



東京大学
THE UNIVERSITY OF TOKYO

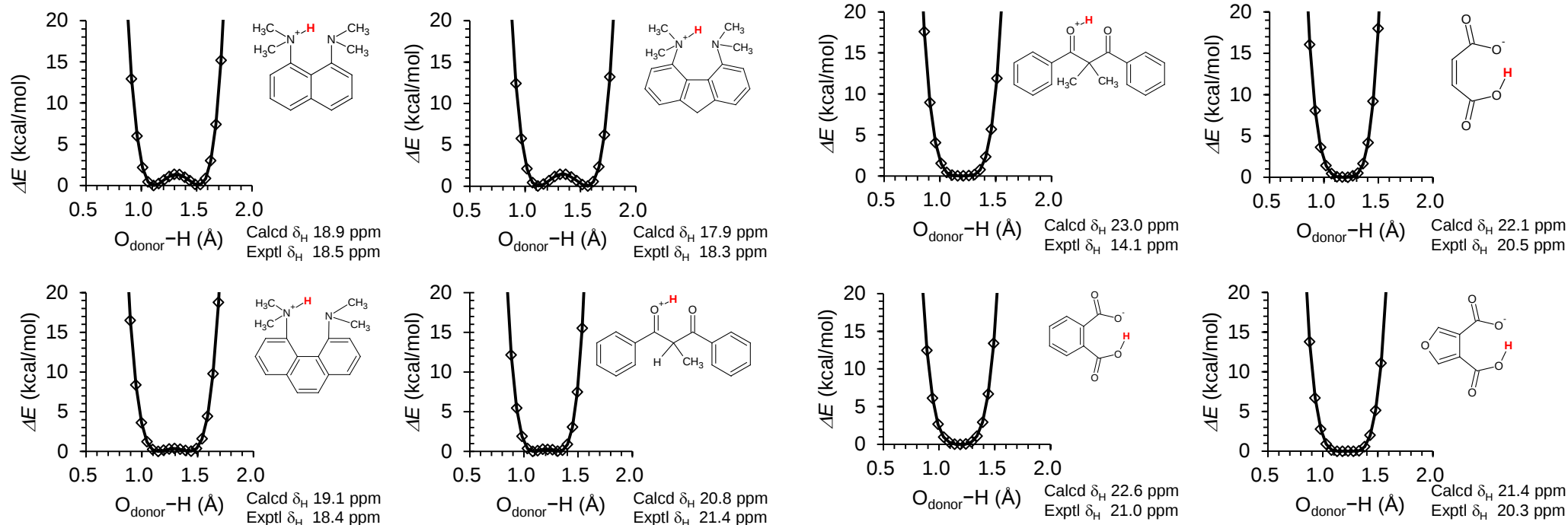
Electron and proton transfer reactions in photosynthetic reaction centers

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石北 央

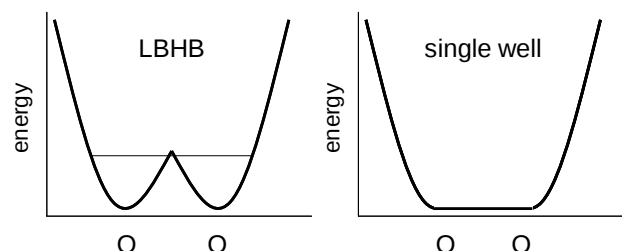
Low-barrier H-bonds
really exist?

Can we identify Low-barrier H-bond at the DFT level?



LBHB: $pK_a(\text{donor}) = pK_a(\text{acceptor})$

LBHB can be unambiguously identified in the potential-energy profile at the DFT level (with neither solving the nuclear Schrödinger equation nor considering dynamics)



