Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information.

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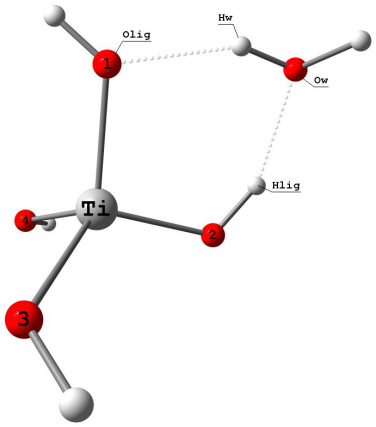
1 Water splitting by $Ti(OH)_4$ in the ground state

To investigate if the reaction $Ti(OH)_4 + H_2O \xrightarrow{h\nu} Ti(OH)_3HOH\cdots OH^{\bullet}$ can proceed in the ground state, we begin by studying the ground state energy profiles.

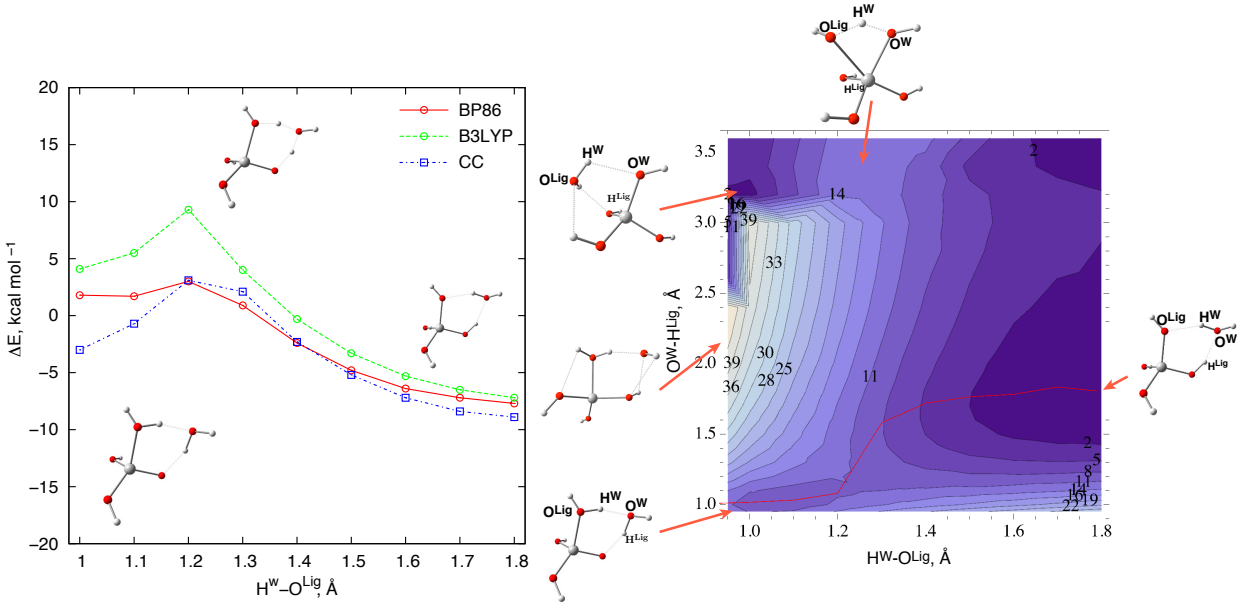
The energy profiles along the H^W-O^{lig} distance (see labels in Fig. S1) are shown in Fig. S2. The ground state PESs feature moderate activation energies of 11-16 kcal/mol. The calculated transition state barriers are 11 (BP86), 16 (B3LYP) and 14 (CCSD(T)) kcal/mol. Although the barriers are low, the reactions do not lead to the formation of a hydroxyl radical, instead, during the shortening of O^{lig}–H^W distance, an H^{lig} atom from a neighbouring OH ligand moves to the water oxygen (O^W). This amounts to a relay of an H atom between the ligands of the $Ti(OH)_4$ molecule resulting in an oxo-titanium compound $TiO(OH)_2H_2O$ (see Fig. S3).

Fig. S1: Structure and the labelling of the atoms of the reactant complex $Ti(OH)_4\cdots H_2O$.



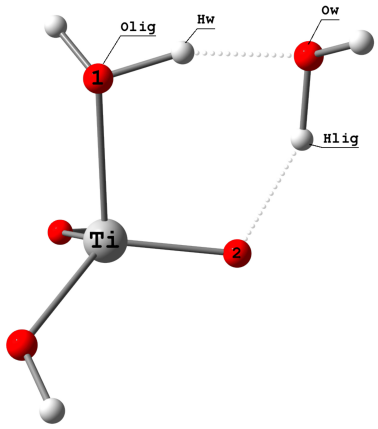
To prevent a spontaneous transfer of H^{lig} to the OH remnant of water and investigate the possibility of $OH^{\bullet}$ radical formation in the ground state we have performed a two-dimensional PES scan whereby H^W-O^{lig} and O^W-H^{lig} coordinates have been fixed, while all the other coordinates have been optimised. The obtained potential energy surface (PES) is shown in Fig. S2 (right). The red curve on the plot shows the path taken in the one-dimensional energy scan along H^W-O^{lig}.

Fig. S2: Ground state PES (in kcal/mol).
Left: energy profiles along the H^W-O^{Lig} distance relative to free $Ti(OH)_4$ and H_2O. The ground state reactions do not correspond to the process $Ti(OH)_4 + H_2O \xrightarrow{h\nu} Ti(OH)_3HOH\cdots OH^\bullet$, but rather to a relay of an H-atom from one OH ligand to the other via the water molecule, which results in an oxo-titanium species (see inset). Single point CCSD(T) calculations on the BP86 geometries are shown in the plot ('CC')).
Right: 2D PES along the H^W-O^{Lig} and O^W-H^{Lig} coordinates. The two coordinates have been kept fixed, whereas all other coordinates have been optimised. The energies are with respect to the reactant complex energy. The red curve represents the projection of the 1D PES (BP86 in the left panel). The $OH^\bullet$ radical formation is energetically prohibited (∼40 kcal/mol).



At longer O^W-H^{Lig} (≥2.5 Å) the incident water coordinates to the Ti atom and the shortening of H^W-O^{Lig} leads to the transfer of H-atom from the coordinated water to the OH-ligand, whereby the nascent water ligand decoordinates from the titanium site. This results in a structure similar to the reactant complex at H^W-O^{Lig} ∼1.0 Å, O^W-H^{Lig} ∼3.2 Å. As can be seen that at O^W-H^{lig} distances between 1.5 and 2.4 Å the energy rises to 40 kcal/mol. Only this region corresponds to the formation of an $OH^\bullet$ radical. Therefore, in the ground state the $OH^\bullet$ radical formation is energetically not feasible.

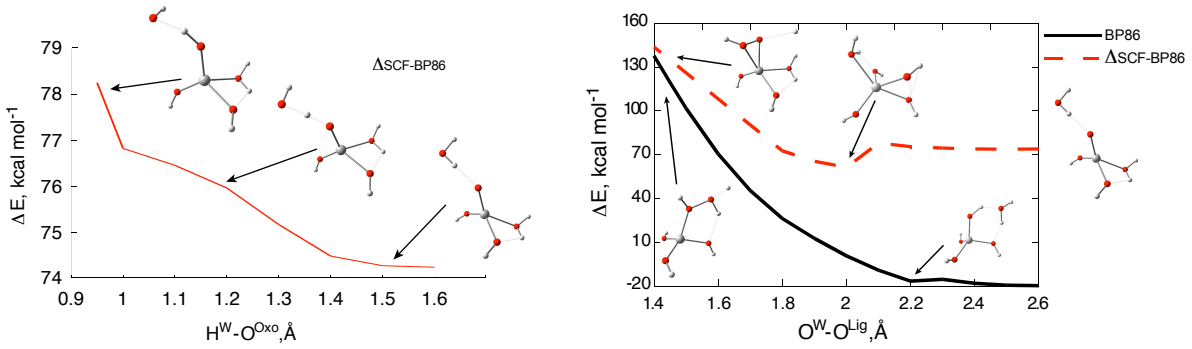
Fig. S3: Structure of $TiO(OH)_2H_2O\cdots H_2O$ complex obtained upon shortening of $O^{lig}-H^{w}$ coordinate in the ground state.



1.1 Reactivity of the oxo-titanium species $TiO(OH)_2H_2O$.

We follow the same lines as in the $Ti(OH)_4$+H_2O study and first study the H-abstraction by the oxo-moiety of the oxo-titanium. The excited state PES (ΔSCF-BP86) along the H^W-O^{Oxo} distance is shown in Fig. S4 (left). There is no stable minimum on the curve, however, the energy penalty for the water OH bond breaking is small ∼4 kcal/mol.

Fig. S4: Left panel: Excited state (ΔSCF-BP86) energy profile for the water H-abstraction reaction by the $TiO(OH)_2H_2O$.
Right panel: Ground (BP86) and excited (ΔSCF-BP86) state energy profiles for the O-O bond formation reaction by the $TiO(OH)_2H_2O$.



Additionally, we studied the nucleophilic attack of water on the oxo moiety. The energy curves of the O^W-O^{Lig} bond formation reaction are shown in Fig. S4 (right). The ground state scan leads very quickly to the reproduction of the $Ti(OH)_4$+H_2O system and then, naturally, follows the same repulsive potential that was observed in the reaction with $Ti(OH)_4$ (see main text). On the excited (ΔSCF-BP) state a small barrier is surmounted after which the water molecule coordinates to Ti. Subsequent shortening of the O-O bond is energetically prohibited (≥60 kcal/mol).

Hereby we have found that the oxo-titanium species is not superior to the $Ti(OH)_4$ system, but has similar traits. Namely, it is also capable of OH bond breaking in the excited state and is inactive in the ground state. Likewise, $TiO(OH)_2H_2O$ is inert towards a nucleophilic attack of water on its oxo-moiety.

To conclude, the reaction $Ti(OH)_4 + H_2O \xrightarrow{h\nu} Ti(OH)_3HOH\cdots OH^{\bullet}$ can proceed either

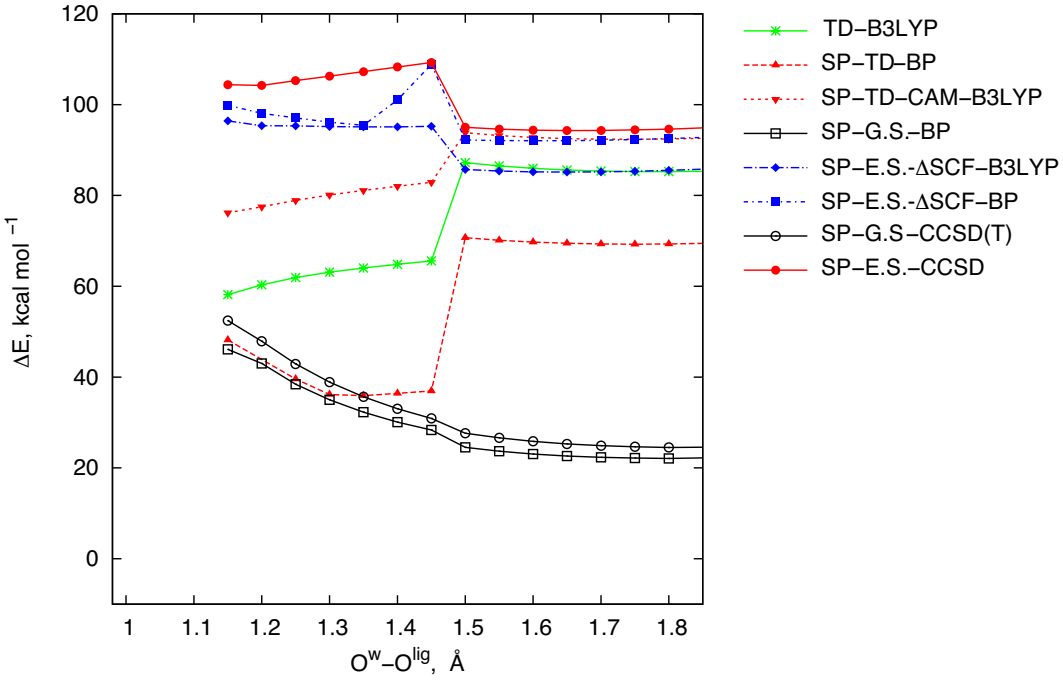
directly or via a precursor oxo-titanium species with comparable activation barriers. In each case the excitation is crucial for the generation of an $OH^{\bullet}$ radical.

2 TDDFT treatment of the water H-abstraction reaction by $Ti(OH)_4$.

Herein we investigate the excited state reaction of $Ti(OH)_4$ with water using the TDDFT method for geometry optimisations. Energy profiles along a one-dimensional (H^W-O^{Lig}) relaxed TD-B3LYP scan are shown in Fig. S5. The single point energies using TD-DFT and ΔSCF with different functionals together with the excited CCSD and ground state CCSD(T) results have been plotted. The excited (S_1) state CCSD results were obtained by adding the CCSD(T) ground state energies and the CCSD excitation energies. It is evident that in the Franck-Condon region the TDDFT and ΔSCF curves are parallel to the CCSD ones. TDDFT performs better with hybrid functionals in agreement with our benchmark calculations in the main text and with the recent work of Berardo et al.[1,2] Using the range-separated CAM-B3LYP brings TDDFT results very close to the CCSD values. At H^W-O^{Lig}=1.45 Å there is an abrupt drop in TDDFT curves. This is reflected in large geometric transformations, namely the ligand OH that initially donated an H-bond to water turns $\sim$180° and now accepts an H-bond from the rotated water. After the drop water bridges two OH ligands. Although it is obvious that this sudden drop is due to the unfortunate reaction coordinate, it should be noted that the energy profiles from CCSD and ΔSCF methods do not show a lowering of energy, but a raise.

