Supporting Information

Mechanism of Proton-Coupled Electron Transfer in the S₀-to-S₁ Transition of Photosynthetic Water Oxidation As Revealed by Time-Resolved Infrared Spectroscopy

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Figure S1. TRIR measurement scheme to obtain the signals of the pure contribution of the $S_0 \rightarrow S_1$ transition.



Figure S2. FTIR difference spectra upon the (a) 1st, (b) 2nd, (c) 3rd, and (d) 4th flashes of the PSII core complexes from *T. elongatus* in H₂O (black lines) and D₂O (red lines) buffers. (A) Strongly hydrogen-bonded OH(OD)/NH(ND) region; (B) protein vibration region including the COO⁻ stretching vibrations of carboxylate groups. Dashed lines indicate the monitoring frequencies of TRIR measurements at 2500 (H₂O), 1900 (D₂O), and 1400 (H₂O and D₂O) cm⁻¹. Spectra were reorganized from the data in ref. 1.



Figure S3. Heat signal correction of the TRIR traces at (A, C) 1400, (B) 2500, and (D) 1900 cm⁻¹ in H₂O (A, B) and D₂O (C, D) buffers. (a) Heat signal corresponding to a laser power of 21 mJ cm⁻² pulse⁻¹ (blue lines) calculated by subtraction of the TRIR trace upon a flash with 7 mJ cm⁻² pulse⁻¹ (black lines) from that upon a flash with 28 mJ cm⁻² pulse⁻¹ (green lines). (b–e) Heat-corrected TRIR traces (red lines) obtained by subtraction of a heat signal corresponding to a laser power of 7 mJ cm⁻² pulse⁻¹ (blue lines) from the raw TRIR traces by flashes with 7 mJ cm⁻² pulse⁻¹ (black lines). (b) 1st flash; (c) 2nd flash; (d) 3rd flash; (e) 4th flash after 30 min dark adaptation. The heat signal corresponding to 21 mJ cm⁻² pulse⁻¹ (a, blue line) by a factor of 3.

References

(1) Noguchi T.; Sugiura M. FTIR detection of water reactions during the flash-induced S-state cycle of the photosynthetic water oxidizing complex. *Biochemistry* **2002**, *41*, 15706–15712.