion pair state will prevent such a raid excimer formation by a slight geometrical change as observed in ethylacetate solution, leading to the clear-cut observation of the ion pair state in 10 ps∿100 ps time regions.

At longer delay times of 100 ps∿a few ns, both absorption bands due to neutral S_1 (LE) state and ion pair state decay and excimer state is formed. In the course of the excimer formation (slow process), probably the intramolecular CS will take place, which accelerates the excimer formation. This is in accordance with the fact that the decay of LE fluorescence as well as rise of excimer (ca. 400 ps) are faster than those in n-hexane solution although the viscosity of acetonitrile is higher than that of n-hexane.

1.B. 1,2-D(9-A)E.

Analogous photoinduced ET and excimer formation processes seem to occur also in the case of 1,2-D(9-A)E in polar solvents according to our picosecond laser photolysis studies. We have confirmed actually formation of transient ion pair state in several 10 ps∿several 100 ps regions in the case of acetone and acetonitrile solutions, although its absorption spectrum is not so prominent as in the case of the 1,2-D(1-A)E in acetonitrile. At any rate, the general features of intramolecular ET state and excimer formation are similar to the case of 1,2-D(1-A)E.

2. Energetics of intramolecular photoinduced charge separation, charges recombination (CR) and excimer formation in 1,2-dianthrylethanes

We examine above experimental results on the basis of theoretical considerations on the energy gap dependences of the photoinduced CS and CR of the ion pair state. We extend similar considerations to the problems of photoinduced CS and CR of ion pair in porphyrin dimer and porphyrin-acceptor systems in the next section.

By using the oxidation and reduction potentials of anthracene chromophore and by taking into consideration the coulombic attraction between cation and anion moieties in acetonitrile solution, the free energy of the ion pair state above the ground state has been estimated to be $-\Delta G^\circ_{ip}=2.85$ eV.[7b] Since the energy of the LE state is $\Delta E(S_1)=3.18$ eV, the energy gap for the photoinduced CS reaction is given by $\Delta G^\circ_{et}=-0.33$ eV. On the basis of the results of theoretical calculations on the energy gap dependence of the CS reaction rate constant,[11] k_{CS} in acetonitrile at $-\Delta G^{\circ}_{et}$=0.33 eV is estimated to be $k_{CS} \approx 10^{11} \sim 10^{10}$ s^{-1}. This is in agreement with the fast photoinduced ion pair formation observed in acetonitrile solution of 1,2-dianthrylethanes as described above. For the CR reaction to the ground state, the experimental as well as theoretical studies[9,11c] predict $k_{CR} \approx 10^{7} \sim 10^{8}$ s^{-1}. Therefore, contrary to the rapid photoinduced CS, the CR deactivation is much slower. However, in the case of 1,2-dianthrylethanes, the lifetime of the ion pair state becomes much shorter than k_{CR} due to the conversion to the excimer state. Although the energy of the excimer state above the ground state is not clear, a rough estimation using the energy of the observed excimer fluorescence and excimer binding energy of 9-MA indicate that the excimer state is rather close to the ion pair state. If the mutual approach of the chromophores in the present system is prevented by fixing them by rigid spacer, the lifetime of the ion pair state may become much longer.

As described above, results of the picosecond laser photolysis studies on the 1,2-dianthrylethanes can be reasonably well understood on the basis of the energy gap dependence of the CS and CR rate constant as theoretically predicted and observed for many aromatic donor-acceptor systems.[9,11] The present system gives a clear-cut example of the intramolecular radical ion pair state formation in the excited composite system with identical halves, and it should be noted that the CR of the intramolecular ion pair state is much slower compared with the photoinduced CS, which is very favorable for the efficient energy storage.

3. On the photoinduced CS and CR of radical ion pair state in porphyrin dimer models and porphyrin-quinone systems.

In relation to the above results of picosecond laser photolysis studies on 1,2-dianthrylethanes, we discuss here similar problems in porphyrin dimer model compounds which we have investigated by picosecond laser photolysis.[1j] In the biological photosynthetic RC, the primary photoinduced CS takes place between porphyrins, and not between porphyrin and quinone. Moreover, compared with the very fast photoinduced CS among porphyrins, the CR of the ion pair state seems to be considerably slower in the biological RC, which enhances the CS efficiency. This result is somewhat similar to that of 1,2-dianthrylethanes as discussed above in 2. Therefore, it is very important to elucidate the dynamics and mechanisms of photoinduced CS and CR of ion pair state in model systems containing porphyrins and metal porphyrins. In this respect, we have made picosecond time-resolved transient absorption as well as picosecond time-resolved fluorescence studies on photoinduced electron transfer (ET) in hybrid dimers of porphyrin connected by flexible covalent chains, i.e. tetratolylporphinato Zn(II) (ZnP) combined by 1,3-dioxypropane chain with tetratolylporphinato Fe(III) (Fe(III)PCl) or tetratolylporphinato Mn(III) (Mn(III)PCl), abbreviated as ZnP/Fe(III)PCl and ZnP/Mn(III)PCl, respectively.

