Experimental and theoretical studies of H_2O oxidation by neutral $Ti_2O_{4,5}$ clusters under visible light irradiation

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Table SI-1. Cartesian Coordinates for Optimized Geometries (Å), Total Energies at 0 K (E_{0K}, a.u.) and Zero Point Correction Energies (ZPCE, a.u.) at B3LYP/TZVP Level. For the conical intersection $(S_1/S_0)_{CI}$, Calculations Are at CASSCF(10, 7)/6-31g(d) Level, and Its Cartesian Coordinates for Optimized Geometries (Å) and Eigenvalues of CI Matrix of Ground State and First Excited State Are Given.

Figure 3. $Ti_2O_5 + H_2O \rightarrow Ti_2O_4 + H_2O_2$

$^1Ti_2O_5$ E_{0K} = -2075.40787183; ZPCE = 0.016773

Ti	-1.35732300	0.20716700	-0.03670000
O	-1.22325500	2.03157100	0.16692300
O	0.47113000	0.19081700	0.17004100
Ti	0.63725400	2.04528800	0.31816600
O	-2.58957400	-0.92813500	-0.80104500
O	-2.58838900	-0.92358200	0.67226700
O	1.36354300	2.71412200	-0.96998600

^1H_2O E_{0K} = -76.4606225962; ZPCE = 0.021187

O	-0.04155000	0.02668600	0.00000000
H	0.92028000	0.06430400	0.00000000
H	-0.32716000	0.94591000	0.00000000

G1 E_{0K} = -2151.92133134; ZPCE = 0.041470

Ti	-1.46922700	0.11753500	-0.14661500
O	-1.32338400	1.94107700	-0.23831100
O	0.30420300	0.10601100	0.30799700
Ti	0.51613400	1.97738800	0.17882700
O	-2.64058900	-1.12943700	-0.84719500
O	-2.81712400	-0.85738100	0.59468900
O	1.48290800	2.47277000	-1.03994300
O	1.23750200	3.11762200	1.84212900
H	1.97076200	3.72852300	1.69405300
H	0.96462500	3.16710500	2.76581200

G1/G2 E_{0K} = -2151.89661603; ZPCE = 0.041934

Ti	-1.00315700	-0.29766400	-0.00000400
O	0.32565200	-0.35046300	-1.27300300
O	0.32565100	-0.35050400	1.27299400
Ti	1.63698700	0.07024200	0.00000500
O	-2.68861700	-1.02509600	-0.00000400
O	-2.68902100	0.44510600	0.00000500

O	3.02957000	-0.77312800	-0.00000800
O	0.01575600	2.04178300	0.00001300
H	-0.24809300	2.55084100	-0.77935500
H	-0.24810400	2.55086500	0.77936100

G2 E_{0K} = -2151.90350059; ZPCE = 0.042052

Ti	-1.26856100	0.07402700	-0.11413400
O	-0.70591500	1.46034400	0.97112800
O	0.30332700	0.39108200	-1.06100300
Ti	0.83073600	1.83149900	-0.00426100
O	-2.90109500	0.22861000	-0.89560400
O	-2.77349600	-1.05291400	-0.20986700
O	0.82950000	3.27138000	-0.76304700
O	-0.37791000	-1.70698700	0.81802800
H	0.39338000	-2.05732700	0.35475500
H	-1.02664700	-2.42074500	0.89168400

G2/G3 E_{0K} = -2151.88865566; ZPCE = 0.038224

Ti	0.78116400	-0.00972900	0.07663100
O	-0.58464800	-0.33724000	1.24707100
O	-0.52917200	0.67804900	-1.02783700
Ti	-1.93272900	0.32262600	0.13742200
O	1.74766700	-1.33120800	-0.73775800
O	2.62788800	-0.82008600	0.32159000
O	-2.96408900	-0.80936900	-0.39976500
O	2.21797300	1.43619800	0.07168800
H	2.38183700	2.14352800	-0.56021700
H	2.82763400	0.44197400	0.05114500