To make the interpretation clearer one should consider a more smooth reaction path, that does not involve such strong geometric transformations. To this end we fix the distance between the water oxygen and the OH ligand hydrogen (the one that will turn 180 degrees in the one-dimensional scan). The two dimensional relaxed scan along the H^W-O^{Lig} and O^W-H^{Lig} (Fig. S6) has been performed in the lowest singlet excited state using the TD-B3LYP/TZ2P approach. In contrast to the ΔSCF results (see main text) the TDDFT optimisation spontaneously leads to the isolation of the OH radical. The red curve on the 2D plot in Fig. S6 represents the path along the 1D-H^W-O^{Lig}-scan (Fig. S5). The considerable

Fig. S5: Relaxed excited state TD-B3LYP/TZ2P scan along the H^W-O^{Lig} distance. Single point calculations using the TD-B3LYP optimised geometries are plotted.



drop on the one-dimensional plot is reflected in the turn of the red path towards large O^W-H^{Lig} values. Since the left part of this plot corresponds to the OH radical formation, we examine the cut at O^W-H^{Lig} =2.0 Å, which is gives a representative reaction coordinate without abrupt features.

The 1D plot along H^W-O^{Lig} with O^W-H^{Lig} distance fixed to 2.0 Å is shown in Fig. S7. It is evident that before H^W-O^{Lig} =1.4 Åall the excited state curves, except TD-BP, are in a reasonable agreement and the best match with the CCSD results is seen with the TD-CAM-B3LYP and ΔSCF-BP results. However beyond the mentioned point the TDDFT results diverge. This behaviour is an indication of the artefact of the method. Notably, the ΔSCF-BP results follow the same trend as the CCSD ones even at shorter distances (when one water OH bond is broken and the OH radical is formed).

To investigate the source of the breakdown we have traced back the HOMO-LUMO gaps along the reaction coordinate. The values of the gaps together with the excitation

Fig. S6: Relaxed 2D excited state TD-B3LYP/TZ2P scan along the H^W-O^{Lig} and O^W-H^{Lig} distances. The energies are in kcal mol^{-1}, relative to the lowest energy point.

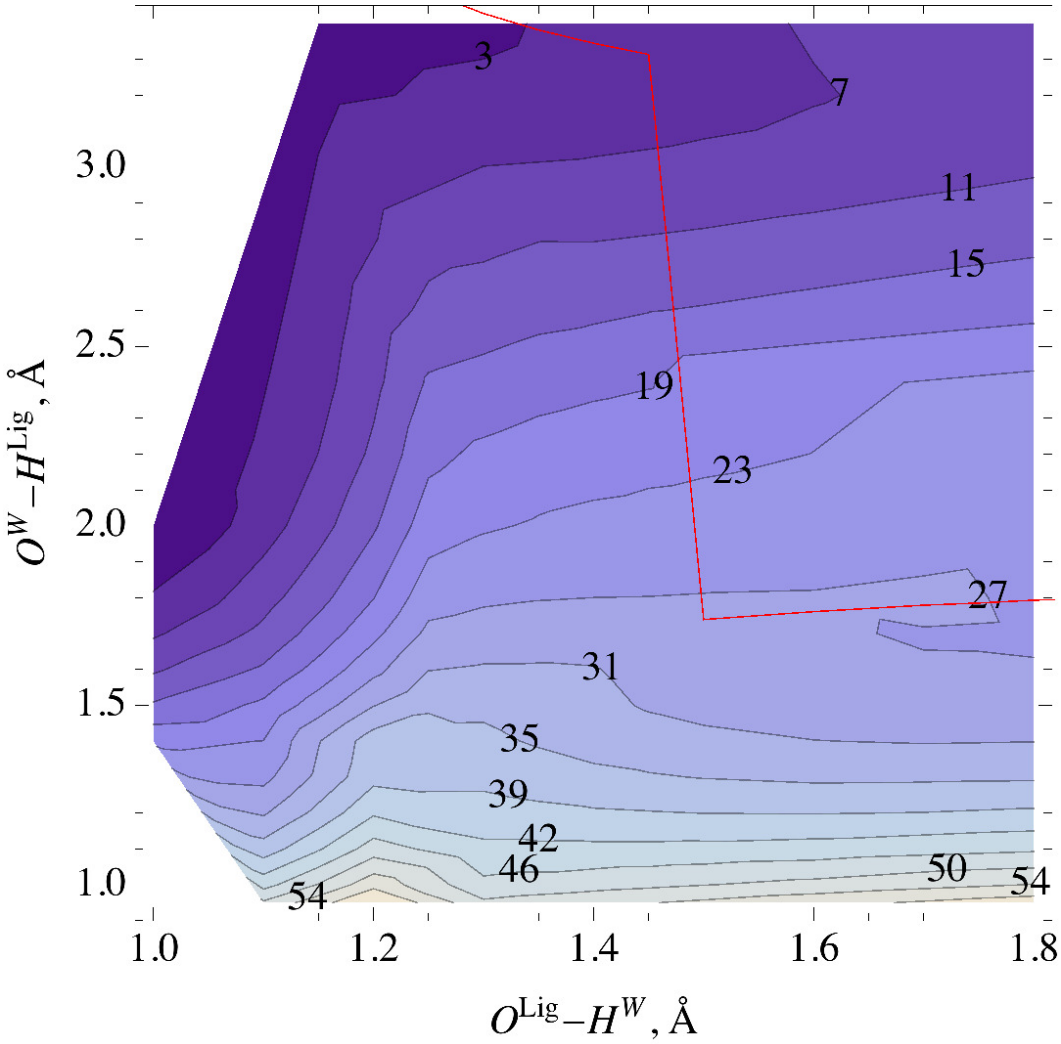
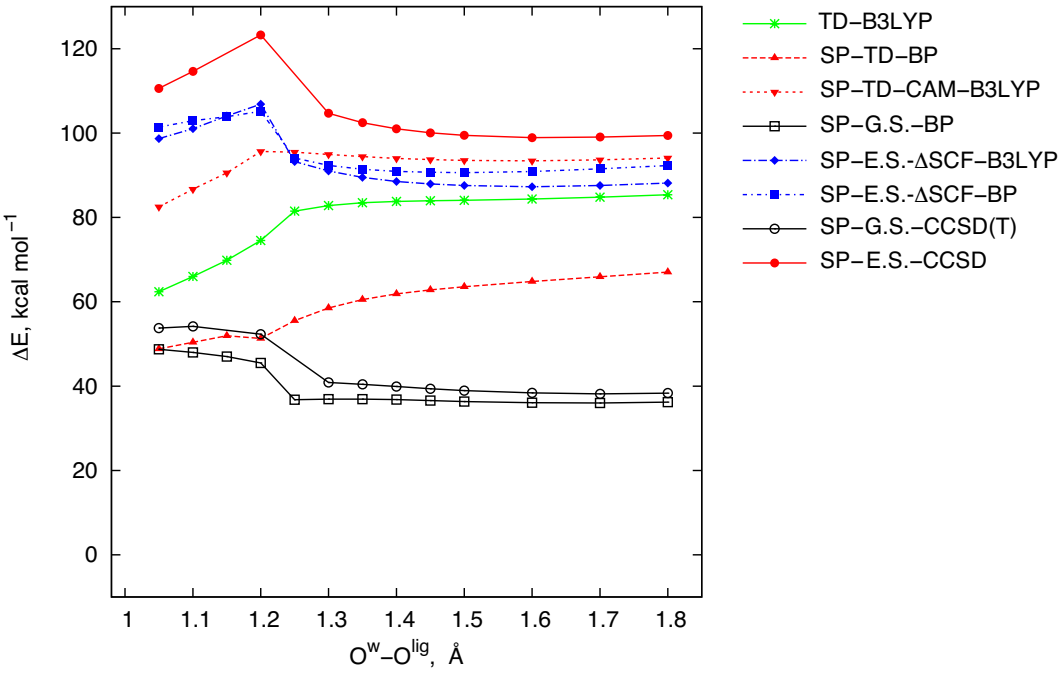


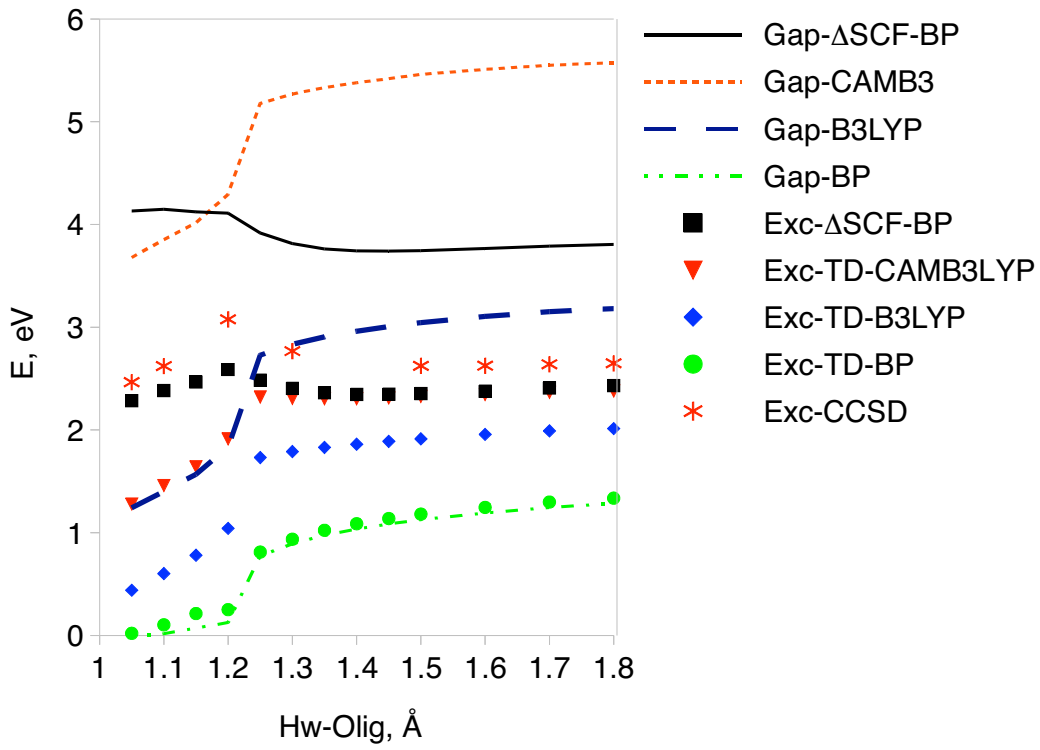
Fig. S7: Relaxed excited state TD-B3LYP/TZ2P scan along the H^W-O^{Lig} distance with the O^W-H^{Lig} distance fixed to 2.0 Å. Single point calculations using the TD-B3LYP optimised geometries are plotted.



energies are depicted in Fig. S8. It is evident that the TDDFT excitation energies follow the corresponding closed shell reference DFT gaps. At H^W-O^{Lig} $\leq$1.4 Å the gaps get smaller, until at a given point they tend to diminish. The CAM-B3LYP method has the largest gap and hence its excitation energies survive somewhat longer. But this does not salvage the method at too short distances.

We therefore prove that the TDDFT study of the water H-abstraction reaction by $Ti(OH)_4$ must be confined to the Franck-Condon region and is not generally applicable for this investigation. On the other hand, we have presented another strong evidence that the ΔSCF-BP approach gives very reasonable results.

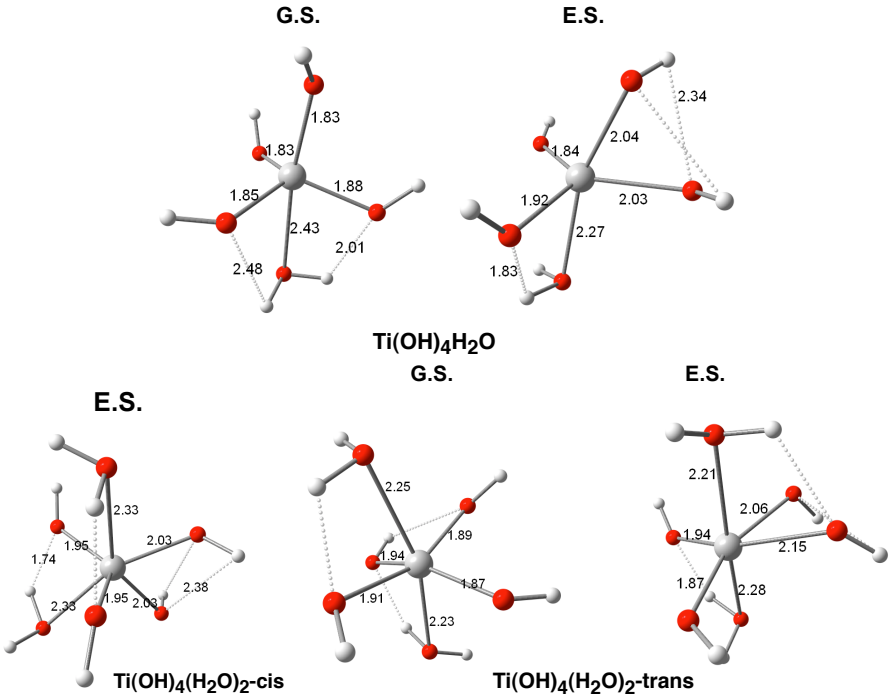
Fig. S8: HOMO-LUMO band gaps and the excitation energies at the geometries obtained by the TD-B3LYP relaxed scan along the H^W-O^{Lig} distance with the O^W-H^{Lig} distance fixed to 2.0 Å.



