

Supplementary Information for

**Protonation structure of the photosynthetic water oxidizing complex in
the S_0 state as revealed by normal mode analysis using quantum
mechanics/molecular mechanics calculations**

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Table S1. Mulliken spin densities of the Mn ions in the optimized structures of the S₀ and S₁ models

S state	model	Mn	Mulliken spin density
S ₀	O4H/H ₂ O(W2)	Mn1	3.83
		Mn2	2.96
		Mn3	3.90
		Mn4	3.89
	O4H/OH ⁻ (W2)	Mn1	3.86
		Mn2	2.89
		Mn3	3.86
		Mn4	3.87
	O5H/H ₂ O(W2)	Mn1	3.85
		Mn2	2.98
		Mn3	3.84
		Mn4	3.89
	O5H/OH ⁻ (W2)	Mn1	3.86
		Mn2	2.96
		Mn3	3.82
		Mn4	3.86
S ₁	H ₂ O(W2)	Mn1	3.86
		Mn2	2.95
		Mn3	2.83
		Mn4	3.91
	OH ⁻ (W2)	Mn1	3.86
		Mn2	2.93
		Mn3	2.81
		Mn4	3.87

Table S2. Metal-metal distances (Å) in the optimized structures of the S₀ and S₁ models in comparison with the experimental distances

		calculation						experiment	
		S ₀				S ₁		S ₀ rich (SFX 3F) ^a	S ₁ (SFX 0F) ^a
		O4H/ H ₂ O(W2)	O4H/ OH ⁻ (W2)	O5H/ H ₂ O(W2)	O5H/ OH ⁻ (W2)	H ₂ O(W2)	OH ⁻ (W2)		
Ca	Mn1	3.57	3.53	3.37	3.38	3.40	3.40	3.38	3.43
	Mn2	3.38	3.39	3.42	3.42	3.41	3.42	3.43	3.38
	Mn3	3.52	3.45	3.55	3.55	3.41	3.39	3.54	3.51
	Mn4	3.71	3.72	4.20	4.09	3.96	3.99	4.01	3.83
Mn1	Mn2	2.74	2.74	2.77	2.77	2.77	2.76	2.76	2.77
	Mn3	3.53	3.43	3.20	3.21	3.12	3.10	3.27	3.24
	Mn4	5.13	5.13	5.24	5.12	5.02	5.08	4.98	4.86
Mn2	Mn3	2.87	2.88	2.79	2.81	2.76	2.79	2.86	2.85
Mn3	Mn4	2.85	2.89	3.09	3.04	2.91	2.97	2.85	2.74
average		3.48	3.46	3.51	3.49	3.42	3.43	3.45	3.40

^a Kern et al.¹

Table S3. Calculated frequencies and assignments of the prominent vibrations in the infrared spectra of the S_0 and S_1 states with the O4H/OH⁻(W2) and OH⁻(W2) structures, respectively ^a

S state	frequency (cm ⁻¹) ^b	intensity (km/mol)	assignment
S_0	1458	113	D342
	1454	224	D170
	1450	189	D61
	1429	219	E333, E354, D342
	1426	245	E333, E354
	1418	159	E354, D342, A344
	1416	137	D342, A344, H190
	1411	105	E189, D342
	1371	412	A344
	1358	110	D170, A344
	1340	157	E189
	1320	109	A344, E189, Y _Z
	1311	275	E189, A344, Y _Z
	1297	115	Y _Z , H190
	1288	175	Y _Z , H190
	1287	110	H337
S_1	1462	195	D61
	1448	204	D170, Y _Z
	1431	225	E333
	1414	220	E189
	1404	104	D342, E354, A344
	1397	347	E354, D342, H337
	1384	105	D170,
	1373	421	A344
	1339	216	E189
	1322	95	A344, Y _Z
	1313	223	E189
	1287	255	Y _Z , H190

^a Corresponding to the spectra in Fig. 3b.

^b Scaled by a factor of 0.988.

