Ultrafast Phenomena VI

Proceedings of the 6th International Conference,
Mt. Hiei, Kyoto, Japan, July 12–15, 1988

Editors: T. Yajima, K. Yoshihara,
C. B. Harris, and S. Shionoya

With 487 Figures

Springer-Verlag Berlin Heidelberg New York
London Paris Tokyo

Contents

Femtosecond Excited-State Reaction Dynamics of Retinal-Containing Photosystems

W. Zinth, J. Dobler, K. Dressler, and W. Kaiser

Physik Department E11, Technische Universität München, Arcisstraße 21, D-8000 München 2, Fed. Rep. of Germany

Bacteriorhodopsin (BR) is one of the best studied photoreactive systems. It functions as a light-driven proton pump building up a proton gradient across the cell membrane of halobacterium halobium /1/. The reaction scheme of BR may be understood as follows: In the primary step, light absorption initiates the isomerization of the retinal chromophore from the all-trans to the 13-cis configuration. This reaction establishes the starting condition for the subsequent much slower proton transport process /2-4/. It is the purpose of this paper to reveal the ultrafast molecular processes which proceed during the primary reaction. Due to the recent development of femtosecond techniques these ultrafast phenomena may now be directly studied /5,6,7/.

In our experiments we work with amplified pulses from a CPM dye-laser (Cu vapor pumped amplifier) for excitation (λ = 620 nm) and with probe pulses at different wavelengths selected from a femtosecond continuum. The change of transmission of the sample induced by the exciting pulses is measured with high precision as a function of time delay. The time resolution of the experiment depends on the width Δt of the cross-correlation function between exciting and probing pulses. Typical values of Δt = 90 fs are obtained in our apparatus permitting the investigation of dynamic processes faster than 50 fs.

The choice of the probing wavelength is of major importance for the interpretation of the observed absorption transients. (i) At short probing wavelengths in the region of the 0-0 transition of the molecule the absorption changes may be related to different processes, e.g. to cross relaxation of an inhomogeneous ground-state distribution, to excited-state processes, and to the formation of photoproducts. (ii) Working at longer wavelengths in the fluorescent region of the molecule, the ground-state processes may be neglected, i.e. a more straightforward interpretation of the experiment is possible /5,6/.

Time resolved changes of absorption observed on light-adapted Bacteriorhodopsin at room temperature are shown in Fig.1 for three probing wavelengths in the gain region of BR. At long probing wavelengths (λ = 850 nm, Fig.1c) a pronounced gain is found (the transmitted pulse is larger than the incident pulse). The gain decays at later time with a time constant of 500 fs. A slight 180 fs contribution is present at very early times. With decreasing probing wavelength the 500 fs contribution disappears. At 735 nm (Fig.1b) a 180 fs process dominates the decay of the gain. Fig.1a is taken at a still shorter probing wavelength of 660 nm, where the S_1-S_0 absorption of BR may still be neglected. At late times the build-up (with 500 fs) of an induced absorption of the intermediate J is seen. Around time zero we observe a very short-lived gain. A detailed analysis of the experimental data with a precise determination of time zero and of the cross-correlation function reveals that the gain around time zero is due to an additional intermediate with a lifetime of approximately 50 fs (50±25 fs).

Springer Series in Chemical Physics, Vol. 48: Ultrafast Phenomena VI
Editors: T. Yajima • K. Yoshihara • C.B. Harris • S. Shionoya

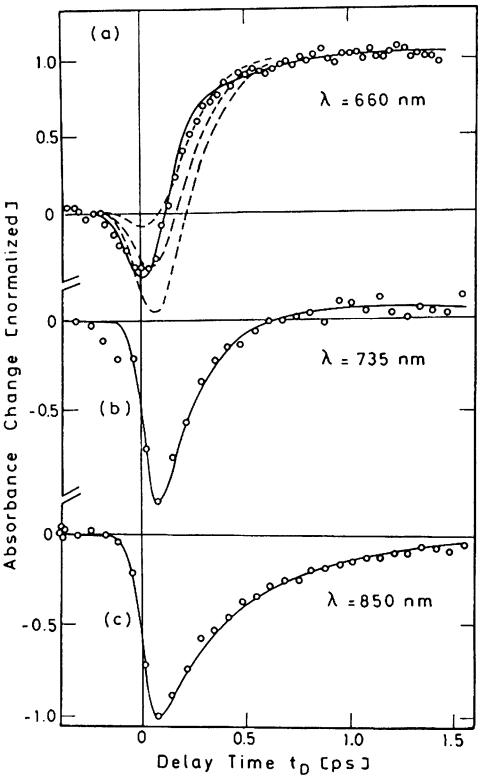

Fig. 1 Time-resolved changes of absorption (negative values correspond to gain) induced by exciting femtosecond pulses at λ = 620 nm. The probing wavelengths are λ = 660 nm (a), λ = 735 nm (b), λ = 660 nm (c). The solid curves are calculated using the decay kinetics discussed in the text. The broken curves are calculated excluding the 50 fs kinetic.