3 Stability and reactivity of $Ti(OH)_4(H_2O)_{0,1,2}$ systems

The titanium atom in $Ti(OH)_4$ is undercoordinated and in an aqueous solution can possibly afford one or two water molecules in its shell. The optimised structures of $Ti(OH)_4(H_2O)_{1,2}$ are shown in Fig. S9. The corresponding energies relative to the free ground state $Ti(OH)_4$ and water molecules are given in Tab. S1

Fig. S9: Structures of the coordinatively saturated $Ti(OH)_4(H_2O)_{1,2}$ compounds.



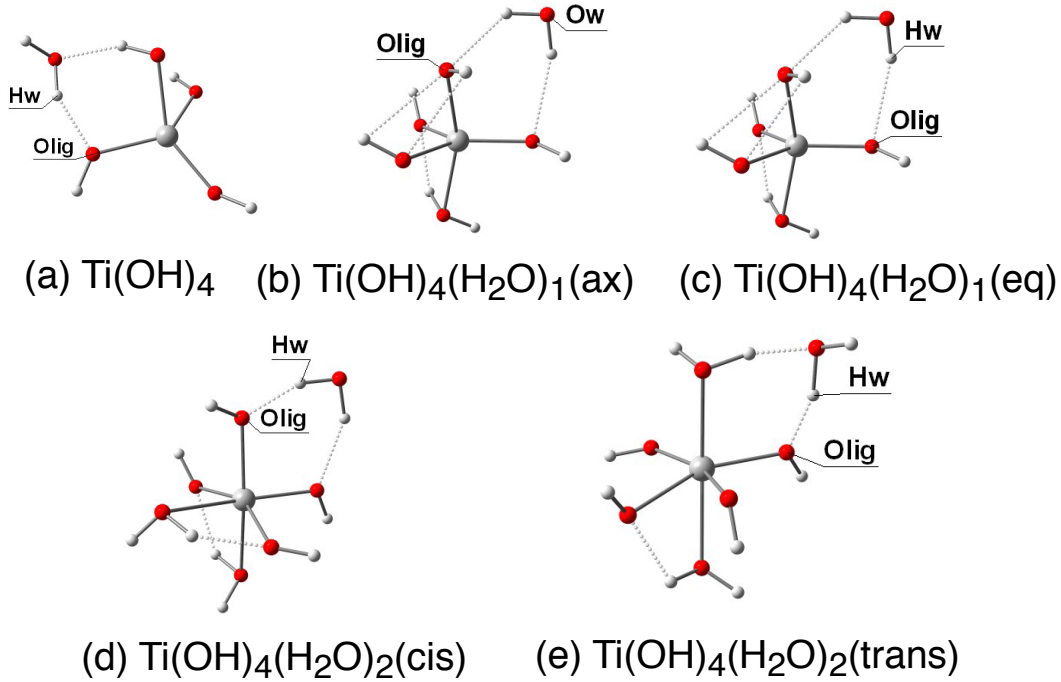
Tab. S1

Ground state			
	ΔE	ΔH	ΔG
$Ti(OH)_4$	0.0	0.0	0.0
$Ti(OH)_4H_2O$	-3.8	-2.1	8.4
$Ti(OH)_4(H_2O)_2$-cis	–	–	–
$Ti(OH)_4(H_2O)_2$-trans	4.7	7.9	29.4
Excited state			
	ΔE	ΔH	ΔG
$Ti(OH)_4$	92.1	92.4	93.4
$Ti(OH)_4H_2O$	80.4	82.5	93.8
$Ti(OH)_4(H_2O)_2$-cis	75.7	79.5	102.0
$Ti(OH)_4(H_2O)_2$-trans	74.6	78.2	98.1

In the ground state the $Ti(OH)_4(H_2O)_{1,2}$ compounds are within 5 kcal/mol from $Ti(OH)_4$. However, their free energies are considerably higher (∼8-29 kcal/mol). The major contribution comes from the entropic effect, which renders the $Ti(OH)_4(H_2O)_{1,2}$ molecules unstable.

In the excited state, all $Ti(OH)_4(H_2O)_{1,2}$ conformers are significantly lower in energy (∼12-18 kcal/mol) than $Ti(OH)_4$. The entropic effect, however, raises their energies above $Ti(OH)_4$. The single water-coordinated $Ti(OH)_4H_2O$ becomes energetically accessible ($\Delta\Delta G$=0.4 kcal/mol), whereas the doubly-coordinated $Ti(OH)_4(H_2O)_2$ are less favored, being 5 (trans) and 9 (trans) kcal/mol higher than $Ti(OH)_4$. The possibility of the additional coordination in the excited state can be explained by the geometry of $Ti(OH)_4$, which features wider openings of the ∠OTiO angles (>109°) in the excited state.

Fig. S10: Structures of compounds $Ti(OH)_4(H_2O)_n \cdots H_2O$, n=0 (a); n=1 (b, c) and n=2(d, e). The labels indicate the atoms, the distance between which is varied in the H-abstraction reactions.



From the above analysis it is seen that $Ti(OH)_4$ is stable in the ground state, whereas in the excited state it can attach an additional water molecule. The reactivity of $Ti(OH)_4(H_2O)_{1,2}$

Fig. S11: Relaxed potential energy scans along the Hw-Olig coordinate. The energies are with respect to the reactant complex (RC). The corresponding structures are depicted in Fig. S5

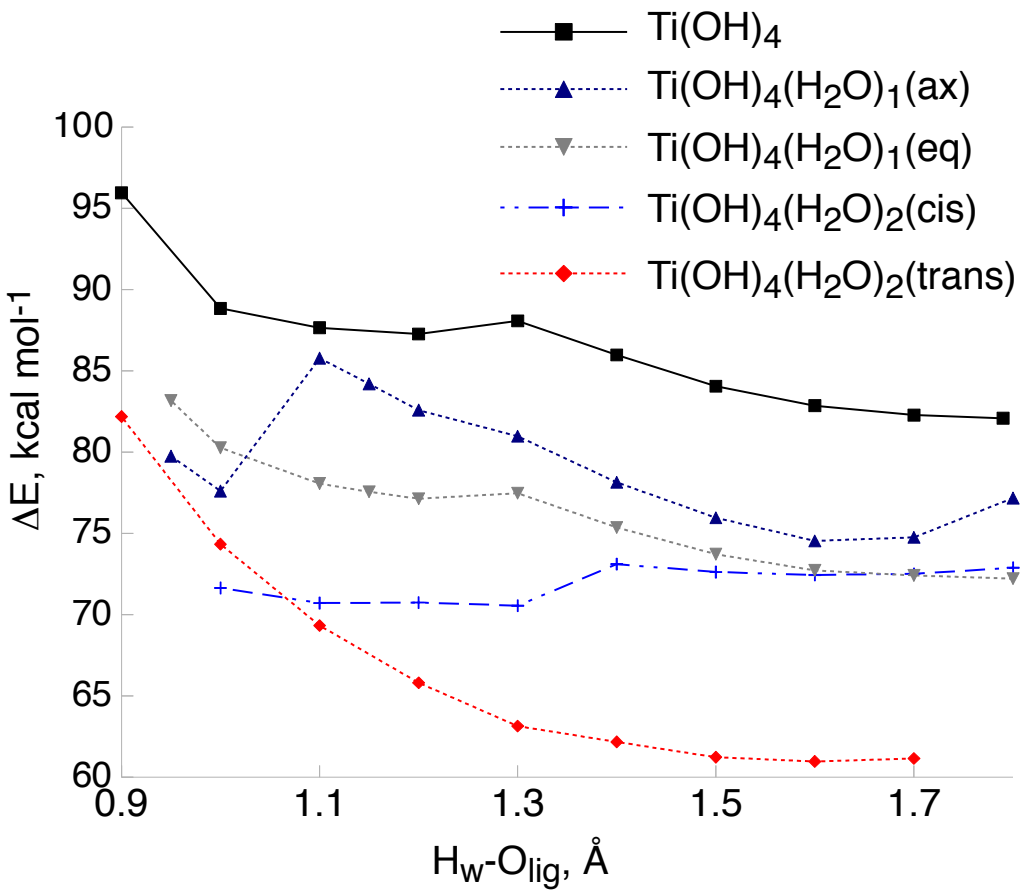


Fig. S12: Structures of compounds $Ti(OH)_4(H_2O)_n \cdots H_2O$, n=0 (a); n=1 (b) and n=2(c, d). The labels indicate the oxygen atoms, the distance between which is shortened in the O-O bond formation reactions.

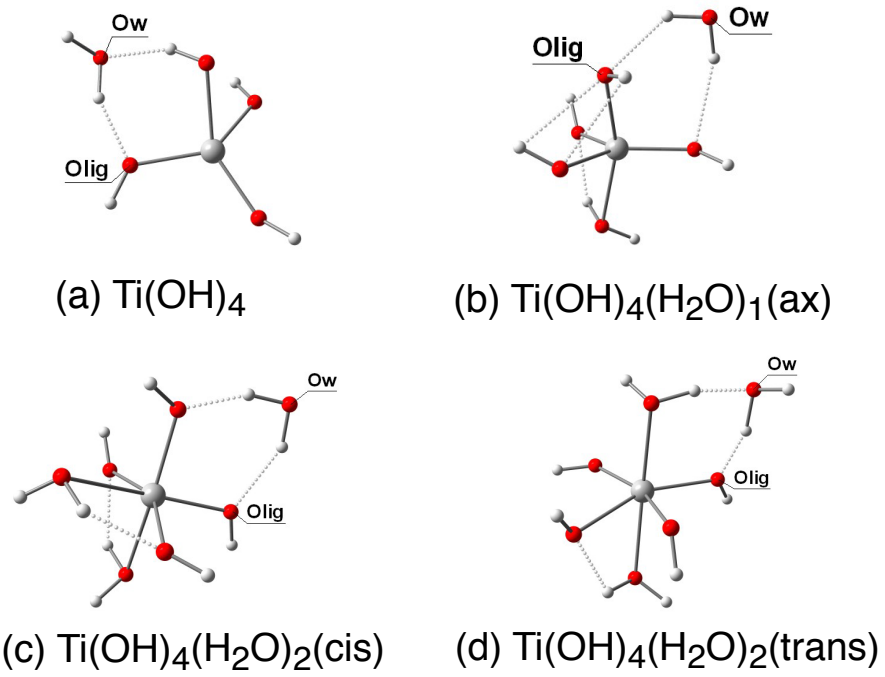
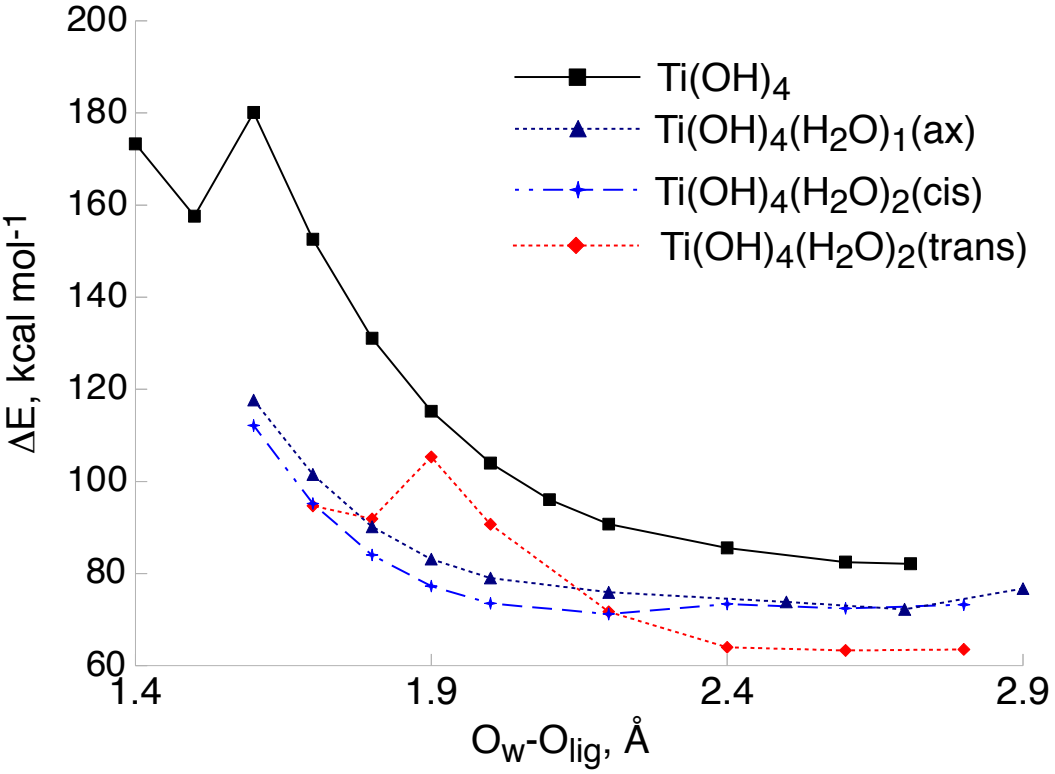


Fig. S13: Relaxed potential energy scans along the Ow-Olig coordinate. The energies are with respect to the reactant complex (RC). The corresponding structures are depicted in Fig. S11



with water was found to be similar to that of $Ti(OH)_4$ (see the SI for details of this study), therefore in the next sections we concentrate on the reactions driven by $Ti(OH)_4$.

