Molecular Structures and Energetics of the $(TiO_2)_n$ (n = 1−4) Clusters and Their Anions

Shenggang Li and David A. Dixon*,[1]

Chemistry Department, The University of Alabama, Shelby Hall, Box 870336,

Tuscaloosa, Alabama 35487-0336

Supporting Information Geometry parameters at different computational levels, relative energies for different structures of a given cluster at 0 K at the B3LYP/aD, BP86/aD, PW91/aD levels and at 298 K at the CCSD(T) level, electron detachment energies to the ground state and first triplet excited states of the neutral clusters at the B3LYP/aD, BP86/aD, PW91/aD levels, reorganization energies and adiabatic energy gaps at the B3LYP/aD, BP86/aD, PW91/aD levels, clustering energies at 0 K at the B3LYP/aD, BP86/aD, and PW91/aD levels and at 298 K at the CCSD(T) level, DFT atomization energies, heats of formation at 0 K and 298 K at the B3LYP/aD, BP86/aD, and PW91/aD levels, zero-point energies and electronic energies (E_e) at different computational levels calculated at the B3LYP/aD, BP86/aD, PW91/aD, CCSD(T)/aD, and CCSD(T)/aT optimized geometries, CCSD T_1 diagnostics, and Cartesian coordinates in Angstroms optimized at the B3LYP/aD, BP86/aD, PW91/aD, CCSD(T)/aD, and CCSD(T)/aT levels. Figure S1 showing structures of the rutile (a) and anatase (b) phases of bulk TiO_2 and Figure S2 showing additional high energy structures of $(TiO_2)_n^-$ (n = 2−4).

[1] Email: dadixon@bama.ua.edu

Table S1. Optimized bond lengths (Å) and bond angles (°) for $(TiO_2)_n$ and $(TiO_2)_n^-$ (n = 1, 2) at the CCSD(T), B3LYP, BP86, and PW91 levels.

	TiO_2 / TiO_2^- $^1A_1$ / $^2A_1$ (C_{2v})		Ti_2O_4 / $Ti_2O_4^-$ ^1A_g / ^2A_g (C_{2h})				Ti_2O_4 / $Ti_2O_4^-$ $^1A_1$ / $^2A_1$ (C_{2v} ***a***)				Ti_2O_4 / $Ti_2O_4^-$ $^1A_1$ / $^2A_1$ (C_{3v})			
	Ti=O	O=Ti=O	Ti=O	Ti−O	O=Ti−O	O−Ti−O	Ti=O	Ti−O	O=Ti−O	O−Ti−O	Ti=O	Ti−O	O=Ti−O	O−Ti−O
							$(TiO_2)_n$							
CCSD(T)/aT	1.666	112.4	1.648	1.863	114.9	85.9	1.645	1.870	116.9	86.0	1.632	2.006	133.9	77.2
												1.767		90.2
CCSD(T)/aD	1.672	112.9	1.653	1.868	115.5	86.1	1.650	1.876	117.5	86.2	1.654	2.020	133.7	77.5
												1.788		90.0
B3LYP/aD	1.645	112.1	1.630	1.849	114.6	85.4	1.628	1.856	116.3	85.6	1.632	2.003	133.8	77.3
												1.769		90.1
BP86/aD	1.656	110.6	1.643	1.853	113.0	85.6	1.641	1.859	114.3	85.8	1.647	2.005	133.4	78.0
												1.781		90.2
PW91/aD	1.654	110.4	1.642	1.850	112.7	85.6	1.639	1.857	114.0	85.7	1.645	2.002	133.4	78.0
												1.779		90.1
							$(TiO_2)_n^-$							
CCSD(T)/aT	1.696	114.3	1.694	1.889	129.1	88.7	1.683	1.883	125.1	88.3	1.679	1.974	131.8	80.5
												1.823		88.8
CCSD(T)/aD	1.702	114.9	1.700	1.897	130.1	89.1	1.689	1.889	125.5	88.5	1.684	1.982	131.8	80.5
												1.829		88.8
B3LYP/aD	1.679	113.9	1.675	1.873	125.8	87.9	1.670	1.873	125.4	88.5	1.673	1.970	130.8	81.9
												1.828		89.9
BP86/aD	1.688	112.0	1.682	1.876	122.3	87.6	1.679	1.876	122.6	88.4	1.686	1.977	130.7	82.1
												1.831		90.3
PW91/aD	1.685	111.8	1.680	1.873	121.9	87.5	1.677	1.874	122.4	88.3	1.684	1.974	130.7	82.0
												1.829		90.2

Table S2. Relative energies at 0 K (ΔE_{0K}, kcal/mol) for the low-lying states of $(TiO_2)_n$ and $(TiO_2)_n^-$ (n = 2−4) calculated at the B3LYP/aD, BP86/aD, and PW91/aD levels.

		B3LYP[a]	BP86	PW91
$(TiO_2)_n$				
Ti_2O_4	^1A_g (C_{2h})	0.0	0.0	0.0
	$^1A_1$ (C_{2v} ***a***)	5.7	6.1	6.2
	$^1A_1$ (C_{3v})	15.3	13.5	12.7
Ti_3O_6	$^1A'$ (C_s ***a***)	0.0	0.0	0.0
	^1A (C_2)	9.0	7.9	8.7
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	0.0	0.0	0.0
	^1A_g (C_{2h} ***a***)	5.2	4.4	4.5
	$^1A_1$ (C_{2v} ***b***)	9.7	10.9	11.4
$(TiO_2)_n^-$				
$Ti_2O_4^-$	$^2A_1$ (C_{2v} ***a***)	0.0	0.0	0.0
	^2A_g (C_{2h})	0.1	−0.3	−0.3
	$^2A_1$ (C_{3v})	8.2	8.3	7.4
$Ti_3O_6^-$	$^2A'$ (C_s ***a***)	0.0	0.0	0.0
	^2B (C_2)	30.6	22.6	23.4
$Ti_4O_8^-$	^2A_g (C_{2h} ***a***)	0.0	0.0	0.0
	$^2A_1$ (C_{2v} ***a***)	0.5	0.8	0.7
	$^2A_1$ (C_{2v} ***b***)	−4.2	−3.4	−3.3

[a] ZPEs from BP86/aD.

Table S3. Relative energies at 298 K (ΔH_{298K} and ΔG_{298K}, kcal/mol) for the low-lying states of $(TiO_2)_n$ and $(TiO_2)_n^-$ (n = 2−4) calculated at the CCSD(T) level.

Molecule	State	$\Delta H_{0K\rightarrow 298K}$[a]	$\Delta G_{0K\rightarrow 298K}$[a]	ΔH_{298K}[b]	ΔG_{298K}[b]
Ti_2O_4	^1A_g (C_{2h})	+0.00	+0.00	0.00	0.00
	$^1A_1$ (C_{2v} ***a***)	+0.03	−0.03	5.57	5.51
	$^1A_1$ (C_{3v})	+0.12	−0.07	12.96	12.77
Ti_3O_6	$^1A'$ (C_s ***a***)	+0.00	+0.00	0.00	0.00
	^1A (C_2)	+0.11	−0.42	15.27	14.74
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	+0.00	+0.00	0.00	0.00
	^1A_g (C_{2h} ***a***)	+0.08	−0.44	5.29	4.77
	$^1A_1$ (C_{2v} ***b***)	+0.42	−0.47	16.39	15.50
$Ti_2O_4^-$	$^2A_1$ (C_{2v} ***a***)	+0.00	+0.00	0.00	0.00
	^2A_g (C_{2h})	+0.02	−0.08	1.65	1.55
	$^2A_1$ (C_{3v})	−0.25	+0.89	6.41	7.55
$Ti_3O_6^-$	$^2A'$ (C_s ***a***)	+0.00	+0.00	0.00	0.00
	^2B (C_2)	+0.46	−0.95	41.68	40.27
$Ti_4O_8^-$	^2A_g (C_{2h} ***a***)	+0.00	+0.00	0.00	0.00
	$^2A_1$ (C_{2v} ***a***)	+0.02	+0.19	0.19	0.36
	$^2A_1$ (C_{2v} ***b***)	+0.24	−0.12	1.03	0.67

[a] BP86/aD.

[b] $\Delta H_{298K} = \Delta E_{0K} + \Delta H_{0K\rightarrow 298K}$ and $\Delta G_{298K} = \Delta E_{0K} + \Delta G_{0K\rightarrow 298K}$, where ΔE_{0K} is taken from Table 1.

Table S4. Electron detachment energies (ADEs / VDEs, eV) of $(TiO_2)_n^-$ (n = 1−4) to the ground states of the neutral for the low-lying structures calculated at the B3LYP/aD, BP86/aD, and PW91/aD levels.

		B3LYP[a]	BP86	PW91
ADEs				
TiO_2^-	$^2A_1 \rightarrow {}^1A_1$ (C_{2v})	1.75	1.68	1.62
$Ti_2O_4^-$	$^2A_1 \rightarrow {}^1A_1$ (C_{2v} ***a***)	2.15	2.12	2.06
	$^2A_g \rightarrow {}^1A_g$ (C_{2h})	1.90	1.86	1.81
	$^2A_1 \rightarrow {}^1A_1$ (C_{3v})	2.21	2.08	2.02
$Ti_3O_6^-$	$^2A' \rightarrow {}^1A'$ (C_s ***a***)	3.11	2.87	2.82
	$^2B \rightarrow {}^1A_g$ (C_2)	2.17	2.23	2.18
$Ti_4O_8^-$	$^2A_g \rightarrow {}^1A$ (C_{2h} ***a***)	3.01	2.94	2.90
	$^2A_1 \rightarrow {}^1A_1$ (C_{2v} ***a***)	2.76	2.72	2.67
	$^2A_1 \rightarrow {}^1A_1$ (C_{2v} ***b***)	3.38	3.37	3.34
VDEs				
TiO_2^-	$^2A_1 \rightarrow {}^1A_1$ (C_{2v})	1.79	1.71	1.65
$Ti_2O_4^-$	$^2A_1 \rightarrow {}^1A_1$ (C_{2v} ***a***)	2.43	2.35	2.30
	$^2A_g \rightarrow {}^1A_g$ (C_{2h})	2.25	2.10	2.04
	$^2A_1 \rightarrow {}^1A_1$ (C_{3v})	2.46	2.25	2.20
$Ti_3O_6^-$	$^2A' \rightarrow {}^1A'$ (C_s ***a***)	3.54	3.17	3.12
	$^2B \rightarrow {}^1A$ (C_2)	2.30	2.36	2.31
$Ti_4O_8^-$	$^2A_g \rightarrow {}^1A_g$ (C_{2h} ***a***)	3.74	3.60	3.56
	$^2A_1 \rightarrow {}^1A_1$ (C_{2v} ***a***)	3.62	3.51	3.47
	$^2A_1 \rightarrow {}^1A_1$ (C_{2v} ***b***)	4.05	3.90	3.87

[a] ZPEs from BP86/aD.

