Effects of hydrogen/deuterium exchange on photosynthetic water cleavage in PS II core complexes from spinach

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Abstract H/D isotope exchange effects on $P680^{+\bullet}$ reduction by Y_z and electron abstraction from the water oxidizing complex (WOC) in redox state S_3 by Y_Z^{OX} were analyzed in PS II core complexes from spinach by measurements of laser flash induced absorption changes at 820 nm and 355 nm. The results obtained reveal: (1) the rate of Y_z oxidation by $P680^{+\bullet}$ is almost independent of the substitution of exchangeable protons by deuterons; and (2) the reaction between Y_Z^{OX} and the WOC in S_3 exhibits a kinetic H/D isotope exchange effect of similar magnitude as that recently observed in PS II membrane fragments [Renger, G., Bittner, T. and Messinger, J. (1994) Biochem. Soc. Trans. 22, 318–322]. Based on these results it is inferred that photosynthetic dioxygen formation comprises the cleavage of at least one hydrogen bond.

Key words: Photosystem II; Water cleavage; Isotope exchange

1. Introduction

Photosynthetic water cleavage into dioxygen and metabolically bound hydrogen takes place in a multimeric integral protein complex referred to as photosystem II. The overall process comprises three different reaction sequences: (a) photooxidation of a special Chl-*a* component (P680) and subsequent stabilization of the primary charge separation by rapid electron transfer to a specially bound plastoquinone (Q_A) (for a review see [1]); (b) cooperation of four oxidizing redox equivalents in a manganese-containing unit giving rise to oxidation of two water molecules into dioxygen and four protons (for reviews, see [2–4]); and (c) plastoquinone reduction under proton uptake (for a review, see [5]). Protons are not only products and substrates in reaction sequences (b) and (c), respectively, but also affect the functional and structural pattern of PS II either through modulation of electrostatic interactions between protonizable groups or as constituents of hydrogen bonds. Exchange of protons to deuterons can affect both, the rate constants of individual reaction steps and/or the structural stability of a protein complex.

Previous studies had revealed that the thermal stability of the water oxidizing complex (WOC) was enhanced in isolated thylakoids and PS II membrane fragments when the samples were suspended in D_2O [6,7]. Latest analyses led to the conclusion that the kinetics of the elementary reactions in sequence (a) remain virtually unaffected after substitution of exchangeable protons by deuterons [8] while the kinetics of sequence (c) becomes markedly retarded [9]. Of special interest are kinetic H/D exchange experiments in reaction sequence (b) for a deeper understanding of the mechanism of water oxidation that is still an unresolved problem (for a list of questions see [4]). Few studies have been performed so far. The kinetics of proton release coupled with univalent oxidation steps were shown to be significantly retarded if PS II membrane fragments are suspended in D_2O at slightly alkaline pH [10]. However, as predicted previously [11] the proton release reflects an electrostatic response of the protein matrix rather than the intrinsic protolytic reactions of water oxidation [12] and therefore these isotope effects are not directly related to the latter process. Studies on the kinetics of the redox transitions in the water oxidizing complex (WOC) were performed by measuring absorption changes at 355 nm induced by a train of saturating laser flashes in dark adapted PS II membrane fragments. The results obtained reveal [7] that H/D-exchange causes comparatively small effects on the redox transitions:

$$Y_Z^{OX} S_i + w_{i+1} H_2O \rightarrow Y_z S_{i+1} + n_i H^+_{lumen} + \delta_{i3} O_2 \quad (1)$$

where Y_z is the redox active tyrosine of polypeptide D1 [13,14] that mediates the oxidation of the WOC by $P680^{+\bullet}$ [2–4]; n_i is the number of protons released and w_i is the number of substrate water molecules that are bound in the redox transition $S_i \rightarrow S_{i+1}$, S_i represents the redox state of the WOC with i = 0,... 3 under normal turnover conditions and δ_{i3} is the Kronecker symbol ($\delta_{i3} = 1$ for i = 3, otherwise zero). This formulation tacitly implies that S_4 does not exist as the highest oxidation state of the manganese cluster in the WOC because is assumed to cause an oxidant-induced reduction of S_3 to $S_0 + O_2$ ([7], see also [15]).

