

# First principles study of water oxidation catalyzed by a tetraruthenium-oxo core embedded in polyoxometalate ligands (Supplementary Information)

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## I. INFLUENCE OF BASIS SET ON THE STRUCTURAL AND ELECTRONIC PROPERTIES

To test the influence of the choice of the basis set on the properties of interests we use a simplified model of the Ru<sub>4</sub>-POM molecule, where each of the two  $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$  units is replaced with four Cl<sup>-</sup> ions, as to maintain the octahedral coordination of the Ru atoms. This simplified model (Ru<sub>4</sub>-Cl) has already been used in Ref. ? to compute the Raman spectra of the various intermediates. Here we consider the initial state **S**<sub>0</sub>, where each Ru atom is in oxidation state IV and is bonded to one water molecule. We monitor the most relevant distances, namely all the Ru-Ru distances as well as the distances between Ru and water. We also test the convergence of the Mulliken charges on the Ru atoms and the the atomic spin densities of the Ru atoms. Our reference is the aug-TZV2P-MOLOPT calculation, and in Table I we report the mean unsigned error (MUE) and the maximum absolute error (MAE) of all the quantities monitored. While the distances do not depend strongly on the choice of the basis set, the Mulliken charges and the atomic spin densities are more sensitive. While the latter quantity converges as the quality of the basis set increases, the Mulliken charge does not. However, rather than in the absolute value of the Mulliken atomic charges, we are interested in the difference between the Ru Mulliken charge upon oxidation, i.e. when Ru<sup>IV</sup> is oxidized to Ru<sup>V</sup>. To this end, we monitor the difference between the Ru Mulliken charges for **S**<sub>0</sub>, where all four Ru are in oxidation state IV, and **S**<sub>4</sub>, where all Ru atoms are in oxidation state V. This difference is shown in the last column of Table I. We can see that this quantity does not depend strongly on the basis set used and the errors are always small.

We also tested the influence of the basis set used to describe Cl. The last row of Table I shows the comparison between the previously defined aug-TZV2P-MOLOPT calculation, where Cl was described with the DVZP basis set, and one which also Cl is described using the aug-TZV2P-MOLOPT basis set. The main difference is a  $\sim 0.014$  Å shorter distance of the Ru-Cl bond using the larger basis set, while the Mulliken charges and the atomic spin densities are scarcely influenced. In our calculations we therefore used the aug-TZV2P basis set for O and H and the DVZP basis set for Cl, which ensures sufficiently converged results for distances, spin densities and Mulliken charge differences.

Basis	distance (Å)		charge (e)		spin (e)		charge difference (e)	
	MUE	MAE	MUE	MAE	MUE	MAE	MUE	MAE
DZVP	$1.3 \times 10^{-2}$	$3.1 \times 10^{-2}$	$6.2 \times 10^{-2}$	$6.8 \times 10^{-2}$	$4.2 \times 10^{-1}$	$6.0 \times 10^{-1}$	$3.6 \times 10^{-2}$	$4.9 \times 10^{-2}$
TZVP	$9.8 \times 10^{-3}$	$1.3 \times 10^{-2}$	$8.1 \times 10^{-2}$	$8.2 \times 10^{-2}$	$1.7 \times 10^{-2}$	$2.7 \times 10^{-2}$	$1.5 \times 10^{-3}$	$4.6 \times 10^{-3}$
TZV2P	$5.8 \times 10^{-3}$	$9.4 \times 10^{-3}$	$1.3 \times 10^{-2}$	$1.6 \times 10^{-2}$	$1.2 \times 10^{-2}$	$2.2 \times 10^{-2}$	$6.8 \times 10^{-3}$	$1.0 \times 10^{-2}$
aug-TZV2P	$5.6 \times 10^{-3}$	$7.1 \times 10^{-3}$	$1.1 \times 10^{-1}$	$1.2 \times 10^{-1}$	$2.5 \times 10^{-3}$	$4.1 \times 10^{-3}$	$9.4 \times 10^{-3}$	$1.9 \times 10^{-2}$
aug-QZV2P	$4.3 \times 10^{-3}$	$5.7 \times 10^{-3}$	$1.5 \times 10^{-1}$	$1.6 \times 10^{-1}$	$3.9 \times 10^{-3}$	$5.9 \times 10^{-3}$	$1.6 \times 10^{-2}$	$2.3 \times 10^{-2}$
aug-TZV2P-MOLOPT	0	0	0	0	0	0	0	0
aug-TZV2P-MOLOPT(Cl)	$1.4 \times 10^{-2}$	$1.7 \times 10^{-2}$	$1.2 \times 10^{-2}$	$1.2 \times 10^{-2}$	$1.2 \times 10^{-3}$	$2.7 \times 10^{-3}$	$2.3 \times 10^{-2}$	$2.8 \times 10^{-2}$

TABLE I: Convergence of the Ru-Ru, Ru-H<sub>2</sub>O and Ru-Cl distances, Ru Mulliken charges and Ru atomic spin densities of the **S**<sub>0</sub> state of Ru<sub>4</sub>-Cl as a function of the basis set used for O and H. The functional used in this test is PBE, the basis set for Ru and Cl are DVZP-MOLOPT and DVZP, respectively. The last two columns report the difference in the Ru Mulliken charges between the **S**<sub>0</sub> and **S**<sub>4</sub> states of Ru<sub>4</sub>-Cl. The last row shows the comparison between the aug-TZV2P-MOLOPT calculation, where Cl is described with the DVZP basis set, and one which also Cl is described using the aug-TZV2P-MOLOPT basis set. MUE is the mean unsigned error, while MAE is the maximum absolute error.