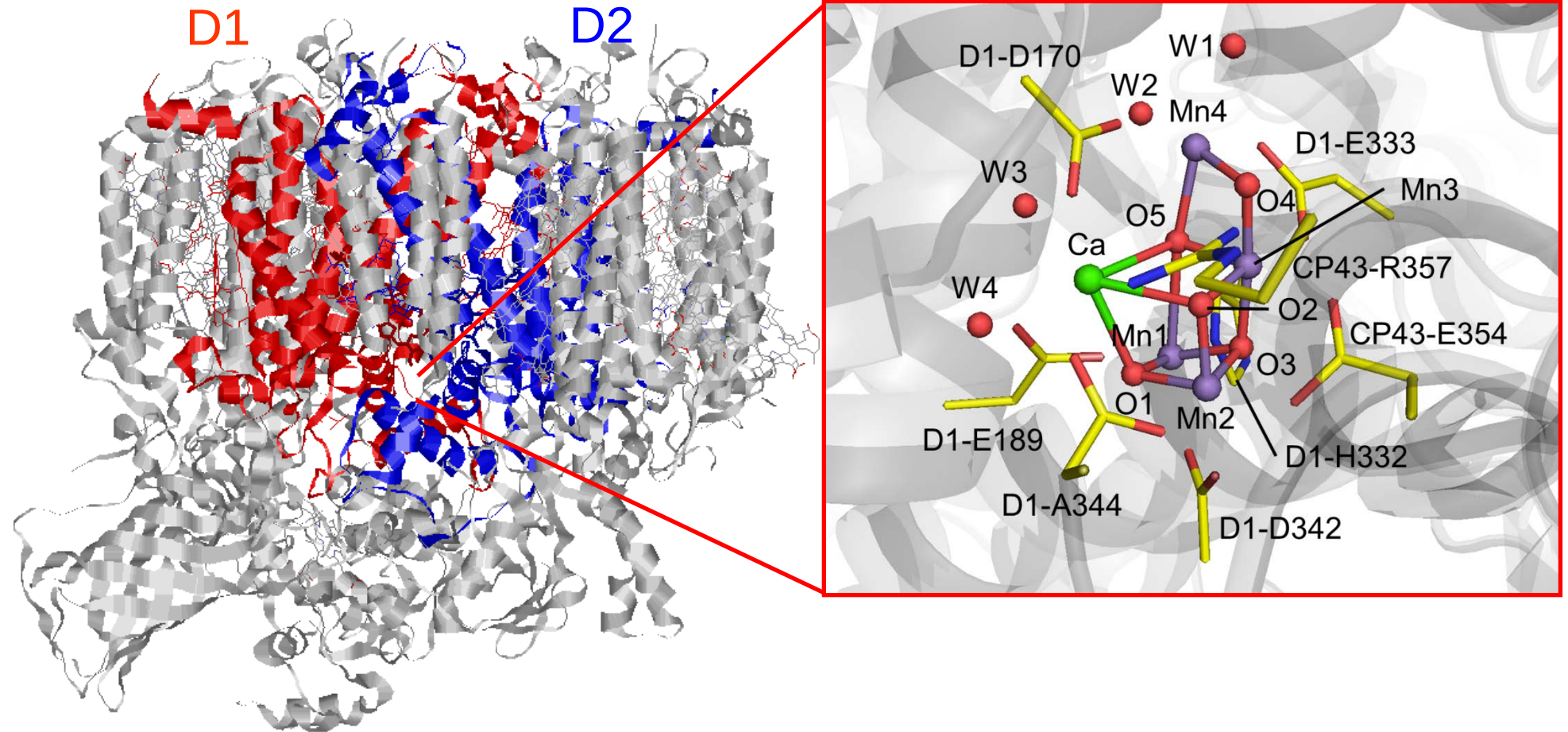
Does a low-barrier H-bond also exist
in a protein environment?

A short H-bond in photosystem II

Light-driven water-splitting enzyme Photosystem II

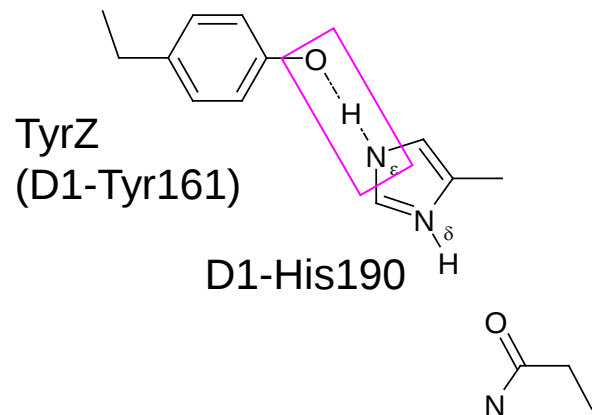


2 substrate water molecules are catalyzed at the Mn_4CaO_5 cluster



QM/MM (Quantum Mechanics/ Molecular Mechanics)