Table S4. Calculated frequencies and assignments of the prominent vibrations in the infrared spectra of the S_0 and S_1 states with the O5H/H₂O(W2) and H₂O(W2) structures, respectively ^a

S state	frequency (cm ⁻¹) ^b	intensity (km/mol)	assignment
S_0	1424	227	D61, E333
	1396	100	E333
	1391	174	E189, A344, D342, E354
	1387	166	E189, A344, D342
	1385	221	E354, D342, A344
	1375	475	D170
	1373	168	D342, E354, D170, A344
	1366	358	D342, E354,
	1360	102	D170, E354, A344, R357
	1359	105	D170, R357
	1353	288	A344, E354, D342, D170
	1313	121	E189, H332
	1311	134	H332, E189
	1285	177	E189
	1277	99	Y _z , H190
	1253	327	Y _z , H190
S_1	1424	209	D61
	1416	98	D342
	1398	207	D170, E333
	1394	428	E333, D170
	1381	277	E189, D342, E354
	1380	147	D61
	1378	185	D342, E189, E354
	1369	293	E354, D342
	1342	392	A344
	1304	212	E189
	1273	204	E189, Y _z
	1253	329	Y _z , H190

^a Corresponding to the spectra in Fig. 3c.

^b Scaled by a factor of 0.965.

Table S5. Calculated frequencies and assignments of the prominent vibrations in the infrared spectra of the S_0 and S_1 states with the O5H/OH⁻(W2) and OH⁻(W2) structures, respectively ^a

S state	frequency (cm ⁻¹) ^b	intensity (km/mol)	assignment
S_0	1426	194	D61
	1410	243	D170, E333
	1407	223	W333, D170
	1388	106	E189, A344, E354, H190
	1386	172	E354, A344, E189
	1380	96	D61
	1374	124	D342, E354, A344
	1367	322	E354, D342, H337
	1355	106	D170
	1347	402	A344
	1314	221	E189, H332
	1291	128	E189, A344
	1260	258	Y _z , H190
S_1	1431	195	D61
	1418	204	D170, Y _z
	1401	225	E333
	1384	220	E189
	1375	104	D342, E354, A344
	1368	347	E354, D342, H337
	1355	105	D170,
	1344	421	A344
	1310	216	E189
	1294	95	A344, Y _z
	1285	223	E189
	1260	255	Y _z , H190

^a Corresponding to the spectra in Fig. 3d.

^b Scaled by a factor of 0.967.

Table S6. Coordination distances (Å) of the Mn and Ca ions in the optimized structures of the S₀ and S₁ models