Recently, it has been proposed that Y_Z^{OX} acts as a hydrogen abstractor from the substrate in the WOC [16]. This idea would imply the existence of kinetic H/D isotope exchange effects. The present study addresses this problem by analyzing two particular reactions in PS II core complexes with high oxygen evolution capacity: (a) the reduction of $P680^{+\bullet}$ by Y_z; and (b) the oxidant-induced reduction of S_3 by Y_Z^{OX}.

2. Materials and methods

PS II core complexes with high oxygen evolution capacity were isolated from spinach according to the method described in [17] with slight modifications. In order to achieve a high extent of H/D exchange the

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Abbreviations: 2,6-DCBQ, 2,6-dichloro-*p*-benzoquinone; FWHM, full-width at half-maximum; MES, morpholinoethane sulfonic acid; Q_A, bound plastoquinone-9 acceptor of PS II; P680, photoactive chlorophyll of PS II; PS II, photosystem II; WOC, water oxidizing complex; Y_z, redox active tyrosin between WOC and P680.

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samples were lyophylized and resuspended in either H_2O (control) or D_2O (deuterated PS II core complexes). It was shown that the oxygen evolution capacity is not significantly affected by this treatment (data not shown). The light saturated oxygen evolution rates of the samples were 1300 ± 100 μmol O_2/mg Chl·h in the presence of 0.5 mM 2,6-DCBQ as electron acceptor.

Flash-induced absorption changes at 820 nm in the ns time domain were measured with the equipment described in [18]. The samples were excited with repetitive laser flashes (FWHM≈100 ps) at a frequency of 1 Hz.

Absorption changes at 355 nm induced in dark adapted PS II core complexes by excitation with a train of single turnover flashes were monitored with a laser flash photometer as used in [7]. A laser flash (FWHM = 9 ns) frequency of 10 Hz was used in order to eliminate effects due to the rapid decay of redox states S_2 and S_3 in PS II core complexes [19,20]. The signals were monitored with an electrical bandwidth of 5 kHz.

The assay contained: PS II core complexes at 20 and 100 μg Chl/ml for the measurement of absorption changes at 355 and 820 nm, respectively, 10 mM NaCl, 20 mM $CaCl_2$, 20 mM MES/NaOH pH 6.5 and 100 μM 2,6-DCBQ/100μM $K_3[Fe(CN)_6]$ as electron acceptors.

3. Results

In PS II with a functionally competent WOC the reduction of $P680^{+\bullet}$ by Y_Z takes place via multiphasic kinetics in the ns and μs-range [21–24] that depend on the redox state S_i of the WOC [25,26]. In order to permit a reliable kinetic analysis, the absorption changes at 820 nm were monitored in three different time domains. The results obtained for control and H/D exchanged PS II core complexes are depicted in Fig. 1.

At a first glance it is readily seen that H/D exchange does not lead to marked kinetic changes. For a more detailed inspection the data were analyzed within the framework of triexponential decay kinetics:

$$\Delta A_{830}^{\mathrm{corr}}(t) = \Delta A_{830}^{\mathrm{corr}}(0) \sum_{i=1}^{3} a_i e^{-t/\tau_i} \quad (2)$$

The very fast relaxation observed in the 10 ns time domain was omitted because it does not reflect $P680^{+\bullet}$ reduction by Y_z but originates from the remaining part of kinetics ascribed to $Pheo^{-\bullet}$ oxidation by Q_A [27] and singlet state decay of chlorophylls [18]. Therefore, $\Delta A_{820}^{\mathrm{corr}}(t)$ and $\Delta A_{820}^{\mathrm{corr}}(0)$ are the transient and initial amplitude, respectively, corrected for the contribution owing to these very fast reactions. Furthermore, the multiphasic decay in the μs-time domain were not deconvoluted into individual components because its unambigous assigment is still a matter of debate and its contribution to the overall decay is comparatively small. For the sake of simplicity they are described by a 'global' component with a fixed τ_3-value of 5 μs. It was checked that this simplifying description of the μs-kinetics does not significantly affect the values of τ_1, τ_2, a_1 and a_2 (data not shown). Table 1 compiles the results gathered from the kinetic deconvolution according to Eqn. 2 of the experimental data of Fig. 1. Three features emerge from Table 1: (i) in about 75% of oxygen evolving PS II core complexes, the $P680^{+\bullet}$-reduction takes place with ns-kinetics and this fraction remains virtually invariant to H_2O/D_2O exchange; (ii) the kinetics in the ns-time domain can be satisfactorily described by a biexponential decay with τ_i-values of about 30 ns and 170 ns, respectively; and (iii) H_2O/D_2O exchange only leads to a marginal kinetic effect of less than 15% for τ_1 (~30 ns) and virtually no change for τ_2 (~170 ns).