QM/MM calculations (B3LYP / LACVP**+)



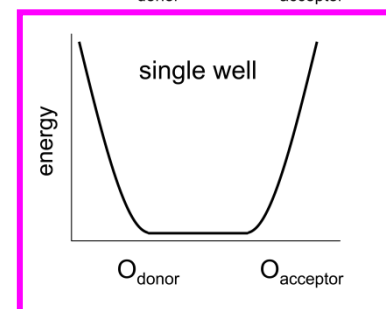
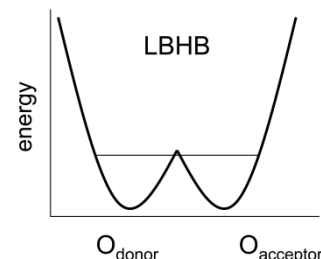
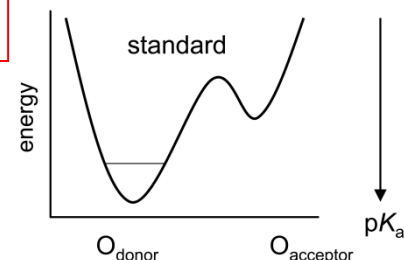
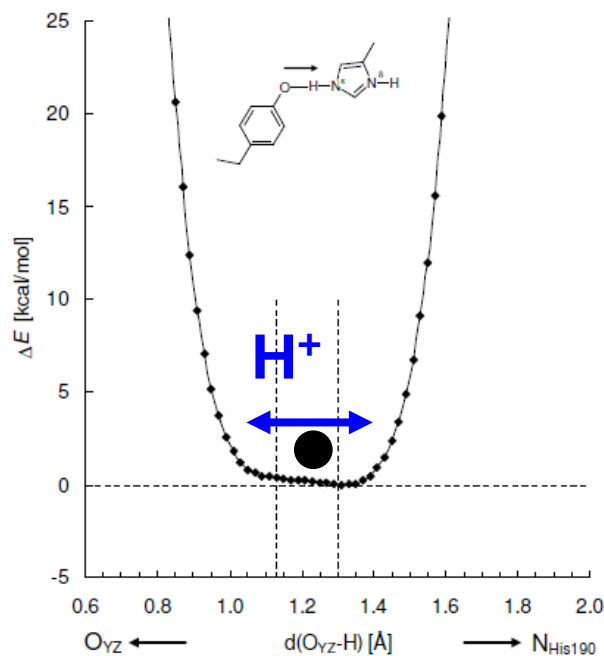
Umena, Kawakami, Shen, Kamiya
(2011) *Nature* 473, 55

$O_{\text{TyrZ}}-N_{\text{His190}} = 2.46 \text{ \AA}$
Remarkably short!

(PDB) $O_{\text{Tyr}}-N_{\text{His}}$ distance = $2.46 \text{ \AA}$

(calc.) $O_{\text{Tyr}}-N_{\text{His}}$ distance = $2.47 \text{ \AA}$

The unusually short H-bond seems to be quantumchemically reasonable!

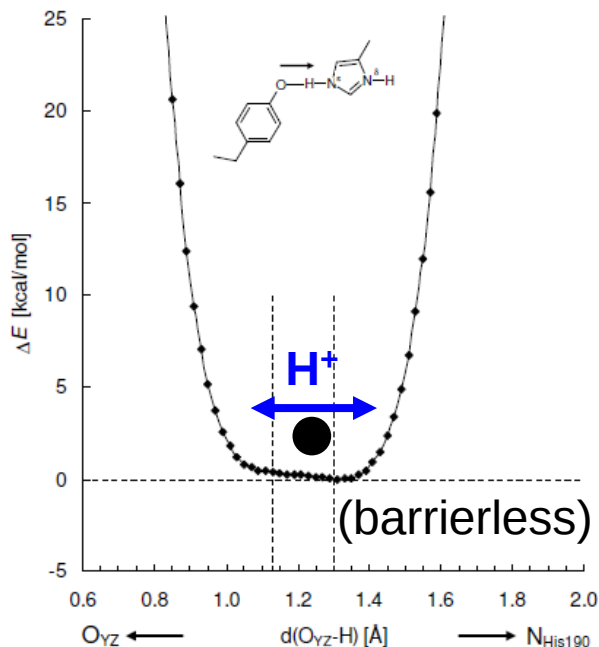


This is why TyrZ...His can mediate proton-coupled electron transfer (PCET)

