2269-15

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Ab-initio modeling of Ru-based homogeneous catalysts for water oxidation

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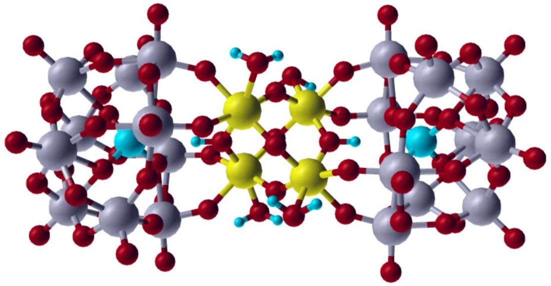
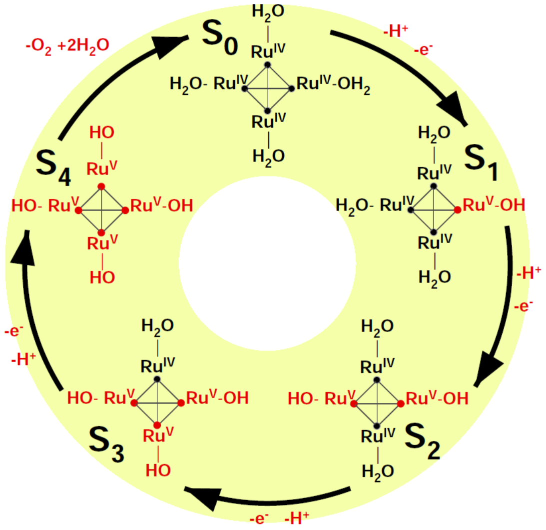
Ab-initio modeling of Ru-based homogeneous catalysts for water oxidation





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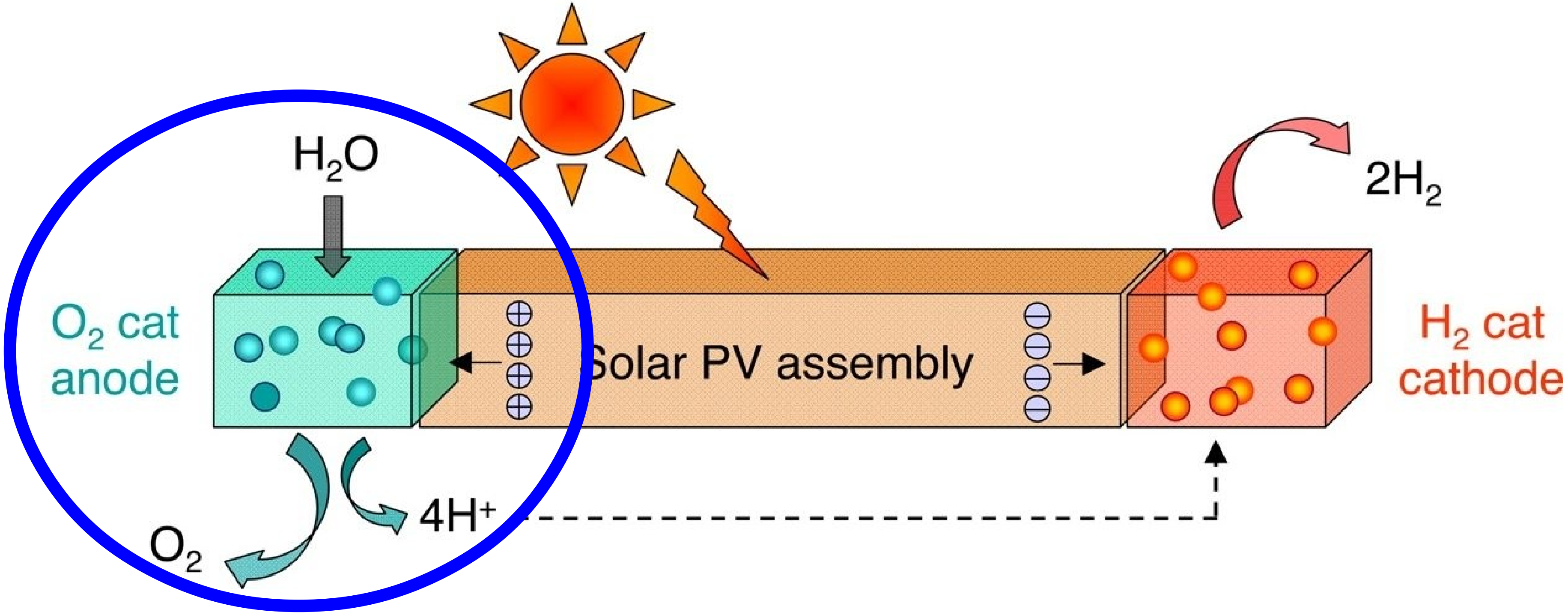
ICTP-SISSA Workshop on New Materials for Renewable Energy
Trieste, 17-21 October 2011

Artificial photosynthesis: using light to make fuels



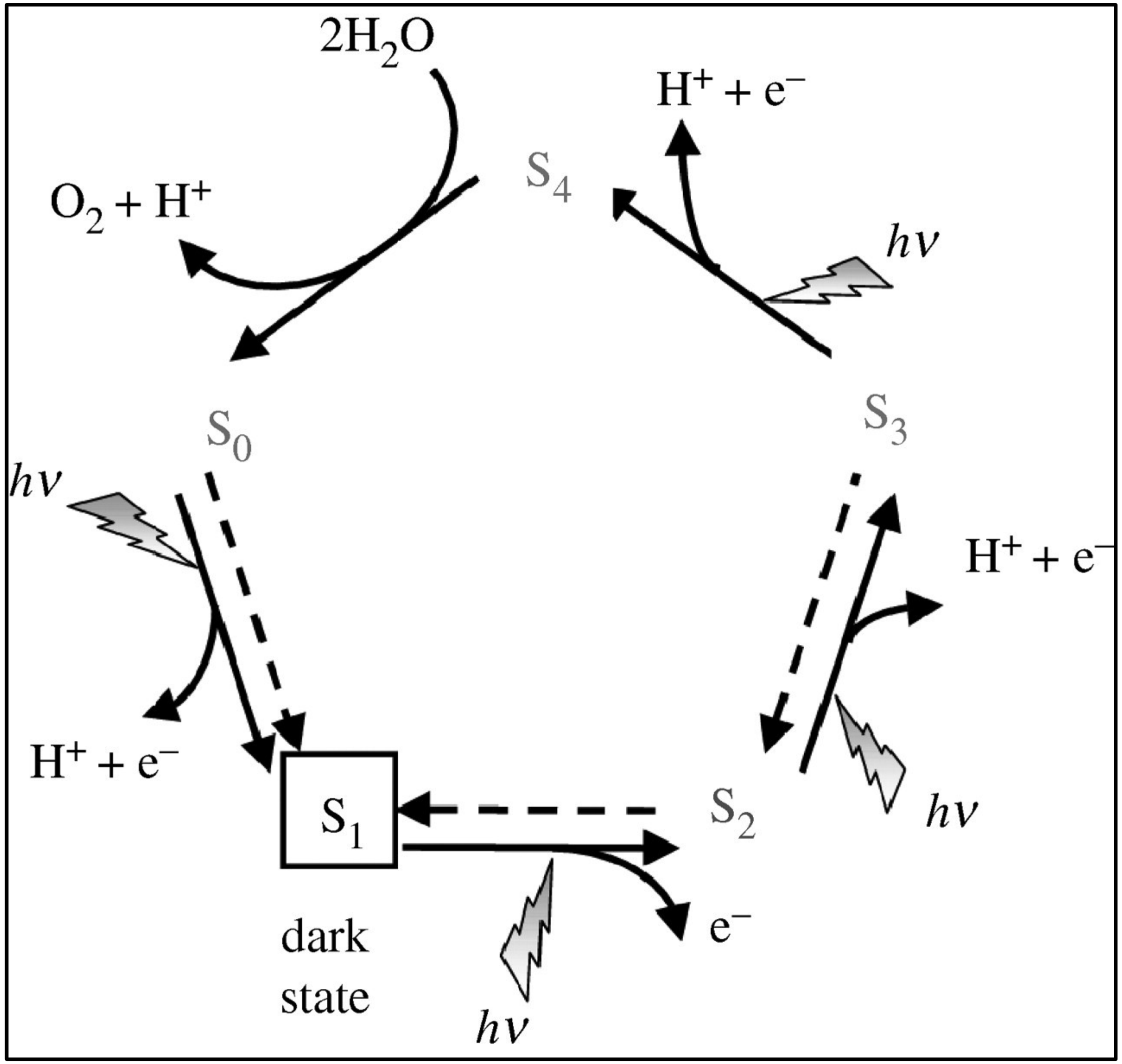
Overall reaction: $2H_2O \rightarrow O_2 + 2H_2$ $(\Delta G^0 = 4.92\ \mathrm{eV},\ E^0 = -1.23\ \mathrm{V})$

Oxidation: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $(E^0 = 1.23\ \mathrm{V})$

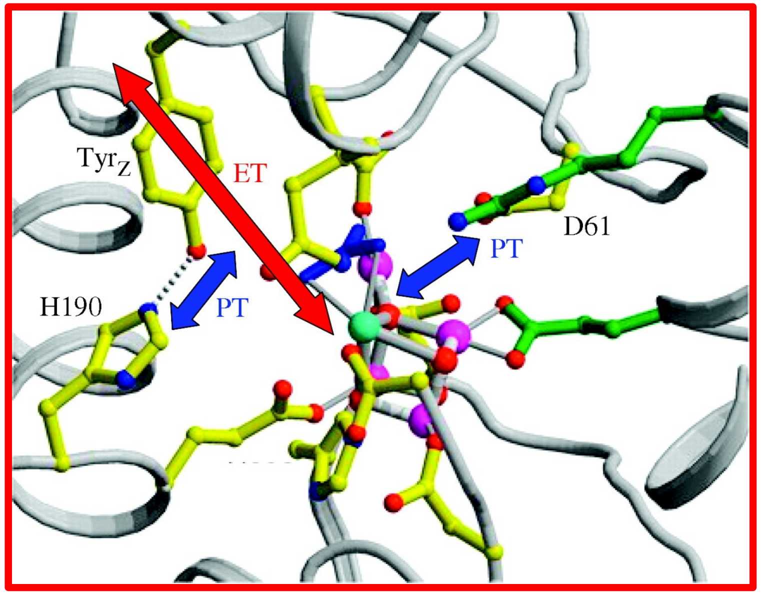
Reduction: $2H^+ + 2e^- \rightarrow H_2$ $(E^0 = 0.00\ \mathrm{V})$

Figure from: Lewis and Nocera, PNAS **103**, 15729 (2006)

Natural photosynthesis: PSII



- The Mn_3CaO_4-Mn catalyst is oxidized four times, through a series of PCET/ET/PT steps
- S4 is the active state that oxidizes water

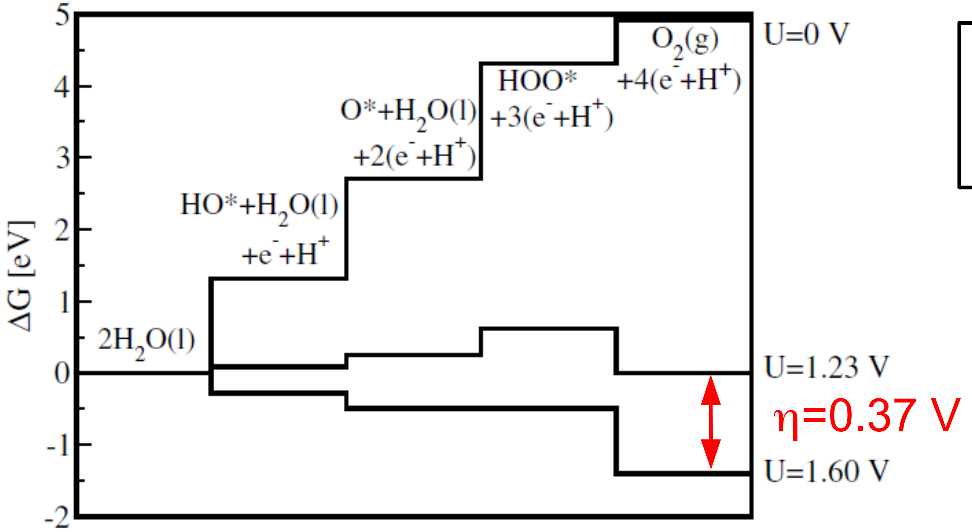


Requirements for water oxidation catalysts

The ideal water oxidation catalyst should be:

(1) **<u>Efficient:</u>** minimize the overpotential (η) avoiding the formation of high energy intermediates such $OH^{\bullet}$ or H_2O_2

RuO_2(110)



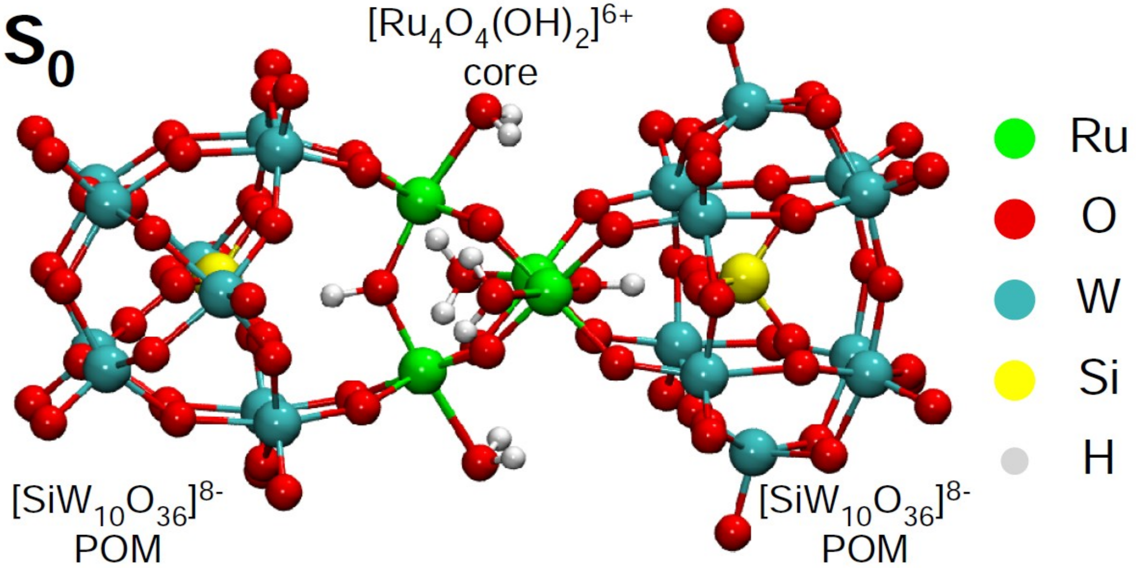
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
$$(E^0 = 1.23\ V,\ \Delta G^0 = 4.92\ eV)$$

(2) **<u>Stable:</u>** organic ligands of organometallic catalysts are typically easily oxidized, reducing the lifetime of the catalyst

(3) **<u>Cheap:</u>** we should minimize the use of precious metals such as Pt, Ru, Ir, ...