The experimental data indicate that there exists an interesting rapid sequence of events in S_1, the excited electronic state, with time values of τ_1 = 50 ps, τ_2 = 180 ps, and τ_3 = 500 ps.

Taking into account the spectral properties of the transient signal and the known molecular data of retinal the following microscopic picture of the very early reactions is suggested (see Fig.2): The incident photons promote the retinal to the Franck-Condon state S_1** on the S_1 potential surface, where a number of vibrational modes are displaced relative to the S_1 equilibrium position /8/. Within 50 fs after light absorption an equilibration of vibrational modes occurs. During this first reaction the molecule remains practically unchanged along the coordinates of the low-frequency modes. The following slower reactive motion of the retinal is related to the 180 fs gain kinetics. In this process, part of the isomerization (presumably a rotation by 60 to 90 degree around the C13-C14 double bond) takes place and the molecules arrive at the bottom of the S_1 potential surface. From this energy position the isomerization continues to form the intermediate product J or the molecule returns via internal conversion to the original ground state with a time constant of 500 fs. Numerical estimates of the isomerization motion support the present interpretiations.

In conclusion it should be noted that additional experiments on other retinal containing systems gave evidence for a very similar hierarchy of events, indicating that the reaction mechanisms found in Bacteriorhodopsin is of a more general nature.

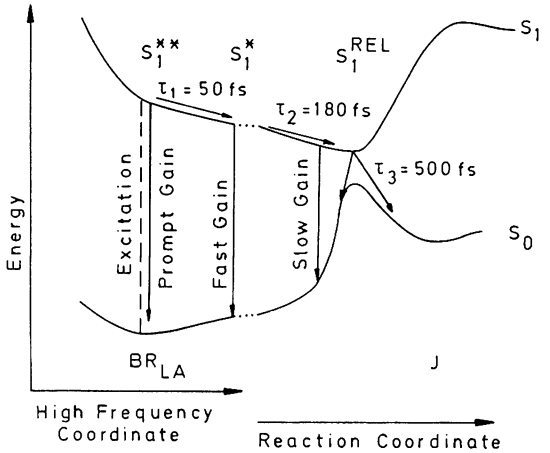

Fig.2 Schematic of the ground-state (S_0) and excited-state (S_1) potential energy surfaces as a function of the high-frequency vibrational and the low-frequency reactive coordinates.

Acknowledgement: the experimental work was done in collaboration with Prof. D. Oesterhelt.

References

1. J.K. Lanyi: In Bioenergetics, ed. L. Ernster (Elsevier, Amsterdam 1984) p.314; W. Stockenius, R.A. Bogomolni, Ann. Rev. Biochem. 52, 587 (1982)
2. M.C. Nuss, W. Zinth, W. Kaiser, E. Kölling, D. Oesterhelt: Chem. Phys. Lett. 117, 1 (1985)
3. H.J. Polland, M.A. Franz, W. Zinth, W. Kaiser, E. Kölling, D. Oesterhelt: Biophys. J. 49, 651 (1986); H.J. Polland, W. Zinth, W. Kaiser: In Ultrashort Phenomena, Vol.4, eds. D.H. Auston, K.B. Eisenthal (Springer, Berlin 1984) p. 456
4. H.J. Polland, M.A. Franz, W. Zinth, W. Kaiser, E. Kölling, D. Oesterhelt: Biochem. Biophys. Acta 767, 635 (1984)
5. J. Dobler, W. Zinth, W. Kaiser, D. Oesterhelt: Chem. Phys. Lett. 144, 215
6. W. Zinth: Naturwiss. 75, 173 (1988) (1988)
7. R.A. Mathies, C.H. BritoCruz, W.T. Pollard, C.V. Shank: Science 240, 777 (1988)
8. E.J. Heller, Acc. Chem. Res. 14, 368 (1981)