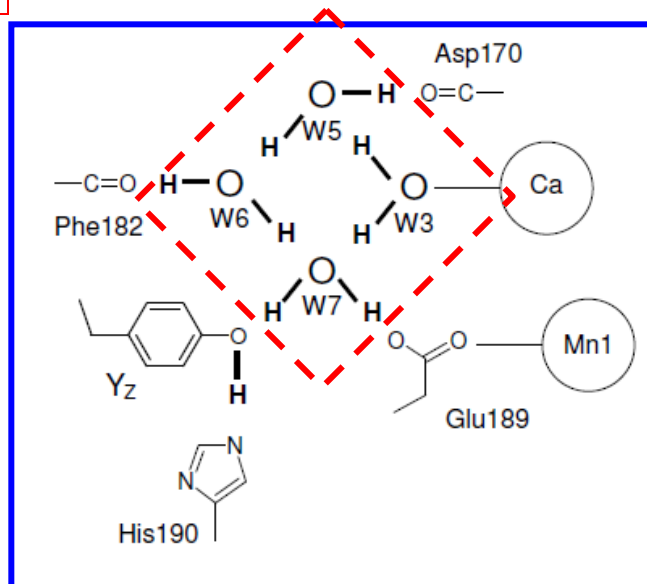
What makes the TyrZ...His190 distance so short?

QM/MM calculations (B3LYP / LACVP**+)

$O_{\text{Tyr}}-N_{\text{His}}$ distance = **2.47 Å**

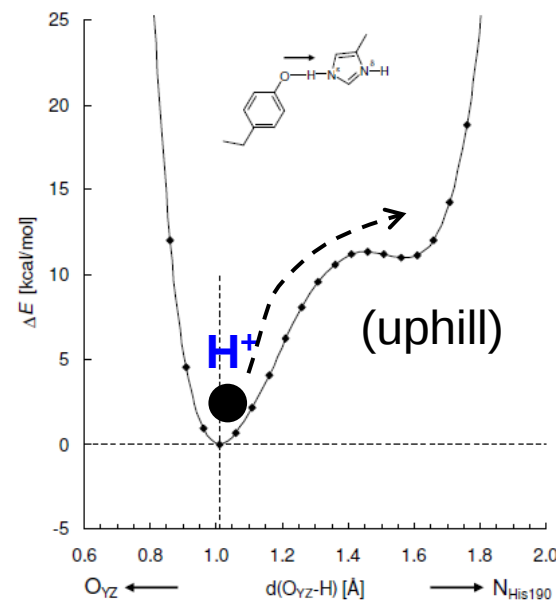


polar environment in PSII

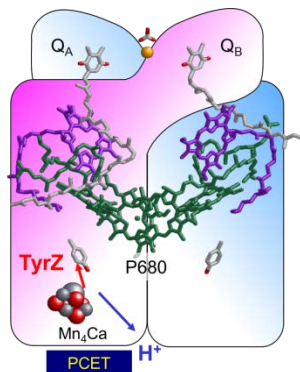


Removal of waters

$O_{\text{Tyr}}-N_{\text{His}}$ distance = **2.71 Å**



Single-well



A cluster of water molecules near Mn_4Ca
 → Matching pK_a between TyrZ and His190

The barrier-less H-bond facilitates PCET

Standard
 (asymmetric double-well)