Table S5. Electron detachment energies (ADEs / VDEs, eV) of $(TiO_2)_n^-$ (n = 1−4) to the first triplet excited states of the neutral for the low-lying structures calculated at the B3LYP/aD, BP86/aD, and PW91/aD levels.

		B3LYP[a]	BP86	PW91
ADEs				
TiO_2^-	$^2A_1 \rightarrow {}^3B_2$ (C_{2v})	3.68	3.71	3.66
$Ti_2O_4^-$	$^2A_1 \rightarrow {}^3B_1$ (C_{2v} ***a***)	4.81	4.48	4.42
	^2A_g (C_{2h}) $\rightarrow {}^3A''$ (C_s)	4.13	4.56	4.51
	$^2A_1 \rightarrow {}^3A_2$ (C_{3v})	4.21	4.27	4.23
$Ti_3O_6^-$	$^2A' \rightarrow {}^3A'$ (C_s ***a***)	5.15	4.90	4.85
	^2B (C_2) $\rightarrow {}^3A$ (C_1)	4.30	4.84	4.81
$Ti_4O_8^-$	$^2A_g \rightarrow {}^3B_g$ (C_{2h} ***a***)	5.65	5.15	5.12
	$^2A_1 \rightarrow {}^3A_2$ (C_{2v} ***a***)	5.61	5.16	5.12
	$^2A_1 \rightarrow {}^3A_1$ (C_{2v} ***b***)	4.93	4.63	4.59
VDEs				
TiO_2^-	$^2A_1 \rightarrow {}^3B_2$ (C_{2v})	3.81	3.83	3.78
$Ti_2O_4^-$	$^2A_1 \rightarrow {}^3B_1$ (C_{2v} ***a***)	5.09	4.74	4.70
	$^2A_g \rightarrow {}^3B_g$ (C_{2h})	5.27	4.86	4.81
	$^2A_1 \rightarrow {}^3A_2$ (C_{3v})	4.35	4.38	4.34
$Ti_3O_6^-$	$^2A' \rightarrow {}^3A'$ (C_s ***a***)	5.40	5.09	5.05
	$^2B \rightarrow {}^3A$ (C_2)	5.63	5.13	5.08
$Ti_4O_8^-$	$^2A_g \rightarrow {}^3B_g$ (C_{2h} ***a***)	5.90	5.31	5.28
	$^2A_1 \rightarrow {}^3A_2$ (C_{2v} ***a***)	5.90	5.34	5.31
	$^2A_1 \rightarrow {}^3A_1$ (C_{2v} ***b***)	5.18	4.85	4.81

[a] ZPEs from BP86/aD.

Table S6. Calculated reorganization energies[a] (ΔE_{reorg}, eV) for $(TiO_2)_n$ (n = 1−4) at the B3LYP/aD, BP86/aD, and PW91/aD levels.

		B3LYP[b]	BP86	PW91
TiO_2	$^1A_1$ (C_{2v})	0.04	0.03	0.03
Ti_2O_4	$^1A_1$ (C_{2v} ***a***)	0.28	0.24	0.24
	^1A_g (C_{2h})	0.35	0.24	0.23
	$^1A_1$ (C_{3v})	0.25	0.17	0.17
Ti_3O_6	$^1A'$ (C_s ***a***)	0.43	0.30	0.30
	^1A (C_2)	0.13	0.13	0.13
Ti_4O_8	^1A_g (C_{2h} ***a***)	0.73	0.66	0.66
	$^1A_1$ (C_{2v} ***a***)	0.86	0.79	0.80
	$^1A_1$ (C_{2v} ***b***)	0.67	0.53	0.54

[a] The reorganization energy is calculated as the difference between the ADE and VDE for the ground state of the neutral cluster.

[c] ZPEs from BP86/aD.

Table S7. Calculated adiabatic energy gaps[a] (ΔE_{gap}, eV) of $(TiO_2)_n$ (n = 1−4) at the B3LYP/aD, BP86/aD, and PW91/aD levels.

		B3LYP[b]	BP86	PW91
TiO_2	$^1A_1 \rightarrow {}^3B_2$ (C_{2v})	1.93	2.03	2.04
Ti_2O_4	^1A_g (C_{2h})$\rightarrow {}^3A''$ (C_s)	2.24	2.70	2.71
	$^1A_1 \rightarrow {}^3B_1$ (C_{2v} ***a***)	2.66	2.36	2.36
	$^1A_1 \rightarrow {}^3A_2$ (C_{3v})	1.99	2.19	2.20
Ti_3O_6	$^1A' \rightarrow {}^3A'$ (C_s ***a***)	2.04	2.03	2.03
	^1A (C_2) $\rightarrow {}^3A$ (C_1)	2.13	2.61	2.62
Ti_4O_8	$^1A_1 \rightarrow {}^3A_2$ (C_{2v} ***a***)	2.85	2.44	2.45
	$^1A_g \rightarrow {}^3B_g$ (C_{2h} ***a***)	2.64	2.21	2.22
	$^1A_1 \rightarrow {}^3A_1$ (C_{2v} ***b***)	1.55	1.26	1.25

[a] The energy gap is calculated as the energy difference between the first triplet excited state and the ground state of the neutral cluster.

[b] ZPEs from BP86/aD.

Table S8. Normalized and differential clustering energies at 298 K (ΔH_{298K} and ΔG_{298K}, kcal/mol) for $(TiO_2)_n$ (n = 2−4) calculated at the CCSD(T) level.

		$\Delta H_{0K\rightarrow 298K}$[a]	$\Delta G_{0K\rightarrow 298K}$[a]	ΔH_{298K}[b]	ΔG_{298K}[b]
Normalized					
Ti_2O_4	^1A_g (C_{2h})	+0.32	−6.01	61.56	55.23
Ti_3O_6	$^1A'$ (C_s ***a***)	+0.38	−8.21	85.41	76.82
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	+0.44	−9.65	98.79	88.70
Differential					
Ti_2O_4	^1A_g (C_{2h})	+0.63	−12.01	123.09	110.45
Ti_3O_6	$^1A'$ (C_s ***a***)	+0.50	−12.61	131.58	118.47
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	+0.64	−13.97	138.94	124.33

[a] BP86/aD.

[b] $\Delta H_{298K} = \Delta E_{0K} + \Delta H_{0K\rightarrow 298K}$ and $\Delta G_{298K} = \Delta E_{0K} + \Delta G_{0K\rightarrow 298K}$, where ΔE_{0K} is taken from Table 8.

Table S9. Normalized and differential clustering energies at 0 K (ΔE_{0K}, kcal/mol) for $(TiO_2)_n$ (n = 2−4) calculated at the B3LYP/aD, BP86/aD, and PW91/aD levels.

		B3LYP[a]	BP86	PW91
Normalized				
Ti_2O_4	^1A_g (C_{2h})	57.9	55.1	56.0
Ti_3O_6	$^1A'$ (C_s ***a***)	77.5	73.2	74.7
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	88.4	83.4	85.2
Differential				
Ti_2O_4	^1A_g (C_{2h})	115.8	110.2	112.1
Ti_3O_6	$^1A'$ (C_s ***a***)	116.7	109.5	112.0
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	121.1	113.9	116.5

[a] ZPEs from BP86/aD.

Table S10. Atomization energies at 0 K ($\Sigma D_{0,\ 0K}$, kcal/mol) for $(TiO_2)_n$ (n = 1−4) calculated at the B3LYP/aD, BP86/aD, and PW91/aD levels.

		B3LYP	BP86	PW91
TiO_2	$^1A_1$ (C_{2v})	288.94	334.77	338.39
Ti_2O_4	^1A_g (C_{2h})	693.71	779.73	788.88
Ti_3O_6	$^1A'$ (C_s ***a***)	1099.48	1223.96	1239.32
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	1509.68	1672.63	1694.20

[a] ZPE and SO corrections from Table 10 .

Table S11. Atomization energies at 0 K ($\Sigma D_{0,\ 0K}$, kcal/mol) for $(TiO_2)_n$ (n = 1−4) calculated at the B3LYP/aT//B3LYP/aD, BP86/aT//BP86/aD, and PW91/aT//PW91/aD levels.[a]

		B3LYP	BP86	PW91
TiO_2	$^1A_1$ (C_{2v})	288.46	335.03	338.25
Ti_2O_4	^1A_g (C_{2h})	692.57	780.43	788.88
Ti_3O_6	$^1A'$ (C_s ***a***)	1097.30	1224.63	1239.02
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	1507.01	1673.91	1694.18

[a] ZPE and SO corrections from Table 10.

Table S12. Heats of formation at 0 and 298 K ($\Delta H_{f,\,0K}$ and $\Delta H_{f,\,298K}$, kcal/mol) calculated at the B3LYP/aD, BP86/aD, and PW91/aD levels.[a]

Molecule		B3LYP[b]		BP86[b]		PW91[b]	
		$\Delta H_{f,\,0K}$[e]	$\Delta H_{f,\,298K}$[f]	$\Delta H_{f,\,0K}$[e]	$\Delta H_{f,\,298K}$[f]	$\Delta H_{f,\,0K}$[e]	$\Delta H_{f,\,298K}$[f]
TiO_2	$^1A_1$ (C_{2v})	−58.6	−59.2	−104.4	−105.0	−108.0	−108.6
Ti_2O_4	^1A_g (C_{2h})	−233.0	−234.8	−319.0	−320.8	−328.2	−329.9
Ti_3O_6	$^1A'$ (C_s ***a***)	−408.4	−411.2	−532.9	−535.7	−548.2	−551.1
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	−588.2	−592.3	−751.2	−755.2	−772.8	−776.8

[a] Error bars due to errors in the heats of formation of the atoms are ±0.7 for TiO_2, ±1.4 for Ti_2O_4, ±2.1 for Ti_3O_6, ±2.8 for Ti_4O_8.

[b] Using the atomization energies calculated at the B3LYP/aD, BP86/aD, and PW91/aD levels from Table S10.

[e] $\Delta H_{f,\,0K}$ (Ti_nO_{2n}) = n $\Delta H_{f,\,0K}$ (Ti) + 2n $\Delta H_{f,\,0K}$ (O) − $\Sigma D_{0,\,0K}$ (Ti_nO_{2n}), where the experimental $\Delta H_{f,\,0K}$ (58.98±0.02, 112.4±0.7 kcal/mol for O and Ti) were used for the atoms.