Ru_4-POM

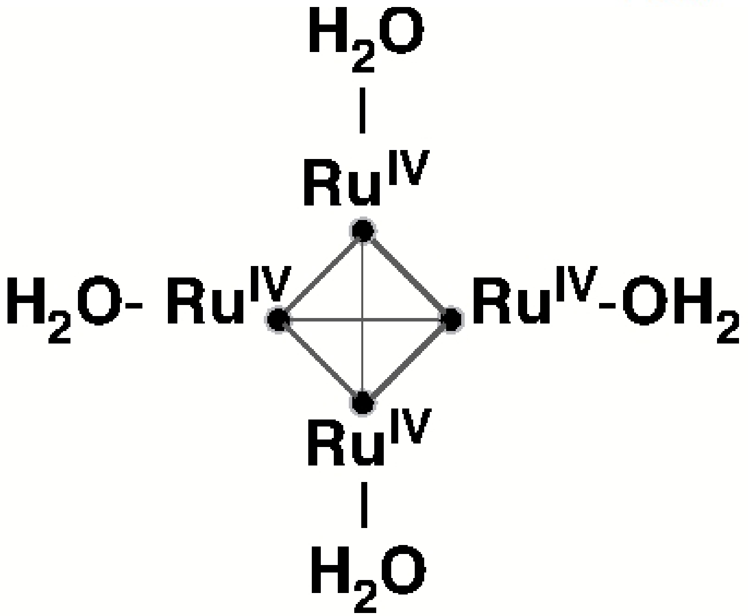
Synthesized by two research groups:
Sartorel *et al.* JACS **130**, 5006 (2008)
Geletii *et al.* Angew. Chem. **47**, 3896 (2008)



RED: $4Ce^{4+} + 4e^- \rightarrow 4Ce^{3+}$ (pH 1.8)

OX: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

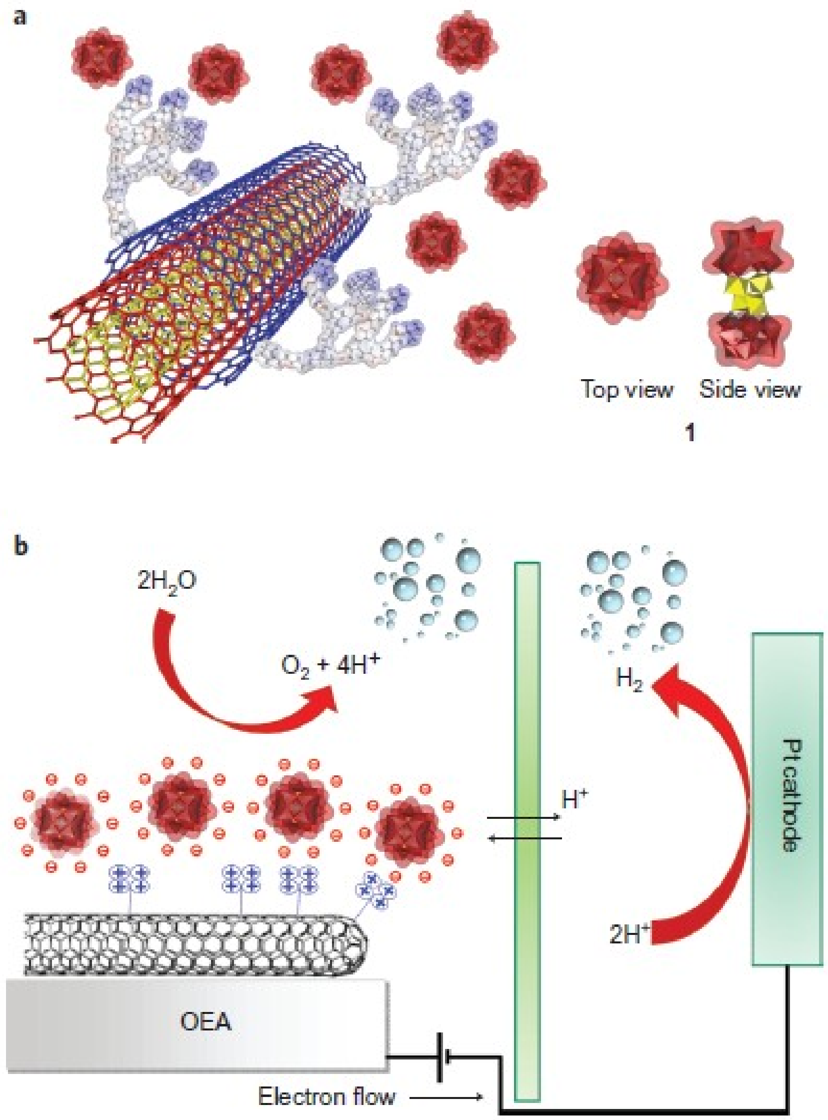
WHY Ru_4-POM?
- Small overpotential ~ 0.35 V
- No deactivation over days
- High turnover rate (~ 450 cycles/h)



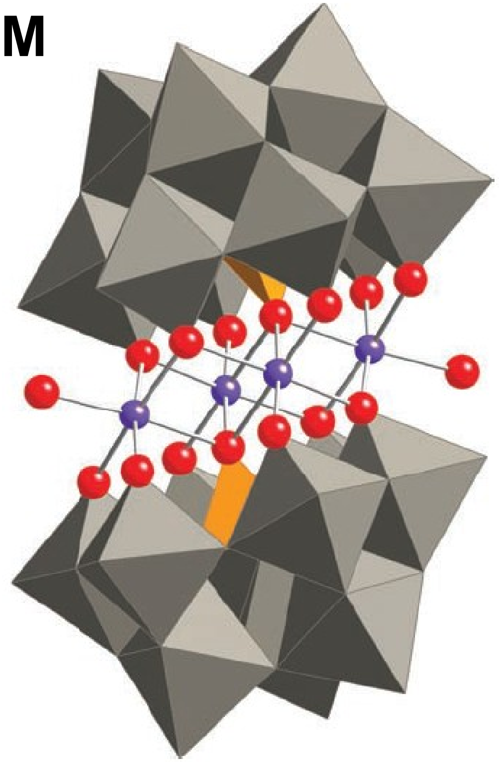
Ru_4-POM

- Ru_4-POM has been adsorbed on functionalized nanotubes, on top of a conducting electrode, thus creating an anodic material for WAT-OX.

- The catalytic performance seen in the homogeneous phase is preserved also in the heterogeneous one



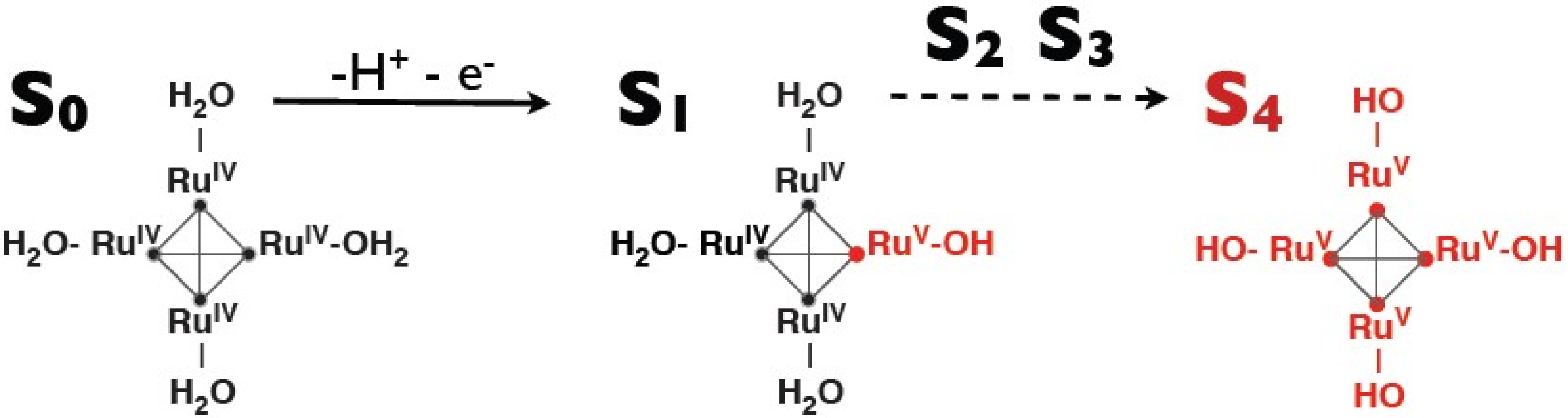
Co_4 - POM

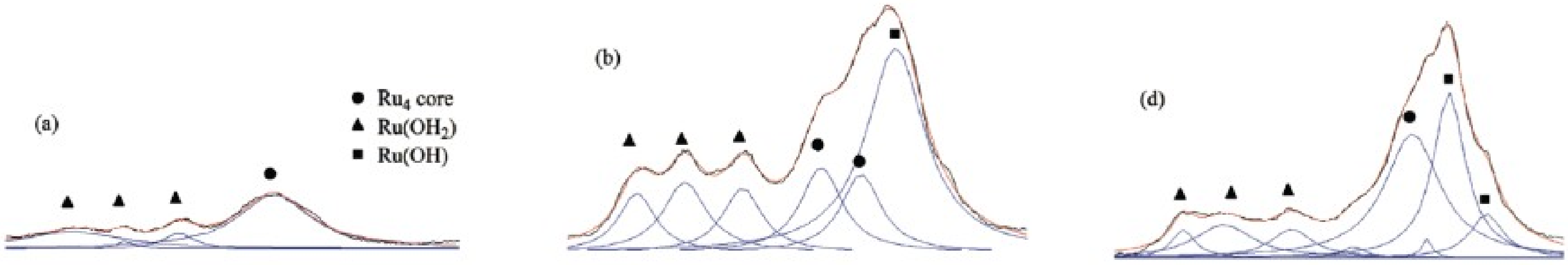


Yin et al., Science **328**, 342-345 (2010)

Ru_4-POM

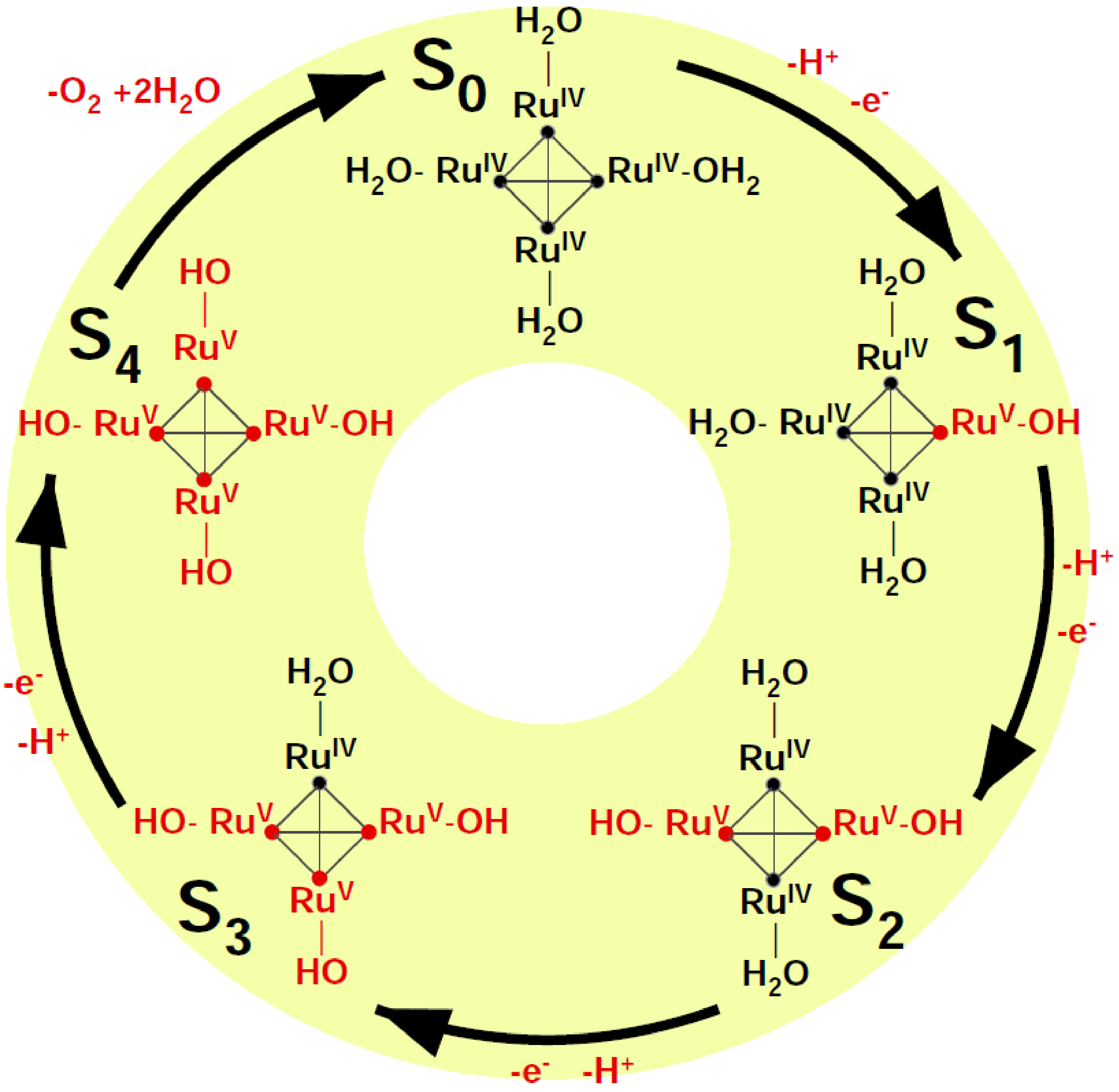
- 5 reaction intermediates (S_0-S_4) have been identified and characterized through Raman spectroscopy
- The energetics of 3 steps (S_0-S_3) has been determined through cyclic voltammetry (also pH dependency)
- 4 PCET steps: Ru(IV)-H_2O → Ru(V)-OH

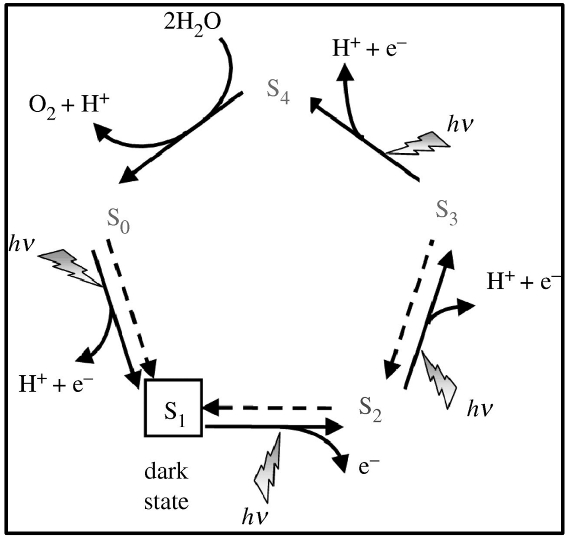




Sartorel et al. J.AM. CHEM. SOC., 131, 16051 (2009)

Proposed reaction clycle: PCET





Proposed reaction clycle: PCET

- Investigate the mechanism of O-O bond formation
- Determine the energetics of the catalytic cycle and the origin of the overpotential

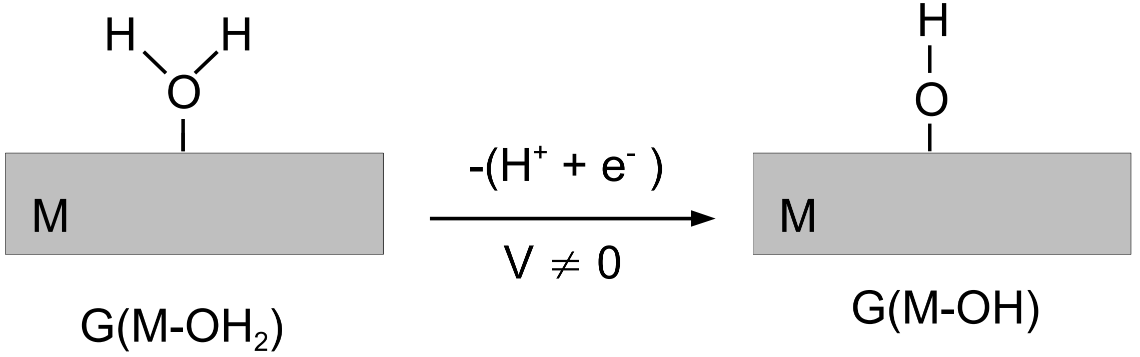
Computational approach

Electronic structure

- GGA (PBE) / Hybrid (HSE06, B3LYP) exchange-correlation functionals (CP2K)

Nørskov's approach for the energetics of PCET

- $\frac{1}{2}\,\mu(H_2) = \mu(H^+) + \mu(e^-)$
- $\Delta G \simeq \Delta E^{DFT} + \Delta ZPE^{DFT} - T\Delta S$



$$\Delta G(V) = G(M\text{-}OH) + \underbrace{\mu(H^+) + \mu(e^-)}_{} - G(M\text{-}OH_2)$$

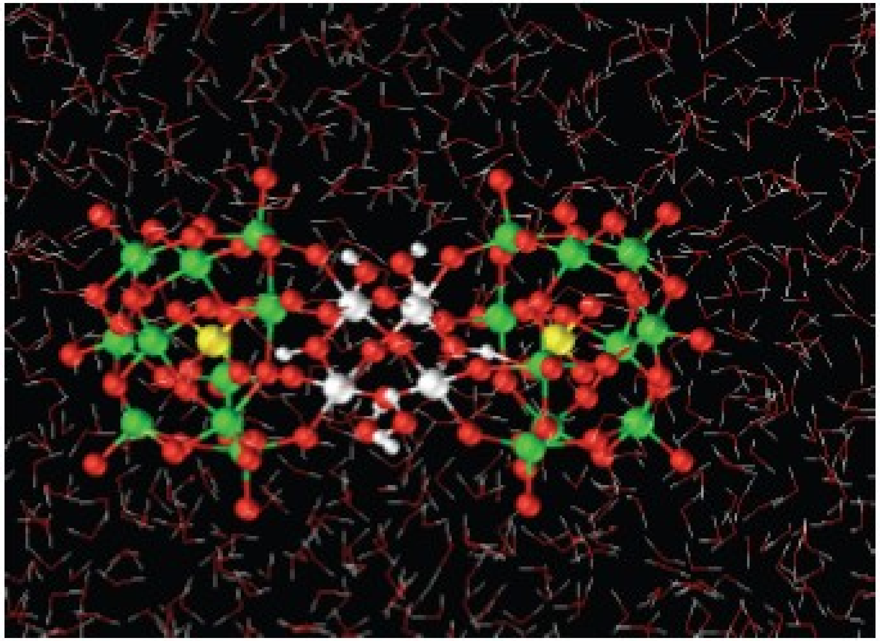
$$= G(M\text{-}OH_2) + 1/2\mu(H_2) - eV - G(M\text{-}OH)$$

$$= \Delta G(V{=}0) - eV$$

Computational approach

Solvent effects?