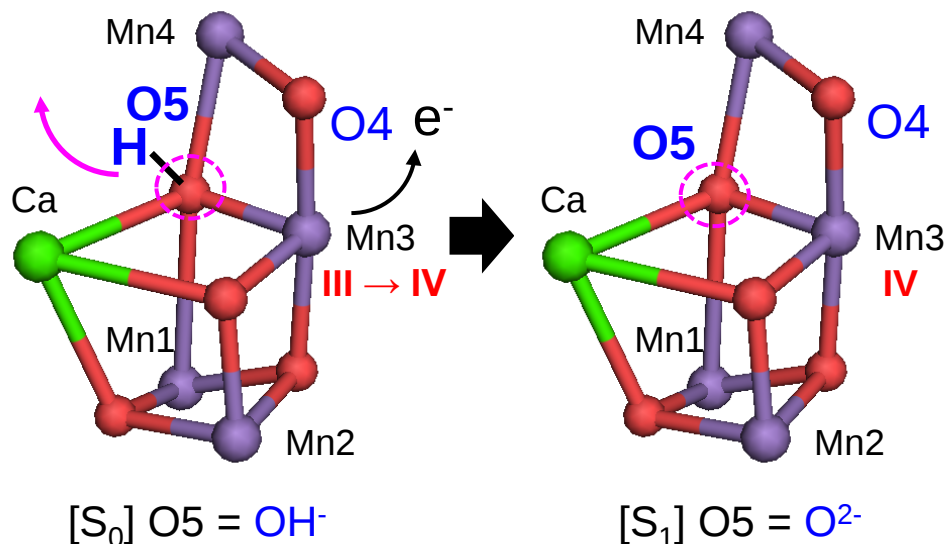
H^+ release from H_2O
in photosystem II

Identification of the H^+ releasing site in the S_0 -to- S_1 transition

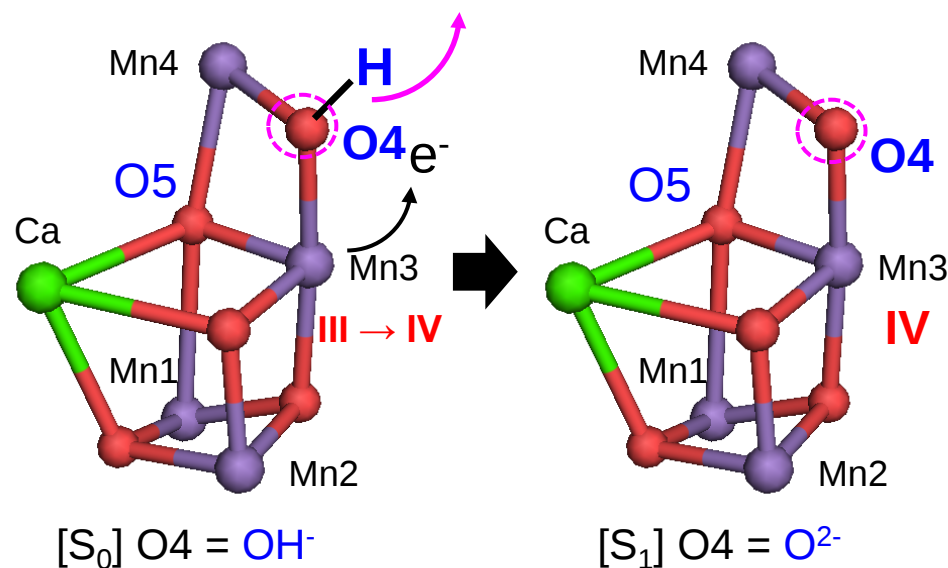
“O5 or O4”, which is the substrate?

Note: in the oxidation of the crystal structure, the substrate water is considered to be OH^- .