3.1 Water splitting and O-O bond formation reactions by $Ti(OH)_4(H_2O)_{0,1,2}$.

As shown above, the $Ti(OH)_4$ molecule is stable both in the ground and the lowest excited states in the gas phase. However, in a water solution, the titanium atom may take on more waters. To estimate the effect of this additional coordination on the reactivity, we studied the H-abstraction and the direct O-O bond formation reactions with different conformations of titanium tetrahydroxide. Since the free energies of the ground state $Ti(OH)_4(H_2O)_{1,2}$ compounds are significantly higher than those of $Ti(OH)_4$, (see Tab. S1) we only consider here the excited state reactions.

3.2 Water splitting.

The reactant complexes of the $Ti(OH)_4(H_2O)_{0,1,2}$ species with a water molecule are illustrated in Fig. S11. In the compound $Ti(OH)_4(H_2O)_1 \cdots H_2O$ the water H-atom (Hw) can be transferred to either the oxygen (Olig) of the axial OH ligand (Fig. S11 b) or that of the equatorial ligand (Fig. S11 c). The system $Ti(OH)_4(H_2O)_2$ has cis and trans conformers (Fig. S11 d, e). The transition of Hw to the Olig of any of the OH ligands are equivalent.

From the plot in Fig. S11 it is evident, that the systems with only one extra water ligand behave similarly to the $Ti(OH)_4$ molecule, although, the transfer of Hw to the axial Olig has a somewhat higher barrier (11.2 kcal/mol) than to the equatorial Olig (6.0 kcal/mol).

The Reactions of water with $Ti(OH)_4(H_2O)_2$ is more different. The H-abstraction by the cis conformer is virtually barrierles ($\sim$0.2 kcal/mol). The transfer of Hw atom to the Olig in the trans-conformer results in a simultaneous relay of an H-atom from the nearby water ligand to the remnant of water, similarly to the mechanism observed in the $Ti(OH)_4$+H_2O reaction in the ground state (see the main text). To check if it is energetically feasible to form a hydroxyl radical, we constrained the OH bond lengths of the water ligand and carried

out the relaxed scan ($Ti(OH)_4(H_2O)_2$(trans) in Fig. S11). It is seen, that there is an energy penalty of around 14 kcal/mol (corresponding to the Hw-Olig distance of ca. 0.98 Å) to the $OH^{\bullet}$ radical formation, which is still reasonable.

3.3 Nucleophilic attack.

To study the possibilities of O-O bond formation between the oxygen of the incident water (Ow) and the oxygen of an OH ligand (Olig) relaxed scans along the Ow-Olig (see labels in Fig. S12) were performed. The corresponding PESs are shown in Fig. S13. In the system $Ti(OH)_4(H_2O)_1 \cdots H_2O$ only the approach to the Olig of the axial OH ligand is shown, since the attack at the equatorial OH leads quickly to the formation of $Ti(OH)_4(H_2O)_2$ (cis) compound. The relaxed scans for the other compounds are propagated until the systems break down to form compounds with one more or one less water ligand. It is evident, that in each case the energy barriers are too high ($\geq$40 kcal/mol) for the reactions to proceed spontaneously.

From the above studies we infer that the reaction mechanisms observed for $Ti(OH)_4$+H_2O do not change significantly when $Ti(OH)_4$ is replaced by its coordinatively saturated species.

4 Cartesian coordinates of the key intermediates

4.1 Optimised geometries of the substrate molecules

$^1H_2$

BP86: -1.1723103812 CCSD(T): -1.1723103812

H 0 0 0.3745079

H 0 0 -0.3745079

$^2OH^\bullet$

BP86: -75.6412823877 UCCSD(T): -75.6412822907

O 0.6539658 -3.51609 0.2697869

H 1.0026787 -2.6374483 -0.012261

$^2OH^\bullet$ (B3LYP geom)

B3LYP: -0.34215934 UCCSD(T): -75.6414814125

O 0 0 2.211137

H 0 0 1.236025

$^2OOH_2$

BP86: -150.718502406 UCCSD(T): -150.7185006506

O 0.6552538 -3.517902 0.2699839

H 0.9759687 -2.6287963 -0.009253

O -0.6626378 -3.3532881 0.4826259

^1H_2O

BP86: -76.3369945521 CCSD(T): -76.3369945521

O -0.0172465 -1.761931 -0.3708988

H -0.0172465 -1.0001733 0.215041

H -0.0172465 -2.5236887 0.215041

^1H_2O (B3LYP geom)

B3LYP: -0.62712589 CCSD(T): -76.3369645121

O -0.8809418 -2.3379923 0

H -0.158625 -1.7006825 0

H -0.4498049 -3.1993051 0

$^1H_2O_2$

BP86: -151.3648285999 CCSD(T): -151.3648285999

O -0.112877 -3.41114 -0.068109

H 0.6345318 -2.7920942 0.039207

O -0.054398 -4.1114638 1.2250637

H 0.2775799 -4.9827316 0.9322997

$^3O_2$

BP86: -150.1346120368 UCCSD(T): -150.1346130104

O 0 0 0.6129558

O 0 0 -0.6129558

4.2 Ground and excited state stationary structures of the reactant $Ti(OH)_4$(R) and corresponding product (P) of H-abstraction, $Ti(OH)_3H_2O$

$^1Ti(OH)_4$ (G.S. geometry)

BP86: 1.95510464 CCSD(T): -1152.0073339806 CCSD-ex: 0.2258958

Ti 0 0 0.000176

O 0.408463 -1.412581 1.075608

O -1.413303 -0.405653 -1.07524

H -2.007516 -1.169882 -1.004803

O -0.408463 1.412581 1.075608

H -1.171167 2.007632 0.994781

O 1.413303 0.405653 -1.07524

H 2.007516 1.169882 -1.004803

H 1.171167 -2.007632 0.994781

$^1Ti(OH)_4$ (E.S. geometry)

BP86: -1.8083389 CCSD(T): -1151.9013008537 CCSD-ex: 0.0582457

Ti 0.16401 0.001477 0.144557

O 0.125608 -0.2136959 1.9439815

O -1.0575427 1.0961497 -1.0524537

H -0.9783417 0.9552897 -2.0182074

O 1.8087695 0.2038519 -0.6249808

H 2.7254802 0.13333 -0.3199709

O -1.3745646 -1.0620837 -0.6309768

H -1.2823866 -1.4713476 -1.5123766

H -0.3682919 -0.071966 2.7632592

$^2Ti(OH)_3H_2O$ (G.S. geometry)

BP86: -2.02504026 UCCSD(T): -1152.5582369267

Ti 0.011258 0.122962 -0.3630109

O -0.5660218 1.2708646 -1.6241495

O 1.5481376 -1.4127726 0.3352339

H 1.7540525 -0.9523247 1.1761237

O 0.8134068 0.9584047 1.1116827

H 0.6349768 1.8479385 1.4517396

O -1.0246787 -1.4285796 -0.2161949

H -1.9368275 -1.5443216 -0.5229479

H -0.7706748 1.9535025 -2.2740584

H 0.9078507 -2.1214604 0.5515708

4.3 Stationary structures of the reactant $Ti_2O_2(OH)_4$(R) and corresponding products (P) of H-abstraction

^{1}R (G.S. geometry)

BP86: -2.86612811

Ti -0.464672 1.111454 -2.156558

Ti -0.205651 1.517553 0.510058

O 0.88664 1.148903 -0.928476

O -0.77554 -0.576186 -2.777927

H -0.921606 -0.883936 -3.686566

O -1.549877 1.531795 -0.728951

O -0.376847 2.382606 -3.444405

H -0.077611 3.294366 -3.571088

O 0.113078 3.104279 1.343924

H 0.135935 4.024666 1.041554

O -0.31762 0.163255 1.720332

H -0.516516 -0.776668 1.583174

^{2}P-term (G.S. geometry)

BP86: -2.93609497

Ti -0.48619 1.25258 -2.118454

Ti -0.288815 1.771647 0.548633

O 0.872889 1.394961 -0.918675

O -0.607119 -0.451033 -2.789173

H -0.886621 -0.726758 -3.676413

O -1.617308 1.558463 -0.697754

O -0.544739 2.54681 -3.402167

O -0.47742 2.97876 1.920532

H -0.404075 3.878991 2.261684

O 1.336995 0.600726 1.532859

H 1.898577 0.571701 0.725531

H -0.36324 3.496208 -3.454035

H 1.833122 1.081001 2.220527

^{2}P-br (G.S. geometry)

BP86: -2.95215123

Ti -0.367066 1.360822 -2.13813

Ti 0.080701 1.701205 0.561045

O 1.017515 1.918208 -0.989312

O 0.001383 -0.289421 -2.838538

H -0.095403 -0.655456 -3.730764

O -1.51205 1.221678 -0.512856

O -0.904177 2.651395 -3.298666

H -0.909474 3.611872 -3.416756

O -0.123574 3.246978 1.519949

H -0.013987 4.180567 1.285208

O 0.685251 0.308801 1.580903

H 1.24009 -0.443218 1.320519

H -2.421007 0.939901 -0.327726

4.4 Stationary structures of the reactant $Ti_3O_3(OH)_6$ (R) and corresponding products (P) of H-abstraction

^{1}R (G.S. geometry)

BP86: -4.33549653

Ti -3.029843 0.724751 -2.517931

Ti -0.786833 2.054915 -0.401673

Ti -2.198565 3.967635 -2.767871

O -1.871205 0.755891 -1.133631

O -2.490652 -0.456257 -3.78318

H -1.693429 -1.002177 -3.866419

O -4.701294 0.315393 -1.915183

H -5.28566 -0.398902 -2.214934

O -3.040696 2.434249 -3.209294

O 0.957511 1.595983 -0.666289

H 1.632781 1.387648 -0.001522

O -1.14899 2.23787 1.36689

H -1.457091 2.992848 1.891798

O -1.141948 3.574875 -1.308229

O -1.154191 4.500066 -4.16235

H -1.067695 5.380227 -4.560699

O -3.394281 5.25454 -2.307946

H -4.363595 5.260897 -2.343842

^{2}P-term (G.S. geometry)

BP86: -4.41505331

Ti -2.171894 0.387496 -1.594339

Ti -0.95242 3.450652 -1.585118

Ti -2.729929 2.547949 -4.122168

O -1.257995 1.809401 -0.855959

O -0.996948 -0.990761 -1.858921

H -0.963282 -1.832863 -1.378586

O -3.525828 -0.108943 -0.474719

H -4.457996 -0.296826 -0.66665

O -2.76789 0.946956 -3.228673

O 0.376593 3.073161 -3.155055

H 1.099771 2.434982 -3.035009

O -0.466476 4.924311 -0.612761

H -0.262115 5.128111 0.311643

O -2.291349 3.742633 -2.875105

O -1.086957 2.484945 -5.152074

H -0.967871 3.000475 -5.965828

O -4.189908 3.061006 -5.1062

H -4.893219 2.52281 -5.503109

H -0.108393 2.851462 -4.063239

^{2}P-br (G.S. geometry)

BP86: -4.40565156

Ti -2.165694 0.414526 -1.704764

Ti -0.806715 3.389128 -1.657151

Ti -2.595885 2.602189 -4.157763

O -1.007966 1.68592 -1.052868

O -1.244311 -1.098163 -2.158768

H -0.704786 -1.666648 -1.586749

O -3.408331 0.084945 -0.410362

H -4.295763 -0.300278 -0.477182

O -2.93015 1.042628 -3.221681

O 0.984549 3.834014 -1.791019

H 1.552814 4.04069 -1.031005

O -1.774407 4.554262 -0.654271

H -2.445937 4.396145 0.028011

O -1.085129 3.745737 -3.58659

O -1.958005 2.100089 -5.789526

H -1.31635 1.429111 -6.073744

O -4.088462 3.631247 -4.19601

H -4.654629 3.974595 -4.90376

H -0.419483 4.187182 -4.149886

4.5 Stationary structures of the reactant $Ti_3O_4(OH)_4$ (R) and corresponding products (P) of H-abstraction

$Ti_3O_4(OH)_4$

Fout:510

^{1}R (G.S. geometry)