[f] $\Delta H_{f,\,298K}$ (Ti_nO_{2n}) = $\Delta H_{f,\,0K}$ (Ti_nO_{2n}) + $\Delta H_{0K\rightarrow298K}$ (Ti_nO_{2n}) − n $\Delta H_{0K\rightarrow298K}$ (Ti) − 2n $\Delta H_{0K\rightarrow298K}$ (O). The experimental enthalpy change from 0 K to 298 K ($\Delta H_{0K\rightarrow298K}$) is 1.04 and 1.15 kcal/mol for O and Ti respectively. The enthalpy change from 0 K to 298 K for Ti_nO_{2n} calculated at the BP86/aD level is used.

Table S13. Zero-point energies (ZPE) and electronic energies (E_e) calculated at the B3LYP/aD, BP86/aD, and PW91/aD levels. All energies are shown in Hartree.

		B3LYP/aD		BP86/aD		PW91/aD	
		ZPE	E_e	ZPE	E_e	ZPE	E_e
Neutral singlet states							
TiO_2	$^1A_1$ (C_{2v})	0.005351	-208.518579	0.005189	-208.589836	0.005202	-208.527435
Ti_2O_4	^1A_g (C_{2h})	0.014229	-417.225181	0.013818	-417.358719	0.013845	-417.236948
	$^1A_1$ (C_{2v} ***a***)	0.014064	-417.215928	0.013673	-417.348788	0.013702	-417.226874
	$^1A_1$ (C_{3v})	0.013609	-417.200173	0.013138	-417.336537	0.013173	-417.216021
Ti_3O_6	$^1A'$ (C_s ***a***)	0.022758	-625.932877	0.021954	-626.125934	0.021999	-625.945889
	^1A (C_2)	0.022605	-625.918532	0.021933	-626.113375	0.021970	-625.932038
	^1A (C_1)	0.022191	-625.920233	–	–	–	–
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	0.031351	-834.647752	0.030205	-834.900346	0.030239	-834.662005
	^1A_g (C_{2h} ***a***)	0.031022	-834.639092	0.029903	-834.893075	0.029948	-834.654553
	$^1A_1$ (C_{2v} ***b***)	0.030730	-834.631485	0.029429	-834.882247	0.029461	-834.643038
Anions							
TiO_2^-	$^2A_1$ (C_{2v})	0.004981	-208.582438	0.004840	-208.651187	0.004858	-208.586494
$Ti_2O_4^-$	$^2A_1$ (C_{2v} ***a***)	0.012065	-417.293637	0.012354	-417.425257	0.012376	-417.301272
	^2A_g (C_{2h})	0.011405	-417.293417	0.012252	-417.425599	0.012288	-417.301732
	$^2A_1$ (C_{3v})	0.012972	-417.280888	0.012607	-417.412295	0.012639	-417.289814

$Ti_3O_6^-$	$^2A'$ (C_s ***a***)	0.022118	-626.046622	0.021359	-626.230791	0.021396	-626.048917
	^2B (C_2)	0.019891	-625.996744	0.020292	-626.193770	0.020313	-626.010563
$Ti_4O_8^-$	^2A_g (C_{2h} ***a***)	0.029025	-834.748354	0.028671	-835.000009	0.028718	-834.759715
	$^2A_1$ (C_{2v} ***a***)	0.028814	-834.747456	0.028625	-834.998648	0.028692	-834.758579
	$^2A_1$ (C_{2v} ***b***)	0.029524	-834.755032	0.028659	-835.005479	0.028680	-834.764891
Neutral singlet states at anion geometries							
TiO_2	$^1A_1$ (C_{2v})	–	-208.516623	–	-208.588240	–	-208.525870
Ti_2O_4	$^1A_1$ (C_{2v} ***a***)	–	-417.204409	–	-417.338745	–	-417.216666
	^1A_g (C_{2h})	–	-417.210657	–	-417.348415	–	-417.226826
	$^1A_1$ (C_{3v})	–	-417.190420	–	-417.329662	–	-417.209132
Ti_3O_6	$^1A'$ (C_s ***a***)	–	-625.916682	–	-626.114227	–	-625.934138
	^1A (C_2)	–	-625.912095	–	-626.107134	–	-625.925709
Ti_4O_8	^1A_g (C_{2h} ***a***)	–	-834.611015	–	-834.867710	–	-834.628964
	$^1A_1$ (C_{2v} ***a***)	–	-834.614466	–	-834.869810	–	-834.631206
	$^1A_1$ (C_{2v} ***b***)	–	-834.606267	–	-834.862109	–	-834.622548
Neutral triplet states							
TiO_2	$^3B_2$ (C_{2v})	0.002474	-208.446104	0.003651	-208.513667	0.003654	-208.450746
Ti_2O_4	^3B_g (C_{2h})	0.011754	-417.106816	0.009715	-417.251119	0.009717	-417.129100
	$^3A''$ (C_s)	0.012614	-417.140857	0.011613	-417.257282	0.011651	-417.135195
	$^3B_1$ (C_{2v} ***a***)	0.012225	-417.114797	0.010180	-417.258540	0.010203	-417.136589
	$^3A_2$ (C_{3v})	0.010765	-417.124959	0.011237	-417.254088	0.011263	-417.133098

Ti_3O_6	$^3A'$ (C_s ***a***)	0.019458	-625.855376	0.019497	-626.049012	0.019525	-625.868658
	^3A (C_2)	0.019414	-625.793959	0.017312	-626.008812	0.017341	-625.827386
	^3A (C_1)	0.020949	-625.838223	0.019934	-626.015385	0.019950	-625.833572
Ti_4O_8	$^3A_2$ (C_{2v} ***a***)	0.026275	-834.538923	0.026219	-834.806784	0.026236	-834.568004
	^3B_g (C_{2h} ***a***)	0.026629	-834.538663	0.026446	-834.808402	0.026445	-834.569422
	$^3A_1$ (C_{2v} ***b***)	0.026834	-834.572505	0.027153	-834.833707	0.027158	-834.594662
Neutral triplet states at anion geometries							
TiO_2	$^3B_2$ (C_{2v})	–	-208.442624	–	-208.510570	–	-208.447503
Ti_2O_4	$^3B_1$ (C_{2v} ***a***)	–	-417.106730	–	-417.251123	–	-417.128686
	^3B_g (C_{2h})	–	-417.099844	–	-417.247087	–	-417.125102
	$^3A_2$ (C_{3v})	–	-417.121217	–	-417.251272	–	-417.130242
Ti_3O_6	$^3A'$ (C_s ***a***)	–	-625.848291	–	-626.043740	–	-625.863380
	^3A (C_2)	–	-625.789807	–	-626.005203	–	-625.823719
Ti_4O_8	^3B_g (C_{2h} ***a***)	–	-834.531711	–	-834.804752	–	-834.565726
	$^3A_2$ (C_{2v} ***a***)	–	-834.530475	–	-834.802436	–	-834.563606
	$^3A_1$ (C_{2v} ***b***)	–	-834.564855	–	-834.827399	–	-834.588323

Table S14. Electronic energies (E_e) calculated at the B3LYP/aT//B3LYP/aD, BP86/aT//BP86/aD, and PW91/aT//PW91/aD levels. All energies are shown in Hartree.

		B3LYP	BP86	PW91
Neutral singlet states				
TiO_2	$^1A_1$ (C_{2v})	-208.555539	-208.625094	-208.563107
Ti_2O_4	^1A_g (C_{2h})	-417.298811	-417.429509	-417.308741
	$^1A_1$ (C_{2v} ***a***)	-417.289511	-417.419563	-417.298672
	$^1A_1$ (C_{3v})	-417.274425	-417.407657	-417.288225
Ti_3O_6	$^1A'$ (C_s ***a***)	-626.042589	-626.231512	-626.053098
	^1A (C_2)	-626.028603	-626.219521	-626.039829
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	-834.794412	-835.041736	-834.805574
	^1A_g (C_{2h} ***a***)	-834.784504	-835.033743	-834.797399
	$^1A_1$ (C_{2v} ***b***)	-834.780084	-835.025729	-834.788650
Anions				
TiO_2^-	$^2A_1$ (C_{2v})	-208.619039	-208.686187	-208.621858
$Ti_2O_4^-$	$^2A_1$ (C_{2v} ***a***)	-417.366273	-417.495305	-417.372146
	^2A_g (C_{2h})	-417.366053	-417.495747	-417.372734
	$^2A_1$ (C_{3v})	-417.354609	-417.483137	-417.361511
$Ti_3O_6^-$	$^2A'$ (C_s ***a***)	-626.155979	-626.336409	-626.155922
	^2B (C_2)	-626.105993	-626.299319	-626.117504
$Ti_4O_8^-$	^2A_g (C_{2h} ***a***)	-834.893556	-835.140962	-834.902489
	$^2A_1$ (C_{2v} ***a***)	-834.893968	-835.140506	-834.902255
	$^2A_1$ (C_{2v} ***b***)	-834.902539	-835.148428	-834.909726
Neutral singlet states at anion geometries				
TiO_2	$^1A_1$ (C_{2v})	-208.553209	-208.623210	-208.561244
Ti_2O_4	$^1A_1$ (C_{2v} ***a***)	-417.276874	-417.408565	-417.287541
	^1A_g (C_{2h})	-417.283107	-417.418327	-417.297794
	$^1A_1$ (C_{3v})	-417.264432	-417.400637	-417.281204
Ti_3O_6	$^1A'$ (C_s ***a***)	-626.025680	-626.219406	-626.040984
	^1A (C_2)	-626.020770	-626.212535	-626.032775

Ti_4O_8	^1A_g (C_{2h} ***a***)	-834.755871	-835.008203	-834.771723
	$^1A_1$ (C_{2v} ***a***)	-834.760768	-835.011302	-834.774982
	$^1A_1$ (C_{2v} ***b***)	-834.753653	-835.004766	-834.767486
Neutral triplet states				
TiO_2	$^3B_2$ (C_{2v})	-208.483325	-208.548985	-208.486648
Ti_2O_4	$^3A''$ (C_s)	-417.214733	-417.328115	-417.207159
	$^3B_1$ (C_{2v} ***a***)	-417.187678	-417.328775	-417.207952
	$^3A_2$ (C_{3v})	-417.198032	-417.324115	-417.204330
Ti_3O_6	$^3A'$ (C_s ***a***)	-625.964736	-626.154511	-625.975955
	^3A (C_1)	-625.948551	-626.121669	-625.941570
Ti_4O_8	$^3A_2$ (C_{2v} ***a***)	-834.685279	-834.948291	-834.711783
	^3B_g (C_{2h} ***a***)	-834.683595	-834.948967	-834.712267
	$^3A_1$ (C_{2v} ***b***)	-834.720079	-834.976654	-834.739909
Neutral triplet states at anion geometries				
TiO_2	$^3B_2$ (C_{2v})	-208.480117	-208.546216	-208.483776
Ti_2O_4	$^3B_1$ (C_{2v} ***a***)	-417.179714	-417.321320	-417.200081
	^3B_g (C_{2h})	-417.172669	-417.317253	-417.196453
	$^3A_2$ (C_{3v})	-417.194133	-417.321273	-417.201471
Ti_3O_6	$^3A'$ (C_s ***a***)	-625.958017	-626.149479	-625.970921
	^3A (C_2)	-625.898214	-626.110641	-625.930927
Ti_4O_8	^3B_g (C_{2h} ***a***)	-834.677068	-834.945662	-834.708921
	$^3A_2$ (C_{2v} ***a***)	-834.677098	-834.944169	-834.707621
	$^3A_1$ (C_{2v} ***b***)	-834.712823	-834.970578	-834.733821

Table S15. Electronic energies (E_e) at the CCSD(T)/aD, CCSD(T)/aT, CCSD(T)/aQ, and CCSD(T)/CBS levels, core-valence correlation corrections (ΔE_{CV}) at the CCSD(T)/awCVDZ and CCSD(T)/awCVTZ levels, and scalar relativistic corrections (ΔE_{SR}) at the CISD/aT level. All energies are shown in Hartree. The T_1 diagnostic are also listed.