1) Substrate = O5

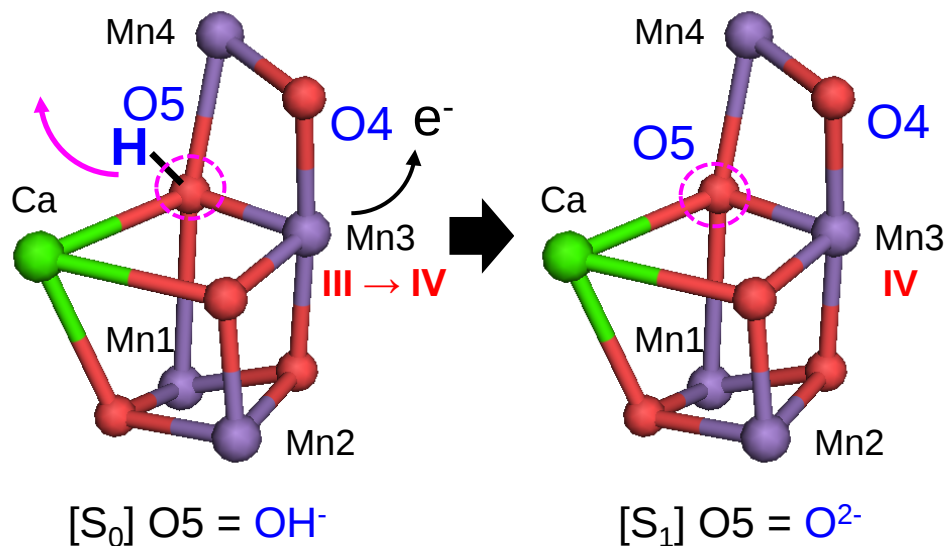


2) Substrate = O4



Identification of the H⁺ releasing site in the S₀-to-S₁ transition

1) Substrate = O5



O5 is close to Ca²⁺ and is apparently interesting...

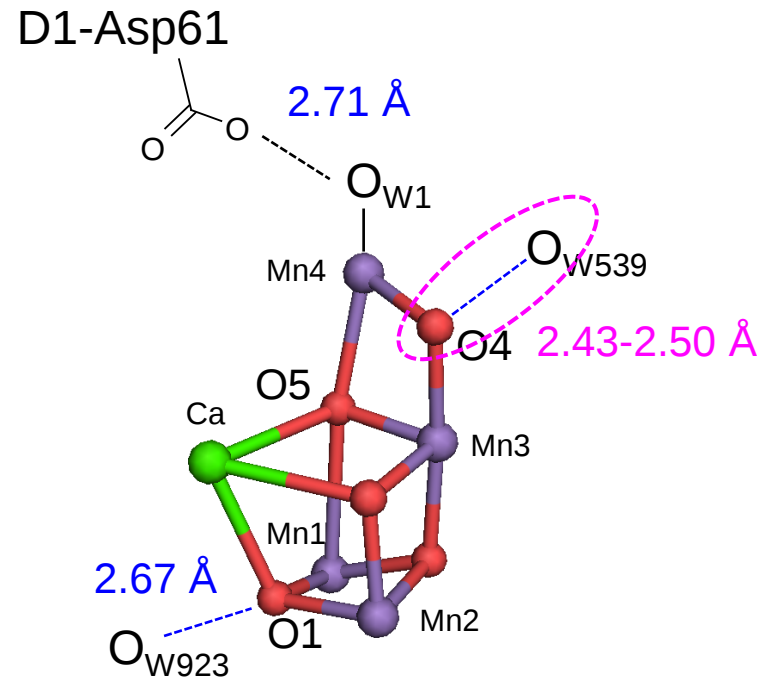
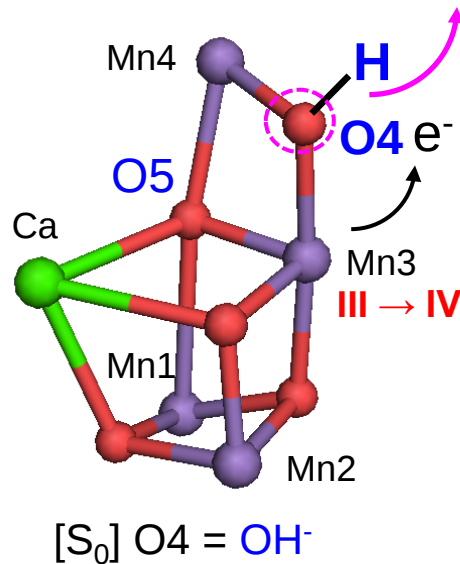
However, O5 has no H-bond partner in the crystal structures
(Umena et al. *Nature* 2011, Suga et al. *Nature* 2015)



no proton transfer from O5
(The activation energy for proton release must be high)