It has to be emphasized that according to single flash experiments in dark-adapted samples [25,26] the 30 ns component is very likely the composite of 20 ns and 50 ns kinetics that are dominating in systems with the WOC in redox states S_0/S_1 and S_2/S_3, respectively. Therefore, four component analyses were performed (data not shown). They did not improve the fit of the experimental data but blurred any possible difference between samples dissolved either in H_2O or D_2O. Therefore, the 30-ns kinetics will be used as representative of the very fast $P680^{+\bullet}$ reduction by Y_z.

The most interesting result of this part of the study is the finding that the kinetics of $P680^{+\bullet}$ reduction by Y_z in the ns-time domain remain almost invariant to H_2O/D_2O exchange. This phenomenon readily excludes the possibility that a cleavage of the OH-bond in Y_z is rate limiting for its oxidation by $P680^{+\bullet}$. A more detailed analysis reveals that also the break of a possible hydrogen bond can only affect the rate determining step if the strength of this bond is sufficiently weak (for further considerations see section 4).

With respect to water oxidation to dioxygen, the S_3 reaction with Y_Z^{OX} is of central relevance. Regardless of its mechanistic interpretation (see [7,15] and References therein), this reaction is of special interest for two reasons: (i) it leads to oxygen evolution; and (ii) it is the only univalent redox step induced by in the WOC that becomes markedly retarded in PS II core complexes compared with PS II membrane fragments [20]. A similar feature was observed in PS II membrane fragments deprived of the extrinsic regulatory subunits of 18 kDa (PS II–Q-protein) and 23 kDa (PS II-P-protein) by NaCl-washing [28]. The retardation by a factor of 3–4 might reflect a change of the reaction coordinate. On the basis of H_2O/D_2O exchange experiments it was recently concluded that Y_Z^{OX} reduction by S_3 in PS II membrane fragments is not rate limited by the cleavage of a covalent OH bond but probably comprises the break of at least one hydrogen bond [7]. It is therefore interesting to check whether or not an analogous phenomenon also exists in PS II core complexes. The kinetics of the redox transition in the WOC can be monitored by measurements of absorption changes in the range of 350–360 nm where the difference spectrum of Y_Z^{OX}/Y_z is close to zero [20,29,30]. The measurements were performed in samples preilluminated with one flash to attain the redox state $Y_Z^{OX}S_1$ before the flash train. Fig. 2 shows laser flash induced absorption changes at 355 nm measured in lyophilized samples dissolved either in H_2O (top) or D_2O (bottom). Two striking features emerge from these traces: (i) the slow phase of the rise kinetics of the absorption changes induced by the second flash becomes markedly retarded in D_2O dissolved samples; and (ii) the relaxation kinetics of the absorption changes due to the 3rd and 4th flash are also slowed down in D_2O dissolved samples. The former effect indicates that in PS II core complexes the S_2 oxidation by Y_Z^{OX} exhibits a markedly more pronounced H/D isotope exchange effect (a factor of about 2) than previously reported [7] for PS II membrane

Table 1
Relaxation kinetics of 820 nm absorption changes in PS II core complexes from spinach with high oxygen evolution capacity

Lifetime (rel. ampl. %)	H_2O		D_2O	
τ_1/ns (a_1)	32 ± 4	(32 ± 3)	36 ± 3	(33 ± 3)
τ_2/ns (a_2)	168 ± 5	(43 ± 2)	169 ± 13	(39 ± 2)
τ_3 (a_3)	nd	(24 ± 2)	nd	(27 ± 2)

nd = not determined.