BP86: -3.74456233

TI 1.795843 -0.527127 0.113294

O 0.003145 -0.145051 0.654719

O 1.755009 0.937814 -0.882033

TI -0.019408 1.574099 -0.486783

O -0.079933 2.906146 0.455485

O 1.87057 -2.025212 -0.923994

TI -1.784639 -0.580048 0.107091

O -1.872456 -2.194305 -0.717956

O -1.738677 0.83587 -0.955751

H -1.563521 -2.483316 -1.591428

O -3.001148 -0.48146 1.452923

H -3.437723 0.308333 1.812549

O 2.979308 -0.511091 1.482837

H 3.518629 0.186896 1.887471

H 2.318873 -2.866847 -0.740253

^{2}P-term (G.S. geometry)

BP86: -3.83297526

Ti 0.694623 -0.307431 -0.809001

O -1.015314 0.070301 -0.186845

O 0.684098 1.109419 -1.850349

Ti -1.07269 1.816788 -1.320744

O -1.095138 3.224781 -0.481961

O 0.36771 -1.940303 -1.768896

Ti -2.873772 -0.225585 -0.758744

O -2.19029 -2.045259 -1.569536

O -2.787357 1.093889 -1.923852

H -1.16001 -2.118398 -1.69143

O -4.236045 -0.360953 0.452225

H -4.984812 0.182726 0.739178

O 2.015849 -0.425044 0.439882

H 2.734407 0.173722 0.697597

H 0.870056 -2.754217 -1.599692

H -2.602708 -2.48748 -2.329909

^{2}P-br (G.S. geometry)

BP86: -3.80526073

Ti 0.890941 -0.270425 -0.850757

O -1.040366 -0.120038 -0.096426

O 0.677194 1.098848 -1.944529

Ti -1.06215 1.733964 -1.278786

O -1.124151 3.020659 -0.25086

O 0.979838 -1.832472 -1.803646

Ti -2.954741 -0.34639 -0.856844

O -3.159615 -1.989926 -1.626467

O -2.73806 0.965905 -2.005299

H -2.996325 -2.27024 -2.541372

O -4.087998 -0.00624 0.528676

H -4.515458 0.833668 0.765574

O 1.994187 -0.001751 0.569088

H 2.478786 0.786293 0.86479

H 1.33218 -2.708359 -1.579961

H -1.046935 0.026076 0.870155

^{2}P-br2 (G.S. geometry)

BP86: -3.84225609

Ti 0.732264 -0.290431 -0.797977

O -1.060375 0.063838 -0.239269

O 0.716142 1.169992 -1.816152

Ti -1.037374 1.798941 -1.321495

O -1.108524 3.17417 -0.432528

O 0.701202 -1.813503 -1.834019

Ti -2.83877 -0.382385 -0.771131

O -2.813097 -2.000642 -1.593968

O -2.786474 1.107537 -2.093934

H -2.069767 -2.370287 -2.103757

O -4.1169 -0.245337 0.50938

H -4.274401 0.394646 1.222303

O 1.962183 -0.282305 0.539879

H 2.549304 0.4109 0.880784

H 1.211584 -2.623682 -1.67179

H -3.491374 1.418328 -2.682793

^{2}P-oxo-term (G.S. geometry)

BP86: -3.86915208

Ti 2.272181 1.441074 4.722556

O 1.36981 2.939312 5.523875

O 1.555105 1.876337 3.118075

Ti 0.754739 3.477478 3.704617

O 1.370399 5.035884 2.983116

O 1.464244 -0.088789 5.38024

Ti -0.468652 3.045368 6.105264

O -0.814538 1.375222 6.727729

O -0.964522 3.301817 4.345945

H -0.369539 0.591244 6.342778

O -0.910792 4.364626 7.279839

H -1.209604 5.282463 7.194494

O 4.082183 1.509292 4.811702

H 4.798533 1.805397 4.22956

H 1.892001 -0.821453 5.852569

H 1.077669 5.946992 2.836793

4.6 Stationary structures of $Ti(OH)_4(H_2O)_{1,2}$ compounds

$^1Ti(OH)_4(H_2O)$ (G.S. geometry)

BP86: -2.48051319

Ti -2.207238 0.005092 1.096729

O -4.564941 0.469224 1.424487

O -2.4222 0.7017 2.825799

O -0.396133 -0.263901 1.079951

O -2.456603 1.220692 -0.270069

H -4.638115 1.290802 0.905918

H -1.649118 0.739134 3.412622

H -2.616773 0.982422 -1.19784

H -4.376193 0.765403 2.339601

O -2.808833 -1.699308 0.808373

H 0.230804 0.27384 0.570023

H -2.176522 -2.422675 0.660087

$^1Ti(OH)_4(H_2O)$ (E.S. geometry)

BP86: -2.34631607

Ti -2.340861 0.149404 1.042985

O -4.557056 0.38867 1.495669

O -2.519718 0.731841 2.858853

O -0.477366 -0.683666 0.949763

O -2.342108 1.470394 -0.237313

H -4.887283 1.13343 0.962382

H -1.762035 0.987294 3.408307

H -2.15496 1.613344 -1.174802

H -4.280968 0.77387 2.368335

O -2.343225 -1.873298 0.918523

H -0.269135 -1.149566 0.11448

H -2.009189 -2.334723 1.71249

$^1Ti(OH)_4(H_2O)_2-$cis. (E.S. geometry)

BP86: -2.8732057

Ti -0.255399 -0.288314 0.05578

O 1.962175 -0.949438 0.319635

O -1.142741 1.754113 -0.620143

O -2.202976 -0.747503 0.384085

O 0.564851 0.659674 1.544108

O -0.629385 -2.242777 0.443359

O 0.162183 0.047587 -1.816936

H 1.951914 -0.271711 1.049963

H -0.707021 1.519493 -1.48536

H -2.636726 -1.239312 -0.340949

H 0.143644 1.371185 2.051661

H -0.857657 -2.43938 1.373395

H 0.731473 -0.511143 -2.369159

H 2.502072 -0.560909 -0.389882

H -0.609723 2.4778 -0.248514

$^1Ti(OH)_4(H_2O)_2$−trans. (G.S. geometry)

BP86: -2.98623008

Ti -2.563856 0.075386 1.036476

O -4.439801 1.287474 0.799341

O -2.436994 -1.08774 -0.425507

O -2.068902 0.812205 2.757981

O -0.441268 -0.496598 1.416826

O -2.144859 1.58981 -0.052537

H -3.864238 1.947963 0.32679

H -2.522042 -2.052309 -0.371295

H -2.552241 0.394046 3.491026

H -0.572646 -0.092361 2.319043

H -1.800762 1.395931 -0.940655

H -4.685897 1.670775 1.660177

O -3.715603 -1.084991 1.979284

H -0.283692 -1.44972 1.527182

H -4.440697 -1.54819 1.52927

^{1}Ti(OH)$_4$(H$_2$O)$_2$−trans. (E.S. geometry)

BP86: -2.87491652

Ti -2.485325 0.288011 1.129951

O -4.408709 1.39597 0.624393

O -2.84824 -1.179738 -0.273917

O -2.487482 1.014139 2.850715

O -0.6026 -0.856683 1.31599

O -2.079104 1.653271 -0.185834

H -3.788589 1.899813 0.018897

H -3.789414 -1.278028 -0.514389

H -2.760416 0.557633 3.661235

H -0.136541 -0.573681 2.122479

H -1.36526 1.64026 -0.841327

H -4.550633 1.976389 1.394814

O -3.016257 -1.658517 1.885215

H -1.058118 -1.702146 1.543812

H -3.915175 -2.026679 1.816635

4.7 Intermediate structures of the reactions of H-abstraction and H_2 formation by $Ti(OH)_4$ in the gas phase

4.7.1 Intermediates of the H-abstraction reaction from H_2O

^{1}RC1 (G.S. geometry)

BP86: -2.48681932 CCSD(T): -1228.3595864051 CCSD-ex: 0.2137248

Ti 0.088915 0.047508 -0.167723

O -0.000363 0.9413647 -1.7537745

O 1.4751216 -1.2006157 -0.2122909

H 2.2236584 -1.1626137 -0.8298078

O 0.3587809 1.2810086 1.1527227

H -0.025352 1.2748506 2.0441144

O -1.3444006 -0.9774457 0.15497

H -1.1941857 -1.9611244 0.2308369

H -0.6129398 0.7687328 -2.4875003

O -0.156499 -3.463065 0.2040779

H 0.6261278 -2.8741202 0.071488

H -0.004872 -3.8971419 1.0594977

^{1}TS1 (G.S. geometry)

BP86: -2.46927152 CCSD(T): -1228.3377939416

Ti 0.076026 0.058953 -0.15122

O 0.172943 0.8343648 -1.8125645

O 1.4016846 -1.4403816 -0.019438

H 2.1863674 -1.5137066 -0.5857398

O 0.3147029 1.3108296 1.1708767

H -0.168237 1.3615636 2.0109154

O -1.2661816 -0.9665317 0.083583

H -0.9195827 -2.2543204 0.108963

H -0.4004179 0.6374118 -2.5706013

O -0.2620019 -3.1827121 0.083488

H 0.7165078 -2.4551353 0.044716

H -0.3203829 -3.612438 0.9537567

^{1}PC1 (G.S. geometry)

BP86: -2.47241204 CCSD(T): -1228.3490788672

Ti 0.053177 0.084607 -0.14515

O 0.1996179 0.8121978 -1.8330615

O 1.4626906 -1.4488716 -0.017451

H 2.1761554 -1.5364376 -0.6712128

O 0.3147479 1.3235416 1.1926767

H -0.2085519 1.4021266 2.0058814

O -1.2817066 -0.8985257 0.076225

H -0.8995797 -2.5032613 0.105363

H -0.3883699 0.6266358 -2.5825133

O -0.2678359 -3.3018321 0.077221

H 0.9133197 -2.3371073 0.029022

H -0.3859509 -3.7648589 0.9231867

^{1}RC1 (E.S. geometry)

BP86: -2.3436207 CCSD(T): -1228.2508579934 CCSD-ex: 0.0504252

Ti 0.2192179 0.09289 0.078467

O -0.6193368 0.3455469 -1.6949995

O 1.2634606 -1.3461656 0.7022238

O 0.7918718 1.7107995 0.6644978

O -1.4692146 -0.9883227 -0.098435

H -0.5320689 -0.3221269 -2.4005563

H 2.1765714 -1.2950776 1.0252207

H 0.5800728 2.5642933 1.0662437

H -1.1963757 -1.8800075 -0.4696799

O -0.045209 -3.2791681 -0.6913918

H 0.5982088 -2.7953422 -0.105261

H -0.2892689 -4.0832029 -0.2048739

^{1}TS1 (E.S. geometry)

BP86:-2.33577201 CCSD(T): -1228.2272168714 CCSD-ex: 0.0399999

Ti 0.110891 0.098136 -0.2770319

O -0.3460629 1.2367637 -1.6207535

O 1.4561256 -1.4341526 -0.3109159

O 0.4156929 0.8338798 1.3788666

O -1.2522686 -1.4244436 -0.3687239

H -0.2921569 1.4190336 -2.5692553

H 2.3694163 -1.3106536 -0.009248

H 0.3093119 1.7321865 1.7258395

H -1.0956047 -2.2102854 -0.9286437

O -0.055467 -2.9523282 0.7909758

H 0.8633688 -2.2345774 0.3061609

H -0.3682589 -2.5528883 1.6261795

^{1}PC1 (E.S. geometry)

BP86: -2.33286315

Ti 0.039261 0.087697 -0.2879679

O -0.5027149 1.1996277 -1.6181945

O 1.5611686 -1.3572126 0.153295

H 2.0238734 -1.0451547 0.9526197

O 0.7570078 1.0576457 1.1197287

H 0.4512089 1.8558095 1.5748016

O -1.2206037 -1.4037726 -0.2462149

H -1.3368216 -2.0019894 -1.0074267

H -0.2488339 1.8256985 -2.3096964

O -0.127301 -3.2354991 0.4499349

H 1.0330507 -2.1728334 0.3896309

H -0.6889288 -3.1390921 1.2443927

^{3}RC1 (Triplet state B3LYP E.S. geometry)

B3LYP/def2-TZVPP: CCSD(T):-1228.2576590776 CCSD-ex: 0.0587616

Ti 0.2682119 0.079389 0.134199

O -0.4622249 -0.016943 -1.7298625

O 1.3993146 -1.3306616 0.5993588

H 2.2317614 -1.3882186 1.0745677

O 0.5809238 1.7787145 0.6916098

H 0.2666839 2.6815612 0.7621958

O -1.5558226 -0.7805768 0.02817

H -1.4640176 -1.7104425 -0.2613839

H -0.4462519 -0.8688808 -2.1901894

O -0.16248 -3.1442691 -0.8433678

H 0.5588328 -2.8000522 -0.2815309

H -0.2067479 -4.0920919 -0.6858638

^{3}TS1 (Triplet state B3LYP E.S. geometry)