Basis	$\Delta E$ (eV)	$d(\text{Ru-O}_{\text{H}_2\text{O}})$ (Å)
DZVP	0.253	2.51
DZVP-MOLOPT	0.200	2.53
TZV2P	0.176	2.50
aug-TZV2P	0.153	2.47
aug-TZV2P-MOLOPT	0.167	2.50
aug-QZV2P	0.163	2.46

TABLE II: Convergence of  $\Delta E = -(E(\text{Ru-H}_2\text{O})-E(\text{Ru-OH})-1/2E(\text{H}_2))$  (in eV) as function of the basis set of O and H. For Ru we use the DZVP-MOLOPT basis set. The exchange and correlation functional used is PBE.

## II. INFLUENCE OF BASIS SET AND XC FUNCTIONAL ON THE ENERGETICS

To test the influence of the choice of the basis set and XC functional on the energetics of our systems, we investigate the bonds between a single Ru atom and  $\text{H}_2\text{O}$  or OH. To this end we model the isolated Ru- $\text{H}_2\text{O}$  and Ru-OH molecules using six different basis sets and three XC functionals, the GGA-PBE and two hybrids, namely the B3LYP and the HSE06 functionals. The main quantity we monitor is a total energy difference  $\Delta E$  defined as  $\Delta E = -(E(\text{Ru-H}_2\text{O})-E(\text{Ru-OH})-1/2E(\text{H}_2))$ . This can be viewed as the binding energy of a H atom in a Ru-bonded  $\text{H}_2\text{O}$ , referenced to the half the  $\text{H}_2$  molecule as opposed to the isolated H atom. Since removing a H atom is equivalent to performing a PCET reaction, where a proton and an electron are removed from the system,  $\Delta E$  is the relevant quantity to be monitored to test the dependence of the energetics of the catalytic cycle on the choices of basis set and XC functional.

In Table II we show the results, obtained using the PBE functional for the exchange and correlation, employing six different types of Gaussian basis sets for the O and H atoms. From Table II we can see that the TZV2P basis set yields results converged within 0.02 eV. Since, however, in our study we will deal with anions, which require the use of diffuse functions, we will employ the aug-TZV2P basis set, which leads to results for  $\Delta E$  converged within 0.01 eV.

	PBE	B3LYP	HSE06
$\Delta E$	0.15	0.33	0.54
		Ru- $\text{H}_2\text{O}$	
$E_b(\text{H}_2\text{O})$	0.13	-0.02	0.06
$d(\text{Ru-O})$	2.47	2.41	2.48
$Q(\text{Ru})$	-0.04	-0.06	-0.06
		Ru-OH	
$E_b(\text{OH})$	3.02	2.41	2.36
$d(\text{Ru-O})$	1.89	1.91	1.90
$Q(\text{Ru})$	0.26	0.35	0.35

TABLE III: Interaction of OH and  $\text{H}_2\text{O}$  with a Ru atom as a function of the XC functional.  $\Delta E$  is defined as  $-(E(\text{Ru-H}_2\text{O})-E(\text{Ru-OH})-1/2E(\text{H}_2))$ .  $E_b(\text{H}_2\text{O})$  is defined as  $-(E(\text{Ru-H}_2\text{O})-E(\text{Ru})-E(\text{H}_2\text{O}))$  and  $E_b(\text{OH}) = -(E(\text{Ru-OH})-E(\text{Ru})-E(\text{OH}))$ .  $Q(\text{Ru})$  is the Mulliken charge on the Ru atom and  $d(\text{Ru-O})$  is the distance, in Å, between Ru and O. The basis set for O and H is aug-TZV2P, while for Ru we use the DZVP-MOLOPT basis set. All energies are in eV.

In Table III we explore the effect of the XC functional on the quantity  $\Delta E$  defined above. We can see that the effect is very large, and that hybrid functionals tend to bind the H atom in Ru- $\text{H}_2\text{O}$  considerably more strongly compared to the PBE functionals. To rationalize this result we have computed, separately, the binding energy of OH and  $\text{H}_2\text{O}$  to the Ru atom in Ru-OH and Ru- $\text{H}_2\text{O}$ . These are shown in Table III. While the Ru- $\text{H}_2\text{O}$  bond is only weakly affected by the change of functional, the description of the Ru-OH bond experiences a large dependence on it, which almost completely accounts for the variation seen in  $\Delta E$ . While the Ru- $\text{H}_2\text{O}$  bond is a weak metal-ligand bond that does not involve a significant charge transfer (see  $Q(\text{Ru})$  in the middle panel of Table III), the Ru-OH bond is a strong bond that involves a partial charge transfer of electrons from Ru to OH (see  $Q(\text{Ru})$  at the bottom of Table III). Using the Mulliken population analysis, we quantify this charge transfer to be 0.26  $e$  in PBE, 0.35 in B3LYP and 0.35 in HSE06. In spite of the smaller charge transfer in PBE, this functional yields a stronger bond compared to the hybrid functionals. We find that the Ru-O distances (1.89 Å in PBE, 1.91 Å in B3LYP and 1.90 Å in HSE06 in the case of Ru-OH) are only marginally affected by the change of functional.

This study, therefore, suggests that we can expect significant variations of the predicted energetics upon the change in XC functionals. In particular, hybrid functionals lead to an increase in the binding energy of the H atom in Ru- $\text{H}_2\text{O}$

compared to the PBE functional. This, at least partially, explains the reason why hybrid functionals lead to larger total energies and free energy differences for PCET reactions compared to the GGA functionals, as we saw in the main text.

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