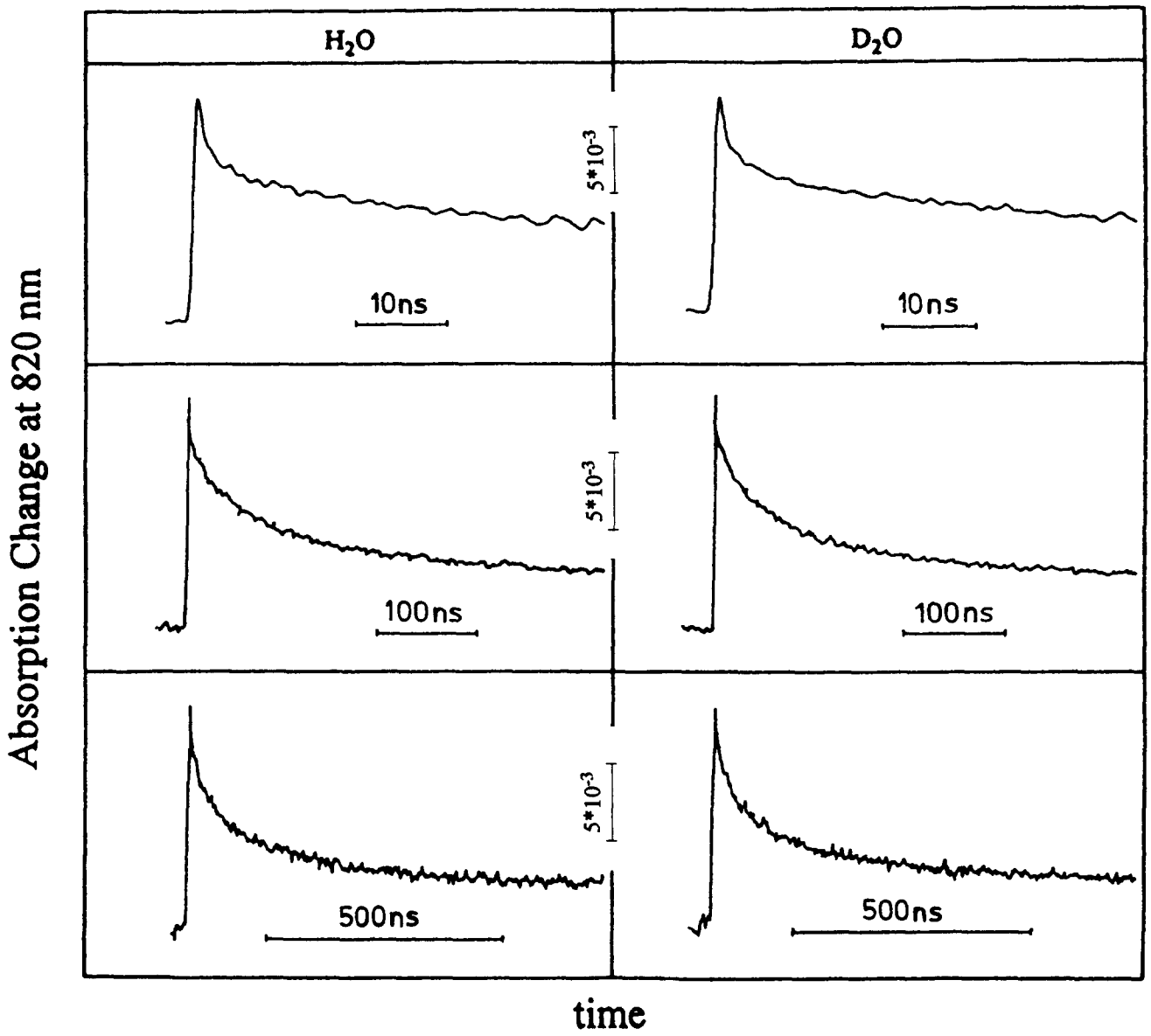

Fig. 1. Laser flash induced absorption changes at 820 nm as a function of time in PS II core complexes dissolved either in H_2O (left side) or D_2O (right side). Experimental details as described in section 2.

fragments (factor 1.1–1.2). This phenomenon will be analyzed in a forthcoming paper while the retardation of the S_3 reaction with Y_Z^{OX} will be discussed in this study. Fig. 3 shows the normalized decay of the 355 nm absorption changes after the 3rd flash. A kinetic analysis reveals that the relaxation is bi-exponential with lifetimes of $\tau_1 \sim 5$ ms (relative amplitude >70%) and $\tau_2 \sim 15$ ms (relative amplitude about 25%) in samples dissolved in H_2O and $\tau_1 = 8.5$ ms (relative amplitude about 70%), $\tau_2 \sim 15$ ms (relative amplitude about 30%) in D_2O dissolved PS II core complexes. The dominating fast component is ascribed to Y_Z^{OX} reduction by S_3 while the slower one probably reflects $Q^{-\bullet}{}_A$ reoxidation by the exogenous acceptor and will not be discussed here (the amplitude ratio of both phases is consistent with the difference spectra of S_3/S_0 and $Q^{-\bullet}{}_A/Q_A$ at 355 nm [31,32]).