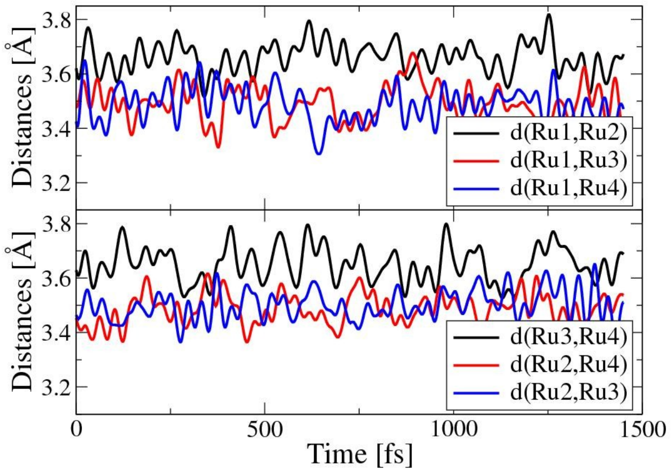
- Energetics computed in **vacuum**. For PCET reactions implicit solvent calculations show very small solvent effects on the energetics (~0.01 eV per PCET step)

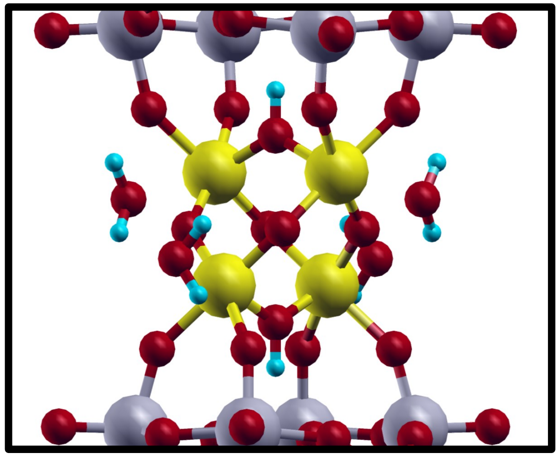


QM/MM calculations in 1800 TIP3P water molecules to study the effect of the solvent on the structural and electronic properties of Ru_4-POM

Molecule in solution: QM/MM (PBE)

Ru-Ru distances



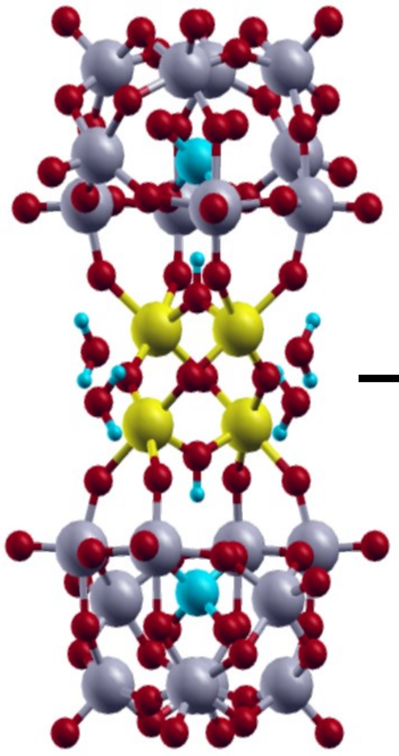


The distortion of the Ru tetrahedron is correctly captured only when solvent effects are included

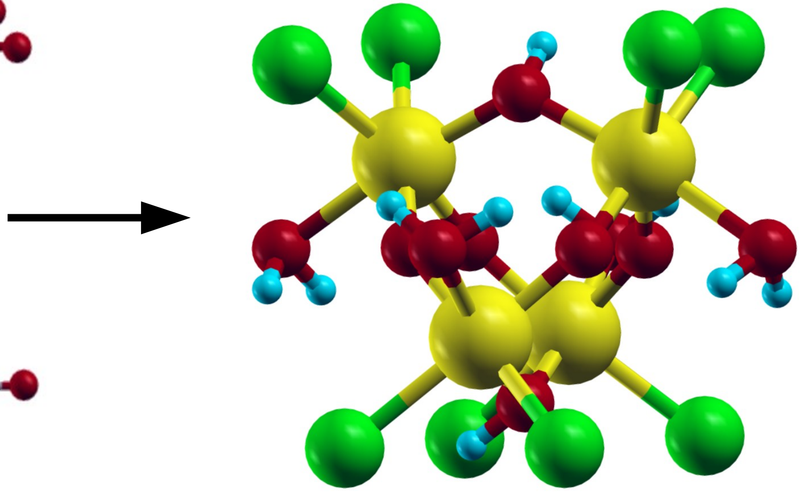
Distance	Vacuum	QM/MM	Exp
μ-OH	3.55	3.67	3.66
μ-O	3.53	3.49	3.47

Simplified cluster for hybrids

To reduce the computational cost associated with the use of **hybrid functionals** we replace the POM ligands with Cl atoms:



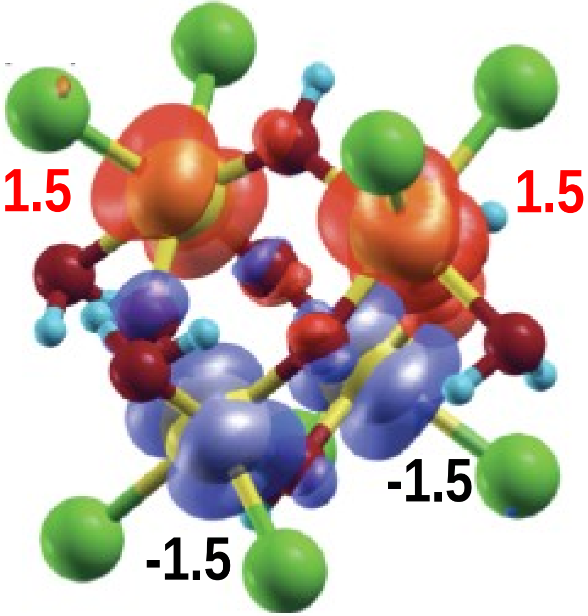
Ru_4-POM

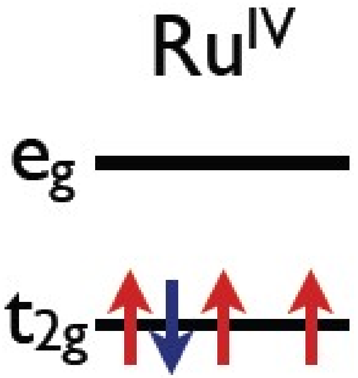


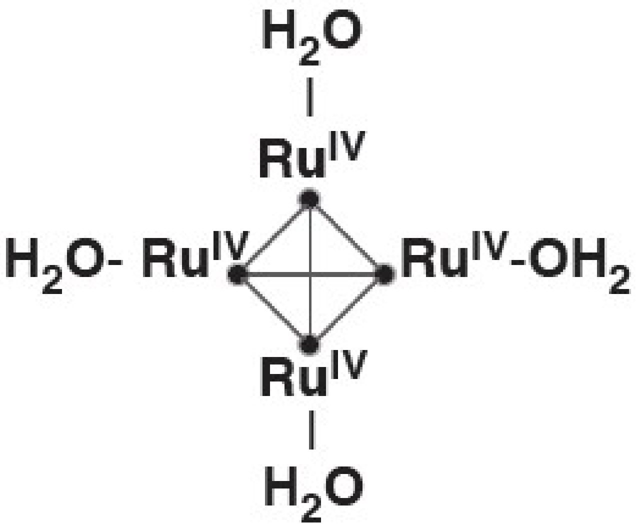
Ru_4-Cl

Simplified cluster for hybrids

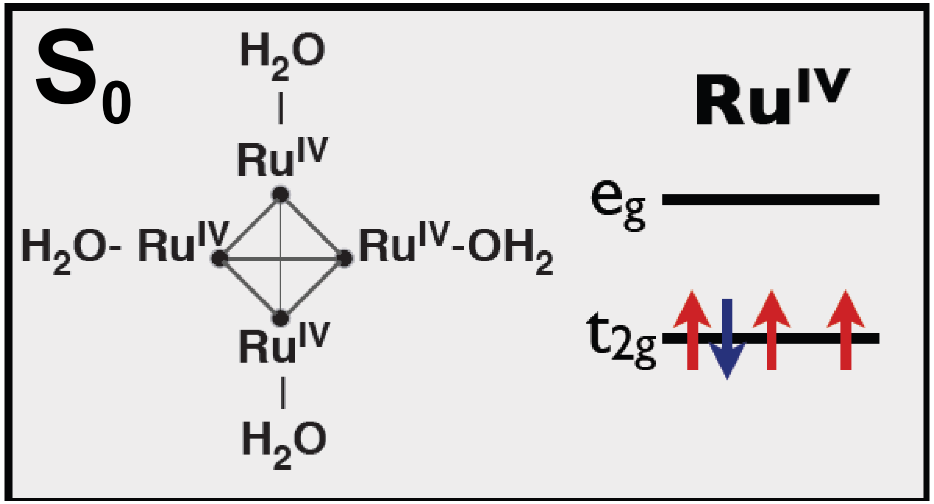
- All calculations predict a singlet ground state - Diamagnetic EPR silent
- Ru spin polarization 1.5: Ru(IV) with 2 unpaired spins per Ru atom
- Antiferromagnetic coupling of Ru centers across μ-OH bridges
- HOMO-LUMO 1.92/1.68 eV (B3LYP/HSE06)
- Frontiers orbitals always localized on the Ru_4O_6 core
- Four highest occupied states in 0.37 eV energy window

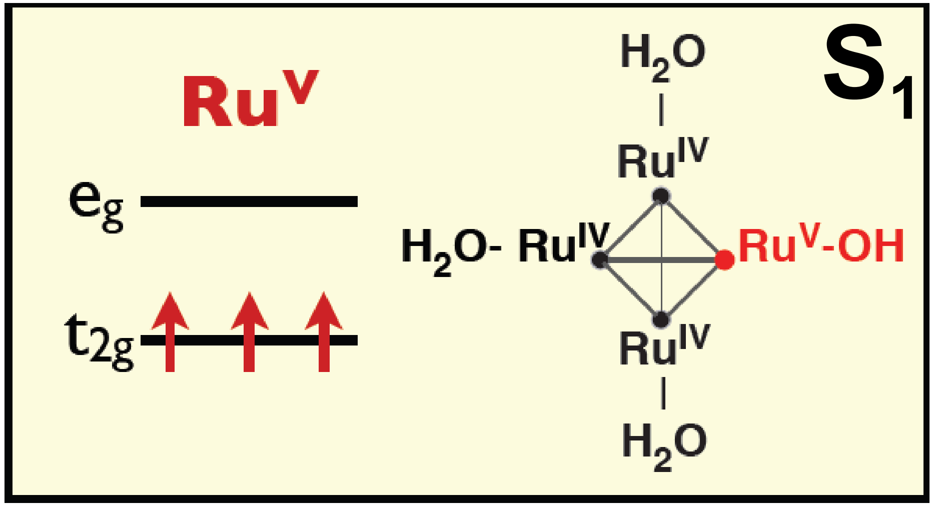


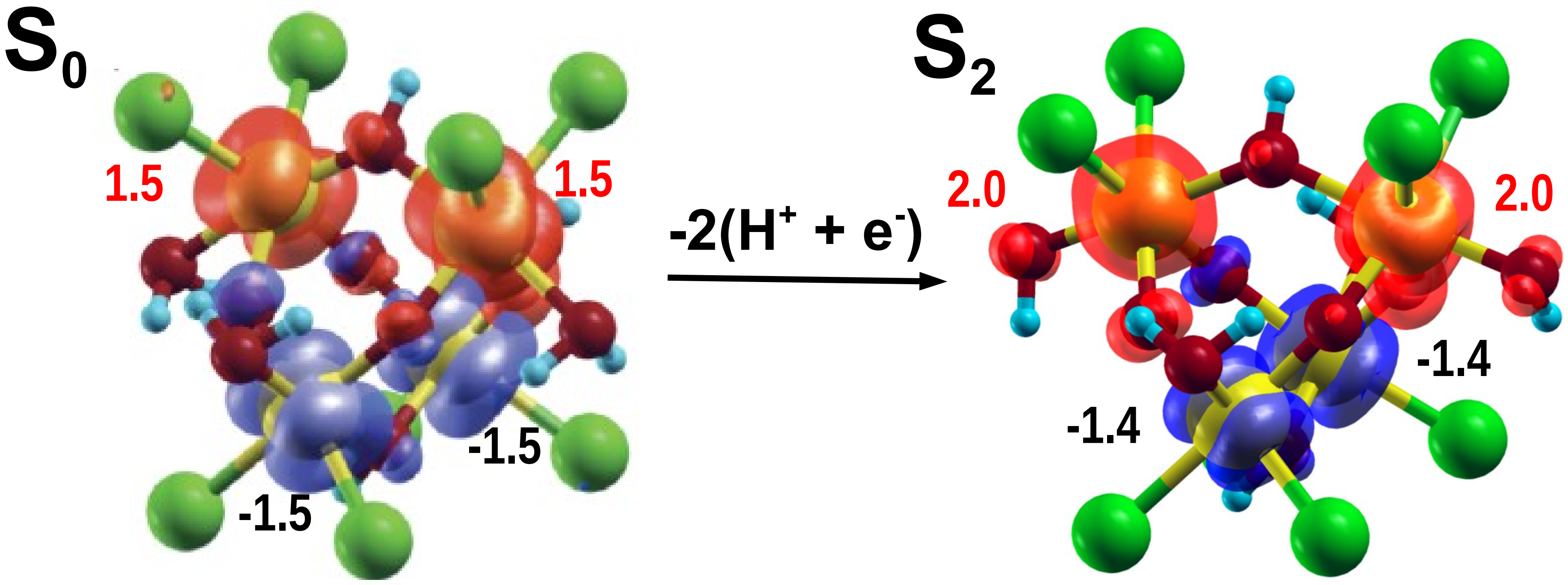




Analysis of spin density

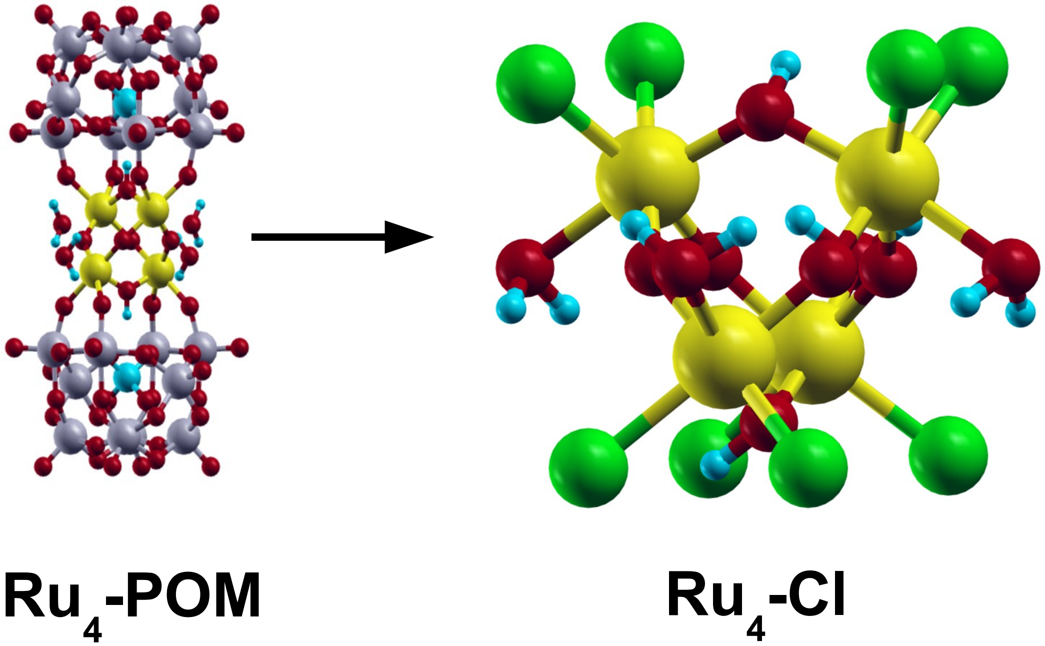






Energetics of the simplified cluster

To reduce the computational cost associated with the use of hybrid functionals we replace the POM ligands with Cl atoms:



System	ΔE (eV) Ru$_4$-POM	ΔE (eV) Ru$_4$-Cl
S0	0.00	0.00
S1	1.03	1.01
S2	1.92	2.10
S3	3.02	3.28
S4	4.04	4.39

