Ultrafast Processes in Spectroscopy 1991

Proceedings of the Seventh International Symposium on Ultrafast Processes in Spectroscopy held in Bayreuth, Germany, 7–10 October 1991

Emil Warburg — Symposium
EPS — Meeting

Edited by A Laubereau and A Seilmeier

Institute of Physics Conference Series Number 126
Institute of Physics, Bristol and Philadelphia

Contents

b) Ti:Sapphire Lasers and Parametric Oscillators

c) Dye Lasers

IV. Applications to Solid State Physics and Surface Dynamics

V. Applications to Semiconductors

a) Carrier Dynamics in Bulk Semiconductors

b) Carrier Dynamics in Semiconductors of Low Dimensionality

VI. Applications to Molecular Systems

a) Ultrafast Photo-Excitation of Molecules

Inst. Phys. Conf. Ser. No 126: Section VIII
Paper presented at Int. Symp. on Ultrafast Processes in Spectroscopy, Bayreuth, 1991

Low temperature reaction dynamics in the primary electron transfer of photosynthetic reaction centers

W. Zinth*, C. Lauterwasser* and U. Finkele

Physik Department der Technischen Universität München,
8000 München Germany

*Present address: Institut für Medizinische Optik der Ludwig-Maximilians-Universität,
8000 München Germany

ABSTRACT: The primary electron transfer in reaction centers of Rhodobacter (Rb.) sphaeroides is investigated as a function of temperature with subpicosecond time resolution. The experimental results indicate that the electron transfer is not thermally activated and that the same transfer mechanisms are active at low temperatures and at room temperature.

1. INTRODUCTION

Photosynthetic conversion of light energy into chemical energy starts via several electron transfer (ET) reactions in pigment protein complexes called reaction centers (RC's). A series of recent experiments have shown that the most rapid electron transfer processes proceed on the time scale of picoseconds /1-7/. During these reactions an electron is transferred from the primary donor (P), a pair of bacteriochlorophyll molecules via a chain of chromophores to a quinone acceptor molecule. From the structural arrangement /8, 9/ of the chromophores in the reaction centers the following reaction path is suggested: Starting at the primary donor P the electron should be transferred via a monomeric bacteriochlorophyll molecule (B), a bacteriopheophytin molecule (H) to a quinone molecule (Q). A number of picosecond experiments addressed the primary reaction in the reaction centers. In these publications it was shown that several picosecond processes occur in the RC's: A process with a time constant of 200 ps is related with the electron transfer from the bacteriopheophytin to the quinone. A faster time constant of about 3.5 ps was attributed to both, the decay of the electronically excited state P* and to the electron transfer to the pheophytin H /2, 3/. The oberservation of an additional time constant of 0.9 picoseconds was taken as an indication that the monomeric bacteriochlorophyll is involved in the primary reaction process /5-7/. Until now the assignment of the fast kinetic constant to a molecular process is still in discussion. Most probable are the three reaction models which are shown in Figure 1 /5-7/.

2. REACTION MODELS

The structural arrangement of the reaction centers strongly suggests the stepwise electron transfer model of Figure 1 a: According to this model the electronically excited state P* of the special pair decays with the time constant of 3.5 ps. Simultaneously an electron is transferred from the special pair to the monomeric bacteriochlorophyll B. The second electron transfer is faster and carries the electron with a time constant of 0.9 ps to the bacteriopheophytin H. Finally the 200 ps process generates the radical pair P^+Q^- where the electron has reached the quinone.