G3 E_{0K} = -2151.92424059; ZPCE = 0.041390

Ti	0.85248900	0.26287500	-0.18491900
O	-0.40305800	0.01058100	1.14912100
O	-0.58319700	0.59444200	-1.26033200
Ti	-1.86832600	0.31395800	0.06747200
O	1.76919400	-1.26159500	-0.82328000
O	2.47394700	-1.11291500	0.45914400
O	-2.82429300	-0.98179300	-0.15381000
O	1.93406200	1.72981800	-0.06795800
H	1.84181000	2.68215500	-0.14094000
H	3.34173500	-0.77022900	0.18849700

G3/G4 E_{0K} = -2151.82097887; ZPCE = 0.039366

Ti	0.77487300	-0.17502400	-0.08965200
O	-0.60105500	0.07494100	1.11159000
O	-0.49723200	0.10139800	-1.38504100
Ti	-1.89736700	0.37892200	-0.18776100
O	1.47153300	-1.78689900	-0.12019400
O	2.73091200	-0.05637300	0.10290100
O	-3.09008700	-0.72335300	-0.24638700
O	2.03858900	1.70329800	-0.06695000
H	2.28839100	2.08715400	0.78779300
H	3.31580600	-0.13676800	-0.67330500

G4 E_{0K} = -2151.86143453; ZPCE = 0.042703

Ti	-0.69050400	0.44881300	0.05250300
O	0.64737000	-0.02489200	1.27652900
O	0.52151700	-0.14231000	-1.24542900
Ti	1.85377500	-0.56274600	-0.02589300
O	-1.13424500	2.02855500	-0.01844500
O	-2.74833200	-0.21094300	0.25372600
O	3.23177900	0.30668600	-0.13583500
O	-3.16211300	-1.54850300	-0.12967800
H	-3.51820400	-1.87332300	0.71451500
H	-3.39201000	0.38222800	-0.16913500

G4/G5 E_{0K} = -2151.85259661; ZPCE = 0.041957

Ti	-0.71964300	0.46364900	0.02667200
O	0.61416700	0.00206000	1.28078700
O	0.52807800	-0.08499700	-1.27702400
Ti	1.84827300	-0.48232800	-0.02558900
O	-1.07028600	2.06168000	-0.03150000
O	-2.77490300	-0.20255700	0.24405200
O	3.45779400	-0.84662900	-0.05852500
O	-3.12957900	-1.55907800	-0.12789100
H	-3.43299100	-1.90658000	0.72832600
H	-3.46456400	0.35214700	-0.15730900

G5 E_{0K} = -2151.87059193; ZPCE = 0.042637

Ti	-0.71004700	0.55896300	-0.01222100
O	0.54357700	0.01577100	1.26364700
O	0.53924200	-0.06747900	-1.25371400
Ti	1.75687100	-0.61884000	0.02114800

O	-1.03037700	2.16808200	-0.06709600
O	-2.72856700	-0.18899100	0.24354200
O	1.99263700	-2.23729100	0.08009800
O	-3.00854900	-1.55250300	-0.16588100
H	-3.06317300	-1.99065800	0.70071100
H	-3.49767000	0.31533700	-0.06590900

$^1Ti_2O_4$ E_{0K} = -2000.21758572; ZPCE = 0.014185

Ti	-1.44338000	0.09794800	-0.02914900
O	-1.32271600	1.94243700	0.11229100
O	0.39713900	0.11944100	0.19362600
Ti	0.51761500	1.96399000	0.33445900
O	-2.25098300	-0.60805200	1.19901800
O	1.32321900	2.66895200	-0.89566900

$^1H_2O_2$ E_{0K} = -151.611797192; ZPCE =0.026267

O	-0.12571200	-0.05227000	-0.12707000
H	0.72452900	-0.07836400	-0.58864200
O	-0.37354200	1.38454100	-0.12704600
H	-1.22369800	1.41066500	-0.58877200

E1 E_{0K} = -2151.85554739; ZPCE = 0.041489

Ti	-1.42767300	0.17352700	-0.08807700
O	-1.29693500	1.96153600	-0.23797700
O	0.32674300	0.12795900	0.30420200
Ti	0.56185700	2.00560800	0.14463800
O	-2.72075500	-1.18472400	-0.79682400
O	-2.93069600	-0.97808400	0.53334100
O	1.53523100	2.50996000	-1.06414100
O	1.24874000	3.12750200	1.83656100
H	1.98014600	3.74851900	1.72620100
H	0.94915100	3.14941000	2.75352000