		E_e [CCSD(T)]				ΔE_{CV} [CCSD(T)][a,b]		ΔE_{SR}[b]	T_1[c]
		aD[d]	aT[b]	aQ[b]	CBS[e]	awCVDZ	awCVTZ	CISD/aT	
Neutral singlet states									
TiO_2	$^1A_1$ (C_{2v})	-207.761268	-207.892733	-207.935363	-207.959630	-0.400878	-0.502913	-0.107945	0.043
Ti_2O_4	^1A_g (C_{2h})	-415.715963	-415.979408	-416.065014	-416.113764	-0.809856	-1.010921	-0.214893	0.038
	$^1A_1$ (C_{2v} ***a***)	-415.707408	-415.970670	-416.056349	-416.105153	-0.809612	-1.010537	-0.214903	0.038
	$^1A_1$ (C_{3v})	-415.691477	-415.956597	-416.042345	-416.091131	-0.812959	-1.012552	-0.214756	0.039
Ti_3O_6	$^1A'$ (C_s ***a***)	-623.679877	-624.074746	–	–	-1.220998	–	-0.321807	0.036
	^1A (C_2)	-623.655347	-624.051230	–	–	-1.220370	–	-0.321782	0.036
Ti_4O_8	$^1A_1$ (C_{2v} ***a***)	-831.652514	-832.180120	–	–	-1.634062	–	-0.428386	0.036
	^1A_g (C_{2h} ***a***)	-831.644900	-832.170468	–	–	-1.635152	–	-0.428355	0.036
	$^1A_1$ (C_{2v} ***b***)	-831.630718	-832.158996	–	–	-1.628731	–	-0.428628	0.036
Anions									
TiO_2^-	$^2A_1$ (C_{2v})	-207.820244	-207.951691	-207.994424	-208.018761	-0.403861	-0.504712	-0.107694	0.043
$Ti_2O_4^-$	$^2A_1$ (C_{2v} ***a***)	-415.776128	-416.038913	-416.124699	-416.173592	-0.813201	-1.012831	-0.214660	0.040
	^2A_g (C_{2h})	-415.773802	-416.036345	-416.122234	-416.171206	-0.812922	-1.012503	-0.214692	0.039

	$^2A_1$ (C_{3v})	-415.761315	-416.025880	-416.111914	-416.160914	-0.816270	-1.015092	-0.214727	0.047
$Ti_3O_6^-$	$^2A'$ (C_s ***a***)	-623.781378	-624.175801	–	–	-1.225007	–	-0.321873	0.041
	^2B (C_2)	-623.715906	-624.110982	–	–	-1.223368	–	-0.321572	0.045
$Ti_4O_8^-$	^2A_g (C_{2h} ***a***)	-831.741606	-832.268255	–	–	-1.637827	–	–	0.035
	$^2A_1$ (C_{2v} ***a***)	-831.740046	-832.268593	–	–	-1.637166	–	–	0.035
	$^2A_1$ (C_{2v} ***b***)	-831.742488	-832.270860	–	–	-1.633951	–	–	0.035
Neutral singlet states at anion geometries									
TiO_2	$^1A_1$ (C_{2v})	-207.759913	-207.891354	-207.933812	-207.957963	-0.400628	-0.501943	-0.107916	0.044
Ti_2O_4	$^1A_1$ (C_{2v} ***a***)	-415.695730	-415.958114	-416.043473	-416.092091	-0.809521	-1.009035	-0.214821	0.039
	^1A_g (C_{2h})	-415.695647	-415.960153	-416.045527	-416.094081	-0.809162	-1.008086	-0.214742	0.039
	$^1A_1$ (C_{3v})	-415.686702	-415.951711	-416.037240	-416.085882	-0.813207	-1.012041	-0.214743	0.041
Ti_3O_6	$^1A'$ (C_s ***a***)	-623.668484	-624.061944	–	–	-1.221591	–	-0.321741	0.038
	^1A (C_2)	-623.654018	-624.048190	–	–	-1.219535	–	-0.321671	0.037
Ti_4O_8	^1A_g (C_{2h} ***a***)	-831.620761	-832.144681	–	–	-1.636247	–	-0.428320	0.038
	$^1A_1$ (C_{2v} ***a***)	-831.623405	-832.149495	–	–	-1.635463	–	-0.428364	0.038
	$^1A_1$ (C_{2v} ***b***)	-831.610000	-832.136785	–	–	-1.630189	–	-0.428621	0.038
Neutral triplet states									
TiO_2	$^3B_2$ (C_{2v})	-207.677450	–	–	–	–	–	–	0.088
Ti_2O_4	$^3A''$ (C_s)	-417.214733	–	–	–	–	–	–	0.040
	$^3B_1$ (C_{2v} ***a***)	-417.187678	–	–	–	–	–	–	0.049

	$^3A_2$ (C_{3v})	-417.198032	–	–	–	–	–	–	0.040
Ti_3O_6	$^3A'$ (C_s ***a***)	-625.964736	–	–	–	–	–	–	0.051
	^3A (C_1)	-625.948551	–	–	–	–	–	–	0.037
Ti_4O_8	$^3A_2$ (C_{2v} ***a***)	-834.685279	–	–	–	–	–	–	0.042
	^3B_g (C_{2h} ***a***)	-834.683595	–	–	–	–	–	–	0.043
	$^3A_1$ (C_{2v} ***b***)	-834.720079	–	–	–	–	–	–	0.045
Neutral triplet states at anion geometries									
TiO_2	$^3B_2$ (C_{2v})	-207.672723	–	–	–	–	–	–	0.108
Ti_2O_4	$^3B_1$ (C_{2v} ***a***)	-417.179714	–	–	–	–	–	–	0.047
	^3B_g (C_{2h})	-417.172669	–	–	–	–	–	–	0.043
	$^3A_2$ (C_{3v})	-417.194133	–	–	–	–	–	–	0.041
Ti_3O_6	$^3A'$ (C_s ***a***)	-625.958017	–	–	–	–	–	–	0.055
	^3A (C_2)	-625.898214	–	–	–	–	–	–	0.052
Ti_4O_8	^3B_g (C_{2h} ***a***)	-834.677068	–	–	–	–	–	–	0.054
	$^3A_2$ (C_{2v} ***a***)	-834.677098	–	–	–	–	–	–	0.055
	$^3A_1$ (C_{2v} ***b***)	-834.712823	–	–	–	–	–	–	0.042

[a] Calculated as the energy difference between the CCSD(T) energies with and without correlating the Ti $3s^23p^6$ and O $1s^2$ electrons.

[b] With the CCSD(T)/aT geometries for the monomer and dimer, and the B3LYP/aD geometries for the trimer and tetramer. For the triplet states, the B3LYP/aD geometries are used.

[c] At the CCSD(T)/aT level except for the triplet states, which are from the CCSD(T)/aD calculations.

[d] With the CCSD(T)/aD geometries for the monomer and dimer, and the B3LYP/aD geometries for the trimer and tetramer. For the triplet states, the B3LYP/aD geometries are used.

[e] Extrapolated the CCSD(T)/aD, CCSD(T)/aT, and CCSD(T)/aQ energies using the mixed Gaussian/exponential formula. Cardinal numbers of 2, 3, 4 for the aD, aT, aQ basis sets were used.

Table S16. Cartesian coordinates in Angstroms optimized at the B3LYP/aD level for the different structures of the $(TiO_2)_n$ (n = 1−4) clusters and their anions, as well as the first triplet excited states for the low-lying structures of the neutral clusters.

TiO_2 / $^1A_1$ (C_{2v})

TI	0.000000	0.000000	0.386906
O	0.000000	1.364619	-0.531996
O	0.000000	-1.364619	-0.531996

Ti_2O_4 / ^1A_g (C_{2h})

TI	0.000000	1.358493	0.000000
O	0.000000	0.000000	1.254563
O	0.000000	0.000000	-1.254563
TI	0.000000	-1.358493	0.000000
O	1.342483	-2.283197	0.000000
O	-1.342483	2.283197	0.000000

Ti_2O_4 / $^1A_1$ (C_{2v} ***a***)

TI	0.000000	1.361547	-0.271262
O	1.260631	0.000000	-0.300363
O	-1.260631	0.000000	-0.300363
TI	0.000000	-1.361547	-0.271262
O	0.000000	-2.317026	1.046333
O	0.000000	2.317026	1.046333

Ti_2O_4 / $^1A_1$ (C_{3v})

TI	0.000000	0.000000	1.444025
O	0.000000	1.444870	0.423783
O	-1.251294	-0.722435	0.423783
O	1.251294	-0.722435	0.423783
TI	0.000000	0.000000	-0.962731
O	0.000000	0.000000	-2.594907

Ti_2O_4 / $^1A_1$ (C_{2v} ***b***)

O	0.000000	1.420680	-1.924267
O	0.000000	-1.420680	-1.924267
O	1.266339	0.000000	0.797946
O	-1.266339	0.000000	0.797946
TI	0.000000	0.000000	1.860312
TI	0.000000	0.000000	-1.041169

Ti_2O_4 / $^1A_1$ (C_{2v} ***c***)

O	0.000000	0.732077	1.451792
O	0.000000	-0.732077	1.451792
O	0.000000	-1.279826	-1.023135
O	0.000000	1.279826	-1.023135
TI	1.048303	0.000000	-0.155875
TI	-1.048303	0.000000	-0.155875

