

Formation Dynamics and Nature of Tryptophan's Primary Photoproduct in Aqueous Solution

Supplemental Information

Solvent kinetics at pH = 1 and 7

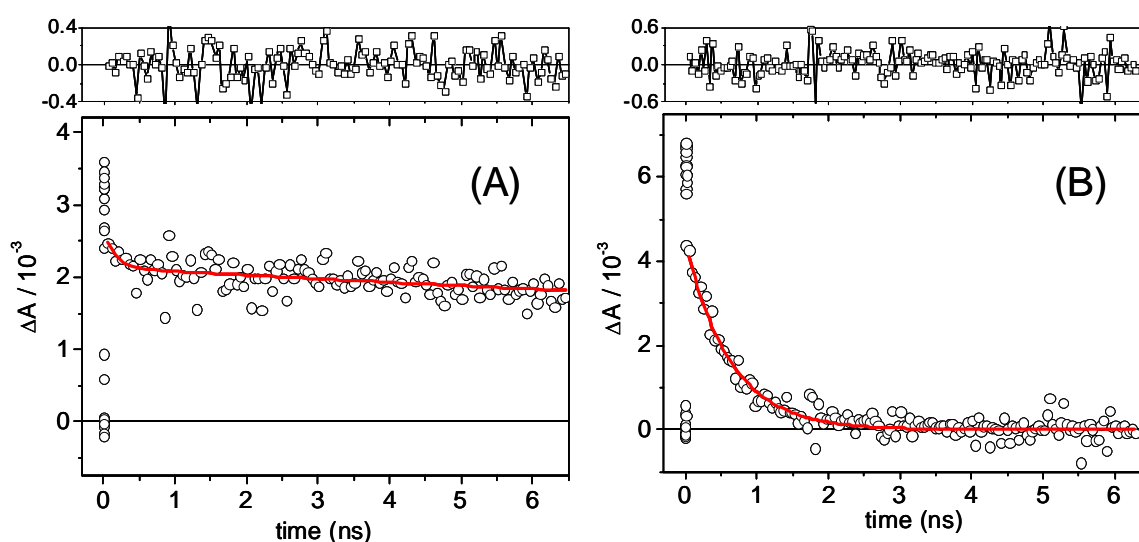


Figure S1. Open circles: transient absorption kinetics of H₂O buffered at pH=7.0 (A) and at pH = 1.0 (B), for $\lambda = 555 \pm 55$ nm (average over a 110-nm window). Solid lines: fit with a bi-exponential decay at $t > 50$ ps. Open squares in upper parts: residuals plots.

Fig. S1 shows the decay of the ϵ_{aq}^- absorption in water at pH=7.0 and pH=1.0, averaged over the range 500-610 nm into one single trace. At pH= 7 (Fig S1 A), for $t > 50$ ps, the decay is bi-exponential with a small-amplitude 150 ± 120 ps and a dominant 40 ± 10 ns component. The short-lived component is

rather inaccurate because its amplitude is only twice the noise level, while the value of the long-lived component is only indicative since it is much longer than the range of times scanned. At pH=1.0 (Fig S1 B), the decay is monoexponential with time constant 0.63 ± 0.03 ns. In the range 500-600nm, the e_{aq}^- kinetics at pH=1 happens to be close to the excited state decay of Trp/H₂O at the same pH.

Global analysis of the transient absorption of Trp/H₂O at neutral pH: Three decay time constants are required.

Fig. S2 illustrates the global analysis of the transient absorption dataset (300 to 650 nm; 50ps to 6 ns) of Trp/H₂O at pH=7.4. A triexponential fit yields better results than a biexponential fit, in terms of evenly distributed residuals (fig. S2 right) and χ^2 . The result of the triexponential fit is as given in the paper: 0.45 ns, 2.9 ns and 40 ns. The need for a third time constant is even better illustrated by analyzing a 20-nm-broad subset of the data centered on 425 as shown in Fig. S3. At this wavelength, which characterizes the photoproduct P formation, the reduced χ^2 improves by a factor of 2 when a third time constant is introduced.

