Probing Mode and Site of Substrate Water Binding to the Oxygen-Evolving Complex in the S 2 State of Photosystem II by 17 O-HYSCORE Spectroscopy

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Probing Mode and Site of Substrate Water Binding to the Oxygen-Evolving Complex in the S_2 State of Photosystem II by ^{17}O-HYSCORE Spectroscopy [*Journal of the American Chemical Society* **2008**, *130*, 786–787 DOI: 10.1021/ja076620i]. Ji-Hu Su Wolfgang Lubitz* and Johannes Messinger*

Additional experiments (see Figure 1) have revealed that the HYSCORE signal reported for the oxygen-evolving complex (OEC) poised in the S_2 state of spinach BBY samples in the presence of ^{17}O-water was incorrectly assigned to the coupling of ^{17}O to the Mn cluster. This signal should instead be assigned to the hyperfine coupling of the axial ^{14}N ligand of the low-spin Fe^{III} center of oxidized cytochrome b559.[1] We have concluded that cytb559 was partially oxidized during 200 K illumination in samples incubated with ^{17}O-water, but to a lesser extent in the ^{16}O control samples.

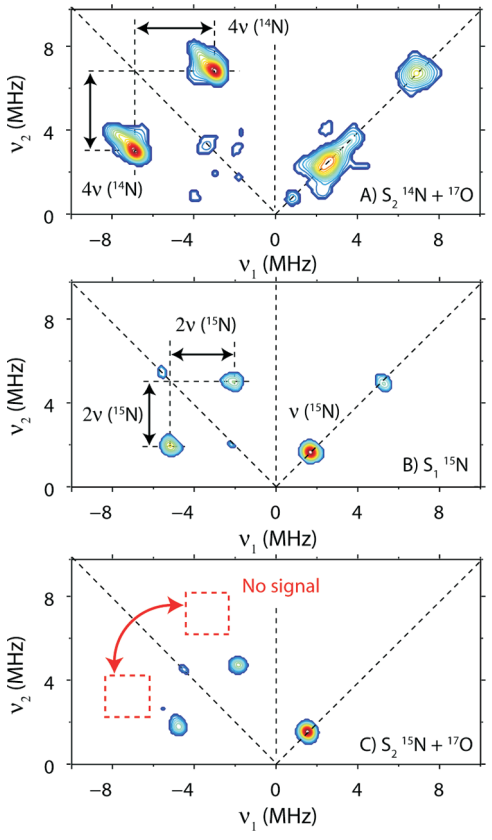

Figure 1. X-band HYSCORE spectra of *T. elongatus* photosystem II core preparations suspended in either buffered $H_2{}^{16}O$ or $H_2{}^{17}O$ medium: (A) S_2 state of ^{14}N-PSII in $H_2{}^{17}O$ medium, (B) S_1 state of ^{15}N-PSII in $H_2{}^{16}O$ medium, and (C) S_2 state of ^{15}N-PSII in $H_2{}^{17}O$ medium. The red boxes show the region where the ^{17}O signal reported in the full article was observed. The S_2 state was generated by 200 K white light illumination for 5 s. All spectra were obtained at the center field of the S_2 multiline EPR spectrum (B_0 = 335 mT). Experimental parameters: (A) $\pi/2$ = 24 ns; τ = 196 ns; t_1, t_2 were varied from 60 to 6720 ns (24 ns steps); shots per point = 50; shot repetition rate = 5 ms. (B,C) $\pi/2$ = 6 ns; τ = 196 ns; t_1, t_2 were varied from 100 to 3172 ns (24 ns steps); shots per point = 100 (B) and 400 (C); shot repetition rate =1 ms; temperature = 4.8 K.

Figure 1A shows the X-band HYSCORE spectrum of the OEC of *Thermosynechococcus elongatus* poised in the S_2 state, measured at the center field of the S_2 EPR spectrum. The two sharp peaks previously assigned to the ^{17}O nucleus of a water-derived ligand to the OEC were observed (left side of panel A). However, they were also seen in the S_1 state and in the absence of ^{17}O-water (data not shown). This signal must therefore arise from the above-mentioned ^{14}N couplings in oxidized cytochrome b559 and/or c550.

To exclude the possibility that the ^{17}O signal seen in the original study (using spinach samples naturally lacking c550) and the cytochrome signal identified above appear in exactly the same spectral position, universal ^{15}N-labeling was employed. Figure 1B,C shows that the two sharp cytochrome peaks shift as compared to panel A, as expected for ^{14}N/^{15}N exchange. No additional signal was observed in the S_2 state spectrum (panel C, red boxes), demonstrating that our original assignment was incorrect.

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