E1/E2 E_{0K} = -2151.83366848; ZPCE = 0.041633

Ti	-0.97534300	-0.31665100	-0.01249800
O	0.16932400	-0.17576700	-1.30319100
O	0.17833200	-0.44147600	1.27392800
Ti	1.71356600	0.03400700	0.03464300
O	-2.84905800	-0.92120200	-0.05567000
O	-2.79505600	0.45289100	0.04553900
O	2.97153700	-0.98039100	-0.08681700

O	0.26866600	2.16558500	0.06705300
H	0.07582800	2.59769000	-0.77676800
H	0.13329900	2.82334800	0.76284600

E2 E_{0K} = -2151.85354884; ZPCE = 0.042280

Ti	0.89874800	-0.10374100	0.06816500
O	-0.31471700	-0.01633600	1.32078800
O	-0.24715500	0.36809400	-1.19304300
Ti	-1.78337600	0.40475800	0.04613700
O	1.77201000	-1.82292100	-0.16455100
O	2.74246600	-0.90096800	0.15827700
O	-3.00368500	-0.64595400	-0.15825200
O	1.99835000	1.72867900	0.01992300
H	1.67359700	2.47829700	-0.49403700
H	2.96086300	1.68524700	-0.04980400

E2/E3 E_{0K} = -2151.82922208; ZPCE = 0.040438

Ti	0.69178900	0.04028400	0.02989100
O	-0.51850700	0.13884900	1.28327800
O	-0.46701700	0.30164300	-1.24207500
Ti	-2.02219100	0.30563500	0.00824900
O	1.83837400	-1.49432300	-0.06213300
O	3.04596100	-0.77762500	-0.02753500
O	-3.02117400	-0.96104200	-0.07837900
O	2.13398100	1.47114900	0.06905100
H	2.35030200	2.30493900	-0.35920500
H	2.82558400	0.65564600	-0.01753900

E3/E4 E_{0K} = -2151.78242914; ZPCE = 0.037991

Ti	0.87764500	-0.17853300	-0.00361000
O	-0.48811500	-0.01096700	1.24104200
O	-0.49559200	-0.13354300	-1.24271800
Ti	-1.83080900	0.04244400	-0.00020100
O	1.70602900	-1.73054900	0.04129600
O	2.82916600	0.04109900	0.12602800
O	-3.65370300	0.19419800	0.00372100
O	2.01707600	1.74060500	-0.15653600
H	2.25089000	2.24048500	0.64108000
H	3.39984200	-0.05326000	-0.65990300

E4 E_{0K} = -2151.79296851; ZPCE = 0.041533

Ti	-0.83258400	0.65626300	0.00424300
O	0.54569300	0.27988600	1.23966900
O	0.49279500	0.22340000	-1.26968800
Ti	1.78051700	-0.10769400	-0.03458100
O	-1.38295100	2.19659000	-0.02955100
O	-2.78420900	-0.25617500	0.23514800
O	3.51724800	-0.72277700	-0.05453600
O	-2.99270700	-1.64250100	-0.13704100
H	-3.17505700	-2.03687200	0.73312600
H	-3.55971000	0.21344500	-0.11393100

$^1Ti_2O_4$* E_{0K} = -2000.11712627; ZPCE = 0.014224

Ti	-0.07141300	-0.39784600	-0.08641400
O	-0.05926400	0.33419900	1.84060900
O	1.85680200	0.33083500	0.10300700
Ti	1.62965200	0.69270500	1.77481300
O	-0.67646100	-1.76492300	-0.71973300
O	2.85998700	0.80783000	3.12245000

$(S_1/S_0)_{CI}$

Ti	0.36577900	-0.37736300	-0.18413200
O	-0.17580000	0.08787700	1.47937800
O	2.02239900	-0.26600200	0.47933800
Ti	1.51132300	0.20912100	2.18809000
O	0.19772000	0.92403800	-1.52716600
O	-2.03444400	-0.01559800	-0.92621200
O	2.03145700	1.51691800	2.90579600
O	0.04024700	-2.09886600	-0.61651900
H	-0.80524300	-2.49601800	-0.77764200
H	-2.14811200	0.62674800	-1.63102000

EIGENVALUES OF CI MATRIX

(1) EIGENVALUE -2147.1979951205

(2) EIGENVALUE -2147.1978220682

Table SI-2. Cartesian Coordinates for Optimized Geometries (Å), Total Energies at 0 K (E_{0K}, a.u.) and Zero Point Correction Energies (ZPCE, a.u.) at B3LYP/TZVP Level.