Ti_3O_6 / $^1A'$ (C_s ***a***)

TI	-0.276993	-0.564058	1.434118
O	1.168219	-0.102305	0.000000
O	-1.198363	-1.305108	0.000000
TI	-0.276993	-0.564058	-1.434118
O	0.083691	-1.452887	-2.748265
O	0.083691	-1.452887	2.748265
TI	0.705530	1.643280	0.000000
O	-0.276993	1.448243	1.417026
O	-0.276993	1.448243	-1.417026

Ti_3O_6 / ^1A (C_2)

TI	0.000000	0.000000	0.070186
O	-0.885873	1.380717	-0.771514
O	0.879206	1.307630	1.004095
O	-0.879206	-1.307630	1.004095
O	0.885873	-1.380717	-0.771514
TI	0.000000	2.714999	0.155349
TI	0.000000	-2.714999	0.155349
O	-0.953948	-3.663727	-0.756295
O	0.953948	3.663727	-0.756295

Ti_3O_6 / ^1A (C_1)

TI	1.343097	-0.812252	0.039546
O	1.060854	0.715999	1.302279
O	1.160018	0.748504	-1.199613
TI	0.449954	1.741399	0.041504
O	-1.305819	1.400026	-0.075090
O	2.687333	-1.731174	0.018600
TI	-1.808897	-0.438847	-0.242814
O	-0.387982	-1.564633	-0.100313
O	-3.170828	-0.917047	0.498987

Ti_3O_6 / $^1A'$ (C_s ***b***)

TI	0.450591	0.837837	1.665865
TI	0.450591	0.837837	-1.665865
TI	-0.724939	-1.807175	0.000000
O	0.982743	1.435514	0.000000
O	-0.362412	-0.807827	-1.503799
O	-0.362412	-0.807827	1.503799
O	-0.362412	1.906314	2.579954
O	-0.017761	-3.270862	0.000000
O	-0.362412	1.906314	-2.579954

Ti_3O_6 / $^1A_1$ (C_{3v})

TI	0.000000	1.930991	-0.220215
TI	-1.672287	-0.965496	-0.220215
TI	1.672287	-0.965496	-0.220215
O	-1.513124	0.873602	-0.330417
O	0.000000	-1.747205	-0.330417
O	1.513124	0.873602	-0.330417
O	0.000000	3.070659	0.936009

O	2.659269	-1.535330	0.936009
O	-2.659269	-1.535330	0.936009

Ti_3O_6 / $^1A_1$ (C_{2v})

TI	0.000000	1.331475	-1.371228
O	1.227596	0.000000	-1.656918
O	-1.227596	0.000000	-1.656918
TI	0.000000	-1.331475	-1.371228
O	0.000000	-1.572530	0.261159
O	0.000000	1.572530	0.261159
TI	0.000000	0.000000	1.795228
O	1.410420	0.000000	2.698197
O	-1.410420	0.000000	2.698197

Ti_4O_8 / $^1A_1$ (C_{2v} ***a***)

TI	0.000000	2.029741	-0.618921
O	1.692413	1.678279	0.289710
O	0.000000	2.765914	-2.058792
O	0.000000	0.000000	2.049982
O	0.000000	0.000000	-0.515803
TI	1.410571	0.000000	0.877932
O	1.692413	-1.678279	0.289710
TI	0.000000	-2.029741	-0.618921
O	0.000000	-2.765914	-2.058792
O	-1.692413	1.678279	0.289710
TI	-1.410571	0.000000	0.877932
O	-1.692413	-1.678279	0.289710

Ti_4O_8 / ^1A_g (C_{2h} ***a***)

TI	0.785839	2.343692	0.000000
O	0.000000	1.785838	1.701381
O	2.078144	3.316563	0.000000
O	1.231627	0.299552	0.000000
O	-1.231627	-0.299552	0.000000
TI	0.000000	0.000000	1.391584
O	0.000000	-1.785838	1.701381
TI	-0.785839	-2.343692	0.000000
O	-2.078144	-3.316563	0.000000
O	0.000000	1.785838	-1.701381
TI	0.000000	0.000000	-1.391584
O	0.000000	-1.785838	-1.701381

Ti_4O_8 / $^1A_1$ (C_{2v} ***b***)

O	0.000000	0.000000	2.314948
TI	1.570968	0.000000	1.359682
TI	-1.570968	0.000000	1.359682
O	1.486102	1.384343	0.342263
O	1.486102	-1.384343	0.342263
O	-1.486102	1.384343	0.342263
O	-1.486102	-1.384343	0.342263
TI	0.000000	1.613542	-0.991713
TI	0.000000	-1.613542	-0.991713
O	0.000000	2.960132	-1.906411

O	0.000000	0.000000	-1.895009
O	0.000000	-2.960132	-1.906411

Ti_4O_8 / ^1A_g (C_{2h} ***b***)

O	0.081969	2.133064	0.000000
TI	-1.572322	1.499034	0.000000
TI	1.781173	1.233221	0.000000
O	-1.781173	0.295127	1.245701
O	-1.781173	0.295127	-1.245701
O	1.781173	-0.295127	1.245701
O	1.781173	-0.295127	-1.245701
TI	-1.781173	-1.233221	0.000000
O	-3.120848	-2.153653	0.000000
TI	1.572322	-1.499034	0.000000
O	-0.081969	-2.133064	0.000000
O	3.120848	2.153653	0.000000

Ti_4O_8 / $^1A_1$ (C_{2v} ***c***)

O	0.000000	0.000000	2.398360
TI	0.000000	1.654084	1.586907
TI	0.000000	-1.654084	1.586907
O	-1.248683	1.781464	0.416459
O	1.248683	1.781464	0.416459
O	-1.248683	-1.781464	0.416459
O	1.248683	-1.781464	0.416459
TI	0.000000	1.688728	-1.180892
O	0.000000	2.972141	-2.183691
TI	0.000000	-1.688728	-1.180892
O	0.000000	0.000000	-1.929897
O	0.000000	-2.972141	-2.183691

Ti_4O_8 / $^1A_1$ (T_d)

O	0.968391	0.968391	0.968391
O	-0.968391	-0.968391	0.968391
O	-1.960599	1.960599	1.960599
O	-0.968391	0.968391	-0.968391
O	1.960599	1.960599	-1.960599
O	0.968391	-0.968391	-0.968391
O	1.960599	-1.960599	1.960599
TI	-1.026808	1.026808	1.026808
TI	1.026808	1.026808	-1.026808
TI	1.026808	-1.026808	1.026808
TI	-1.026808	-1.026808	-1.026808
O	-1.960599	-1.960599	-1.960599

Ti_4O_8 / $^1A_1$ (D_{2d})

O	3.451223	0.000000	1.580807
O	1.559087	1.559087	0.000000
O	0.000000	3.451223	-1.580807
O	-1.559087	1.559087	0.000000
O	-3.451223	0.000000	1.580807
O	-1.559087	-1.559087	0.000000
O	1.559087	-1.559087	0.000000

O	0.000000	-3.451223	-1.580807
TI	-2.496093	0.000000	0.266781
TI	0.000000	-2.496093	-0.266781
TI	2.496093	0.000000	0.266781
TI	0.000000	2.496093	-0.266781

TiO_2^- / $^2A_1$ (C_{2v})

TI	0.000000	0.000000	0.385352
O	0.000000	1.407513	-0.529859
O	0.000000	-1.407513	-0.529859

$Ti_2O_4^-$ / $^2A_1$ (C_{2v} ***a***)

TI	0.000000	1.337798	-0.206580
O	1.306155	0.000000	-0.104080
O	-1.306155	0.000000	-0.104080
TI	0.000000	-1.337798	-0.206580
O	0.000000	-2.758278	0.672174
O	0.000000	2.758278	0.672174

$Ti_2O_4^-$ / ^2A_g (C_{2h})

TI	0.000000	1.348739	0.000000
O	0.000000	0.000000	1.300340
O	0.000000	0.000000	-1.300340
TI	0.000000	-1.348739	0.000000
O	0.978096	-2.708923	0.000000
O	-0.978096	2.708923	0.000000

$Ti_2O_4^-$ / $^2A_1$ (C_{3v})

TI	0.000000	0.000000	1.434587
O	0.000000	1.491659	0.378417
O	-1.291815	-0.745830	0.378417
O	1.291815	-0.745830	0.378417
TI	0.000000	0.000000	-0.908635
O	0.000000	0.000000	-2.581617

$Ti_2O_4^-$ / $^2A_1$ (C_{2v} ***b***)

O	0.000000	1.431888	-1.902333
O	0.000000	-1.431888	-1.902333
O	1.278951	0.000000	0.741656
O	-1.278951	0.000000	0.741656
TI	0.000000	0.000000	1.845867
TI	0.000000	0.000000	-1.001739

$Ti_2O_4^-$ / $^2B_1$ (C_{2v} ***c***)

O	0.000000	0.734321	1.462588
O	0.000000	-0.734321	1.462588
O	0.000000	-1.284772	-1.024901
O	0.000000	1.284772	-1.024901
TI	1.069319	0.000000	-0.159159
TI	-1.069319	0.000000	-0.159159

$Ti_3O_6^-$ / $^2A'$ (C_s)

TI	-0.241423	-0.540480	1.423970
O	1.183894	-0.178144	0.000000
O	-1.267301	-1.193044	0.000000
TI	-0.241423	-0.540480	-1.423970
O	0.021887	-1.469783	-2.769637
O	0.021887	-1.469783	2.769637
TI	0.672838	1.631221	0.000000
O	-0.241423	1.398767	1.539715
O	-0.241423	1.398767	-1.539715

$Ti_3O_6^-$ / ^2B (C_2)

TI	0.000000	0.000000	0.070622
O	-0.895838	1.353785	-0.806347
O	0.902383	1.309095	0.997252
O	-0.902383	-1.309095	0.997252
O	0.895838	-1.353785	-0.806347
TI	0.000000	2.716759	0.127502
TI	0.000000	-2.716759	0.127502
O	-0.801919	-3.952276	-0.638641
O	0.801919	3.952276	-0.638641

$Ti_3O_6^-$ / $^2A_1$ (C_{3v})

TI	0.000000	1.844381	-0.008077
TI	-1.597281	-0.922191	-0.008077
TI	1.597281	-0.922191	-0.008077
O	-1.588585	0.917170	-0.280298
O	0.000000	-1.834340	-0.280298
O	1.588585	0.917170	-0.280298
O	0.000000	3.469894	0.302511
O	3.005016	-1.734947	0.302511
O	-3.005016	-1.734947	0.302511

$Ti_3O_6^-$ / $^2A_1$ (C_{2v})