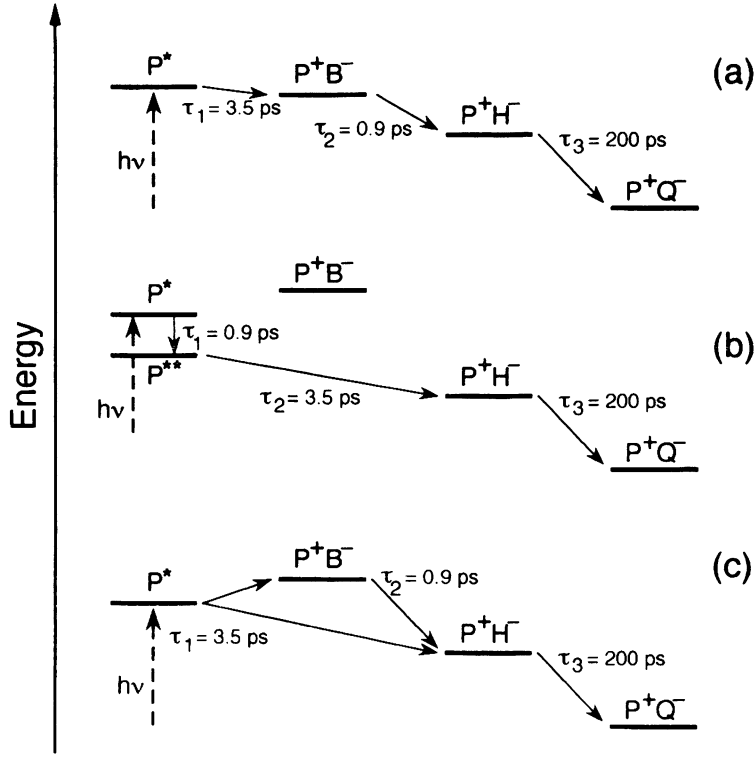

Figure 1: Schematic representation of three reaction models of the primary photosynthetic electron transfer: (a): The stepwise model. (b): unistep superexchange model with a 0.9 ps vibrational relaxation process which leads to a relaxed electronic state P**. (c): branched (parallel) reaction model.

From extensive experimental studies the absorption spectra of the different intermediates of model 1a could be calculated. All these data were fully consistent with the molecular interpretation of a stepwise electron transfer.

In model 1b the fast time constant of 0.9 ps is assigned to an excited state relaxation process of the special pair. Presumably this process is vibrational relaxation from the initially populated Franck-Condon-state. In this reaction model the first electron transfer drives the electron with a time constant of 3.5 ps directly to the bacteriopheophytin H. This fast long-distance electron transfer is only possible if the monomeric bacteriochlorophyll is involved as a virtual intermediate in a superexchange interaction./10-12/. In this case the energy level of the corresponding radical pair P^+B^- is higher than the energy of P*.

When the energy level of state P^+B^- is close to the energy of state P* a branched reaction model becomes possible (see Figure 1c) /12/. In this model two reactions occur in parallel: a direct ET from the special pair P* to the bacteriopheophytin H as well as a stepwise ET via the real intermediate P^+B^-. In this model the 3.5 ps kinetic would reflect the depopulation of the excited special pair while the 0.9 ps time constant is related with the population of the intermediate state P^+B^-. From room temperature experimental data one could conclude that at least 50 % of the reaction centers should use the stepwise reaction path via P^+B^- /5, 6/.

It is the purpose of the present paper to present experimental data on the low temperature reaction dynamics. From the temperature dependence of the observed rates we draw conclusions on the molecular mechanisms of the electron transfer.

3. EXPERIMENTAL

The measurements presented in this paper are obtained on quinone depleted reaction centers from the carotenoid free strain R26.1 of Rb.sphaeroides. Details of the preparation procedures are published in reference /13/. The time resolved absorption experiments are performed using the excite and probe technique with weak subpicosecond pulses (pulse duration $\simeq$ 150 fs) generated by a laser-amplifier-system with a repetition rate of 10 Hz. Details of the experimental system are described in reference /6, 13/. The temporal width of the instrumental response function is below 300 fs.

4. RESULTS

In a first set of time resolved experiments the temperature dependence of the decay of the excited state P* is investigated. In these experiments the transient absorption changes induced by stimulated emission of the radical pair are monitored at a probing wavelength of 920 nm (see Figure 2. At the investigated low temperatures of 25 K the signal closely follows a model function with a single exponential time constant $\tau_1 = 1.4 \pm 0.3$ ps. This time constant as well as the temperature dependence of this time constant is in agreement with the results of previous experimental studies /14/. The most important topic addressed here is the temperature dependence of the fast kinetic component. For this purpose we studied the transient absorption changes at probing wavelengths around 795 nm. In this wavelength range the amplitude of the 3.5 ps kinetic component is very weak and the additonal fast kinetic component is clearly visible at room temperature. In Figure 3 we present the experimental data for a probing wave-

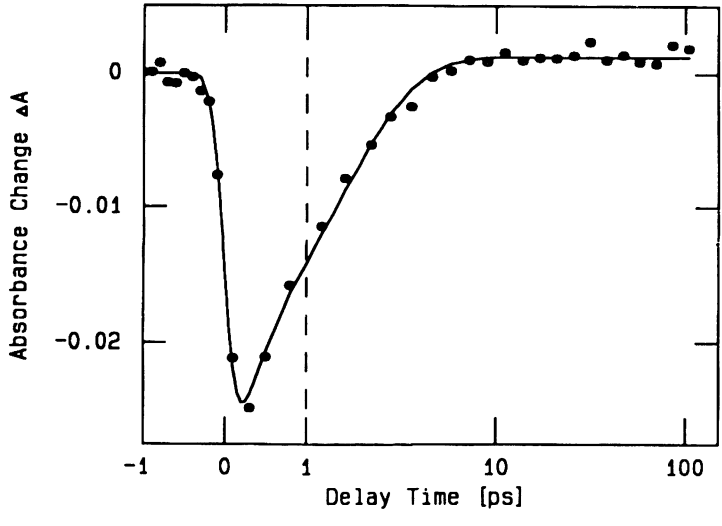

Figure 2: Transient absorption data on RC from Rb. sphaeroides at 25 K. The absorbance change is plotted on a linear scale for delay times $t_D < 1$ps and on a logarithmic scale for longer delay times. Probing wavelength 920 nm. The signal reflects the decay of the excited electronic level P* which is monoexponential with a time constant of $\tau = 1.4$ ps.