(1) $^1Ti_2O_4 + {}^1N_2O \rightarrow {}^1Ti_2O_5 + {}^1N_2$ *(Figure 7)*

$^1Ti_2O_4$ E_{0K} =-2000.21758572; ZPCE =0.014185

Ti	-1.44338000	0.09794800	-0.02914900
O	-1.32271600	1.94243700	0.11229100
O	0.39713900	0.11944100	0.19362600
Ti	0.51761500	1.96399000	0.33445900
O	-2.25098300	-0.60805200	1.19901800
O	1.32321900	2.66895200	-0.89566900

^1N_2O E_{0K} = -184.730161419; ZPCE =0.011050

N	-0.61783900	-1.51417900	0.36945600
N	0.50461300	-1.51418000	0.36945700
O	-1.80265700	-1.51418000	0.36945700

G6 E_{0K} = -2184.97086582; ZPCE = 0.026344

Ti	-1.69427600	-0.24184700	0.09602000
O	-1.64583500	1.55165300	-0.42925600
O	0.16754400	-0.08640600	0.16226200
Ti	0.19916100	1.66296500	-0.41726700
O	-2.45473600	-0.56899400	1.50403800
O	0.81653200	1.81759000	-1.92565200
O	-2.39612500	-1.12057700	-1.85638700
N	-2.24875000	-0.58397600	-2.92501300
N	-2.13382600	-0.11768400	-3.92774700

TS1 E_{0K} = -2184.91200741; ZPCE = 0.023064

Ti	-0.37403400	0.51222100	-0.00012000
O	0.95664800	0.21426000	-1.25329200
O	0.95652400	0.21406100	1.25324600
Ti	2.28735300	-0.10839900	0.00008000
O	-1.13640200	2.02135800	-0.00021600
O	2.82416900	-1.64729000	-0.00010200
O	-2.35901900	0.31334800	0.00069600
N	-3.22519100	-1.02307000	0.00038200
N	-4.20743400	-1.52121100	-0.00063400

$^1Ti_2O_5$ E_{0K} =-2075.40787183; ZPCE =0.016773

Ti	-1.35732300	0.20716700	-0.03670000
O	-1.22325500	2.03157100	0.16692300
O	0.47113000	0.19081700	0.17004100
Ti	0.63725400	2.04528800	0.31816600
O	-2.58957400	-0.92813500	-0.80104500
O	-2.58838900	-0.92358200	0.67226700
O	1.36354300	2.71412200	-0.96998600

$^1N_2$ E_{0K} = -109.567199391; ZPCE = 0.005610

N	-0.00986300	-2.07923600	0.44557300
N	-1.10237800	-2.07923600	0.44557300

(2) $^1Ti_2O_4 + {}^3O_3 \rightarrow {}^1Ti_2O_5 + {}^3O_2$ *(Figure 7)*

$^1Ti_2O_4$ E_{0K} =-2000.21758572; ZPCE =0.014185

Ti	-1.44338000	0.09794800	-0.02914900
O	-1.32271600	1.94243700	0.11229100
O	0.39713900	0.11944100	0.19362600
Ti	0.51761500	1.96399000	0.33445900
O	-2.25098300	-0.60805200	1.19901800
O	1.32321900	2.66895200	-0.89566900

$^3O_3$ E_{0K} = -225.464011856; ZPCE = 0.005005

O	-0.30476400	0.11790800	0.00000000
O	0.96064200	-0.18386400	0.00000000
O	-0.87329600	1.28803600	0.00000000

G8 E_{0K} = -2225.75972848; ZPCE =0.020773

Ti	-1.56893300	-0.04400400	-0.55459100
O	-1.42994700	1.77520200	-0.32979000
O	0.23229700	-0.06851400	-0.34180100
Ti	0.41342600	1.78731800	-0.13944200
O	-2.45935800	-0.83248500	0.87134300
O	1.18877800	2.50675100	-1.36829000
O	-2.21943700	-0.64199800	-2.17266200
O	-2.04739300	-1.10374100	-4.44544700
O	-1.34469600	-0.91293200	-3.46364500