TI	0.000000	1.349573	-0.732098
O	-1.290001	0.000000	-0.910318
O	1.290001	0.000000	-0.910318
TI	0.000000	-1.349573	-0.732098
O	0.000000	-2.685454	-1.691030
O	0.000000	2.685454	-1.691030
TI	0.000000	0.000000	2.327673
O	0.000000	1.389068	1.414066
O	0.000000	-1.389068	1.414066

$Ti_4O_8^-$ / ^2A_g (C_{2h} ***a***)

TI	0.917169	2.309622	0.000000
O	0.000000	1.831560	1.619553
O	2.098254	3.464938	0.000000
O	1.382033	0.335712	0.000000
O	-1.382033	-0.335712	0.000000
TI	0.000000	0.000000	1.313781
O	0.000000	-1.831560	1.619553

TI	-0.917169	-2.309622	0.000000
O	-2.098254	-3.464938	0.000000
O	0.000000	1.831560	-1.619553
TI	0.000000	0.000000	-1.313781
O	0.000000	-1.831560	-1.619553

$Ti_4O_8^-$ / $^2A_1$ (C_{2v} ***a***)

TI	0.000000	2.011664	-0.679385
O	1.585956	1.751772	0.350670
O	0.000000	2.999070	-2.003472
O	0.000000	0.000000	2.206225
O	0.000000	0.000000	-0.726647
TI	1.306378	0.000000	0.883873
O	1.585956	-1.751772	0.350670
TI	0.000000	-2.011664	-0.679385
O	0.000000	-2.999070	-2.003472
O	-1.585956	1.751772	0.350670
TI	-1.306378	0.000000	0.883873
O	-1.585956	-1.751772	0.350670

$Ti_4O_8^-$ / $^2A_1$ (C_{2v} ***b***)

O	0.000000	0.000000	2.493450
TI	1.422857	0.000000	1.306708
TI	-1.422857	0.000000	1.306708
O	1.487914	1.458897	0.321555
O	1.487914	-1.458897	0.321555
O	-1.487914	1.458897	0.321555
O	-1.487914	-1.458897	0.321555
TI	0.000000	1.631322	-0.962309
TI	0.000000	-1.631322	-0.962309
O	0.000000	2.986431	-1.906739
O	0.000000	0.000000	-1.860387
O	0.000000	-2.986431	-1.906739

$Ti_4O_8^-$ / $^2A_1$ (D_{2d})

O	0.000000	1.402906	0.933907
O	0.000000	-1.402906	0.933907
O	-2.754872	0.000000	2.016157
O	-1.402906	0.000000	-0.933907
O	0.000000	2.754872	-2.016157
O	1.402906	0.000000	-0.933907
O	2.754872	0.000000	2.016157
TI	-1.427857	0.000000	1.038017
TI	0.000000	1.427857	-1.038017
TI	1.427857	0.000000	1.038017
TI	0.000000	-1.427857	-1.038017
O	0.000000	-2.754872	-2.016157

$Ti_4O_8^-$ / ^2A_g (C_{2h} ***b***)

O	1.387850	1.713770	0.000000
TI	-0.412104	1.927510	0.000000
TI	2.285788	0.035541	0.000000
O	-1.387850	1.156042	1.264232

O	-1.387850	1.156042	-1.264232
O	1.387850	-1.156042	1.264232
O	1.387850	-1.156042	-1.264232
TI	-2.285788	-0.035541	0.000000
O	-3.936319	-0.041657	0.000000
TI	0.412104	-1.927510	0.000000
O	-1.387850	-1.713770	0.000000
O	3.936319	0.041657	0.000000

$Ti_4O_8^-$ / $^2A_1$ (C_{2v} ***c***)

O	0.000000	0.000000	2.659332
TI	0.000000	1.500185	1.559688
TI	0.000000	-1.500185	1.559688
O	-1.266873	1.742252	0.370574
O	1.266873	1.742252	0.370574
O	-1.266873	-1.742252	0.370574
O	1.266873	-1.742252	0.370574
TI	0.000000	1.682374	-1.166314
O	0.000000	2.989292	-2.175679
TI	0.000000	-1.682374	-1.166314
O	0.000000	0.000000	-1.953828
O	0.000000	-2.989292	-2.175679

$Ti_4O_8^-$ / $^2A_1$ (C_{2v} ***d***)

O	0.000000	2.472625	2.122677
O	-1.654884	1.531331	-0.208310
O	-3.655505	0.000000	-1.850388
O	-1.654884	-1.531331	-0.208310
O	0.000000	-2.472625	2.122677
O	1.654884	-1.531331	-0.208310
O	1.654884	1.531331	-0.208310
O	3.655505	0.000000	-1.850388
TI	0.000000	-1.706684	0.667403
TI	2.563217	0.000000	-0.614919
TI	0.000000	1.706684	0.667403
TI	-2.563217	0.000000	-0.614919

TiO_2 / $^3B_2$ (C_{2v})

TI	0.000000	0.000000	0.470192
O	0.000000	1.281794	-0.646513
O	0.000000	-1.281794	-0.646513

Ti_2O_4 / ^3B_g (C_{2h})

TI	0.000000	1.343787	0.000000
O	0.000000	0.000000	1.261736
O	0.000000	0.000000	-1.261736
TI	0.000000	-1.343787	0.000000
O	1.275739	-2.509935	0.000000
O	-1.275739	2.509935	0.000000

Ti_2O_4 / $^3A''$ (C_s)

TI	-0.281357	-1.429559	0.000000
O	-0.105002	-0.068879	1.256976

O	-0.105002	-0.068879	-1.256976
TI	0.065526	1.255725	0.000000
O	-0.105002	3.153603	0.000000
O	0.908543	-2.537801	0.000000

Ti_2O_4 / $^3B_1$ (C_{2v} ***a***)

TI	0.000000	1.321512	-0.242223
O	1.287212	0.000000	-0.457924
O	-1.287212	0.000000	-0.457924
TI	0.000000	-1.321512	-0.242223
O	0.000000	-2.345597	1.124037
O	0.000000	2.345597	1.124037

Ti_2O_4 / $^3A_2$ (C_{3v})

TI	0.000000	0.000000	1.479118
O	0.000000	1.486591	0.374931
O	-1.287425	-0.743295	0.374931
O	1.287425	-0.743295	0.374931
TI	0.000000	0.000000	-0.949291
O	0.000000	0.000000	-2.581816

Ti_3O_6 / $^3A'$ (C_s)

TI	-0.235743	-0.523929	1.409282
O	1.129643	-0.209592	0.000000
O	-1.284083	-1.132683	0.000000
TI	-0.235743	-0.523929	-1.409282
O	0.083056	-1.530353	-2.747332
O	0.083056	-1.530353	2.747332
TI	0.638691	1.666771	0.000000
O	-0.235743	1.350483	1.570180
O	-0.235743	1.350483	-1.570180

Ti_3O_6 / ^3A (C_2)

TI	0.000000	0.000000	0.144811
O	-0.933792	1.352314	-0.718963
O	0.843527	1.361119	1.057258
O	-0.843527	-1.361119	1.057258
O	0.933792	-1.352314	-0.718963
TI	0.000000	2.699803	0.107338
TI	0.000000	-2.699803	0.107338
O	-0.913071	-3.809516	-0.832590
O	0.913071	3.809516	-0.832590

Ti_3O_6 / ^3A (C_1)

TI	0.064456	-0.047657	-0.011927
O	1.386458	-0.146911	1.254665
O	1.410924	-0.196146	-1.247308
O	-1.330424	-1.247636	-0.002152
O	-1.253999	1.255789	-0.052477
TI	2.768366	-0.290435	0.019755
TI	-2.640736	0.057177	-0.028630
O	-4.537224	0.140850	0.096139
O	3.796027	0.966570	0.008340

Ti_4O_8 / $^3A_2$ (C_{2v} ***a***)

TI	0.000000	1.985731	-0.663777
O	1.538547	1.765781	0.341889
O	0.000000	2.959542	-2.081727
O	0.000000	0.000000	2.185966
O	0.000000	0.000000	-0.711546
TI	1.320207	0.000000	0.904046
O	1.538547	-1.765781	0.341889
TI	0.000000	-1.985731	-0.663777
O	0.000000	-2.959542	-2.081727
O	-1.538547	1.765781	0.341889
TI	-1.320207	0.000000	0.904046
O	-1.538547	-1.765781	0.341889

Ti_4O_8 / ^3B_g (C_{2h} ***a***)

TI	0.898523	2.299123	0.000000
O	0.000000	1.851301	1.569891
O	2.126247	3.499487	0.000000
O	1.361374	0.345941	0.000000
O	-1.361374	-0.345941	0.000000
TI	0.000000	0.000000	1.325202
O	0.000000	-1.851301	1.569891
TI	-0.898523	-2.299123	0.000000
O	-2.126247	-3.499487	0.000000
O	0.000000	1.851301	-1.569891
TI	0.000000	0.000000	-1.325202
O	0.000000	-1.851301	-1.569891

Ti_4O_8 / $^3A_1$ (C_{2v} ***b***)

O	0.000000	0.000000	2.459350
TI	1.434910	0.000000	1.313536
TI	-1.434910	0.000000	1.313536
O	1.461264	1.450112	0.290398
O	1.461264	-1.450112	0.290398
O	-1.461264	1.450112	0.290398
O	-1.461264	-1.450112	0.290398
TI	0.000000	1.617489	-0.929660
TI	0.000000	-1.617489	-0.929660
O	0.000000	2.975670	-1.952466
O	0.000000	0.000000	-1.827325
O	0.000000	-2.975670	-1.952466

Table S17. Cartesian coordinates in Angstroms optimized at the BP86/aD level for the low-lying structures of the $(TiO_2)_n$ (n = 1−4) clusters and their anions, as well as the first triplet excited states of the neutral clusters.