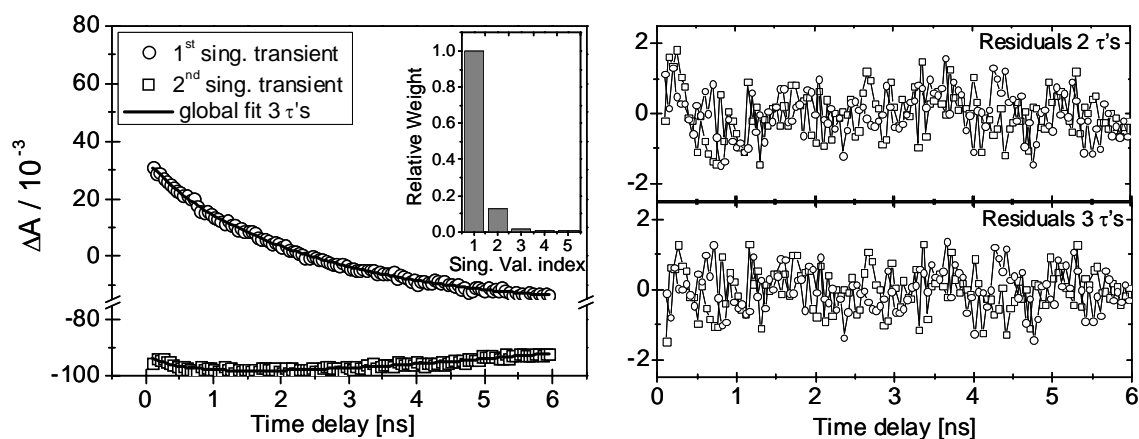


Figure S2. Global analysis of the transient absorption dataset (300 to 650 nm; 50ps to 6 ns) of Trp/H₂O at pH=7.4. Left: only the dominant two Singular Transients (ST) are relevant (the other singular values are $\leq 1\%$ of the dominant one, see inset); solid lines are the global (i.e. simultaneous) fit of the two dominant ST by a

triexponential decay function. Right: residuals of a biexponential (upper part) and triexponential (lower part) global fit to the dominant two ST's. In the former case, systematic deviations are perceptible especially a times < 1 ns, whereas in the later case, the residuals are uniformly spread around zero, attesting a better fit quality (the value of the reduced χ^2 diminishes by 20%).

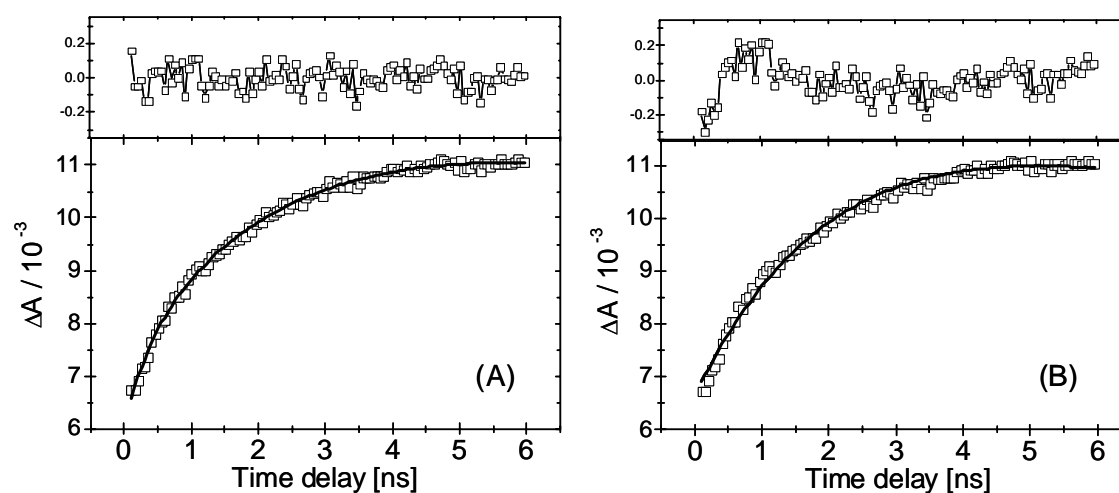


Figure S3. Fit of the transient signal spectrally averaged over a 20-nm broad window centred at 425nm. A triexponential (A) fit (0.4 +/- 0.2 ns; 2.9 +/- 0.2 ns; 40ns fixed after determination from the global analysis) yields a much better result than a biexponential (B) fit (2.3 +/- 0.2 ns; 40 ns also fixed). In the triexponential fit (A), the amplitude of the 0.4 ns component is 20 % of that of the 2.9 ns component, in excellent agreement with the result of the global analysis (see the DADS in Fig. 3 B in the paper)

Primary structure of Zn-binding (35-50)NCp7

Primary structure (35-50)NCp7