B3LYP/def2-TZVPP: -1229.248807186 CCSD(T): -1228.2511839274 CCSD-ex: 0.0699373

Ti -6.9806762 5.5346914 -1.6385668

O -7.0102635 6.1846392 -3.349375

O -5.5232295 4.1609294 -1.423784

H -4.5825752 4.2300967 -1.5884772

O -7.1801285 6.6259275 -0.1761553

H -7.3438912 7.5435689 0.0384098

O -8.2178613 3.8552238 -1.4433374

H -8.7773411 3.5852671 -2.1800849

H -6.883504 5.9526642 -4.2688269

O -6.8613528 2.2319886 -1.846054

H -6.069097 3.100089 -1.6253181

H -7.1671725 1.9035307 -0.9908534

^{3}PC1 (Triplet state B3LYP E.S. geometry)

B3LYP/def2-TZVPP: CCSD(T): -1228.2453554022 CCSD-ex: 0.0357379

Ti 0.102832 0.147158 -0.112434

O -0.04424 0.6627858 -1.8623875

O 1.4966926 -1.4263226 -0.005797

H 2.3227653 -1.4829356 -0.4945299

O 0.2056209 1.5117086 1.1038457

H 0.2055379 1.6390255 2.0545154

O -1.0802487 -1.3286076 0.5264939

H -2.0097844 -1.3875356 0.2777399

H -0.3051439 0.3027029 -2.7125072

O -0.2617709 -3.2085431 -0.3462249

H 0.9345307 -2.2757304 -0.140396

H -0.5342818 -3.512196 0.5330279

4.7.2 Intermediates of the H-abstraction reaction from H_2O_2

^{1}RC2 (G.S. geometry)

BP86: -2.62931869 CCSD(T): -1303.3871536143 CCSD-ex: 0.2106941

Ti 0.052802 0.133655 -0.3063949

O 0.002966 0.9845407 -1.9137805

O 1.3881686 -1.1673927 -0.3048529

H 2.2432574 -1.1212107 -0.7614138

O 0.3661779 1.4070456 0.9596667

H 0.066386 1.4008706 1.8830565

O -1.4099076 -0.8436328 0.038801

H -1.3265846 -1.8261385 0.138833

H -0.6064238 0.8259268 -2.6528783

O -0.1968059 -3.3818331 -0.018862

H 0.5761808 -2.7523392 -0.065953

O 0.042854 -4.0378019 1.2758196

H 0.3109689 -4.9239386 0.9631997

^{1}TS2 (G.S. geometry)

BP86: -2.61191758 CCSD(T): -1303.3650469877 CCSD-ex: 0.1967089

Ti 0.023911 0.088171 -0.3201639

O -0.076098 1.0577687 -1.8709895

O 1.3967116 -1.3755506 -0.4340579

H 2.2611964 -1.3509916 0.006302

O 0.3832819 1.1745247 1.1100907

H -0.013985 1.1197087 1.9941954

O -1.2653166 -1.0110647 -0.087517

H -0.8825548 -2.2293314 0.032052

H -0.7063218 0.9257167 -2.5972583

O -0.1839899 -3.1705881 -0.045661

H 0.7866228 -2.3691483 -0.2279899

O 0.033181 -3.600744 1.3467926

H -0.3618539 -4.4923307 1.2940186

[1]PC2 (G.S. geometry)

BP86: -2.61462357 CCSD(T): -1303.3757696246 CCSD-ex: 0.1978648

Ti 0.01387 0.148203 -0.2753039

O -0.059556 0.8813498 -1.9637494

O 1.4944926 -1.3231936 -0.3130259

H 2.1604534 -1.3773956 -1.0185477

O 0.3596429 1.4033836 1.0232037

H -0.051601 1.4415946 1.9014665

O -1.2379297 -0.9047297 0.086111

H -0.8267268 -2.4480523 0.108502

H -0.7067268 0.6588958 -2.6519963

O -0.1973959 -3.2403761 -0.089736

H 0.9916167 -2.2265324 -0.2389829

O -0.031632 -3.8842799 1.2211927

H -0.5803528 -4.6808147 1.0805757

[1]PC2 (E.S. geometry)

BP86: -2.48210117 CCSD(T): -1303.2761622822 CCSD-ex: 0.0562142

Ti 0.05996 0.2303469 -0.3498379

O -0.4107959 1.1349367 -1.8749315

O 1.4909786 -1.2658266 0.03186

H 2.4211073 -1.2943616 -0.2356129

O 0.3890959 1.4141556 1.0018107

H 0.2181739 1.4351816 1.9550545

O -1.2551706 -1.2288237 -0.2648789

H -1.1690757 -2.1521484 -0.5859008

H -0.4227439 1.0083267 -2.8347652

O 0.044718 -3.3726921 0.00657

H 1.0836957 -2.2147684 0.093996

O -0.166119 -4.0325369 1.2633116

H 0.3910129 -4.8321806 1.1641287

4.7.3 Intermediates of the H-abstraction reaction from $OOH^{\bullet}$

[2]RC3 (G.S. geometry)

BP86: -2.47777203 UCCSD(T): -1302.7463197096

Ti 0.045529 0.105959 -0.2611779

O -0.2220479 0.8984257 -1.8763825

O 1.3458446 -1.2625736 -0.3969359

H 2.2191824 -1.1651317 -0.8091658

O 0.5806428 1.4070566 0.8947017

H 0.3910229 1.4706746 1.8444935

O -1.3284006 -0.8498288 0.3271329

H -1.2412087 -1.8410995 0.4875699

H -0.9174647 0.7130248 -2.5277673

O 0.5476218 -3.661789 0.2907879

H 0.9098187 -2.7307042 0.030238

O -0.7353268 -3.483164 0.6295608

^{2}TS3 (G.S. geometry)

BP86: -2.43883683

Ti -0.141516 0.10489 -0.3098969

O 0.8597198 0.3840979 -1.8008665

O -0.127187 -1.6918225 0.063062

H 0.3649299 -2.6643983 -0.4040859

O 0.6239458 1.0015197 1.0743897

H 0.1927099 1.5354726 1.7604975

O -1.8470575 0.6507018 -0.5563798

H -2.6959912 0.1818369 -0.5668728

H 0.5728918 0.6666218 -2.6837652

O 0.5892398 -3.557637 1.2636496

H 0.102159 -2.3926243 0.9994907

O 0.8344238 -3.8147199 -0.027235

^{2}PC3 (G.S. geometry)

BP86: -2.45373281

Ti -0.161825 0.158917 -0.3214569

O 0.8531198 0.3954479 -1.8139525

O -0.2136279 -1.6396165 0.016533

H 0.6279168 -3.1117761 -0.3975959

O 0.6137408 1.0258497 1.0739037

H 0.2089649 1.5950356 1.7473185

O -1.8378805 0.7922488 -0.5800408

H -2.7021602 0.3518299 -0.5703448

H 0.6222568 0.8550028 -2.6366323

O 0.6047948 -3.7883549 1.3178786

H -0.126748 -2.1232094 0.8801838

O 0.9630377 -3.9658949 0.037299

^{2}PC3 (E.S. geometry)

BP86: -2.37253452 CCSD(T): -1302.6923227806 CCSD-ex: 0.030447

Ti -0.042155 0.7809948 -0.4340129

O 1.1853807 -0.2791309 -1.2805126

O -1.6501905 -0.3462249 0.5675008

H -1.8731915 -0.1981479 1.5014326

O 0.6969848 2.2012074 0.4548629

H 0.3877279 3.0804931 0.7156198

O -1.7110915 1.1537457 -1.3162166

H -1.8234125 1.6987455 -2.1091024

H 1.1553377 -0.8895588 -2.0315334

O 1.1463207 -5.5054925 1.2115907

H -2.3227403 0.119815 -0.006297

O 1.1516067 -6.6635661 0.8099348

4.7.4 Intermediates of the H_2 generation reaction

^{1}RC4 (G.S. geometry)

BP86: -4.13000603 CCSD(T): -2305.1732342035

Ti 5.6366064 -4.7470747 8.8346335

O 5.6569864 -6.0999743 10.0451242

O 6.5341012 -5.1512846 7.3602609

H 3.8959299 -5.8551624 5.8196344

O 3.8237969 -4.3937018 8.4509796

H 3.1781341 -5.0659626 8.7317135

O 6.3803712 -3.2297211 9.5257173

H 6.3467112 -2.9583292 10.4576021

H 6.0718773 -6.974177 9.9672502

H 6.3519452 -5.3500195 6.3988532

Ti 4.2745658 -4.7673757 4.5179237

O 6.0500963 -5.3083205 4.6583357

O 3.1023151 -3.7438349 5.9844033

H 3.3070171 -2.7978902 5.8328494

O 4.4592257 -2.9143492 4.1409218

H 4.5791797 -2.6746662 3.2056011

O 3.416451 -5.5582234 3.1414801

H 3.626754 -6.3563992 2.6316593

H 6.7486391 -4.7087757 4.3414468

H 3.3408241 -4.0045419 6.9311671

^{1}TS (G.S. geometry)

BP86: -4.12025973 CCSD(T): -2305.1609252041

Ti 5.5129615 -4.5510007 8.3099707

O 5.7889604 -5.0369596 10.0486272

O 6.1552423 -5.9945633 7.4151089

H 3.557447 -6.5110072 4.7274557

O 3.608974 -4.4971067 8.2891367

H 3.1511361 -4.7743397 9.0999884

O 6.3474172 -2.8906642 8.3113787

H 6.6676001 -2.5688723 9.1720894

H 6.1466663 -5.8975973 10.3225771

H 6.2850262 -6.1426143 6.4533572

Ti 4.3474238 -4.7978367 4.8133676

O 5.8542504 -5.8609244 4.5197927

O 2.6653423 -4.8879876 5.8650044

H 2.8915802 -4.7857647 6.8520081

O 5.1880405 -3.7648579 6.1500833

H 5.0938046 -2.8006742 6.2505432

O 3.9473469 -3.8430669 3.3469371

H 4.3468918 -3.8116429 2.4622443

H 6.6799731 -5.3643185 4.3614938

H 2.9445472 -5.9893593 5.3823735

[1]PC4 (G.S. geometry)

BP86: -4.17743988 CCSD(T): -2305.2165705163

Ti 5.4936055 -4.7731027 8.6220156

O 6.0094003 -5.0764176 10.3329791

O 6.4006672 -5.7257214 7.4445249

H -0.4292369 -4.5511157 5.9652533

O 3.686282 -5.1499216 8.4259486

H 3.1183861 -5.5870124 9.0806035

O 5.7072584 -2.9946202 8.1131627

H 5.5295254 -2.2284984 8.6829906

H 6.7047721 -5.6594334 10.678941

H 6.2482162 -5.8866113 6.4523532

Ti 4.4589017 -4.4924117 4.6972807

O 5.7450764 -5.8705194 4.8933316

O 3.0402611 -4.9562796 5.7078234

H 3.0976301 -5.0640306 6.6913541

O 5.2879835 -3.0621001 5.3743295

H 5.4663865 -2.8289072 6.3224972

O 3.9045319 -4.3044608 2.9723172

H 4.1655598 -3.627895 2.3267763

H 5.5890354 -6.7592881 4.5329837

H 0.3065489 -4.6420807 5.8459344

4.8 Reactions of H-abstraction and H_2 formation by $Ti(OH)_4$ including explicit water solvent.

4.8.1 Intermediate structures of the reaction of H-abstraction from H_2O.

^{1}RC (G.S. geometry)

B3LYP-D3: -2070.291596619

Ti -11.691922 2.3047821 -0.9658204

O -11.5093503 1.2893642 0.5275147

O -12.4035801 3.895755 -0.534242

O -10.076827 2.4604333 -1.766013

O -12.9307011 1.4945579 -2.0686995

H -12.8125128 4.1625526 0.3435463

H -9.7140956 3.2404759 -2.2774199

H -12.7371119 0.7385298 -2.6844607

H -12.2359036 0.8089006 0.9691291

O -11.9029336 2.5169621 3.1749742

H -12.4890363 1.7474688 3.2356212

H -11.3425506 2.2968739 2.413835

O -13.236504 5.4780359 -2.7149295

H -14.1612865 5.195849 -2.843806

H -12.9389134 5.0232245 -1.9046121

O -8.4316605 0.3089417 -2.1279431

H -8.977125 1.1100722 -1.9494726

H -7.7319352 0.5917127 -2.7248447

O -15.4615034 1.916277 -1.6604227

H -14.4845117 1.7449149 -1.8559251

H -15.9318546 1.1394631 -1.9824616

O -13.5823353 4.2825839 1.7867779

H -13.0049969 3.7917464 2.4101988

H -14.3442351 3.7001785 1.6345961

O -13.7016812 0.4661323 2.0930594

H -14.0382919 -0.4227025 2.2412794

H -14.4523811 1.0110168 1.7721782

O -9.1628144 4.4691297 -3.2150676

H -9.9233654 4.8074569 -3.7557957

H -8.8106312 5.2322952 -2.745878

O -12.4352135 -0.6166478 -3.6351799

H -12.3000996 -0.4741585 -4.5773442

H -11.608729 -1.0565421 -3.3109956

O -15.8561907 4.4048792 -2.9648106

H -16.1783064 4.2463627 -3.8574736

H -15.7938741 3.5285817 -2.5389173

O -15.5479241 2.2323733 1.0489452

H -16.4484797 2.4176603 1.3345328

H -15.5686352 2.1583872 0.0627494

O -10.1173436 -1.6909238 -2.7834085

H -10.1050251 -2.2998814 -2.0387078

H -9.4583046 -0.9849936 -2.5683005

O -11.3138649 5.3455009 -4.5609043

H -12.0755409 5.4117901 -3.92424

H -11.6238768 4.8172447 -5.3021519

[1]PC2 (G.S. geometry)