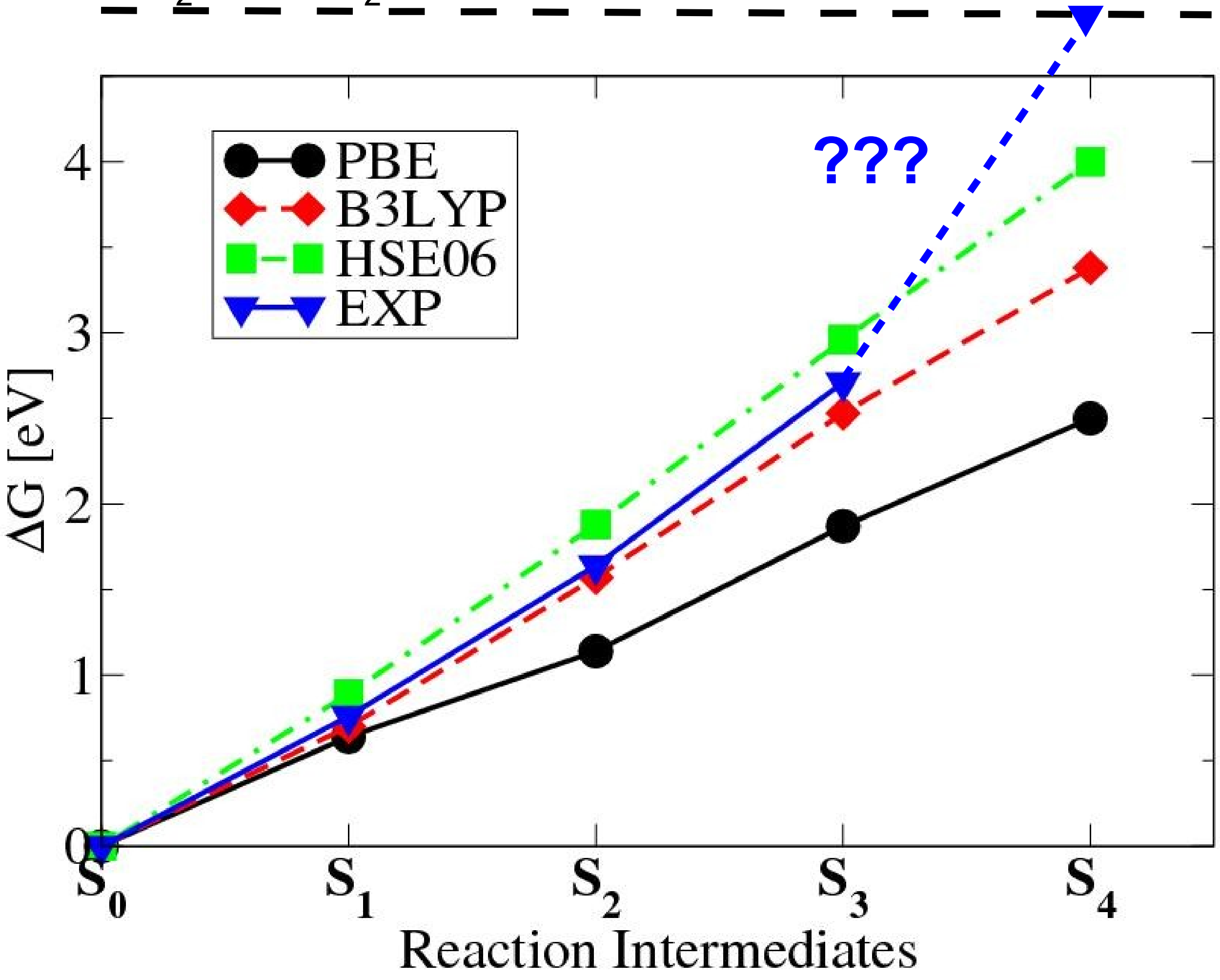
$\Delta E = E(Sn) + n/2E(H_2) - E(S0)$

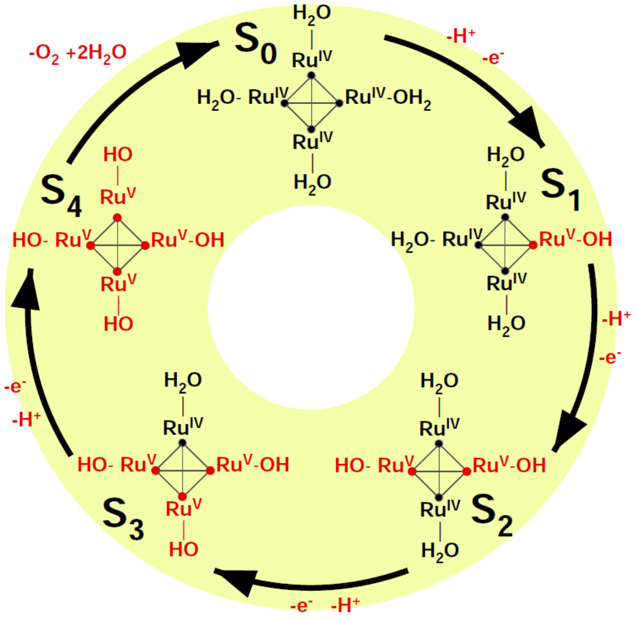
Error of structural simplification: ~ 0.1 eV per PCET event.

$$\Delta E^{hybrid}(Ru_4\text{-POM}) \sim \Delta E^{PBE}(Ru_4\text{-POM}) + \underbrace{[\Delta E^{hybrid}(Ru_4\text{-Cl}) - \Delta E^{PBE}(Ru_4\text{-Cl})]}_{\text{“core” correction}}$$

Energetics of the catalytic cycle

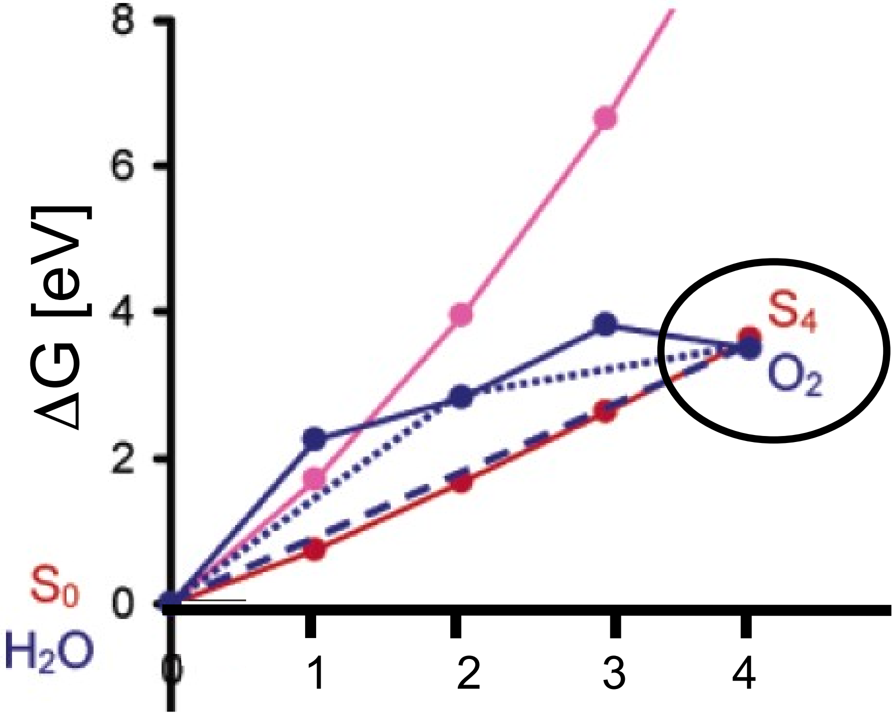
$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad \Delta G^0 = 4.92$ eV

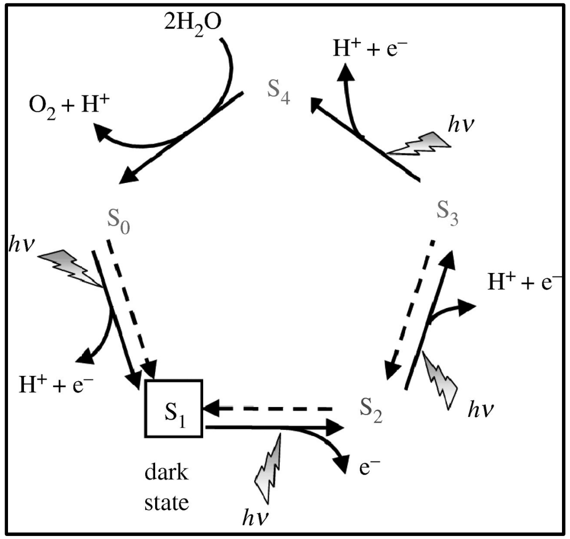




$$\boxed{\Delta G(S0 \rightarrow S4) = 3.38 \ll 4.92\ (4.56)\ \text{eV}}$$

Oxygen evolving complex in PSII





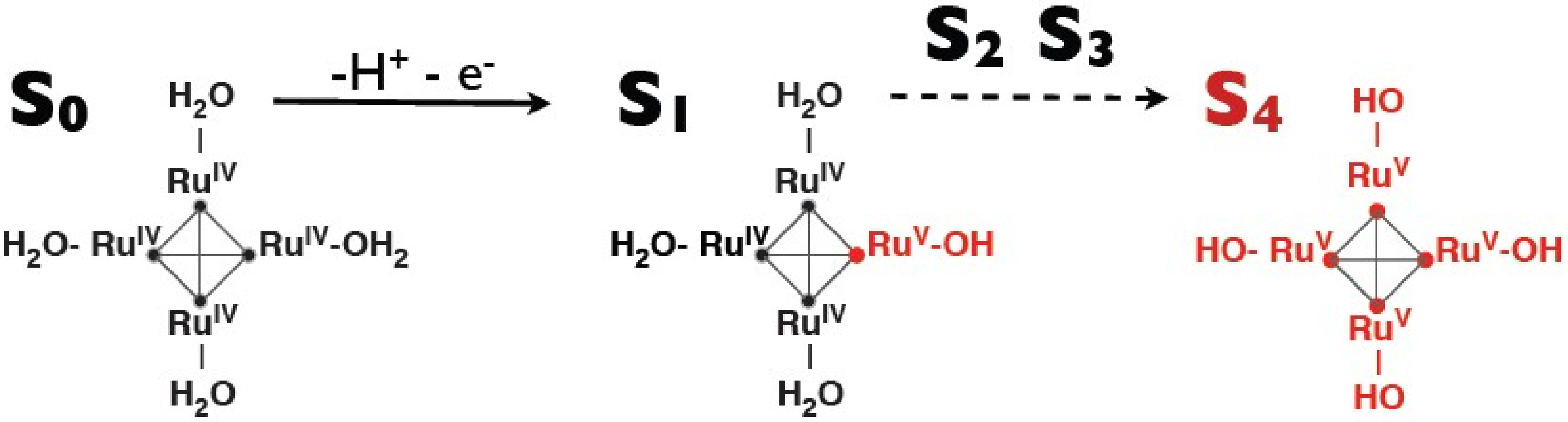
1-e : $H_2O \rightarrow OH^{\bullet} + H^+ + e^-$ ($E^0 = 2.31$ V)

2-e : $2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$ ($E^0 = 1.78$ V)

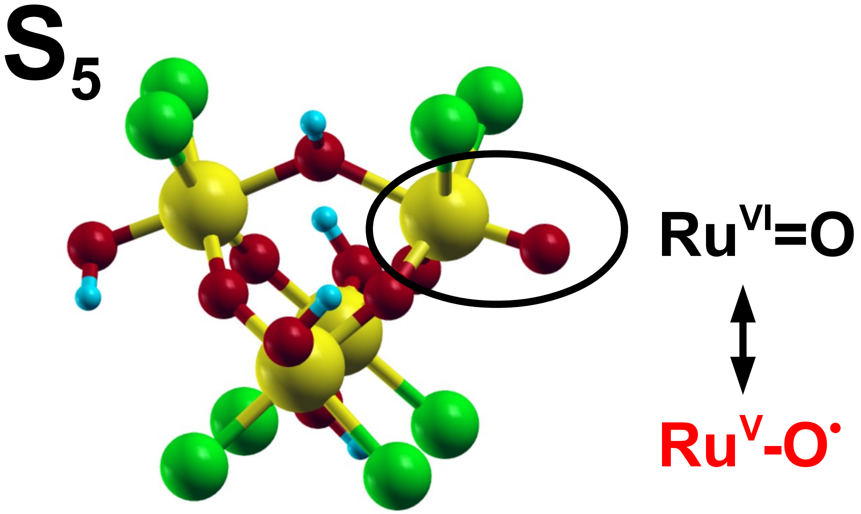
4-e : $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ ($E^0 = 1.23$ V)

Figure from: JP McEvoy and GW Brudvige, Chemical Reviews **106**, 4455 (2006)

Energetics of the catalytic cycle

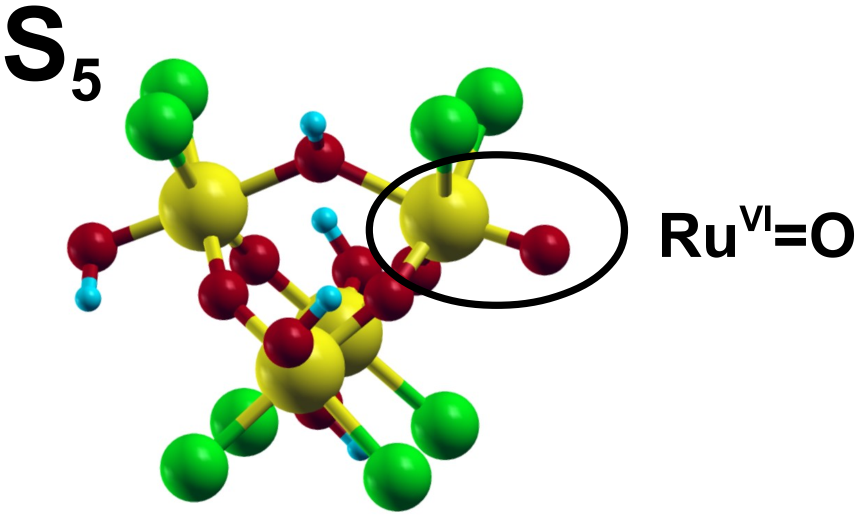


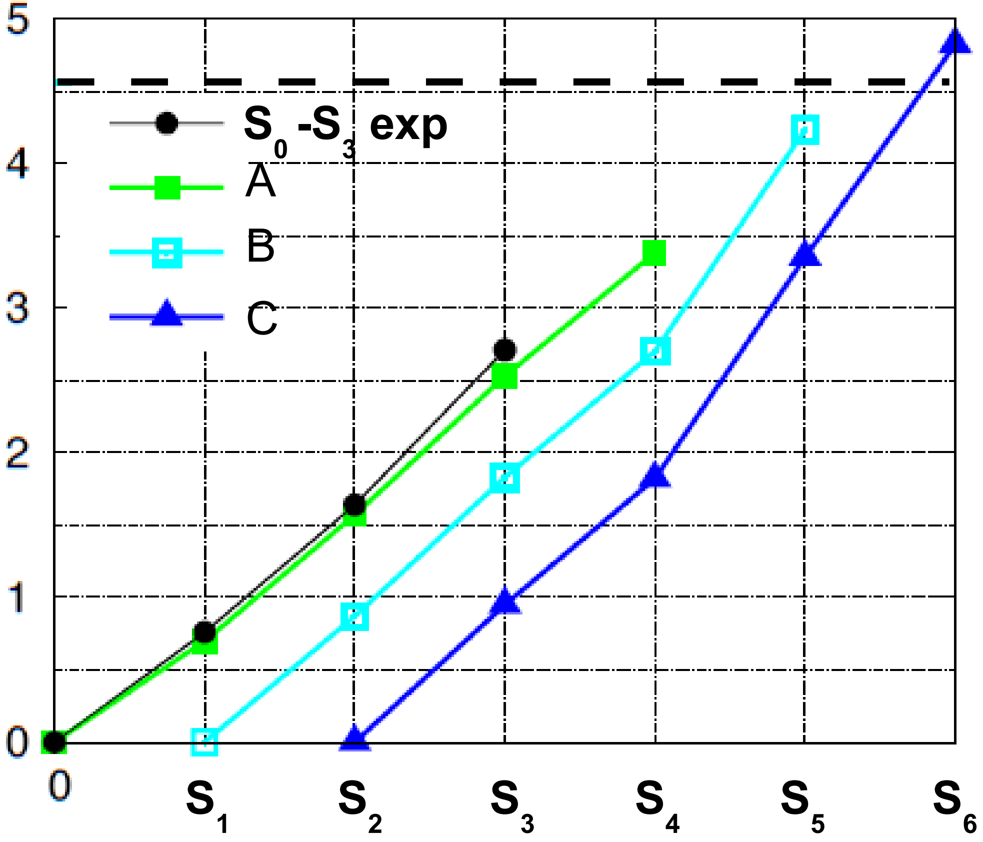
$\Delta G(S0 \rightarrow S4)$ is not sufficient to oxidize water: Higher oxidation states?