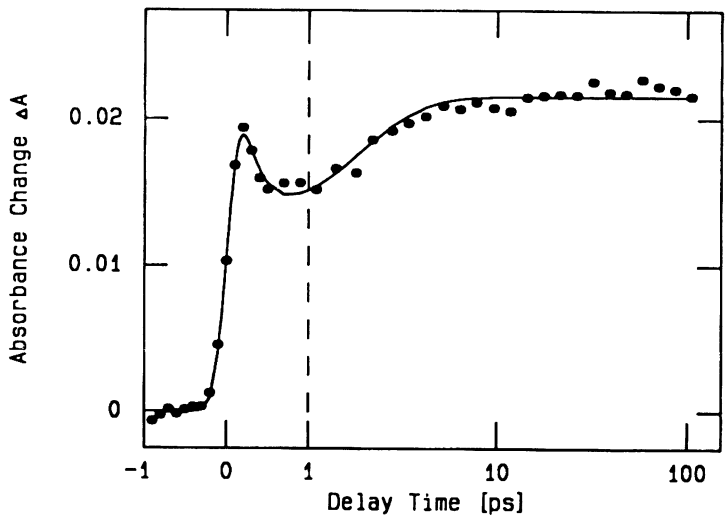

Figure 3: Transient absorption data on RC from Rb. sphaeroides at 25 K. The absorbance change is plotted on a linear scale for delay times t_D < 1ps and on a logarithmic scale for longer delay times. Probing wavelength 794 nm. The transient data show a complex time dependence which can be fitted by a sum of exponential functions with time constants of 0.3 ps and 1.4 ps.

length of 794 nm at a temperature of 25 K. The absorption change rises quickly during the first 100 fs to the pronounced peak. Subsequently an additional fast decay leads to a minimum at t_D = 700 fs. A subsequent slower rise of the absorbance leads to a plateau which is reached after approximately 2 ps. The complex time dependence of the absorbance change excludes the possibility that there is only one, namely the 1.4 ps kinetic component. There must be an additional faster kinetic process which is responsible for the first decay of the absorbance change. From a series of experiments the time constant of this additional kinetic component was determined to be 0.3 ± 0.15 ps. In a set of measurements we have recorded the temperature dependence of the fast kinetic component. These experimental results are summarized in Figure 4: At high temperatures around 300 K the time constant is around 1 ps i. e. we observe a rate of $1 \cdot 10^{12}$ s^{-1}. At lower temperatures a slow rise of the rate constant occurs which accelerates below 100 K. At 25 K a rate constant of 3.3 10^{12} s^{-1} is reached. In Figure 4 the points represent the experimental data; the solid line reflects the results of conventional electron transfer theory /13, 17/. The whole set of experimental results can be summarized as follows: (i) at all temperatures between 300 K and 25 K two time constants are required to explain the experimental data during the first 10 ps.(ii) Qualitatively similar transient absorption features occur at all temperatures (iii) The time constant of the fast kinetic component becomes shorter with decreasing temperature reaching a very small value of t = 0.3 ps at T = 25 K.

5. DISCUSSION

The three reaction models of Figure 1 will now be discussed in the context of the new experimental data. We start with the branched reaction model of Figure 1c. In this model the energy level of state P^+B^- should be of the order of 100 cm^{-1} above the level of P* /12/. At very low temperatures this energy difference prevents the population of state P^+B^-. As a consequence the