H-bonds of the Mn_4CaO_5 cluster

2) Substrate = **O4**



Umena, Kawakami, Shen, Kamiya (2011) *Nature* 473, 55

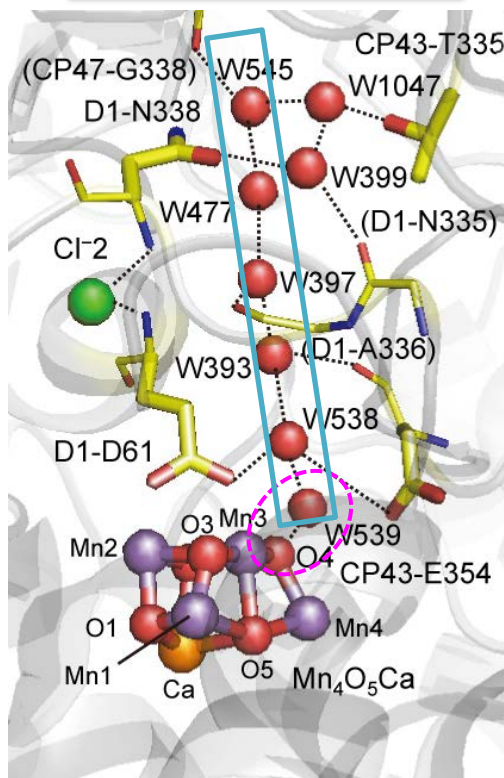
The $\text{O4} \dots \text{O}_{\text{W539}}$ bond is very short ($< 2.5 \text{ \AA}$!)