Energetics of the catalytic cycle

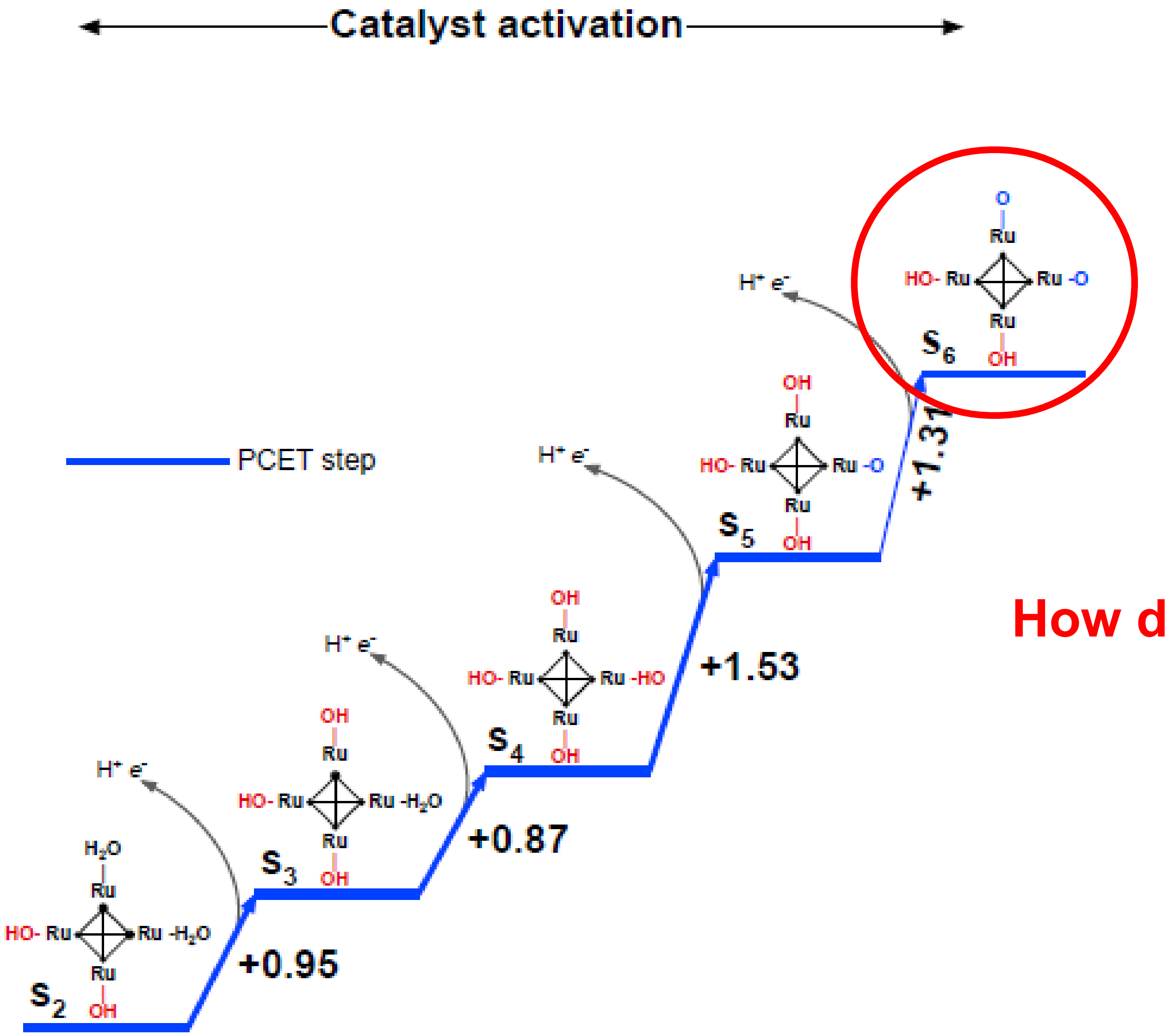
ΔG(S0 → S4) is not sufficient to oxidize water: Higher oxidation states?





- ΔG(S2 → S6) is sufficient to oxidize water.
- In this scheme the O-O bond making step takes place after the catalyst has been oxidized 4 times

Energetics of the catalytic cycle

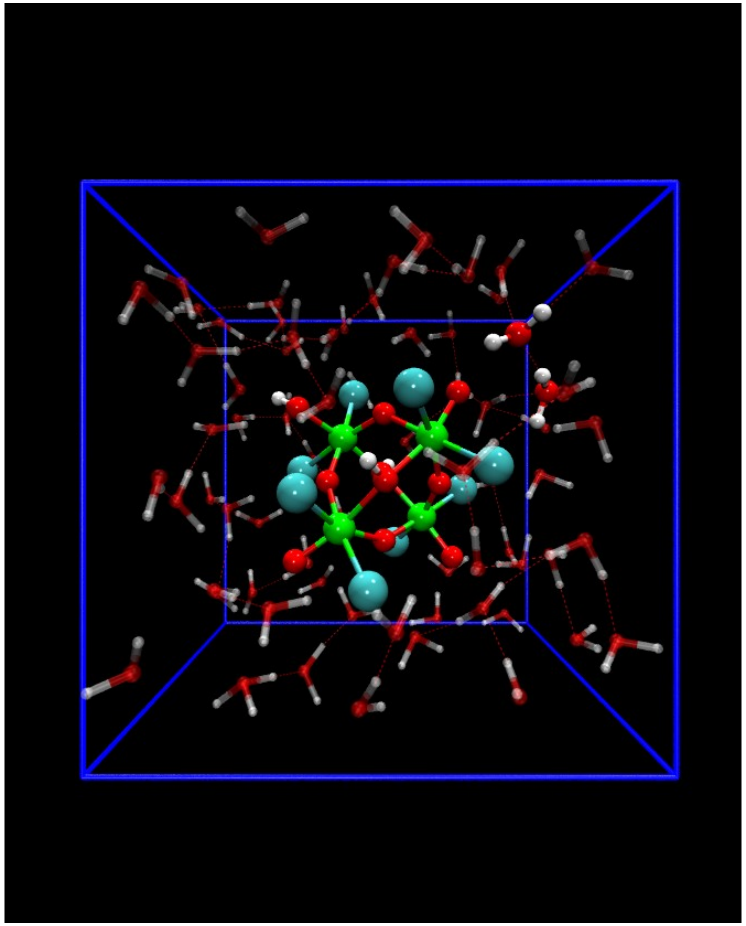


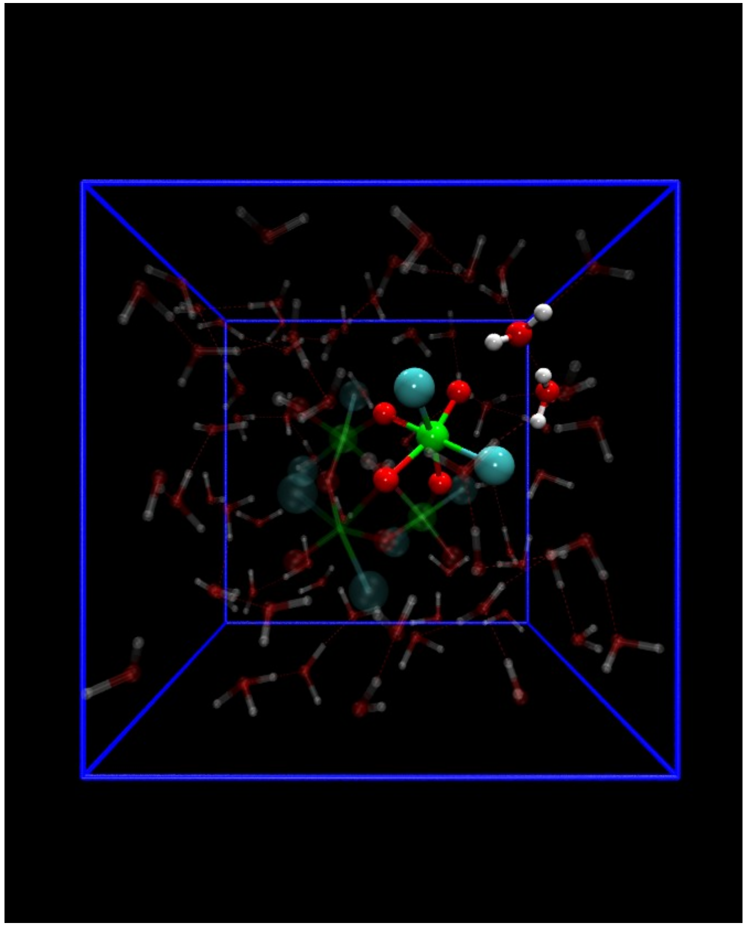
candidate activated intermediate responsible for O-O bond formation

How does the O-O bond form?

DFT simulations of the O-O bond formation

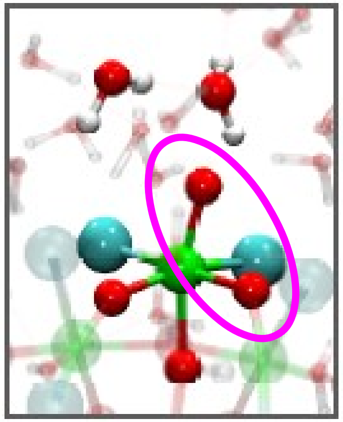
Solvated Ru_4-Cl: PBE simulations





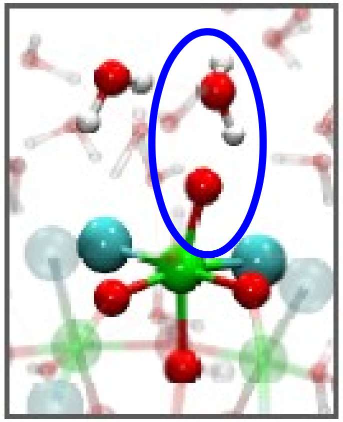
Possible mechanisms of O-O bond formation

Intramolecular paths (direct mechanism)



- oxo ligand - oxo Ru_4O_4 cluster (as in PSII)

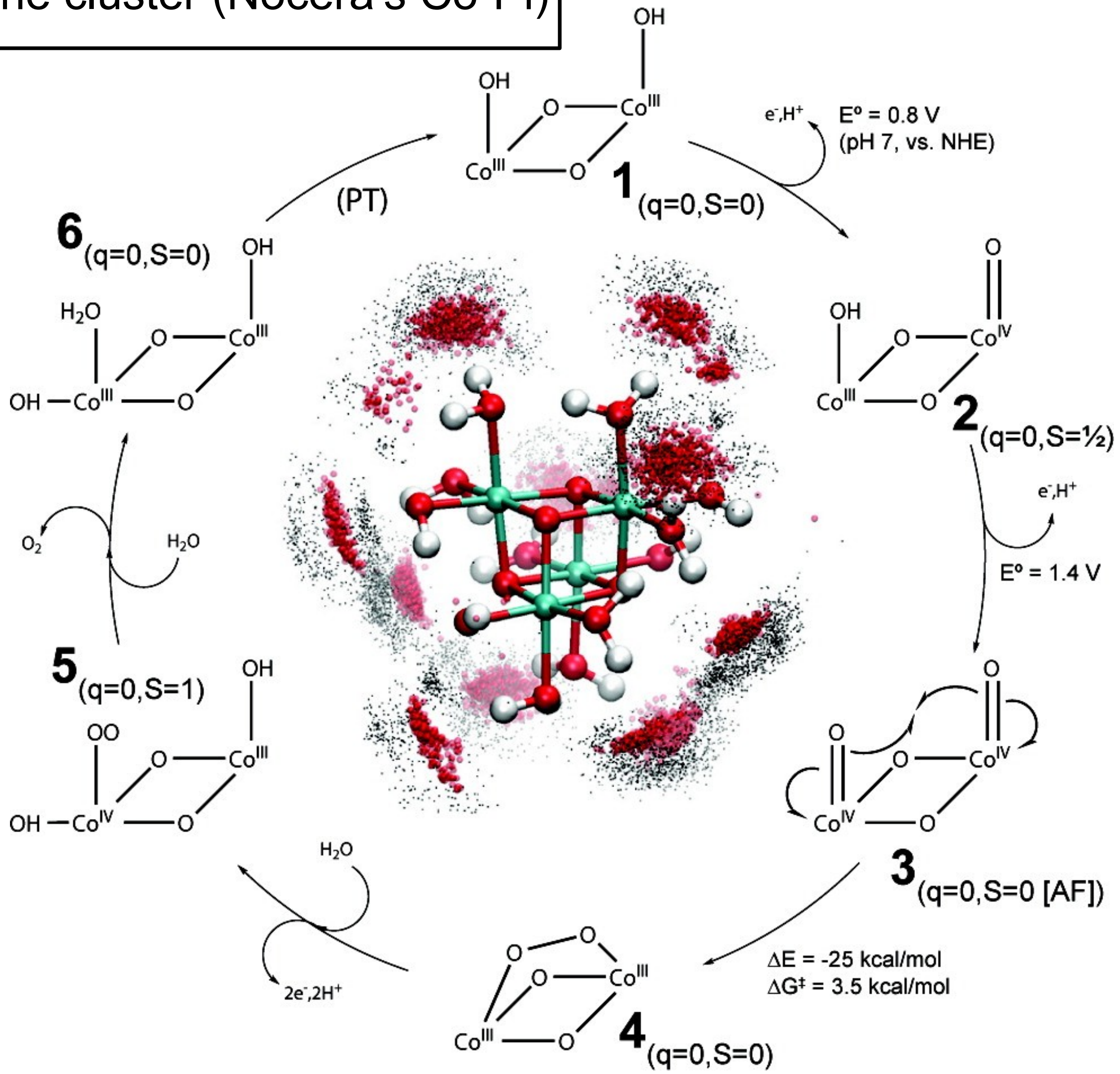
Nucleophilic attack (acid-base mechanism)



- This is the mechanism found in “Blue dimer”

Possible mechanisms of O-O bond formation

Direct O-O formation
Co_4O_4 cubane cluster (Nocera's Co-Pi)



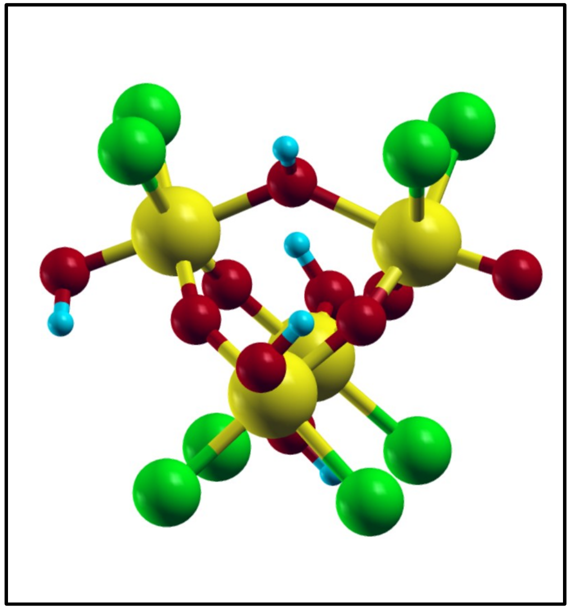
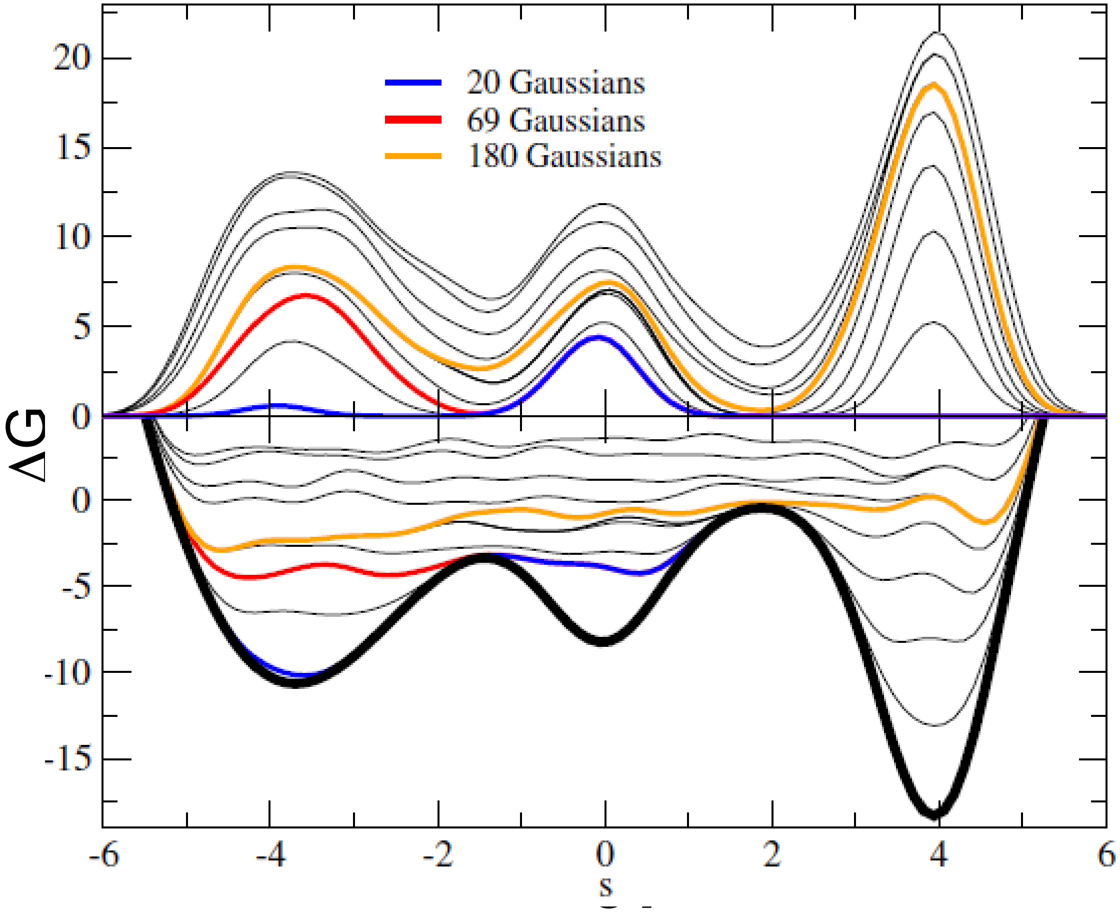


Figure from: LP. Wang and T. van Voohris, J. Phys. Chem. Lett., 2011, **2** (17), pp 2200–2204

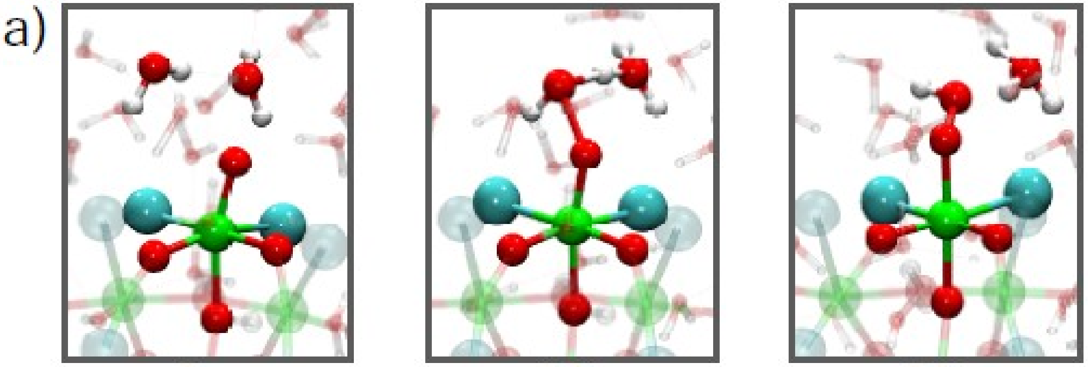
Metadynamics simulations



The method is aimed at reconstructing the multidimensional free energy of complex systems, and is based on an artificial dynamics (metadynamics) performed in the space defined by a few collective variables.