We have confirmed that the strong quenching of ZnP fluorescence in these dimers in dimethylformamide solution is caused by rapid electron transfer from excited ZnP to Fe(III)PCl or Mn(III)PCl moieties with time constant of $30\sim40$ ps, while back ET from Fe(II)PCl or Mn(II)PCl to ZnP^{+} in the same systems is much slower and requires almost 1 ns. On the other hand, the free energy gaps for the photoinduced ET and back ET of these systems are approximately the same and ca. $-\Delta G \sim 1$ eV, which indicates that the rates of two ET reactions should be approximately the same according to the usual theory of ET reaction.[12] We have interpreted this contradictory result by assuming different energy gap dependence for these two ET reactions, on the basis of our new theory.[11]

Namely, by taking into account the fact that the orientational vibration (c-mode) frequency of the polar solvent strongly solvated or coordinated to a charged solute may be considerably larger than that surrounding a neural solute, rate expressions have been given which give a satisfactory interpretation for the difference between the energy gap dependences of CS and CR or "charge generation" reaction and "charge annihilation" reaction. In this treatment, the Franck-Condon factor includes the intramolecular vibrational modes as well as the solvent c-mode. In addition to the c-mode in the first solvent layer, effects of outer solvent layers where the reorientation frequencies around charged and neutral solute are the same should be taken into account in general. However, in the case of large porphyrin molecules, the solvation effect of the outer layer will be weak and we consider only the effect of strong solvation or coordination of the solvent in the first layer to the charged site of porphyrin.

This theory predicts that the rate constant of the charge generation reaction $Zn^{*}P$/Fe(III)PCl or Mn(III)PCl$\rightarrow ZnP^{+}$/Fe(II)PCl or Mn(II)PCl in polar environments will reach a maximum of $\sim10^{11}$ s^{-1} at $-\Delta G^{\circ}\sim1$ eV and will be rather insensitive to small changes of energy gap,[1j,11] while the rate constant of the charge annihilating back ET to the ground state will show a strong energy gap dependence and can take the value of 10^{9} s^{-1} or smaller at $-\Delta G^{\circ}\sim1$ eV in the inverted region.[1j,11d]

Above results on hybrid dimers of metal porphyrins indicate that, even if the energy gap for the photoinduced ET and that of the back ET to the ground state are approximately the same, the back ET rate can be considerably smaller than that of the forward ET. Therefore, if the photoinduced CS takes place in the case of porphyrin dimers with identical halves, much slower CR to the ground state will be realized owing to the similar energy gap relations between the CS and CR process as in the case of 1,2-dianthrylethanes or above hybrid dimers of metal porphyrins. For example, by using the values of oxidation and reduction potentials in polar solvents and excitation energies to S_1 state,[13] the energy gap for the photoinduced ET from S_1 state seems to be ca. $-0.1\sim-0.2$ eV for chlorophylls, bacteriochlorophylls, and pheophytins, while the energy gap between the ET state and the ground state will be ca. $-1.5\sim-1.6$ eV.

On the basis of the above energy gap laws[11d] we have applied to the hybrid dimers of metal porphyrins,[1j] the photoinduced ET in these dimers with identical halves will be sufficiently fast (with time constant of ~10 ps) if the tunneling matrix element is not very small and the back ET will be very slow (with time constant of several 10 ns) due to the small Franck-Condon factor. The energy gap relation for the photoinduced ET is more favorable for the chlorophyll-pheophytin pair, and examination of the model system of chlorophyll dimer combined with pheophytin is a very important problem, although a very clear-cut direct observation with ultrafast laser photolysis does not seem to be available.

On the other hand, porphyrin-quinone pairs can undergo also fairly rapid photoinduced ET owing to the appropriate magnitude of the relevant energy gap,[1] if the tunneling matrix element is not very small, while back ET deactivation in this system is also very rapid in general,[9] especially in polar solutions.[1b] This circumstance is the same also in the case of combined systems.[1c,e] This rapid CR decay is governed by the Franck-Condon factor for this pair.[9] In this respect, it should be emphasized that, as it has been demonstrated already by several groups,[1] the lifetime of the intramolecular ET state in the system where multistep ET seems to be possible is considerably longer than in the system of single step ET, since the multistep ET will more or less suppress the rapid CR decay of ET state in the first step.

4. Concluding remarks

Integrating the above described results and discussions on the photoinduced ET and back ET deactivations in 1,2-dianthrylethanes, porphyrin dimers and porphyrin-quinone systems, we can understand very well the crucial importance of the multistep ET in biological photosynthetic reaction center where the very rapid and highly efficient primary ET takes place among porphyrin dimer and pheophytin and then electron shifts to quinone. In this multistep process, when electron moved to quinone, very small tunneling matrix element prevent the CR decay of the ET state.