TiO_2 / $^1A_1$ (C_{2v})

TI	0.000000	0.000000	0.396998
O	0.000000	1.361529	-0.545873
O	0.000000	-1.361529	-0.545873

Ti_2O_4 / ^1A_g (C_{2h})

TI	0.000000	1.358790	0.000000
O	0.000000	0.000000	1.259175
O	0.000000	0.000000	-1.259175
TI	0.000000	-1.358790	0.000000
O	1.390706	-2.234545	0.000000
O	-1.390706	2.234545	0.000000

Ti_2O_4 / $^1A_1$ (C_{2v} ***a***)

TI	0.000000	1.362141	-0.284550
O	1.265298	0.000000	-0.302256
O	-1.265298	0.000000	-0.302256
TI	0.000000	-1.362141	-0.284550
O	0.000000	-2.265882	1.084768
O	0.000000	2.265882	1.084768

Ti_2O_4 / $^1A_1$ (C_{3v})

TI	0.000000	0.000000	1.444309
O	0.000000	1.456836	0.420630
O	-1.261657	-0.728418	0.420630
O	1.261657	-0.728418	0.420630
TI	0.000000	0.000000	-0.956490
O	0.000000	0.000000	-2.603392

Ti_3O_6 / $^1A'$ (C_s ***a***)

TI	-0.285900	-0.558403	1.425913
O	1.164496	-0.110560	0.000000
O	-1.203241	-1.336885	0.000000
TI	-0.285900	-0.558403	-1.425913
O	0.115377	-1.462564	-2.735050
O	0.115377	-1.462564	2.735050
TI	0.709905	1.646979	0.000000
O	-0.285900	1.457297	1.421150
O	-0.285900	1.457297	-1.421150

Ti_3O_6 / ^1A (C_2)

TI	0.000000	0.000000	0.070399
O	-0.888436	1.388554	-0.774422
O	0.885853	1.306654	1.011337

O	-0.885853	-1.306654	1.011337
O	0.888436	-1.388554	-0.774422
TI	0.000000	2.717054	0.163801
TI	0.000000	-2.717054	0.163801
O	-0.990964	-3.613923	-0.784166
O	0.990964	3.613923	-0.784166

Ti_4O_8 / $^1A_1$ (C_{2v} ***a***)

TI	0.000000	2.030270	-0.607228
O	1.707734	1.684137	0.279754
O	0.000000	2.734818	-2.078740
O	0.000000	0.000000	2.062822
O	0.000000	0.000000	-0.517701
TI	1.411240	0.000000	0.878744
O	1.707734	-1.684137	0.279754
TI	0.000000	-2.030270	-0.607228
O	0.000000	-2.734818	-2.078740
O	-1.707734	1.684137	0.279754
TI	-1.411240	0.000000	0.878744
O	-1.707734	-1.684137	0.279754

Ti_4O_8 / ^1A_g (C_{2h} ***a***)

TI	0.774194	2.341092	0.000000
O	0.000000	1.795403	1.712224
O	2.120303	3.264720	0.000000
O	1.240052	0.297954	0.000000
O	-1.240052	-0.297954	0.000000
TI	0.000000	0.000000	1.391694
O	0.000000	-1.795403	1.712224
TI	-0.774194	-2.341092	0.000000
O	-2.120303	-3.264720	0.000000
O	0.000000	1.795403	-1.712224
TI	0.000000	0.000000	-1.391694
O	0.000000	-1.795403	-1.712224

Ti_4O_8 / $^1A_1$ (C_{2v} ***b***)

O	0.000000	0.000000	2.321750
TI	1.576068	0.000000	1.363605
TI	-1.576068	0.000000	1.363605
O	1.493735	1.392790	0.338467
O	1.493735	-1.392790	0.338467
O	-1.493735	1.392790	0.338467
O	-1.493735	-1.392790	0.338467
TI	0.000000	1.599613	-0.985897
TI	0.000000	-1.599613	-0.985897
O	0.000000	2.954760	-1.913628
O	0.000000	0.000000	-1.925754
O	0.000000	-2.954760	-1.913628

TiO_2^- / $^2A_1$ (C_{2v})

TI	0.000000	0.000000	0.397385
O	0.000000	1.399434	-0.546405
O	0.000000	-1.399434	-0.546405

$Ti_2O_4^-$ / $^2A_1$ (C_{2v} ***a***)

TI	0.000000	1.338826	-0.234233
O	1.307743	0.000000	-0.103333
O	-1.307743	0.000000	-0.103333
TI	0.000000	-1.338826	-0.234233
O	0.000000	-2.700871	0.747473
O	0.000000	2.700871	0.747473

$Ti_2O_4^-$ / ^2A_g (C_{2h})

TI	0.000000	1.354261	0.000000
O	0.000000	0.000000	1.297607
O	0.000000	0.000000	-1.297607
TI	0.000000	-1.354261	0.000000
O	1.132802	-2.597721	0.000000
O	-1.132802	2.597721	0.000000

$Ti_2O_4^-$ / $^2A_1$ (C_{3v})

TI	0.000000	0.000000	1.434006
O	0.000000	1.498756	0.381580
O	-1.297960	-0.749378	0.381580
O	1.297960	-0.749378	0.381580
TI	0.000000	0.000000	-0.907362
O	0.000000	0.000000	-2.593013

$Ti_3O_6^-$ / $^2A'$ (C_s ***a***)

TI	-0.247541	-0.537665	1.417911
O	1.194038	-0.177656	0.000000
O	-1.269938	-1.225186	0.000000
TI	-0.247541	-0.537665	-1.417911
O	0.025726	-1.467958	-2.775359
O	0.025726	-1.467958	2.775359
TI	0.684002	1.627686	0.000000
O	-0.247541	1.409889	1.531143
O	-0.247541	1.409889	-1.531143

$Ti_3O_6^-$ / ^2B (C_2)

TI	0.000000	0.000000	0.077642
O	-0.898243	1.360898	-0.805150
O	0.908443	1.311586	1.009110
O	-0.908443	-1.311586	1.009110
O	0.898243	-1.360898	-0.805150
TI	0.000000	2.719506	0.136813
TI	0.000000	-2.719506	0.136813
O	-0.858503	-3.892382	-0.686953
O	0.858503	3.892382	-0.686953

$Ti_4O_8^-$ / ^2A_g (C_{2h} ***a***)

TI	0.912168	2.302935	0.000000
O	0.000000	1.837702	1.632612
O	2.125287	3.444775	0.000000

O	1.391659	0.331445	0.000000
O	-1.391659	-0.331445	0.000000
TI	0.000000	0.000000	1.315800
O	0.000000	-1.837702	1.632612
TI	-0.912168	-2.302935	0.000000
O	-2.125287	-3.444775	0.000000
O	0.000000	1.837702	-1.632612
TI	0.000000	0.000000	-1.315800
O	0.000000	-1.837702	-1.632612

$Ti_4O_8^-$ / $^2A_1$ (C_{2v} ***a***)

TI	0.000000	2.011136	-0.674002
O	1.597749	1.758211	0.347369
O	0.000000	3.007729	-2.008299
O	0.000000	0.000000	2.217174
O	0.000000	0.000000	-0.736517
TI	1.305854	0.000000	0.882450
O	1.597749	-1.758211	0.347369
TI	0.000000	-2.011136	-0.674002
O	0.000000	-3.007729	-2.008299
O	-1.597749	1.758211	0.347369
TI	-1.305854	0.000000	0.882450
O	-1.597749	-1.758211	0.347369

$Ti_4O_8^-$ / $^2A_1$ (C_{2v} ***b***)

O	0.000000	0.000000	2.491903
TI	1.430825	0.000000	1.304743
TI	-1.430825	0.000000	1.304743
O	1.504655	1.467365	0.317279
O	1.504655	-1.467365	0.317279
O	-1.504655	1.467365	0.317279
O	-1.504655	-1.467365	0.317279
TI	0.000000	1.618294	-0.952301
TI	0.000000	-1.618294	-0.952301
O	0.000000	2.982913	-1.906999
O	0.000000	0.000000	-1.885448
O	0.000000	-2.982913	-1.906999

TiO_2 / $^3B_2$ (C_{2v})

TI	0.000000	0.000000	0.477925
O	0.000000	1.269933	-0.657147
O	0.000000	-1.269933	-0.657147

Ti_2O_4 / ^3B_g (C_{2h})

TI	0.000000	1.350104	0.000000
O	0.000000	0.000000	1.272642
O	0.000000	0.000000	-1.272642
TI	0.000000	-1.350104	0.000000
O	1.344453	-2.427977	0.000000
O	-1.344453	2.427977	0.000000

Ti_2O_4 / $^3A''$ (C_s)

TI	-0.102838	-1.453723	0.000000
O	-0.086969	-0.056438	1.265061
O	-0.086969	-0.056438	-1.265061
TI	-0.086969	1.253367	0.000000
O	-0.529734	3.076798	0.000000
O	1.225639	-2.412943	0.000000

Ti_2O_4 / $^3B_1$ (C_{2v} ***a***)

TI	0.000000	1.327893	-0.251286
O	1.295346	0.000000	-0.479197
O	-1.295346	0.000000	-0.479197
TI	0.000000	-1.327893	-0.251286
O	0.000000	-2.270282	1.170234
O	0.000000	2.270282	1.170234

Ti_2O_4 / $^3A_2$ (C_{3v})

TI	0.000000	0.000000	1.468550
O	0.000000	1.498323	0.384664
O	-1.297586	-0.749162	0.384664
O	1.297586	-0.749162	0.384664
TI	0.000000	0.000000	-0.945072
O	0.000000	0.000000	-2.593554

Ti_3O_6 / $^3A'$ (C_s ***a***)

TI	-0.245474	-0.521636	1.410791
O	1.146310	-0.193714	0.000000
O	-1.286837	-1.165455	0.000000
TI	-0.245474	-0.521636	-1.410791
O	0.114571	-1.508276	-2.761816
O	0.114571	-1.508276	2.761816
TI	0.637252	1.643948	0.000000
O	-0.245474	1.361930	1.573480
O	-0.245474	1.361930	-1.573480

Ti_3O_6 / ^3A (C_2)

TI	0.000000	0.000000	0.161833
O	-0.960976	1.348062	-0.701636
O	0.834822	1.370763	1.086887
O	-0.834822	-1.370763	1.086887
O	0.960976	-1.348062	-0.701636
TI	0.000000	2.710741	0.107597
TI	0.000000	-2.710741	0.107597
O	-0.985507	-3.666800	-0.903663
O	0.985507	3.666800	-0.903663

Ti_3O_6 / ^3A (C_1)

TI	0.062497	-0.052907	-0.068387
O	1.324297	-0.028037	1.268871
O	1.463698	-0.327050	-1.224979
O	-1.348379	-1.259753	-0.001037
O	-1.275825	1.243675	-0.299030
TI	2.762552	-0.294194	0.113573

TI	-2.644309	0.044759	-0.133439
O	-4.400125	0.187164	0.486167
O	3.739300	1.015440	0.012706

Ti_4O_8 / $^3A_2$ (C_{2v} ***a***)

TI	0.000000	1.998423	-0.653972
O	1.563915	1.775065	0.339706
O	0.000000	2.973938	-2.064816
O	0.000000	0.000000	2.186188
O	0.000000	0.000000	-0.715217
TI	1.319958	0.000000	0.890306
O	1.563915	-1.775065	0.339706
TI	0.000000	-1.998423	-0.653972
O	0.000000	-2.973938	-2.064816
O	-1.563915	1.775065	0.339706
TI	-1.319958	0.000000	0.890306
O	-1.563915	-1.775065	0.339706

Ti_4O_8 / ^3B_g (C_{2h} ***a***)

TI	0.893310	2.298770	0.000000
O	0.000000	1.854221	1.593612
O	2.136936	3.477755	0.000000
O	1.371170	0.342573	0.000000
O	-1.371170	-0.342573	0.000000
TI	0.000000	0.000000	1.324472
O	0.000000	-1.854221	1.593612
TI	-0.893310	-2.298770	0.000000
O	-2.136936	-3.477755	0.000000
O	0.000000	1.854221	-1.593612
TI	0.000000	0.000000	-1.324472
O	0.000000	-1.854221	-1.593612

Ti_4O_8 / $^3A_1$ (C_{2v} ***b***)

O	0.000000	0.000000	2.459145
TI	1.440271	0.000000	1.309099
TI	-1.440271	0.000000	1.309099
O	1.476301	1.458949	0.285854
O	1.476301	-1.458949	0.285854
O	-1.476301	1.458949	0.285854
O	-1.476301	-1.458949	0.285854
TI	0.000000	1.608542	-0.926184
TI	0.000000	-1.608542	-0.926184
O	0.000000	2.994203	-1.927340
O	0.000000	0.000000	-1.853912
O	0.000000	-2.994203	-1.927340

Table S18. Cartesian coordinates in Angstroms optimized at the PW91/aD level for the low-lying structures of the $(TiO_2)_n$ (n = 1−4) clusters and their anions, as well as the first triplet excited states of the neutral clusters.