BP86: -2071.113082225

Ti -0.4279873 -0.0512456 -0.2963344

O 0.0402982 -1.6154416 -1.4683579

O 0.5088374 1.2538106 -0.7667909

O -2.2254716 0.3282888 -0.3563798

O 0.1786641 -0.5934645 1.4193295

H 2.1331102 0.9546625 -1.5702586

H -2.6196038 1.2464642 -0.5701092

H -0.1249596 -1.4655123 1.7816592

H 0.61571 -2.3260393 -0.9762324

O 1.3647753 -0.9659369 -3.5462141

H 1.8362459 -1.6520103 -4.0452475

H 0.5299027 -1.4153046 -2.3754022

O 0.7661967 3.8583972 0.0940344

H 1.2513179 3.6862133 0.9382694

H 0.6984534 2.958473 -0.3187193

O -4.0024122 -1.517011 0.3389677

H -3.3721622 -0.7785759 0.0546846

H -4.5890725 -1.1204002 1.0025307

O 2.4539425 0.2082748 2.262868

H 1.5013221 -0.1076617 1.9954474

H 2.6060849 -0.1219674 3.1642442

O 2.8940255 0.4683878 -1.9848371

H 2.0673943 -0.4117573 -3.0506996

H 3.2206103 -0.1064436 -1.2542986

O 1.5199326 -3.2594026 -0.1346239

H 0.9896404 -3.3936197 0.6914534

H 2.2812785 -2.674718 0.1087989

O -3.2629506 2.6836114 -0.8392499

H -2.6867036 3.4350471 -0.4758349

H -3.3503215 2.8711405 -1.7880715

O -0.3486037 -3.261527 1.9556097

H -0.3065734 -3.7053466 2.8179354

H -1.2771126 -3.4731087 1.5756666

O 2.0907532 3.0436574 2.4739

H 1.469114 3.075865 3.2193037

H 2.2746928 2.0802404 2.3455984

O 3.5208026 -1.27933 0.2771402

H 4.4664803 -1.4674455 0.3960585

H 3.248284 -0.701756 1.0545301

O -2.7217146 -3.7168872 0.9990817

H -2.7612226 -4.2627368 0.1971092

H -3.232603 -2.8672672 0.7731609

O -1.7409333 4.659643 0.0393724

H -0.7600115 4.3987286 0.1158042

H -1.9819952 5.0660236 0.8860542

^{1}RC (E.S. geometry)

(E.S.) BP86: -2070.966545925

Ti -11.7294182 2.1294284 -1.0825951

O -11.5256781 2.2432969 0.9309065

O -12.7199688 3.6649186 -0.3567331

O -10.106845 2.1945991 -1.9317864

O -13.0501928 1.0880011 -1.917891

H -13.3881179 3.8691766 0.4171922

H -9.6244765 3.000122 -2.3238876

H -12.9251664 0.3506069 -2.5980028

H -12.22649 1.6467413 1.3473056

O -12.0438841 3.9275797 3.1164118

H -11.9736362 3.3206761 3.8717797

H -11.6290174 3.4374296 2.3608334

O -13.1038738 5.5582304 -2.3112179

H -13.9080725 5.0850556 -2.6488581

H -12.860284 5.0601244 -1.4918681

O -8.6519859 0.0426617 -2.6510767

H -9.1772251 0.8487798 -2.3574827

H -8.0057723 0.3787644 -3.2930988

O -15.5005727 1.7041805 -1.5515684

H -14.5100853 1.4089984 -1.7071832

H -16.0464289 1.0252518 -1.9831934

O -14.3018062 4.1939426 1.5999035

H -13.6390029 4.1261247 2.3416038

H -14.8950975 3.4114307 1.6570465

O -13.4038877 0.6025253 2.0445841

H -13.2999363 -0.2974317 1.6933519

H -14.3029427 0.9050497 1.7439107

O -8.9395568 4.2794683 -3.0229111

H -9.6793865 4.8934722 -3.3379626

H -8.4161027 4.8126548 -2.4025905

O -12.7743882 -0.8918537 -3.6707374

H -12.8536093 -0.6237729 -4.6005968

H -11.8463785 -1.2866087 -3.598617

O -15.3131855 4.0495968 -3.1791092

H -15.1088676 3.6429462 -4.0370789

H -15.4349206 3.2822158 -2.565435

O -15.7119222 1.7554379 1.1217388

H -16.6239461 1.5862013 1.4076084

H -15.7125604 1.7473276 0.1109847

O -10.2972259 -1.8422328 -3.5470424

H -10.140639 -2.6164454 -2.9833701

H -9.6517107 -1.1349731 -3.2249797

O -10.8990949 5.9089501 -3.7509114

H -11.7656476 5.7748747 -3.2465179

H -11.1373427 5.987533 -4.6873994

[1]PC1 (E.S. geometry)

BP86: -2070.95711932

Ti 0.6353292 -0.1343987 -0.2979544

O 1.6101306 -1.5496752 0.5555496

O 0.7895829 1.0301856 1.3589016

O 1.3135926 0.1053327 -2.0213027

O -1.2799513 -0.0616049 -0.4121139

H 0.7881453 0.6523378 2.3487189

H 1.556467 1.0057651 -2.3907056

H -1.7991593 -0.5071929 -1.1488306

H 1.0570342 -2.3411049 0.7930763

O 3.0209842 -1.3553084 2.8038262

H 3.2659775 -2.2540321 3.0773584

H 2.6313064 -1.4506083 1.8771093

O -0.0759746 3.3830202 1.0938744

H -1.004964 3.3003743 1.4933769

H 0.6116556 2.0392178 1.3646968

O 1.2134172 -1.6913012 -3.9854538

H 1.2948534 -1.01203 -3.2406526

H 1.5046939 -1.2313868 -4.7890752

O -2.7130823 0.1454896 1.611767

H -2.1066004 0.0548051 0.7146251

H -3.5989116 -0.1639479 1.3565315

O 0.8797113 -0.0091193 3.6552342

H 1.7037271 -0.5723822 3.5155264

H 0.1126583 -0.6326372 3.6502783

O -0.1819147 -3.4668907 1.5354344

H -0.8248012 -3.7679431 0.8726701

H -0.6937359 -2.8727168 2.1410201

O 1.8695881 2.598018 -2.9172297

H 1.3101184 3.2179391 -2.3669026

H 2.7855639 2.8807956 -2.7621123

O -2.7667243 -1.2816741 -2.2950891

H -3.2198717 -0.6472155 -2.8739854

H -2.2008149 -1.8346322 -2.9236263

O -2.5245479 2.8405158 2.0436871

H -3.2719463 3.2451584 1.5743306

H -2.6394789 1.8512669 1.9310349

O -1.4344772 -1.5811116 3.2023815

H -1.9789861 -1.8263238 3.968268

H -1.9812601 -0.9267072 2.6557783

O -1.2572572 -2.6423051 -4.0119369

H -1.1643655 -3.5998748 -3.8861352

H -0.3124994 -2.2790515 -4.0349887

O 0.3236759 4.2647651 -1.4159603

H 0.1353626 3.9846859 -0.4710377

H -0.5426256 4.4388841 -1.8181186

4.8.2 Intermediates of the H_2 formation reaction.

^{1}RC (G.S. geometry)

B3LYP-D3: -4141.694131806

Ti 0.0830695 -0.5628762 -2.5430944

O -1.0280617 -2.147581 -1.8451465

O -0.6715571 1.0417062 -2.0554645

O 1.9160996 -0.8320643 -2.2698995

O -0.5037284 -1.0016301 -4.3664686

H -1.6120351 1.1276884 -1.7987148

H 2.654997 -0.20196 -2.408049

H 0.1434867 -0.6730614 -5.0266342

H -1.6041763 -2.6172507 -2.5164726

O -2.440753 -1.4817646 0.3063498

H -2.8837676 -2.023917 0.9715517

H -1.5201286 -2.0686847 -0.989421

O 0.3529749 3.0377466 -3.7586243

H -0.1698848 2.8738477 -4.5759829

H -0.0388507 2.4605552 -3.0716423

O 3.7714491 -1.9198188 -4.2291448

H 2.9991518 -1.9124384 -3.6378932

H 4.2636867 -1.1348282 -3.9419727

O -2.5708806 0.110533 -5.538886

H -1.7731203 -0.290994 -5.0645212

H -2.6333447 -0.3579084 -6.379144

O -3.380749 0.6292887 -1.339601

H -3.2406842 -0.1534367 -0.7730709

H -3.8163979 0.2855387 -2.1421756

O -2.42507 -2.9486651 -3.9258795

H -1.7450964 -2.4130297 -4.3866045

H -3.2054587 -2.3711975 -3.8696169

O 4.0990026 0.6989807 -2.9843961

H 3.682396 1.3761354 -3.5714467

H 4.6325031 1.1674715 -2.3351177

O 1.2638419 0.297566 -6.1227468

H 1.8585348 0.9004632 -5.6373816

H 1.8507831 -0.3675026 -6.5483442

O -0.7773693 2.288636 -6.1753462

H -0.1051013 1.6263442 -6.4184477

H -1.571649 1.7588467 -5.9975491

O -4.3226495 -0.6842484 -3.6681694

H -5.2545207 -0.6623948 -3.9084684

H -3.8184919 -0.2832441 -4.4191986

O 3.0738229 -1.6077927 -6.8521936

H 2.8939697 -2.4551634 -7.2697151

H 3.3655615 -1.8059912 -5.9308251

O 2.6730349 2.2768307 -4.6156793

H 1.8098647 2.6283724 -4.2150039

H 3.0302844 2.9800925 -5.1676983

H -1.9564565 -0.7932881 0.8457717

Ti 0.2009533 0.4642218 2.6092447

O 0.448102 -1.5529767 1.9802057

O 1.9452341 0.9439986 2.0860667

O -1.5330939 0.4833424 1.8333904

O -0.1140795 -0.1238003 4.4579212

H 2.7192903 0.5135534 2.5080023

H -2.1562448 1.1941047 1.534616

H -0.7962053 0.271651 5.0160068

H 0.4865606 -2.2269576 2.6970771

O 2.5403391 -1.2599786 0.3923044

H 2.3752763 -1.2726438 -0.575607

H 1.1968498 -1.6851317 1.3411131

O 0.1894464 2.6172664 3.3404378

H 0.2693664 2.6825694 4.3311305

H 1.0687701 2.827576 2.9861758

O -3.2097856 -1.1583934 3.3063624

H -2.6012925 -0.505691 2.8865254

H -4.0712949 -0.7278939 3.3234063

O 1.5495692 0.0628447 6.490238

H 1.0432934 -0.0064101 5.6331516

H 0.8533923 -0.1968409 7.1226524

O 3.9164067 -0.8149006 3.0240462

H 3.7983904 -1.4108475 2.2720266

H 3.6424429 -1.3040058 3.8208275

O 0.3633785 -2.7697408 4.4150233

H 0.1276079 -1.8215248 4.5713527

H 1.2480081 -2.8598161 4.8067908

O -3.3779176 2.2418664 1.001337

H -2.8920571 3.0857821 1.0500423

H -3.5057797 2.0065221 0.0675049

O -1.1297595 -0.3311721 7.2965793

H -1.6392886 -0.3064413 8.1121459

H -1.5299709 -1.0612825 6.7561449

O 0.5408814 2.674632 6.0160552

H -0.235656 2.6692035 6.5869759

H 1.0524571 1.8803476 6.2797599

O 2.9799819 -2.0346392 5.4616543

H 3.6505652 -2.4555246 6.0090913

H 2.6133975 -1.2829404 5.9850702

O -2.2013059 -2.2657665 5.7149759

H -1.4785796 -2.8331416 5.4038726

H -2.593512 -1.8945864 4.8977437

O -1.5709895 4.2230551 1.7213854

H -1.0177481 3.7117624 2.3382061

H -1.7103577 5.0827242 2.1291362

H 2.452745 -0.3245967 0.6589567

^{1}IN1 (G.S. geometry)