The ratio $\tau_1(D_2O)/\tau_1(H_2O) = k_1(H_2O)/k_1(D_2O)$ in different experiments was found to be in the range of 1.6–1.8. This value is somewhat larger than that of PS II membrane fragments (~1.4) but the difference is not considered to be relevant. Therefore it is concluded that a similar H/D isotope exchange effect is characteristic for the oxygen formation step in both, PS II membrane fragments and PS II core complexes.

4. Discussion

The rapid reduction of $P680^{+\bullet}$ by Y_z in oxygen evolving PS II membrane fragments with the WOC in redox state S_1 (20-ns kinetics at room temperature) was recently found to exhibit an activation energy of ~10 kJ/ mol within the range of $250 < T < 300$ K [26]. It was therefore suggested that a hydrogen bond might exist between Y_z and its microenvironment, i.e. an amino acid residue, and that the break of this H-bond could

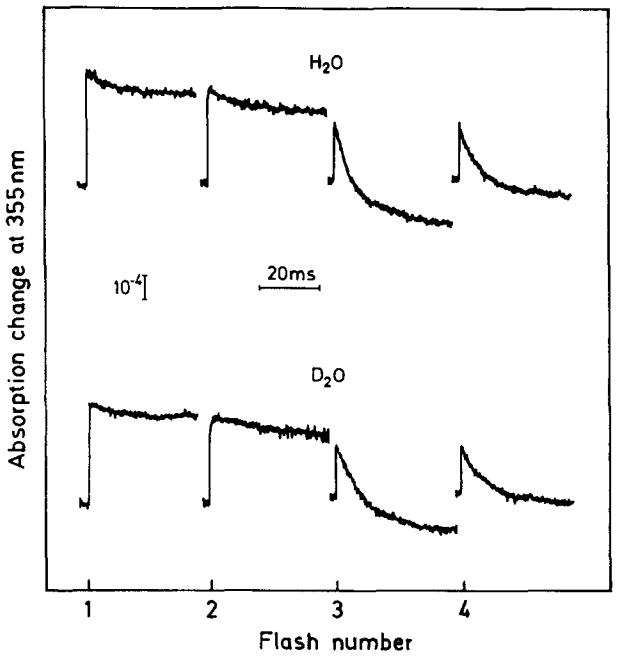

Fig. 2. Absorption changes at 355 nm induced by a train of laser flashes in dark adapted PS II core complexes dissolved in either H_2O (top traces) or D_2O (bottom traces). 10 signals were averaged for improving the signal to noise ratio. Other experimental details as described in section 2.

be rate limiting. If this idea is correct, a kinetic H/D-isotope exchange effect should arise. According to the transition state theory the ratio of the rate constants in D_2O and H_2O dissolved samples is dependent on the difference in zero point energies of bonds that are cleaved in the reaction [see textbooks of Physical Chemistry], i.e.

$$k_H/k_D = \tau_D/\tau_H = \exp\left\{\frac{hc\nu_0(H)}{2k_BT}\left(1-\sqrt{\frac{\mu_H}{\mu_D}}\right)\right\} \quad (3)$$

where k_H and k_D are the rate constants of $P680^{+\bullet}$ reduction by Y_z of samples dissolved in H_2O and D_2O, respectively, τ_H and τ_D the corresponding lifetimes, μ_H and μ_D are the reduced masses of H or D forming the presumed hydrogen normal or deuterated bond, $\upsilon_0(H)$ is the characteristic frequency of the hydrogen bond in H_2O dissolved samples and h = Planck constant, k_B = Boltzmann constant and c = velocity of light (it should be mentioned that there were some typing errors in the formula given in [7]).

Using the extreme value of a possible deuterium effect of 15% for the composite 30 ns kinetics, Eqn. 3 gives a wave number for the hydrogen bond, $\upsilon_0(H)$, that does not exceed 200 cm^{-1}. This value could be reconciled with a hydrogen bond [33]. However, if one considers that 200 cm^{-1} is the absolute upper limit and that the 170-ns kinetics exhibits virtually no isotope effect, the results could be better explained by two other alternatives: (a) the oxidation of Y_z by $P680^{+\bullet}$ does probably not comprise the cleavage of a hydrogen bond in the rate limiting step; or (b) the proton of the OH-group of Y_z is not susceptible to H/D-exchange.