N. M. acknowledges the support by a Grant-in-Aid (No. 62065006) from the Japanese Ministry of Education, Science and Culture.

REFERENCES

1. (a) Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S.; Karen, A.; Okada, T.; Mataga, N. J. Am. Chem. Soc. 1983, 105, 7771. (b) Mataga, N.; Karen, A.; Okada, T.; Nishitani, S.; Sakata, Y.; Misumi, S. J. Phys. Chem. 1984, 88, 4650. (c) Mataga, N.; Karen, A.; Okada, T.; Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S. J. Phys. Chem. 1984, 88, 5138. (d) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J.-C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Liddell, P. A.; Lehman, W. R.; Nemeth, G. A.; Moore, A. L. Nature (London) 1984, 307, 630. (e) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. J. Am. Chem. Soc. 1985, 107, 1080. (f) Brookfield, R. L.; Ellul, H.; Harriman, A.; Porter, G. J. Chem. Soc. Faraday Trans 2. 1986, 82, 219. (g) Joran, A. D.; Leland, B. A.; Felker, P. M.; Zewail, A. H.; Hopfield, J.; Dervan, P. B. Nature (London) 1987, 327, 508.

(h) Harrison, R. J.; Pearce, B.; Beddard, G. S.; Cowan, J. A.; Sanders, J.K.M. Chem. Phys. 1987, 116, 429. (i) Schmidt, J. A.; McIntosh, A. R.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S.; Hurley;, J. K.; Wasielewski, M. R. J. Am. Chem. Soc. 1988, 110, 1733. (j) Mataga, N.; Yao, H.; Okada, T.; Kanda, Y.; Harriman, A. Chem. Phys., 1989, 131, 473.

2. Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. J. Mol. Biol. 1984, 180, 385.

3. (a) Boxer, S. G.; Gottfried, D.; Lockhart, D.; Middendorf, T. J. Chem. Phys. 1987, 86, 2439. (b) Lockhart, D. J.; Boxer, S. G. Biochemistry 1987, 26, 664.

4. For a direct observation with picosecond time-resolved tansient absorption spectral measurements, see for example, (a) Mataga, N. Pure & Appl. Chem. 1984, 56, 1255. (b) Mataga, N. Acta Phys. Polon. 1987, A71, 767. (c) Okada, T.; Mataga, N.; Baumann, W.; Siemiarczuk, A. J. Phys. Chem. 1987, 91, 4490. (d) Nakatani, K.; Okada, T.; Mataga, N.; De Schryver, F. C. Chem. Phys. 1988, 121, 87, and papers cited in these papers.

5. (a) Nakashima, N.; Murakawa, M.; Mataga, N. Bull. Chem. Soc. Jpn. 1976, 49, 854; (b) Rettig, W.; Zander, M. Ber. Bunsenges. Phys. Chem. 1983, 87, 1143.

6. (a) Mataga, N.; Yao, H.; Okada, T.; Rettig, W., J. Phys. Chem., in press. (b) Okada, T.; Yao, H.; Mataga, N., manuscript in preparation.

7. (a) Hayashi, T.; Suzuki, T.; Mataga, N.; Sakata, Y.; Misumi, S. Chem. Phys. Lett. 1976, 38, 599. (b) Hayashi, T.; Suzuki, T.; Mataga, N.; Sakata, Y.; Misumi, S. J. Phys. Chem. 1977, 81, 420.

8. (a) Hayashi, T.; Mataga, N.; Sakata, Y.; Misumi, S. Chem. Phys. Lett. 1976, 41, 325. (b) Hayashi, T.; Mataga, N.; Umemoto, T.; Sakata, Y.; Misumi, S. J. Phys. Chem. 1977, 81, 424.

9. (a) Mataga, N.; Miyasaka, H.; Asahi, T.; Ojima, S.; Okada, T., Ultrafast Phenomena VI, 1988, Springer Verlag, in press. (b) Mataga, N.; Asahi, T.; Kanda, Y.,; Okada, T.; Kakitani, T. Chem. Phys. 1988, 127, 249. (c) Mataga, N. in: "Photochemical Energy Conversion" (Proc. 7th Internat. Conf. Photochemical Conversion and Storage of Solar Energy) eds. J. Norris, D. Meisel, Elsevier, 1988, p. 32.

10. Miyasaka, H.; Masuhara, H.; Mataga, N. Laser Chem. 1983, 1, 357.

11. Kakitani, T.; Mataga, N.; (a) Chem. Phys. 1985, 93, 381; (b) J. Phys. Chem. 1985, 89, 8; (c) ibid. 1986, 90, 993; (d) ibid. 1987, 91, 6277.

12. Marcus, R. A.; Sutin;, N. Biochim. Biophys. Acta. 1985, 811, 265.

13. Seely, G. R. Photochem. Photobiol. 1978, 27, 639.