TS3 E_{0K} = -2225.74876604; ZPCE =0.019485

Ti	0.29366000	0.90247800	0.00198200
O	-0.90630200	0.28199100	1.24828500

O	-0.92652500	0.33093100	-1.25086500
Ti	-2.13615100	-0.34974400	-0.00507900
O	0.96739500	2.59611200	-0.01355600
O	-2.23537000	-1.96949200	-0.03424300
O	2.11786600	0.67536000	0.00341000
O	3.50547700	-1.89977000	-0.28184300
O	2.54431100	-1.53514900	0.33732800

$^1Ti_2O_5$ E_{0K} =-2075.40787183; ZPCE =0.016773

Ti	-1.35732300	0.20716700	-0.03670000
O	-1.22325500	2.03157100	0.16692300
O	0.47113000	0.19081700	0.17004100
Ti	0.63725400	2.04528800	0.31816600
O	-2.58957400	-0.92813500	-0.80104500
O	-2.58838900	-0.92358200	0.67226700
O	1.36354300	2.71412200	-0.96998600

$^3O_2$ E_{0K} = -150.382045971; ZPCE = 0.003689

O	-0.04800900	0.09674900	0.00000000
O	-0.45126700	1.23551400	0.00000000

(3) $^1Ti_2O_4 + {}^1O_3 \rightarrow {}^1Ti_2O_5 + {}^1O_2$ *(Figure 7)*

$^1Ti_2O_4$ E_{0K} =-2000.21758572; ZPCE =0.014185

Ti	-1.44338000	0.09794800	-0.02914900
O	-1.32271600	1.94243700	0.11229100
O	0.39713900	0.11944100	0.19362600
Ti	0.51761500	1.96399000	0.33445900
O	-2.25098300	-0.60805200	1.19901800
O	1.32321900	2.66895200	-0.89566900

$^1O_3$ E_{0K} = -225.497982435; ZPCE = 0.007166

O	-0.34180900	0.07177500	0.00000000
O	0.90568600	-0.10181900	0.00000000
O	-0.78129400	1.25212500	0.00000000

G7 E_{0K} = -2225.74277525; ZPCE = 0.022315

Ti	-1.47549000	0.11379800	-0.65945200
O	-1.33601800	1.88300900	-0.10162600
O	0.36015400	0.06484000	-0.43227900
Ti	0.50097900	1.83435700	0.11420800

O	-2.31161000	-0.87621400	0.37881000
O	1.31562500	2.78340400	-0.93224000
O	-2.29670600	-0.45663700	-2.55426400
O	-2.29396800	-1.57633100	-4.40306400
O	-1.69823000	-1.30463000	-3.35441900

TS2 E_{0K} = -2225.70520441; ZPCE = 0.020860

Ti	-0.29963300	0.43769000	-0.04684500
O	1.19403800	0.67965400	-1.09132900
O	0.85371200	-0.26827800	1.19467100
Ti	2.37835900	-0.06659800	0.13928000
O	-1.26805600	1.81666600	0.37779300
O	2.99108100	-1.48585200	-0.35763500
O	-2.22495100	0.41866100	-0.32257800
O	-4.23550000	-1.06778700	0.00178000
O	-3.02682100	-1.11356600	-0.05689800

$^1Ti_2O_5$ E_{0K} =-2075.40787183; ZPCE =0.016773

Ti	-1.35732300	0.20716700	-0.03670000
O	-1.22325500	2.03157100	0.16692300
O	0.47113000	0.19081700	0.17004100
Ti	0.63725400	2.04528800	0.31816600
O	-2.58957400	-0.92813500	-0.80104500
O	-2.58838900	-0.92358200	0.67226700
O	1.36354300	2.71412200	-0.96998600

$^1O_2$ E_{0K} = -150.320270596; ZPCE = 0.003663

O	-0.04800300	0.09673200	0.00000000
O	-0.45127300	1.23553200	0.00000000