Although the second alternative cannot entirely be excluded [33] it seems to be rather unlikely because the samples were thoroughly lyophilized before addition of D_2O (see section 2). Therefore, if one accepts that Y_z is hydrogen bonded to His-190 [34] the results of this study lead to the conclusion that the break of this bond is probably not rate determining for Y_z oxidation.

In contrast to $P680^{+\bullet}$ reduction by Y_z the kinetics of electron abstraction by Y_Z^{OX} from the WOC in redox state S_3 exhibits a significant H/D isotope exchange effect. Values of 1.4–1.8 were found in PS II membrane fragments [7] and PS II core complexes (this study). In redox proteins a decrease of the electron transfer rate by a factor of 1.4–1.8 can originate either from a lengthening of the distance between the reacting groups by 0.2–0.3 Å [34] or due to an increase of the activation energy. Although a distance change via indirect effects cannot entirely be excluded it seems more reasonable to assume that the decrease of the zero point energy of hydrogen bonds owing to substitution of exchangeable protons by deuterons gives rise to the observed isotope effect. An interpretation within the framework of Eqn. 3 reveals that the cleavage of either one rather strong hydrogen bond or two (three) normal bonds could be involved. This conclusion raises questions on the nature of this (these) hydrogen bond(s). Two alternatives have to be considered: (i) a specific effect related to the functional redox groups and the associated substrate molecules; or (ii) a more distant unspecific modulation of the kinetics by the whole protein matrix. The present data do not permit an unambiguous conclusion. However an indirect line of evidence can be gathered from the finding that the ratio $\tau_D\,(S_3Y_Z^{OX})/\tau_H(S_3Y_Z^{OX})$ is rather similar in PS II membrane fragments and PS II core complexes whereas the overall rate of electron transfer from S_3 to in the control (H_2O) differs by a factor of about 3 between both samples types. Therefore, it appears more likely that the isotope effect is rather specific. Furthermore, latest data on the flexibility of the phenoxy ring indicate that Y_Z^{OX} is probably not hydrogen bonded [35]. As a consequence, the isotope effect is ascribed to the breakage of hydrogen bonds during electron abstraction from S_3 leading to O_2 formation. Since the Y_Z^{OX} reduction by S_3 exhibits almost the same kinetics as oxygen release [36–39] it is reasonable to assume that this (these) hydrogen bond(s) comprise substrate water. This idea is highly supported

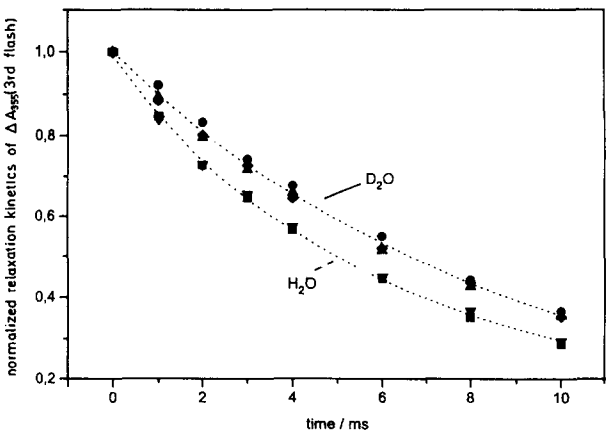

Fig. 3. Normalized relaxation kinetics of absorption changes at 355 nm after the 3rd flash, ΔA_{355} (3rd flash). Data from Fig. 2 are presented in an extended scale. The signals were normalized to the total amplitude of the relaxation kinetics within the 40 ms time window.

by previous findings of an H/D isotope effect on the oxygen release kinetics [40] that is of nearly the same extent as that of the electron transfer from S_3 to Y_Z^{ox} ([7], this study). It is therefore attractive to assume that the substrate itself (either as complexed hydroxyl group(s) or as a preformed peroxidic configuration, for a discussion see [4]) is hydrogen bonded and that the cleavage of this (these) bond(s) affects the rate constant. A highly asymmetric complexation by hydrogen bonds might also be responsible for the quite different $H_2{}^{18}O/H_2{}^{16}O$ exchange rates of the two substrate molecules that eventually give rise to O_2-formation [41]. Further experiments are required to clarify this mechanistically relevant point.

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