B3LYP-D3: -4141.745893772

Ti 0.1083221 -0.9979986 -2.24721

O -1.0607635 -2.7195958 -1.7702385

O -0.837799 -0.2894737 -0.6074639

O 1.906898 -1.3889986 -2.2321578

O -0.437931 -0.0393156 -3.7827659

H -1.8124005 -0.2769074 -0.741699

H 2.6431603 -0.8906148 -1.8045436

H 0.2809301 0.5583506 -4.1076848

H -1.581136 -2.9842484 -2.5602063

O -2.8177845 -2.6927414 0.3494636

H -2.9555619 -3.4957698 0.8613437

H -1.6424637 -2.7649655 -0.9717092

O 0.1284398 2.4438506 -1.1234878

H -0.304682 2.8595692 -1.915677

H -0.0739043 1.4881008 -1.1887928

O 4.0573763 -1.0159316 -4.0800174

H 3.2199669 -1.3596971 -3.7191494

H 4.4906601 -0.6540052 -3.2904318

O -2.5143077 1.2668245 -4.6280228

H -1.7152486 0.7312081 -4.3161019

H -2.4039463 1.3847694 -5.5781358

O -3.6297419 -0.5165428 -1.1328528

H -3.698802 -1.4145777 -0.7644946

H -3.9329038 -0.555981 -2.0606516

O -2.2840895 -2.6195781 -4.2298367

H -1.5973954 -2.0221957 -4.5611896

H -3.0812901 -2.0621151 -4.1679325

O 4.068922 0.0281599 -1.3368127

H 3.6914593 0.9267951 -1.3843701

H 4.2992547 -0.1460293 -0.4050453

O 1.453673 1.8624675 -4.4164338

H 1.9987947 2.0194812 -3.6213537

H 2.0956233 1.5835544 -5.1117076

O -0.7670179 3.3749136 -3.492731

H -0.0304355 3.024503 -4.0283102

H -1.5503763 2.8898928 -3.7985868

O -4.2739287 -0.5966969 -3.844776

H -5.1839465 -0.5067861 -4.1446501

H -3.7630981 0.1779657 -4.1941303

O 3.4445672 0.8612021 -5.9423247

H 3.446393 0.4695861 -6.8202926

H 3.7381588 0.1544364 -5.3155954

O 2.7214554 2.4166767 -1.901675

H 1.8333268 2.4768607 -1.4706843

H 3.1204802 3.2912137 -1.8418669

H -2.5545511 -1.9830949 1.0036308

Ti -0.3852756 -0.1383827 1.391131

O -0.0701884 -2.2822757 1.7804226

O 1.4227365 -0.0021014 0.8099848

O -2.2312809 -0.5257274 1.821255

O 0.1183454 0.1846391 3.3038246

H 2.2719215 0.2032298 1.2181757

H -3.0410038 0.0064566 1.6243661

H -0.6189085 0.3975516 3.8891203

H 0.2638142 -2.425361 2.6953096

O 2.154267 -2.5955125 0.3067305

H 2.1814877 -2.7751026 -0.6452377

H 0.6232553 -2.6723055 1.1998919

O -0.7491662 1.9998498 1.3332251

H -0.3457218 2.4788932 2.1119518

H -0.4143925 2.4053215 0.4934107

O -2.6761574 -0.6467904 4.4776976

H -2.5221443 -0.7032956 3.4997917

H -3.5617009 -0.2862303 4.5818516

O 2.3171727 1.3818271 4.1597572

H 1.4999084 0.957222 3.7674914

H 1.9952024 1.650549 5.035602

O 4.2805146 -0.9278703 1.3103115

H 3.8403136 -1.768093 1.1053638

H 4.2918816 -0.873796 2.2848273

O 1.0684444 -2.0425066 4.335284

H 0.7798354 -1.1493167 4.0017537

H 2.0378963 -1.9955258 4.3292352

O -4.5330229 0.792819 1.2070822

H -4.3093512 1.742631 1.2439193

H -4.4689504 0.5357673 0.2716483

O 0.1761245 1.9643886 5.9632365

H -0.0111102 2.4341881 6.7817292

H -0.1057239 1.0206637 6.1150522

O 0.252927 3.3317362 3.4305294

H -0.0128598 2.9194926 4.2759874

H 1.2023277 3.136306 3.4006809

O 3.8082956 -0.858171 4.0769021

H 4.5075141 -0.9029487 4.7365909

H 3.3602883 0.0201565 4.1905385

O -0.5916009 -0.5917165 6.2837377

H 0.0319101 -1.2488843 5.9304562

H -1.4073275 -0.7137117 5.7542583

O -3.301725 3.2695123 1.3098485

H -2.4215662 2.8515693 1.3568428

H -3.3098799 3.9554644 1.9842568

H 1.9603818 -1.6264136 0.3470741

^{1}IN2 (G.S. geometry)

B3LYP-D3: -4141.805845031

Ti -0.1999327 -1.3715932 -2.0368604

O 0.0387469 -3.157054 -2.393204

O -0.945587 0.1291942 -0.8443582

O 1.5775995 -1.0078204 -2.0296754

O -0.6444966 -0.4111498 -3.6030148

H -1.9155257 0.206243 -0.7424463

H 2.1966053 -0.2642911 -1.8442112

H 0.0328446 0.2559674 -3.8626223

H -0.7230438 -3.7409494 -2.4658043

O -3.3766017 -2.5984688 0.3097406

H -3.7075415 -3.3766862 0.7657686

H -0.0840438 -1.7644287 -0.1661044

O -0.2342801 2.6669214 -1.2603943

H -0.728217 2.9958383 -2.0499526

H -0.4035547 1.6915148 -1.266795

O 3.6379713 -1.0571693 -4.0908736

H 2.8269972 -1.4051134 -3.6874887

H 3.966823 -0.4503137 -3.4038961

O -2.7089718 0.8057191 -4.5569051

H -1.9100434 0.2809863 -4.2108124

H -2.6865152 0.7332331 -5.5168336

O -3.9043449 0.1321449 -0.3215325

H -3.9663228 -0.8123856 -0.0918857

H -4.3187959 0.1875554 -1.1990086

O -2.3284246 -2.047933 -2.0467442

H -2.7031665 -2.4082724 -1.2039937

H -3.0433827 -1.5206924 -2.4562131

O 3.7205811 0.6515441 -1.8032007

H 3.3777877 1.5675811 -1.8077606

H 4.0907856 0.4629503 -0.9231683

O 1.0273994 1.6630547 -4.3999744

H 1.6080151 2.0659015 -3.7284026

H 1.6159374 1.3478734 -5.124898

O -1.2556087 3.1965589 -3.7489372

H -0.4743508 2.8070704 -4.1865268

H -1.9690142 2.5767154 -3.974573

O -4.4412936 -0.4595946 -3.0140939

H -5.2073597 -0.8432683 -3.4512008

H -3.9450858 0.0744238 -3.6879396

O 2.8299359 0.5740015 -6.1140138

H 2.6395077 0.0859408 -6.9203963

H 3.1924766 -0.0791001 -5.4671685

O 2.2650341 2.9284235 -2.1590668

H 1.3817403 2.8846014 -1.6998844

H 2.5026538 3.8578677 -2.2310899

H -2.7144384 -2.1151764 0.9202661

Ti -0.1101577 -0.4162451 1.0262559

O 0.8225171 -2.2753341 1.7397556

O 1.4889869 0.2506253 0.5575229

O -1.8527477 -1.0798757 1.6321878

O 0.264033 0.0569797 2.9533345

H 2.4556807 0.1387718 0.6397558

H -2.4827299 -0.3676177 1.8778133

H -0.5155884 -0.0151253 3.5194539

H 1.2917923 -2.216429 2.6021124

O 2.7410573 -2.7651235 -0.219806

H 2.8806491 -3.6291112 -0.6219984

H 1.4544082 -2.629832 1.0802002

O -0.970904 1.6547717 1.2401671

H -0.6937854 2.0702177 2.0830399

H -0.7217869 2.2484561 0.5034473

O -2.1998881 -1.2478043 4.3504765

H -1.9880193 -1.4884808 3.4232843

H -2.9790182 -0.6825008 4.2564709

O 2.1938085 1.8069419 3.6682381

H 1.475821 1.2551749 3.2619367

H 1.8913033 1.8722669 4.590273

O 4.1476287 -0.4709708 0.7267111

H 3.9358213 -1.4066937 0.5647923

H 4.3164198 -0.3524929 1.684515

O 1.9122196 -1.5894233 4.166537

H 1.3609085 -0.8559607 3.7724624

H 2.8277639 -1.2692572 4.1204788

O -3.8730551 0.6420057 2.5446731

H -3.6394987 1.5784865 2.7110815

H -4.2542646 0.648169 1.6522204

O 0.3309382 1.7564706 5.8377921

H 0.2138778 2.1609401 6.7030687

H 0.1638014 0.7749958 5.9604755

O -0.4745454 3.1476087 3.5853708

H -0.3482035 2.61712 4.4036659

H 0.4086726 3.4914578 3.3986716

O 4.204468 0.0518609 3.444987

H 4.9977973 0.3161822 3.921134

H 3.5473013 0.7960998 3.5368265

O -0.0718868 -0.8416035 6.1098111

H 0.6709968 -1.3085088 5.6876889

H -0.8678676 -1.093949 5.5985405

O -3.1440703 3.3675036 2.601564

H -2.8843438 3.2931285 1.6750091

H -2.2999112 3.4987375 3.0671396

H 2.3126294 -2.218288 -0.9196211

^{1}PC (G.S. geometry)

B3LYP-D3: -4141.862071568

Ti -0.2904284 -0.6075144 -2.2833354

O 0.7398288 -2.1678651 -2.6423586

O -0.9988805 -0.1596376 -0.5500712

O 1.1330002 0.3924038 -2.1799231

O -1.1343402 0.1968471 -3.6989939

H -1.9821471 -0.1288335 -0.5209194

H 2.0811719 0.6803487 -2.2447527

H -0.5550082 0.8983043 -4.1500268

H 0.2262439 -2.9529043 -2.8667692

O -1.7544781 -3.2385446 0.1386289

H -0.7973918 -3.2751221 0.299102

H 0.6761214 -4.987299 -0.5898366

O 0.0425366 2.9000054 -0.5780714

H -0.7428336 2.6602494 -1.1238558

H 0.4908771 2.0644073 -0.3093661

O 3.1192439 -1.2126255 -4.0400262

H 2.2839237 -1.5173437 -3.6387055

H 3.4171443 -0.4635052 -3.4966026

O -3.5770522 0.0584455 -4.7572388

H -2.6329375 0.094679 -4.4542112

H -3.5611394 -0.1268833 -5.700465

O -3.6828994 0.3667621 -0.6901719

H -4.1219619 0.5116553 0.1659938

H -4.2326628 -0.2015549 -1.2600432

O -1.9079621 -2.1272418 -2.2547777

H -1.915844 -2.6013089 -1.368335

H -2.8398829 -1.9199331 -2.4721743

O 3.6306 1.1494123 -2.3353143

H 3.3544375 2.0834766 -2.364749

H 3.8662857 0.9067125 -1.4126663

O 0.4060858 2.017284 -4.770218

H 0.8992382 2.4736505 -4.0641745

H 1.0780944 1.5256232 -5.2918582

O -2.2679064 2.4649862 -2.020783

H -2.071412 1.9914651 -2.8407315

H -2.8772592 1.8700341 -1.5464752

O -4.5301813 -1.3085866 -2.7266697

H -5.2607429 -1.9147852 -2.8804463

H -4.3497161 -0.8190704 -3.5746984

O 2.2820868 0.4664529 -6.0692737

H 2.1493872 0.0291454 -6.9150098

H 2.6144271 -0.2173989 -5.445075

O 1.8628318 3.3562416 -2.5815044

H 1.2190118 3.2830585 -1.8313054

H 1.9954416 4.298402 -2.7282598

H -2.0265726 -2.5375361 0.7726577

Ti -0.1438872 -0.3410285 1.3837221

O 0.7004176 -1.9181059 1.02104

O 1.2063608 0.8744591 0.822764

O -1.9053608 -1.0410404 1.8469892

O 0.3031926 -0.1169874 3.182602

H 2.0148308 0.4723962 0.4354266

H -2.698924 -0.4822902 1.8255313

H -0.3414995 -0.4890256 3.8131284

H 1.3943833 -2.2512776 1.6163335

O 3.1128437 -2.5126192 -1.1850396

H 3.6283272 -2.5762389 -1.9995274

H 1.2124427 -4.4644365 -0.5514919

O -1.2199605 1.8076856 1.6735149

H -0.9335356 2.0966847 2.5648564

H -0.8330582 2.4261188 1.014807

O -1.7465328 -1.4276736 4.6018182

H -1.9196586 -1.5607149 3.6435779

H -2.3547968 -0.7109272 4.8508858

O 2.6033338 1.772273 3.1127314

H 2.0331558 1.5728052 2.3384356

H 2.0834406 1.4940714 3.885701

O 3.6668011 -0.1426156 0.029083

H 3.5212017 -1.0580631 -0.3090468

H 4.112431 -0.1988084 0.8972815

O 2.3843096 -1.8736676 3.4920304

H 1.7675225 -1.1163728 3.3957287

H 3.2637969 -1.4931467 3.3283776

O -3.8815213 1.0974292 1.9486969

H -3.9891638 1.0617524 2.9128946

H -3.0286543 1.5580403 1.8150755

O 1.1803519 1.1623817 5.624675

H 1.5707707 1.4795181 6.445222

H 1.0645982 0.1751862 5.7294737

O -0.8653054 2.4550606 4.3878621

H -0.1173335 1.9636247 4.8155586

H -0.7275091 3.3863622 4.5916649

O 4.4746642 -0.0634274 2.6907455

H 5.3493537 0.1665133 3.0178095

H 3.8632808 0.6960834 2.9113814

O 0.8714976 -1.487194 5.8985337

H 1.4836886 -1.8844741 5.2504778

H -0.0238036 -1.7169821 5.5932471

O -3.2254503 1.051758 4.7737727

H -3.731679 1.3522344 5.5353967

H -2.43273 1.6295636 4.7165837

H 2.1897587 -2.4379583 -1.5012898

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