We focus on the $\text{O4} \dots \text{O}_{\text{W539}}$ H-bond

Changes in the H-bond potential in the S_0 -to- S_1 transition

O4 is linked with the O4-water chain via W539

O4-water chain

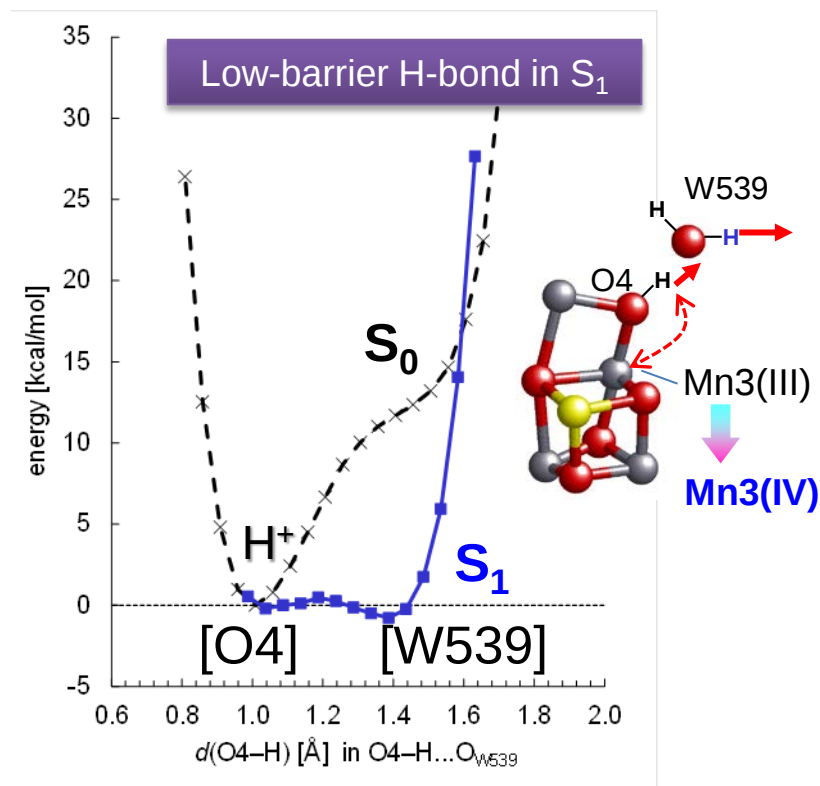


X-ray

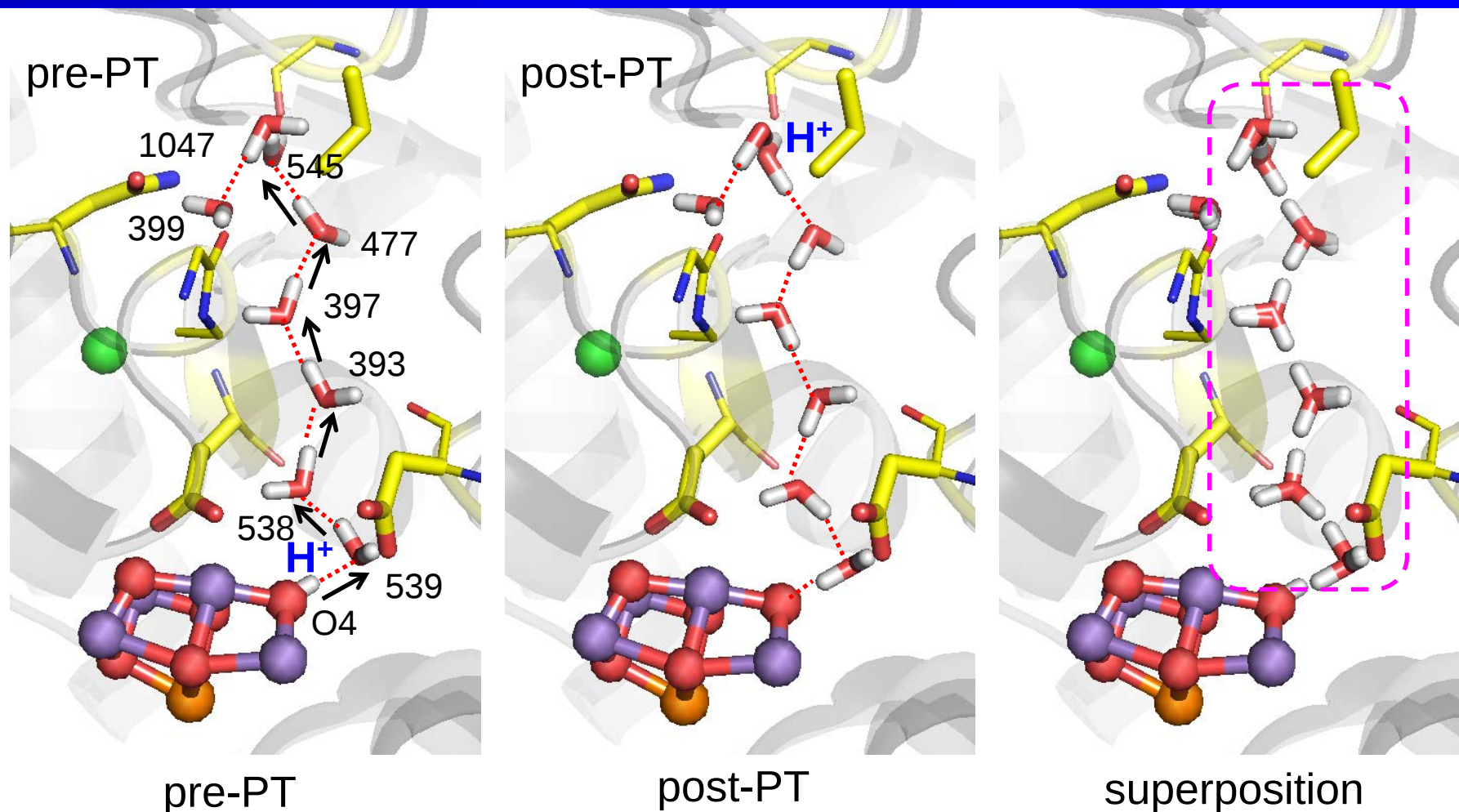
O4...O_{W539} distances:
2.43-2.50 Å (Umena 2011)

QM/MM

2.55 Å in S_0 (Saito 2015)
2.45 Å in S_1 (Saito 2015)



H-bond pattern: before and after PT in the S_0 -to- S_1 transition



O atoms did not move during H^+ transfer



The activation energy is low

- O4 is the deprotonation site
- The O4-water chain is the proton transfer pathway

Saito, Rutherford, Ishikita. (2015) *Nat. Commun.* 6, 8488

Experimental support for the O4-water chain being used in S_0 -to- S_1

Time-resolved infrared spectroscopy

The S_0 -to- S_1 transition:

“the highest rate among the four S-state transitions.”

“The high PCET rate with a relatively small KIE value (~1.2)”

“This result is more consistent with the O4-H structure (Saito et al.) than the O5-H one.”

Simizu, Sugiura, Noguchi. (2018) *J. Phys. Chem. B* 122, 9460

The time-resolved infrared spectroscopy supports
“O4 is the deprotonation site in the S_0 -to- S_1 transition”

Conclusions:

- O4 is the deprotonation site (= substrate water)
- The O4-water chain is the proton transfer pathway

Saito, Rutherford, Ishikita. (2015) *Nat. Commun.* 6, 8488

Kawashima, Takaoka, Kimura, Saito, Ishikita. (2018) *Nat. Commun.* 9, 1247