		W2 = H ₂ O					W2 = OH ⁻				
		S ₁	S ₀				S ₁	S ₀			
			O4H		O5H			O4H		O5H	
		<i>d</i> ^a	<i>d</i> ^a	Δ <i>d</i> ^b	<i>d</i> ^a	Δ <i>d</i> ^b	<i>d</i> ^a	<i>d</i> ^a	Δ <i>d</i> ^b	<i>d</i> ^a	Δ <i>d</i> ^b
Mn1	O1	1.87	1.86	0.01	1.89	-0.02	1.87	1.85	0.02	1.88	-0.01
	O3	1.92	1.88	0.04	1.92	0.00	1.91	1.87	0.04	1.92	-0.01
	O5	2.51	3.29	-0.78	2.25	0.26	2.39	3.05	-0.66	2.22	0.17
	E189	1.87	1.87	0.00	1.88	-0.01	1.90	1.90	0.00	1.90	0.00
	D342	2.25	2.16	0.09	2.27	-0.02	2.29	2.19	0.10	2.30	-0.01
	H332	2.01	2.01	0.00	2.03	-0.02	2.03	2.02	0.01	2.04	-0.01
	ave ^c	2.07	2.18	-0.11	2.04	0.03	2.07	2.15	-0.08	2.04	0.02
Mn2	O1	1.84	1.84	0.00	1.83	0.01	1.84	1.85	-0.01	1.83	0.01
	O2	1.76	1.74	0.02	1.77	-0.01	1.75	1.72	0.03	1.75	0.00
	O3	1.86	1.85	0.01	1.86	0.00	1.86	1.86	0.00	1.87	-0.01
	D342	2.12	2.15	-0.03	2.12	0.00	2.14	2.17	-0.03	2.16	-0.02
	A344	1.90	1.93	-0.03	1.92	-0.02	1.91	1.92	-0.01	1.92	-0.01
	E354	2.02	2.05	-0.03	2.03	-0.01	2.02	2.05	-0.03	2.03	-0.01
	ave ^c	1.92	1.93	-0.01	1.92	0.00	1.92	1.93	-0.01	1.93	-0.01
Mn3	O2	1.85	1.90	-0.05	1.87	-0.02	1.87	1.97	-0.1	1.91	-0.04
	O3	2.00	2.29	-0.29	2.02	-0.02	2.05	2.28	-0.23	2.05	0.00
	O4	1.82	2.15	-0.33	1.86	-0.04	1.77	2.10	-0.33	1.82	-0.05
	O5	1.74	1.86	-0.12	2.25	-0.51	1.75	1.79	-0.04	2.26	-0.51
	E333	1.99	1.97	0.02	1.97	0.02	1.98	2.01	-0.03	1.97	0.01
	E354	2.18	2.10	0.08	2.25	-0.07	2.22	2.16	0.06	2.29	-0.07
	ave ^c	1.93	2.05	-0.12	2.04	-0.11	1.94	2.05	-0.11	2.05	-0.11
Mn4	O4	1.80	1.88	-0.08	1.78	0.02	1.88	1.91	-0.03	1.85	0.03
	O5	2.53	1.86	0.67	3.09	-0.56	2.70	2.09	0.61	2.99	-0.29
	W1	2.16	2.08	0.08	2.11	0.05	2.16	2.16	0.00	2.14	0.02
	W2	2.06	2.1	-0.04	2.11	-0.05	1.83	1.83	0.00	1.86	-0.03
	D170	1.99	2.13	-0.14	1.95	0.04	2.04	2.1	-0.06	2.00	0.04
	E333	1.94	2.15	-0.21	1.95	-0.01	1.98	2.12	-0.14	1.98	0.00
	ave ^c	2.08	2.03	0.05	2.17	-0.08	2.10	2.04	0.06	2.14	-0.04
Ca	O1	2.43	2.45	-0.02	2.43	0.00	2.46	2.47	-0.01	2.45	0.01
	O2	2.64	2.61	0.03	2.67	-0.03	2.63	2.60	0.03	2.67	-0.04
	O5	2.49	2.54	-0.05	2.41	0.08	2.47	2.48	-0.01	2.41	0.06
	W3	2.48	2.48	0.00	2.49	-0.01	2.47	2.49	-0.02	2.49	-0.02
	W4	2.42	2.45	-0.03	2.41	0.01	2.45	2.48	-0.03	2.44	0.01
	D170	2.53	2.49	0.04	2.52	0.01	2.50	2.48	0.02	2.50	0.00

E189	2.77	2.97	-0.20	2.76	0.01	2.85	2.98	-0.13	2.83	0.02
A344	2.60	2.61	-0.01	2.60	0.00	2.62	2.67	-0.05	2.59	0.03
ave ^c	2.55	2.58	-0.03	2.54	0.01	2.56	2.58	-0.03	2.55	0.01

^a Metal-ligand distance

^b Distance change upon the $S_0 \rightarrow S_1$ transition

^c Averages of the metal-ligand distances and their changes upon the $S_0 \rightarrow S_1$ transition

References

1. J. Kern, R. Chatterjee, I. D. Young, F. D. Fuller, L. Lassalle, M. Ibrahim, S. Gul, T. Fransson, A. S. Brewster, R. Alonso-Mori, R. Hussein, M. Zhang, L. Douthit, C. de Lichtenberg, M. H. Cheah, D. Shevela, J. Wersig, I. Seuffert, D. Sokaras, E. Pastor, C. Weninger, T. Kroll, R. G. Sierra, P. Aller, A. Butryn, A. M. Orville, M. N. Liang, A. Batyuk, J. E. Koglin, S. Carbajo, S. Boutet, N. W. Moriarty, J. M. Holton, H. Dobbek, P. D. Adams, U. Bergmann, N. K. Sauter, A. Zouni, J. Messinger, J. Yano and V. K. Yachandra, *Nature*, 2018, **563**, 421-425.