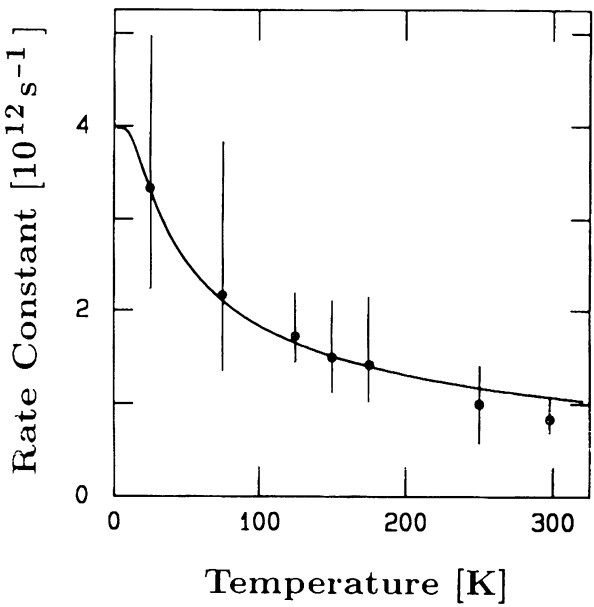

Figure 4: Temperature dependence of the fast rate constant. Points with error bars give the experimental data. The solid line represents the result of conventional electron transfer theory with parameters listed in /13/.

reaction path via P^+B^- is closed and the lifetime of state P* should become longer. In addition the amplitude of the fast kinetic component related to the decay of state P^+B^- should strongly decrease. Both phenomena are not observed experimentally. Therefore the branched reaction model is quite unlikely. In the superexchange model of Figure 1b the fast kinetic component is related to an S_1 vibrational relaxation. It is well known from a number of publications that vibrational relaxation slows down considerably at low temperatures /15, 16/. Experimentally, however, the fast process (which is related in the superexchange model with a vibrational relaxation) accelerates continuously when lowering the temperature. This is in clear contradiction to the interpretation of the fast step being vibrational relaxation. On the other hand the evaluation of the temperature dependent transient absorption data according to the stepwise model of Figure 1a leads to a fully consistent picture.

In conlusion, we have found that the dynamics of the primary electron transfer in reaction centers of Rb. sphaeroides shows transient absorption changes with two picosecond time constants throughout the whole investigated temperature range from 300 K to 25 K. The existence of the two kinetic processes in this temperature range as well as the temperature dependence of time constants and amplitudes strongly support the idea that the primary electron transfer in reaction centers is a stepwise process via the monomeric bacteriochlorophyll molecule.

ACKNOWLEDGEMENT

The authors thank Professor W. Kaiser for numerous discussions; Professor H. Scheer for providing us with the sample and M. Seel for technical assistance with the low temperature set-up.

REFERENCES

[1]N.W.Woodbury, M.Becker, D.Middendorf, W.W.Parson, Biochem. 24 (1985) 7516.
[2]J.Breton, J.L.Martin, A.Migus, A.Antonetti, A.Orszag, Proc. Natl. Acad. Sci. US 83 (1986) 5121.
[3]J.L.Martin, J.Breton, A.J.Hoff, A.Migus, A.Antonetti, Proc. Natl. Acad. Sci. US 83 (1986) 957.
[4]C.Kirmaier, D.Holten, W.W.Parson, Biochim. et Biophys. Acta 810 (1985) 49.
[5]W.Holzapfel, U.Finkele, W.Kaiser, D.Oesterhelt, H.Scheer, H.U.Stilz, W.Zinth, Chem. Phys. Letters 160 (1989) 1.
[6]W.Holzapfel, U.Finkele, W.Kaiser, D.Oesterhelt, H.Scheer, H.U.Stilz, W.Zinth, Proc. Natl. Acad. Sci. US 87 (1990) 5168.
[7]K.Dressler, E.Umlauf, S.Schmidt, P.Hamm, W.Zinth, S.Buchanan, H.Michel, Chem. Phys. Letters 183 (1991) 270.
[8]J.Deisenhofer, H.Michel, EMBO J. 8 (1989) 2149.
[9]C.H.Chang, D.Tiede, J.Tang, U.Smith, J.Norris, M.Schiffer, FEBS Letters 205 (1986) 82.
[10]M.Plato, K.Möbius, M.E.Michel-Beyerle, M.Bixon, J.Jortner, J. Am. Chem. Soc. 110 (1988) 7279.
[11]R.A.Marcus, Chem. Phys. Letters 133 (1987) 471.
[12]M.Bixon, J.Jortner, M.E.Michel-Beyerle, Biochim. et Biophys. Acta 1056 (1991) 301.
[13]C.Lauterwasser, U. Finkele, H. Scheer, W. Zinth; Chemical Physics Letters 183 (1991) 471.
[14]G.R.Fleming, J.L.Martin, J.Breton, Nature 333 (1988) 190.
[15]T.J.Kosic, R.E.Cline, D.D.Dlott, J. Chem. Phys. 81 (1984) 4932.
[16]W.H.Hesselink, D.A.Wiersma, Chem. Phys. Letters 56 (1978) 227.
[17]M.Bixon, J.Jortner, J. Phys. Chem. 90 (1986) 3795.