

Supporting information for “Water oxidation energy diagrams for photosystem II for different charge states, and the effect of removing calcium.”

Per E. M. Siegbahn*

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91, Stockholm, Sweden.

Email: ps@organ.su.se

The choice of fitting parameter for the different functionals.

For the redox step, only computed *relative values* are used. To obtain the actual values used in the diagrams a fitting procedure has been used. First, the relative energies calculated for removing a (H⁺,e⁻)-couple to the gas phase, are fitted to the total experimental driving force of 41.5 kcal/mol, see below. Then, for two steps, S₂ to S₃ and S₃ to S₄, an additional 5 kcal/mol are added to the driving force, giving a total driving force in the diagram of 51.5 kcal/mol. This addition is made to take account of the experimental fact (see reference 31 in the paper) that a proton is repelled from the cluster after P₆₈₀ is oxidized to P₆₈₀⁺.

The driving force of 41.5 kcal/mol is obtained from:

$$4 * (1.25 - 0.8) * 23.063 = 41.5 \text{ kcal/mol}$$

where the redox potential of the oxidant P₆₈₀ of 1.25 V (Ref.17 and 18 in the paper) and the oxidation potential of 0.80 V to oxidize water to O₂ in water at pH = 7 have been used.

The calculated proton affinities (PA) and ionization potentials (IP) are given in the table below.

	H ⁺ on His not on OH	H ⁺ on OH not on His	H+ on both His and OH	No H ⁺
PA- parameter	285.4	270.0	264.0	292.0
IP- parameter	120.5	136.3	141.6	113.4
IP- S ₀ ⁻¹	107.1	119.6	127.4	99.1
PA- S ₁ ⁰	284.7	271.4	264.8	289.1
IP- S ₁ ⁻¹	114.8	118.6	127.5	108.7
PA- S ₂ ⁰	287.0	273.4	266.3	294.3
IP- S ₂ ⁻¹	112.5	125.4	130.1	105.2
PA- S ₃ ⁰	287.5	270.9	266.8	293.5
IP- S ₃ ⁻¹	124.1	138.0	142.8	116.0
ΔE#	+7.7	+9.4	+7.5	+4.9
ΔE-S ₄ ⁰	-10.1	-3.6	-5.6	-8.5
PA- S ₀ ⁰	274.6	273.6	260.7	282.8

The energy difference going to the next level in the diagram is obtained by subtracting the PA-parameter (or EA-parameter) from the calculated PA or IP (going to gas-phase).

The choice of the PA and IP parameters were made to make the best fit to experiments in each case. For example, two critical points in the diagrams are S₁ to S₂ where only an electron leaves the OEC and no proton. This means that the level after S₂ when the proton leaves should be higher in energy. Two other critical points are the beginning of the S₂ to S₃, and S₃ to S₄ transitions where a proton leaves only after P₆₈₀ is oxidized. Also, the fact that a well characterized intermediate has been identified with given oxidation states for each S-state

except S_4 .

The values in the table are enough for obtaining the energy diagrams shown in the paper. As an example, if the next level after S_1^{-1} of -14.1 kcal/mol in the first column should be obtained, one should take the IP of 114.8 kcal/mol in the table and subtract the IP parameter of 120.5 kcal/mol. This means that the next level will be $(114.8-120.5) = -5.7$ kcal/mol higher than S_1^{-1} , that is at -19.8 kcal/mol, etc. To obtain the absolute pK_a values at a certain level, for example at S_1^0 one should take the energy difference to the next level where the proton is removed to bulk at pH=7, that is $(13.4-14.1) = -0.7$ kcal/mol. This energy difference corresponds to $0.7/1.4 = 0.5$ pK_a units. The pK_a at S_1^0 is therefore $7-0.5=6.5$. For the redox potentials the same procedure is used but the reference is now 1.25 V for the oxidation potential of P_{680} . If other parameters should be tried the sum of them has to be the same as in the table. For example, for the first column another set of parameters could be 281.4 and 124.5. The present choice was made to give reasonable diagrams, but it is not necessarily the best choice.

The coordinates for all structures in the first column were given as supporting information in Ref.2.