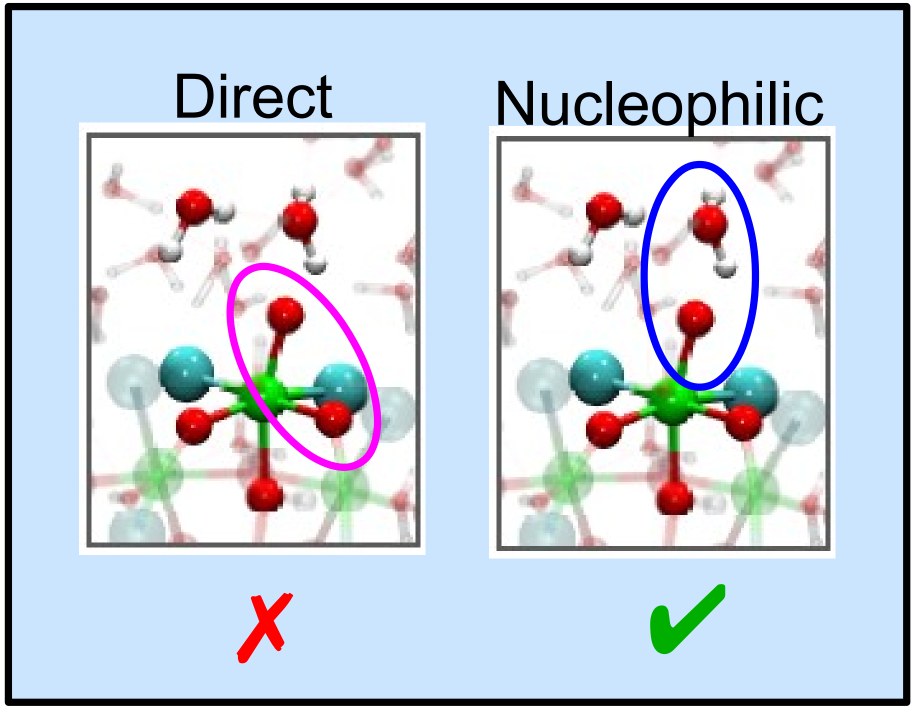
Figure from: Laio and Gervasion Rep. Prog. Phys. **71** (2008) 126601

Metadynamics simulations of the O-O bond formation

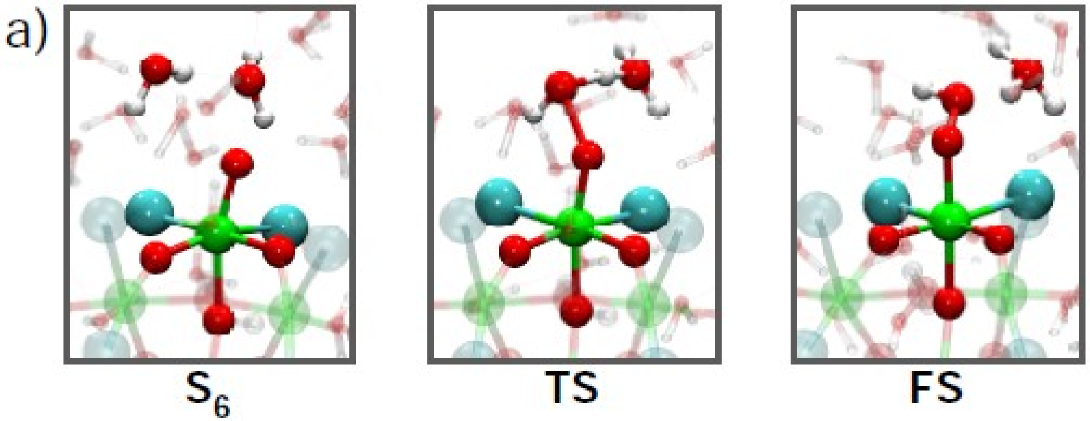


S_6 TS FS

CV1: O-O coordination number → Nucleophilic attack (Acid-base) is favored



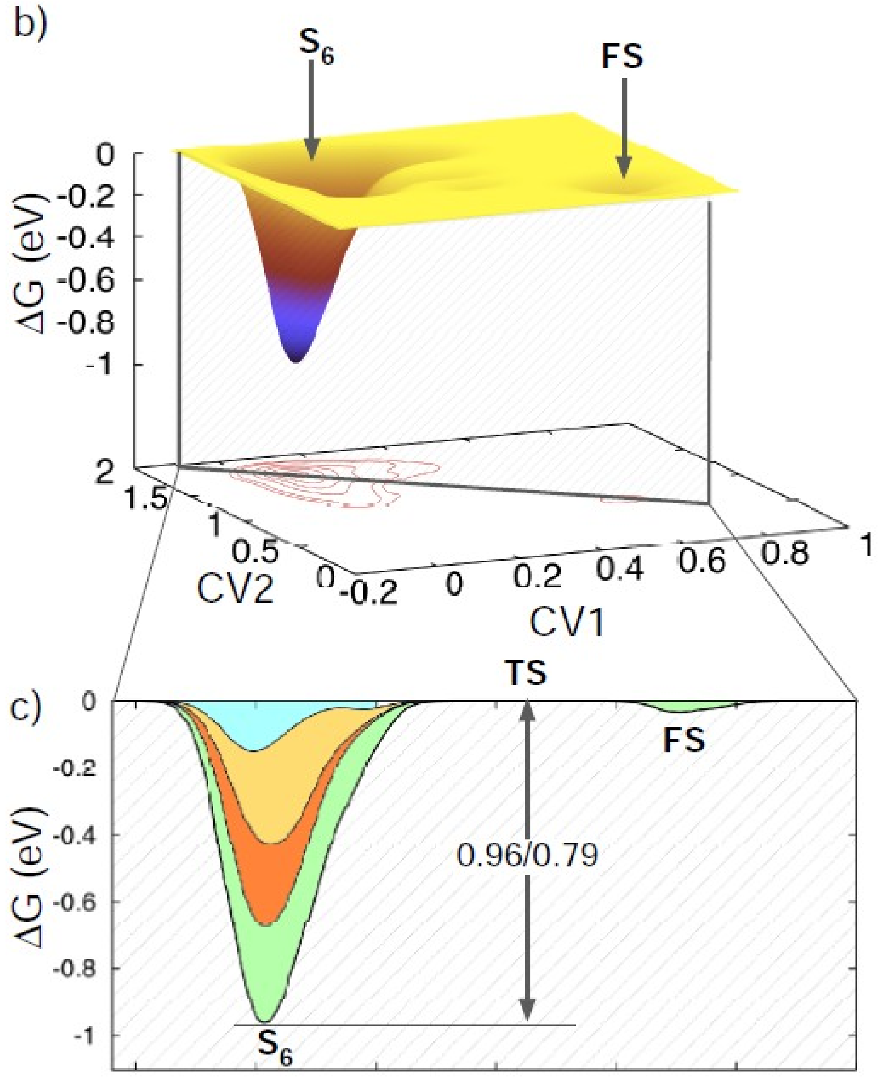
Metadynamics simulations of the O-O bond formation



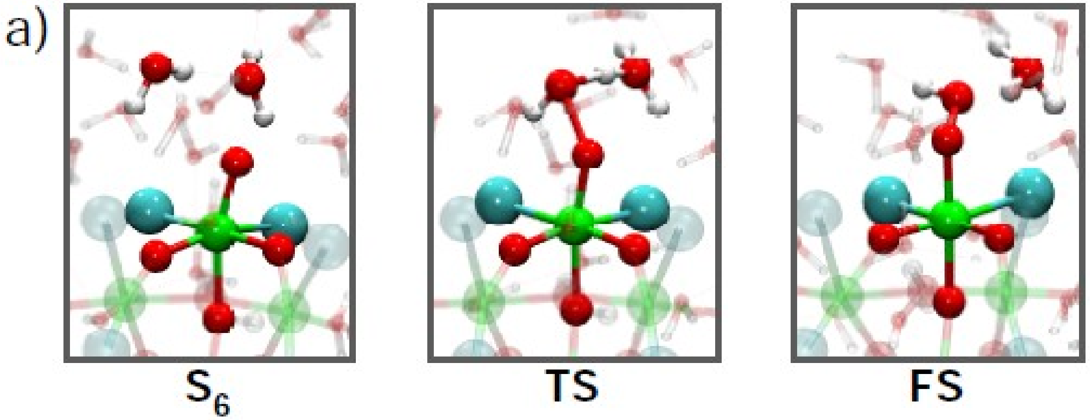
CV1: O-O coordination number

CV2: O-H coordination number

B3LYP correction to PBE activation energy evaluated through single point calculations



Metadynamics simulations of the O-O bond formation

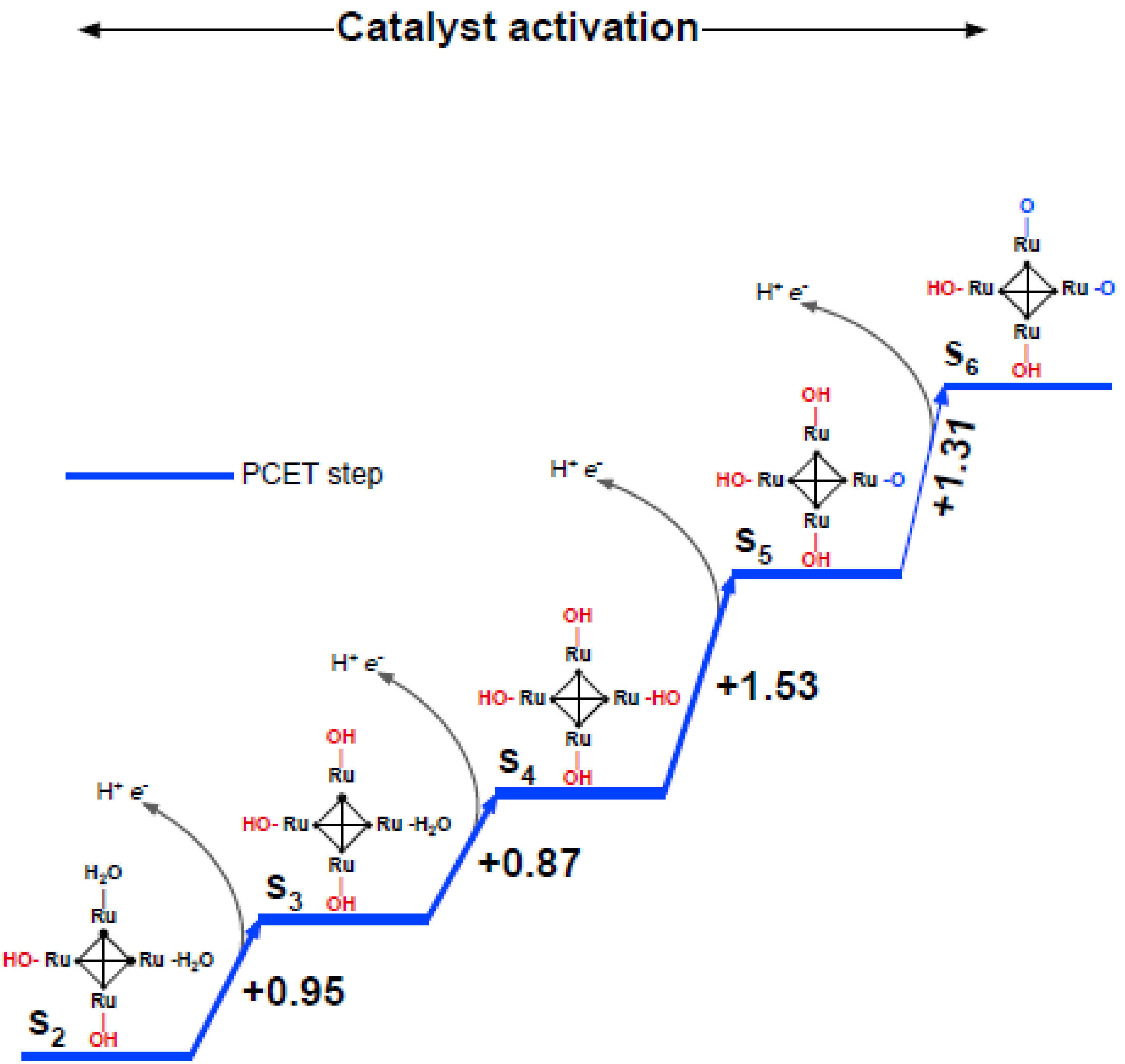


Metadynamics predicts a nucleophilic attack rather than an intramolecular mechanism

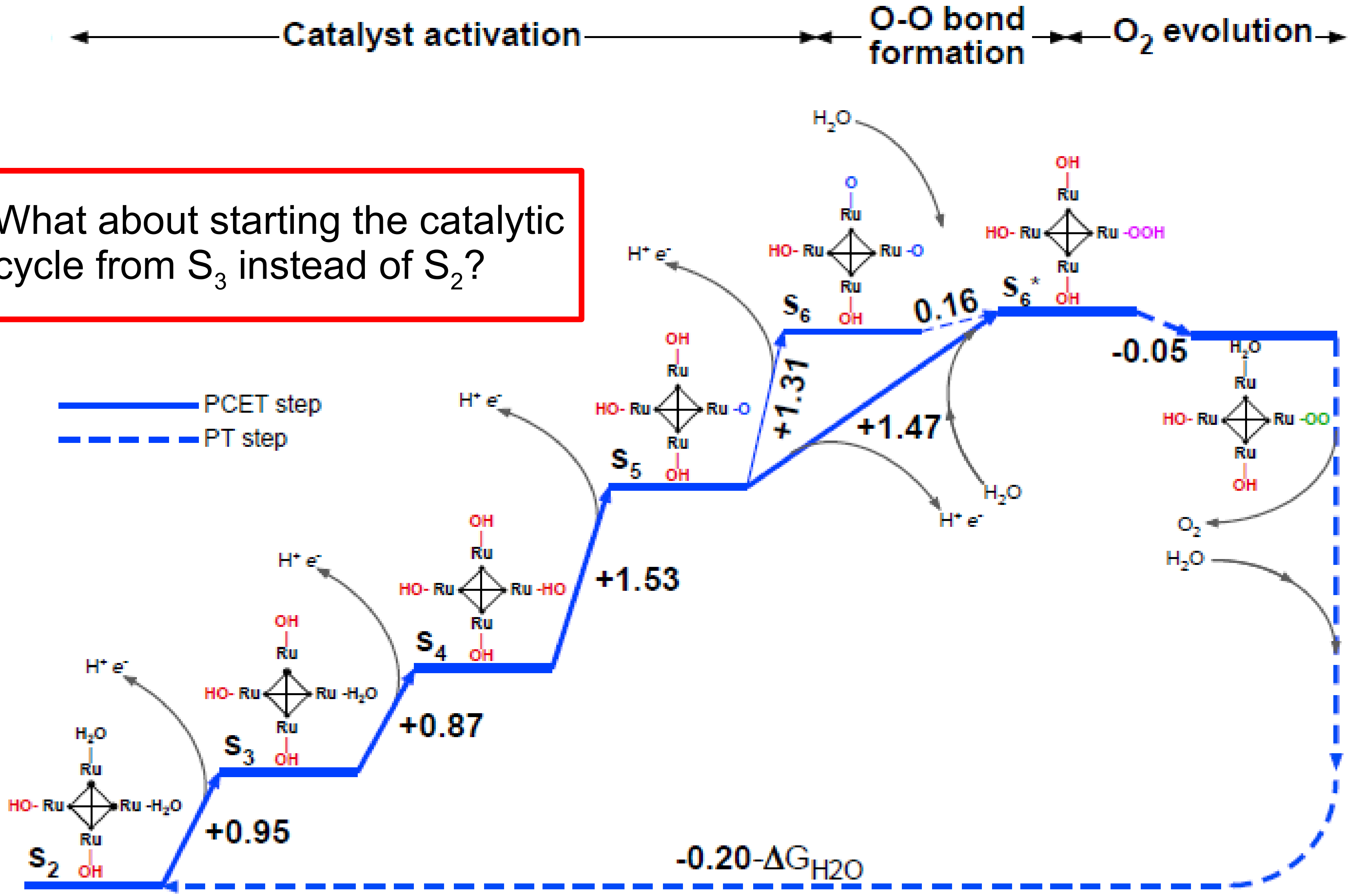
PBE/B3LYP estimate: 0.79 - 0.96 eV
Experimental estimate: 0.83 - 1.01 eV (Blue dimer: 1.12 eV)

The intramolecular mechanism has a prohibitively high activation energy (2.2 eV)

Energetics of the catalytic cycle

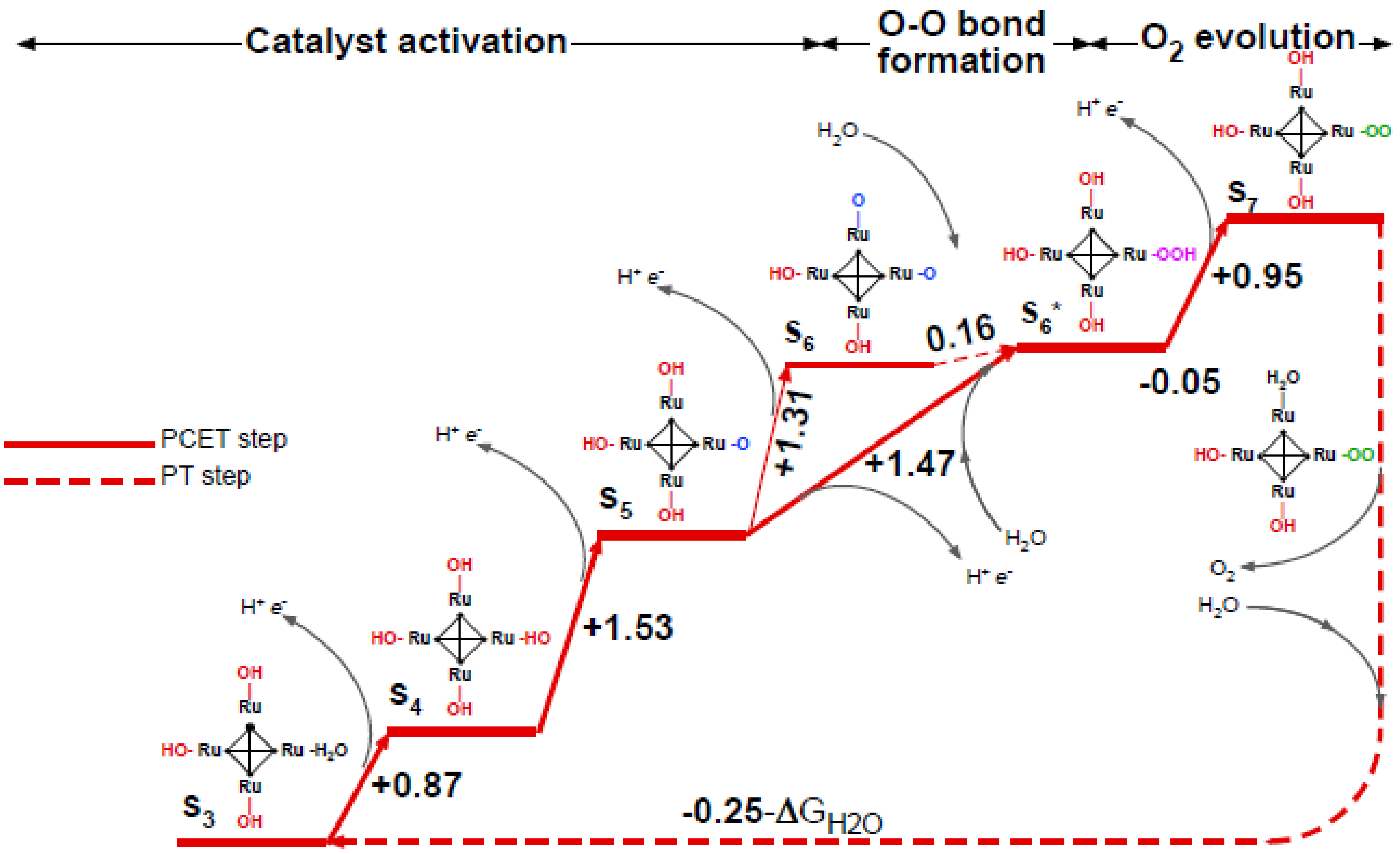


Energetics of the catalytic cycle



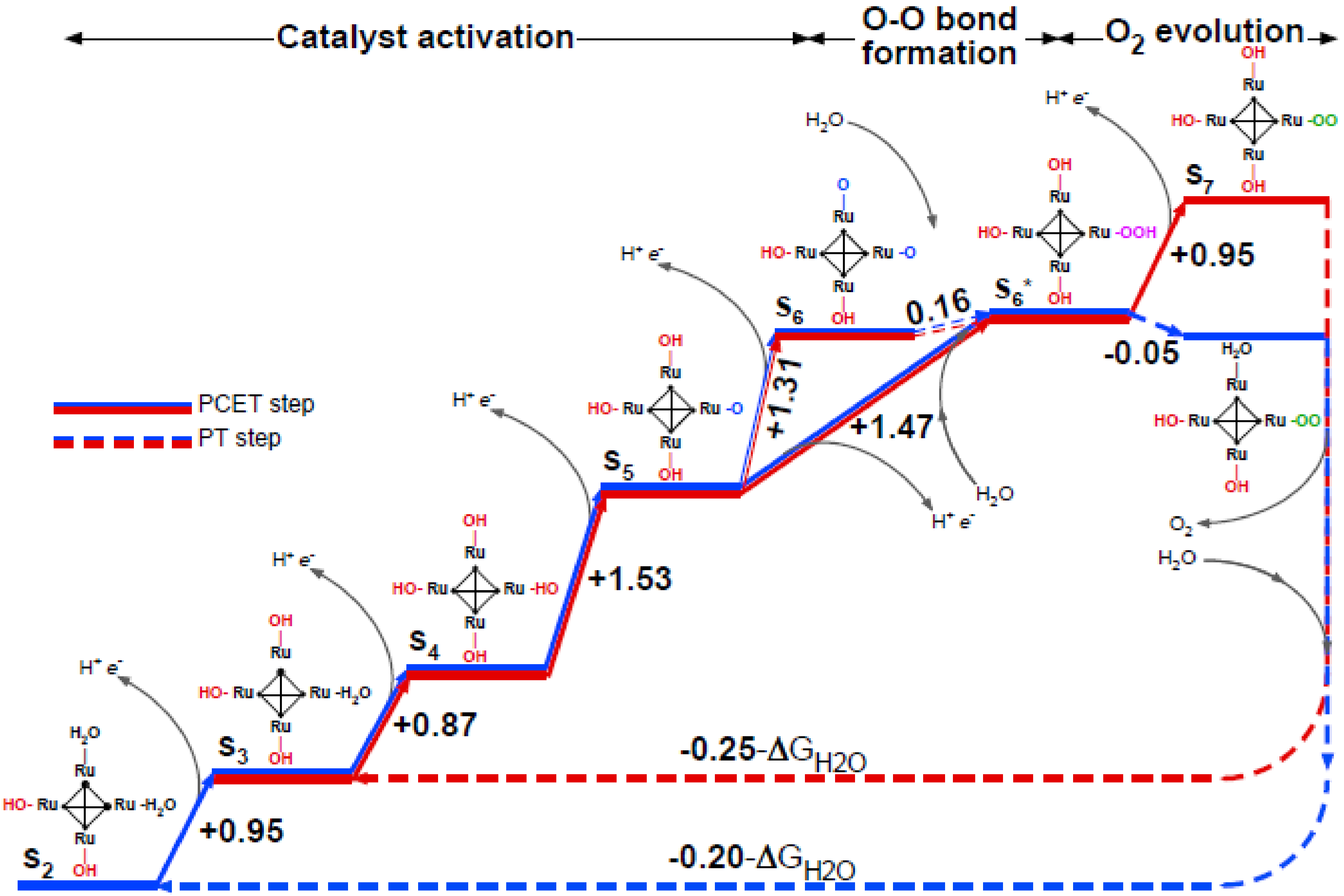
What about starting the catalytic cycle from S_3 instead of S_2?

Energetics of the catalytic cycle



- In this path a <u>single Ru atom</u> is involved in the catalytic process

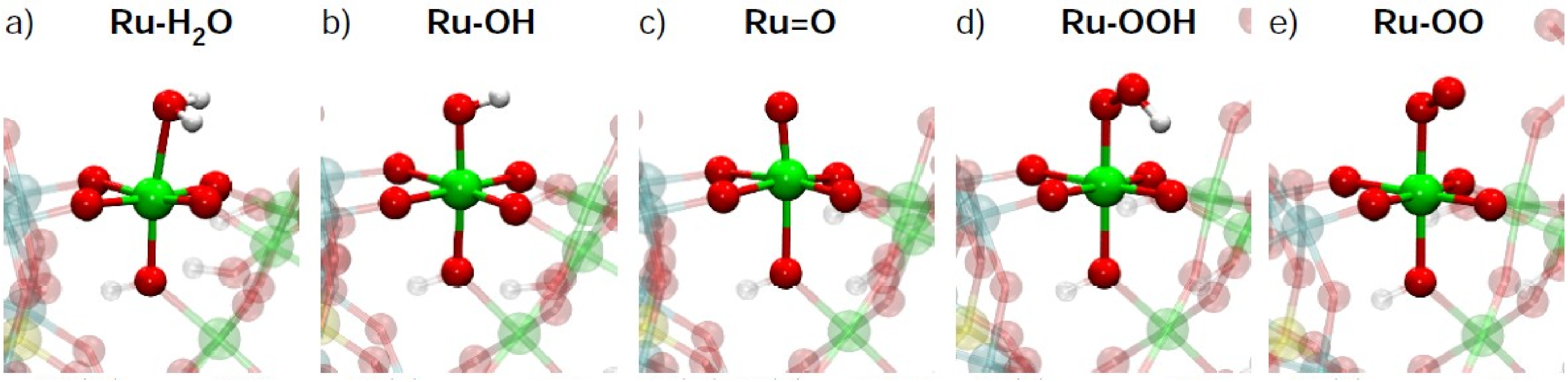
Energetics of the catalytic cycle



- Thermodynamically the two paths are equivalent
- Activation energies of the PCET steps might favor one of the two paths

Intermediates of the catalytic cycle

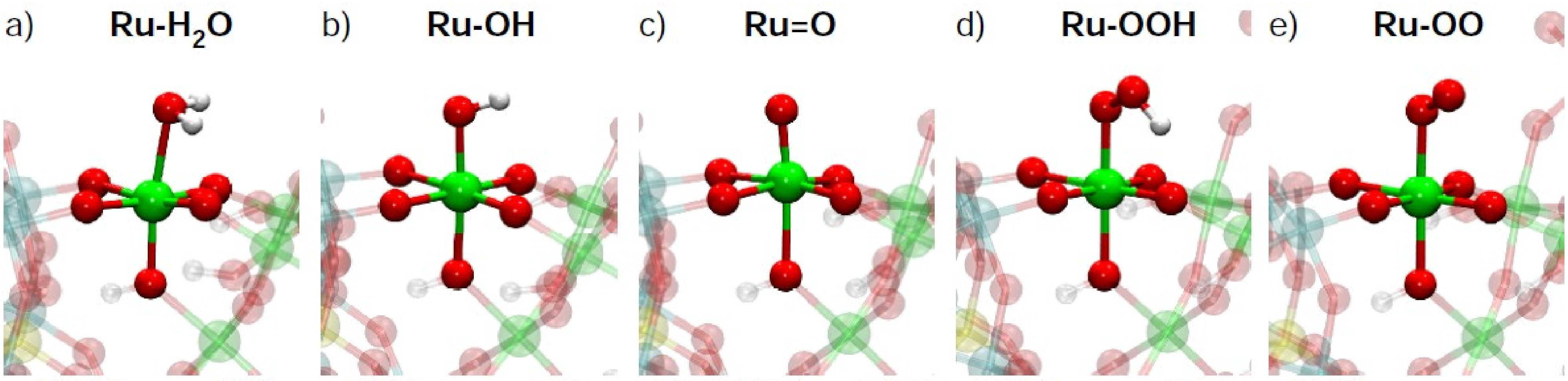
Mechanism on Ru_4-POM



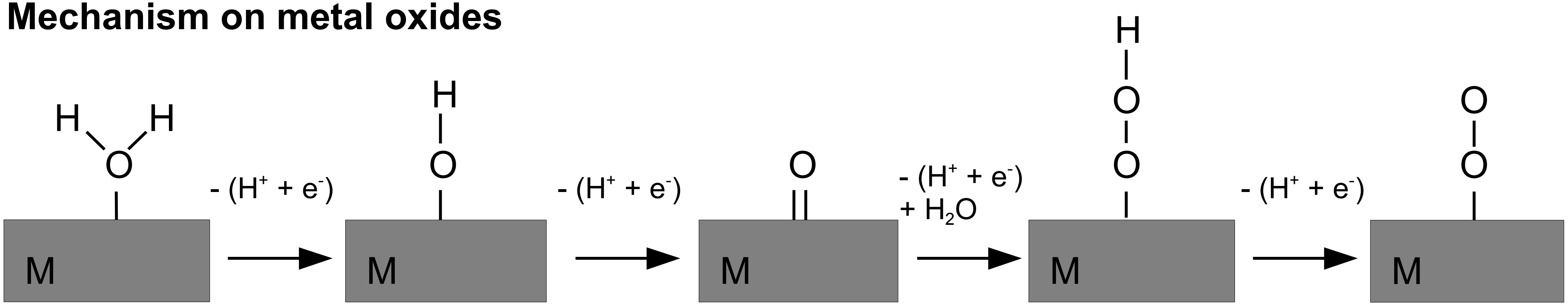
- A reaction mechanism involving **a single Ru ion** (within the Ru_4O_6 core) is possible
- 4 electron reaction, 4 transition metals? Single center (Ru, Ir) catalysts exist.
- Here Ru oxidation state changes between IV and V

Intermediates of the catalytic cycle

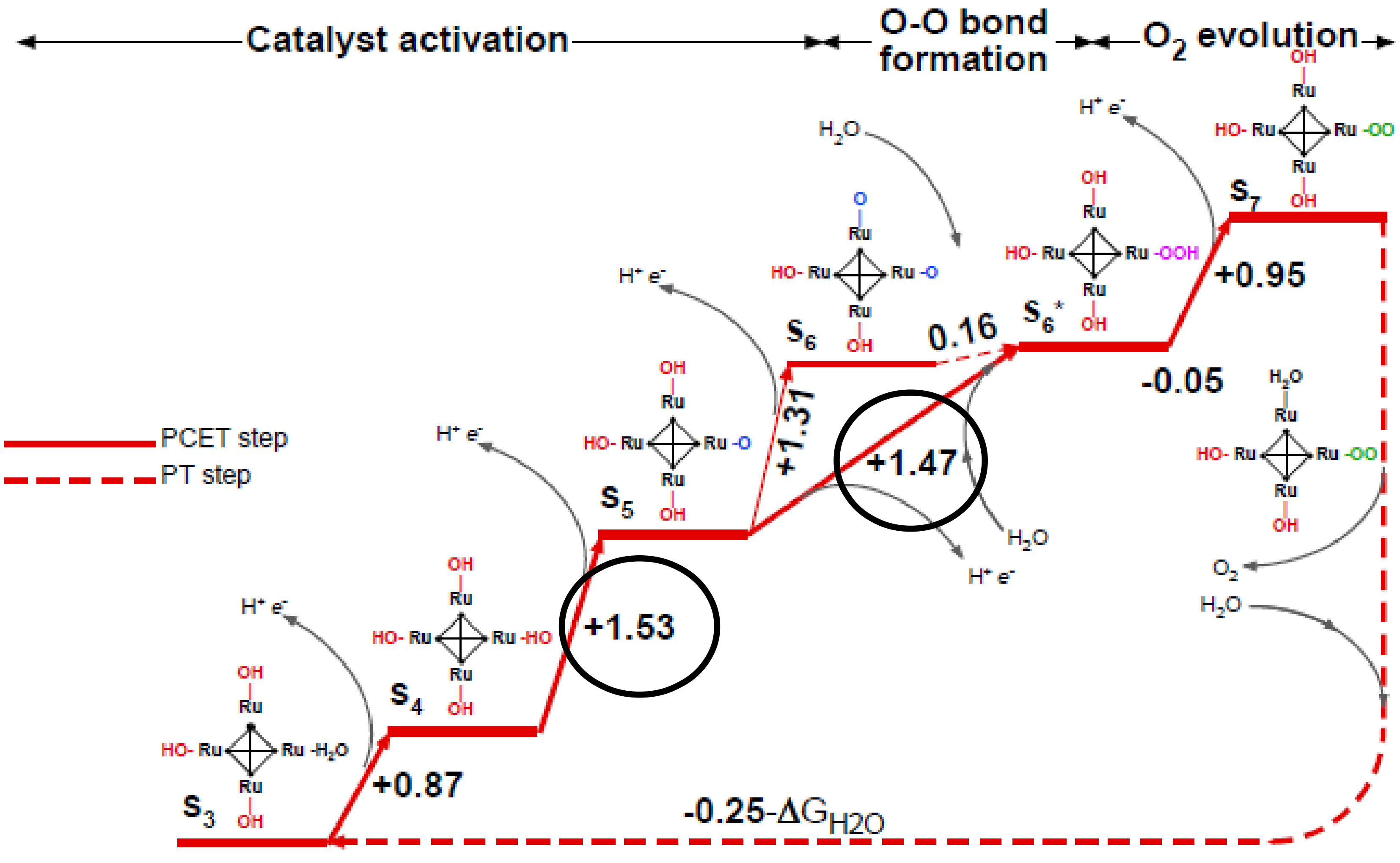
Mechanism on Ru_4-POM



Mechanism on metal oxides



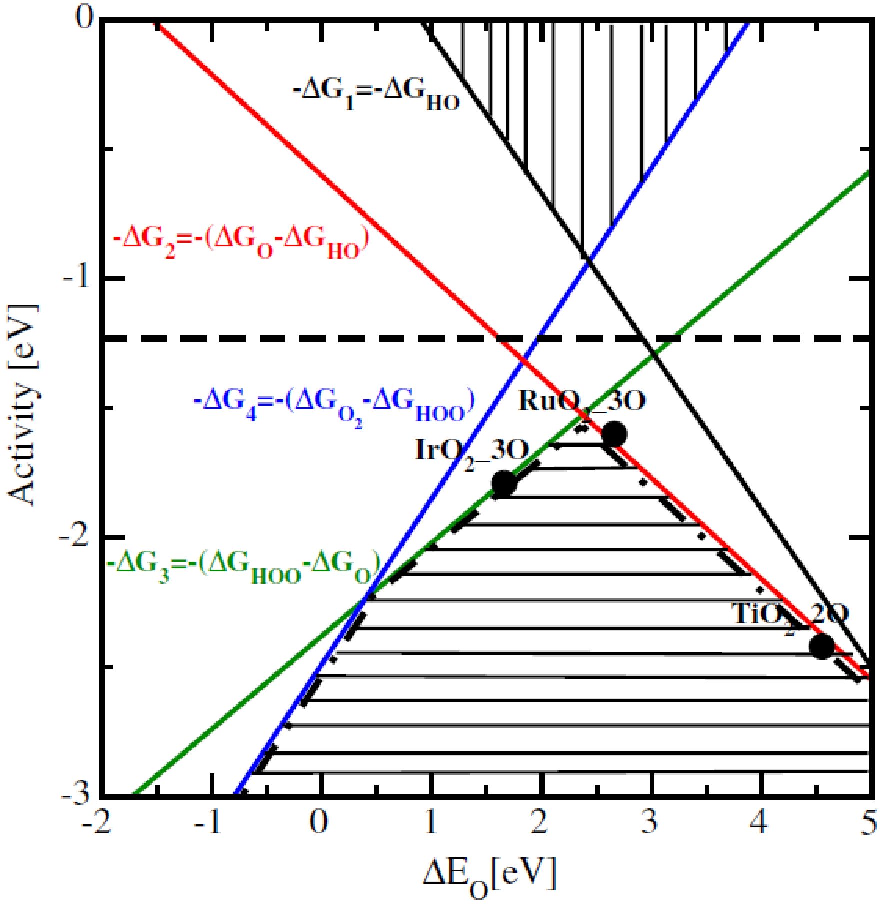
Energetics of the catalytic cycle

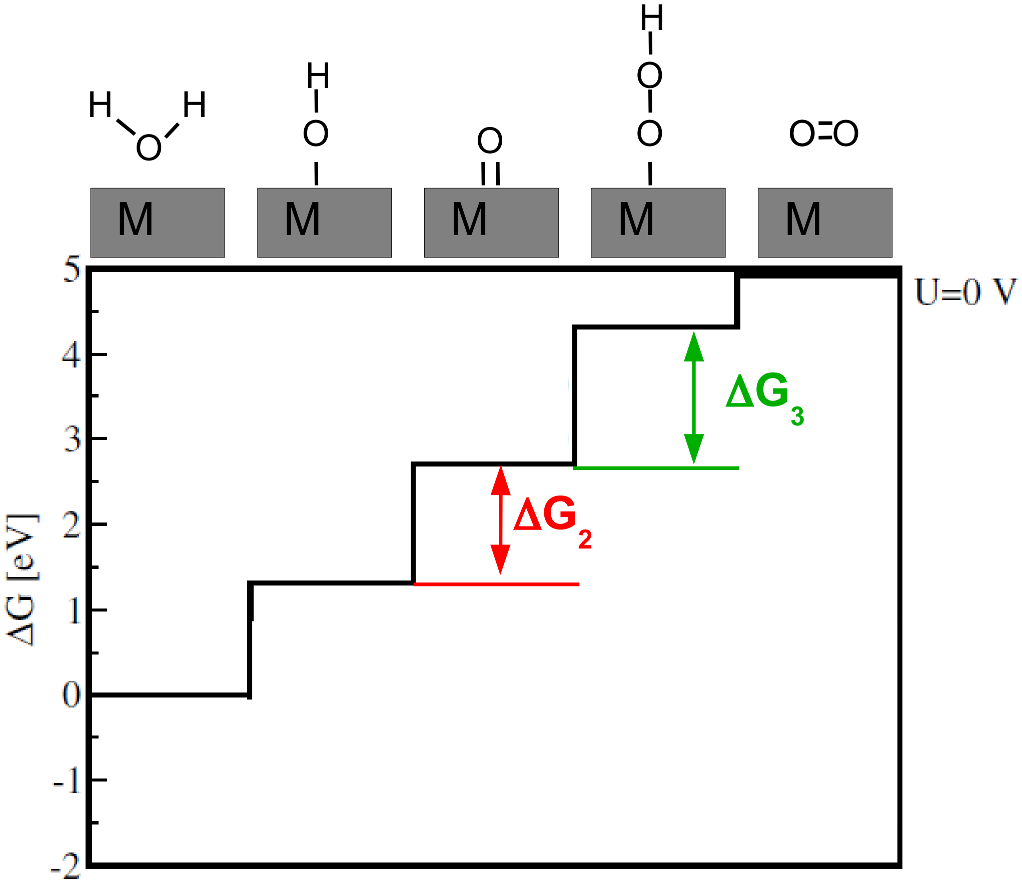


- Overpotential η= 1.53-1.23 = 0.30 eV (exp: 0.35 eV)
- η is determined by the Ru(V)-OH → Ru(VI)=O step

Electrolysis of water on oxide surfaces

Why do we have a finite overpotential?





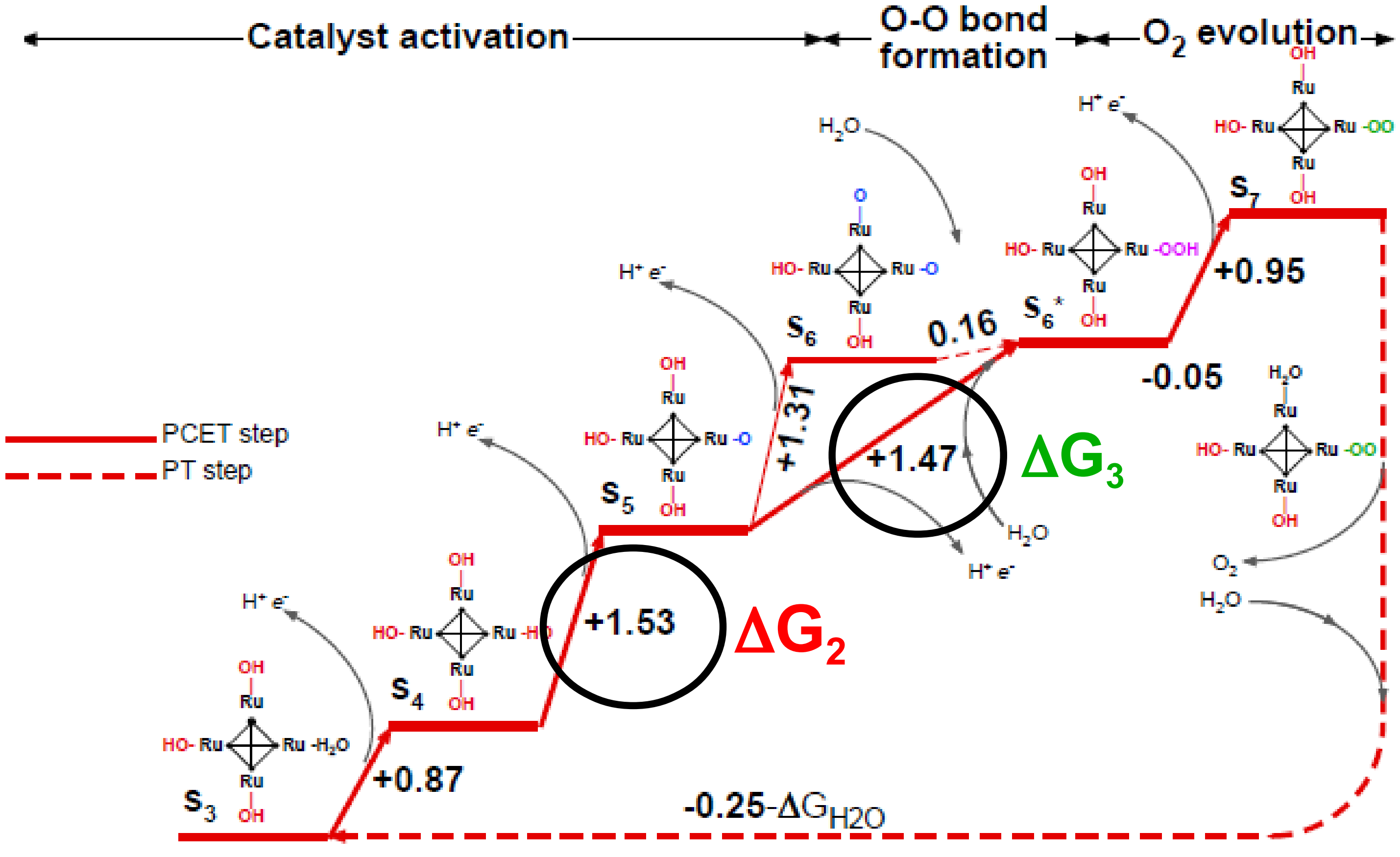
$\Delta G_2 + \Delta G_3 = 3.2$ eV ± 0.2 eV (68%)
± 0.4 eV (95%)

"Ideal" catalyst $\Delta G_2 = \Delta G_3 = 1.6$ eV ($\eta = 0.37 \pm 0.1$ eV)

RuO$_2$ is therefore as good a catalyst for OER as a metal oxide can be

Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

Energetics of the catalytic cycle



Ru_4-POM

$\Delta G_2 + \Delta G_3 = 3.00$ eV

$\eta = 0.30$ eV

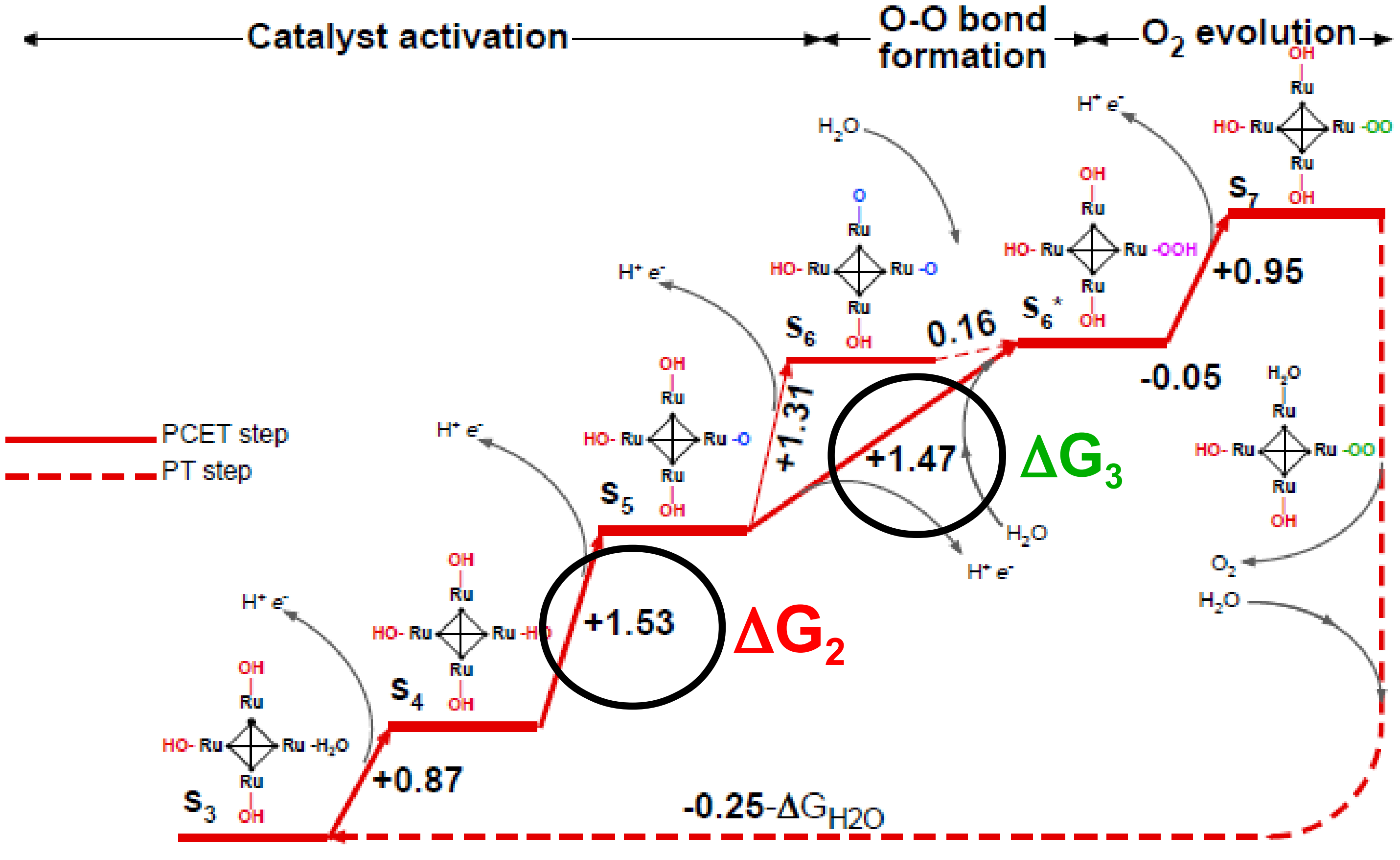
Metal oxides

$\Delta G_2 + \Delta G_3 = 3.2$ eV ± 0.2 eV (68%)

± 0.4 eV (95%)

“Ideal” catalyst $\Delta G_2 = \Delta G_3 = 1.6$ eV ($\eta = 0.37 \pm 0.1$ eV)

Energetics of the catalytic cycle



Ru$_4$-POM

$\Delta G_2 + \Delta G_3 = 3.00$ eV

$\eta = 0.30$ eV

- **Ru$_4$-POM complies with the “universal” constraint on $\Delta G_2 + \Delta G_3$**
- **Ru$_4$-POM is an almost “ideal” catalyst**
- **All atoms in Ru$_4$-POM are active sites**

Summary

- The O-O bond formation takes place through a nucleophilic attack of water molecule on an oxo intermediate

- The overpotential is determined by the formation of the oxo intermediate

- The activation energy of the O-O bond formation is compatible with the observed kinetics

- Paths involving a single Ru center are also possible, suggesting that the efficiency of this catalyst is not linked to cooperative effects of the four Ru centers, but to the favorable spread of the thermodynamic cost among the key intermediates

- The thermodynamics of the reaction cycle promoted by Ru_4-POM can be understood on the basis of the energetics of metal oxides

- Ru_4-POM is an “optimal RuO_2 cluster” where every single atom is a surface atom and hence an active site.

Summary

THANKS TO:

- Stefano Fabris
- Andrea Sartorel and Marcella Bonchio
- EU-FP7 Marie Curie, DEISA, CINECA

(1) S. Piccinin and S. Fabris, *Phys. Chem. Chem. Phys.* **13**, 7666-7674 (2011)
(2) S. Piccinin. A. Sartorel, M. Bonchio and S. Fabris, *submitted*