TiO_2 / $^1A_1$ (C_{2v})

TI	0.000000	0.000000	0.397544
O	0.000000	1.358122	-0.546623
O	0.000000	-1.358122	-0.546623

Ti_2O_4 / ^1A_g (C_{2h})

TI	0.000000	1.358051	0.000000
O	0.000000	0.000000	1.256992
O	0.000000	0.000000	-1.256992
TI	0.000000	-1.358051	0.000000
O	1.396115	-2.221423	0.000000
O	-1.396115	2.221423	0.000000

Ti_2O_4 / $^1A_1$ (C_{2v} ***a***)

TI	0.000000	1.361465	-0.285611
O	1.263031	0.000000	-0.304961
O	-1.263031	0.000000	-0.304961
TI	0.000000	-1.361465	-0.285611
O	0.000000	-2.251145	1.090391
O	0.000000	2.251145	1.090391

Ti_2O_4 / $^1A_1$ (C_{3v})

TI	0.000000	0.000000	1.444165
O	0.000000	1.454269	0.419836
O	-1.259434	-0.727135	0.419836
O	1.259434	-0.727135	0.419836
TI	0.000000	0.000000	-0.956186
O	0.000000	0.000000	-2.601453

Ti_3O_6 / $^1A'$ (C_s ***a***)

TI	-0.285889	-0.558021	1.424583
O	1.163200	-0.110644	0.000000
O	-1.201906	-1.335730	0.000000
TI	-0.285889	-0.558021	-1.424583
O	0.113659	-1.460571	-2.733064
O	0.113659	-1.460571	2.733064
TI	0.711110	1.646207	0.000000
O	-0.285889	1.454781	1.417850
O	-0.285889	1.454781	-1.417850

Ti_3O_6 / ^1A (C_2)

TI	0.000000	0.000000	0.069141
O	-0.887560	1.388567	-0.772659
O	0.883989	1.304840	1.010233

O	-0.883989	-1.304840	1.010233
O	0.887560	-1.388567	-0.772659
TI	0.000000	2.715306	0.164975
TI	0.000000	-2.715306	0.164975
O	-0.994945	-3.600428	-0.786325
O	0.994945	3.600428	-0.786325

Ti_4O_8 / $^1A_1$ (C_{2v} ***a***)

TI	0.000000	2.028446	-0.606673
O	1.705511	1.682182	0.279012
O	0.000000	2.730968	-2.077044
O	0.000000	0.000000	2.059998
O	0.000000	0.000000	-0.516945
TI	1.410693	0.000000	0.878489
O	1.705511	-1.682182	0.279012
TI	0.000000	-2.028446	-0.606673
O	0.000000	-2.730968	-2.077044
O	-1.705511	1.682182	0.279012
TI	-1.410693	0.000000	0.878489
O	-1.705511	-1.682182	0.279012

Ti_4O_8 / ^1A_g (C_{2h} ***a***)

TI	0.773421	2.339178	0.000000
O	0.000000	1.793875	1.709674
O	2.119079	3.260093	0.000000
O	1.238566	0.296996	0.000000
O	-1.238566	-0.296996	0.000000
TI	0.000000	0.000000	1.390858
O	0.000000	-1.793875	1.709674
TI	-0.773421	-2.339178	0.000000
O	-2.119079	-3.260093	0.000000
O	0.000000	1.793875	-1.709674
TI	0.000000	0.000000	-1.390858
O	0.000000	-1.793875	-1.709674

Ti_4O_8 / $^1A_1$ (C_{2v} ***b***)

O	0.000000	0.000000	2.318296
TI	1.576183	0.000000	1.363893
TI	-1.576183	0.000000	1.363893
O	1.490134	1.390037	0.338517
O	1.490134	-1.390037	0.338517
O	-1.490134	1.390037	0.338517
O	-1.490134	-1.390037	0.338517
TI	0.000000	1.597597	-0.986061
TI	0.000000	-1.597597	-0.986061
O	0.000000	2.951488	-1.912493
O	0.000000	0.000000	-1.925452
O	0.000000	-2.951488	-1.912493

TiO_2^- / $^2A_1$ (C_{2v})

TI	0.000000	0.000000	0.397737
O	0.000000	1.395791	-0.546888
O	0.000000	-1.395791	-0.546888

$Ti_2O_4^-$ / $^2A_1$ (C_{2v} ***a***)

TI	0.000000	1.337867	-0.235187
O	1.305614	0.000000	-0.102546
O	-1.305614	0.000000	-0.102546
TI	0.000000	-1.337867	-0.235187
O	0.000000	-2.695192	0.749311
O	0.000000	2.695192	0.749311

$Ti_2O_4^-$ / ^2A_g (C_{2h})

TI	0.000000	1.353700	0.000000
O	0.000000	0.000000	1.294818
O	0.000000	0.000000	-1.294818
TI	0.000000	-1.353700	0.000000
O	1.145317	-2.582568	0.000000
O	-1.145317	2.582568	0.000000

$Ti_2O_4^-$ / $^2A_1$ (C_{3v})

TI	0.000000	0.000000	1.433729
O	0.000000	1.496099	0.380942
O	-1.295659	-0.748049	0.380942
O	1.295659	-0.748049	0.380942
TI	0.000000	0.000000	-0.907115
O	0.000000	0.000000	-2.591016

$Ti_3O_6^-$ / $^2A'$ (C_s ***a***)

TI	-0.247741	-0.537264	1.416435
O	1.192720	-0.177804	0.000000
O	-1.268737	-1.224425	0.000000
TI	-0.247741	-0.537264	-1.416435
O	0.025635	-1.465811	-2.772879
O	0.025635	-1.465811	2.772879
TI	0.684657	1.626535	0.000000
O	-0.247741	1.407914	1.528117
O	-0.247741	1.407914	-1.528117

$Ti_3O_6^-$ / ^2B (C_2)

TI	0.000000	0.000000	0.078012
O	-0.898069	1.360033	-0.802396
O	0.905946	1.310710	1.009467
O	-0.905946	-1.310710	1.009467
O	0.898069	-1.360033	-0.802396
TI	0.000000	2.717501	0.137142
TI	0.000000	-2.717501	0.137142
O	-0.863762	-3.879966	-0.691478
O	0.863762	3.879966	-0.691478

$Ti_4O_8^-$ / ^2A_g (C_{2h} ***a***)

TI	0.911440	2.301347	0.000000
O	0.000000	1.836106	1.630026
O	2.123249	3.441901	0.000000

O	1.390594	0.330771	0.000000
O	-1.390594	-0.330771	0.000000
TI	0.000000	0.000000	1.314238
O	0.000000	-1.836106	1.630026
TI	-0.911440	-2.301347	0.000000
O	-2.123249	-3.441901	0.000000
O	0.000000	1.836106	-1.630026
TI	0.000000	0.000000	-1.314238
O	0.000000	-1.836106	-1.630026

$Ti_4O_8^-$ / $^2A_1$ (C_{2v} ***a***)

TI	0.000000	2.009862	-0.673587
O	1.594797	1.756587	0.347092
O	0.000000	3.006921	-2.005220
O	0.000000	0.000000	2.214675
O	0.000000	0.000000	-0.737317
TI	1.304608	0.000000	0.881717
O	1.594797	-1.756587	0.347092
TI	0.000000	-2.009862	-0.673587
O	0.000000	-3.006921	-2.005220
O	-1.594797	1.756587	0.347092
TI	-1.304608	0.000000	0.881717
O	-1.594797	-1.756587	0.347092

$Ti_4O_8^-$ / $^2A_1$ (C_{2v} ***b***)

O	0.000000	0.000000	2.489155
TI	1.428905	0.000000	1.302617
TI	-1.428905	0.000000	1.302617
O	1.503321	1.466397	0.316915
O	1.503321	-1.466397	0.316915
O	-1.503321	1.466397	0.316915
O	-1.503321	-1.466397	0.316915
TI	0.000000	1.616419	-0.950677
TI	0.000000	-1.616419	-0.950677
O	0.000000	2.979504	-1.904643
O	0.000000	0.000000	-1.883194
O	0.000000	-2.979504	-1.904643

TiO_2 / $^3B_2$ (C_{2v})

TI	0.000000	0.000000	0.479541
O	0.000000	1.264229	-0.659369
O	0.000000	-1.264229	-0.659369

Ti_2O_4 / ^3B_g (C_{2h})

TI	0.000000	1.349086	0.000000
O	0.000000	0.000000	1.271356
O	0.000000	0.000000	-1.271356
TI	0.000000	-1.349086	0.000000
O	1.354390	-2.410429	0.000000
O	-1.354390	2.410429	0.000000

Ti_2O_4 / $^3A''$ (C_s)

TI	-0.098608	-1.454508	0.000000
O	-0.089641	-0.056468	1.263177
O	-0.089641	-0.056468	-1.263177
TI	-0.089641	1.250908	0.000000
O	-0.542138	3.069996	0.000000
O	1.239107	-2.397159	0.000000

Ti_2O_4 / $^3B_1$ (C_{2v} ***a***)

TI	0.000000	1.325465	-0.252363
O	1.294413	0.000000	-0.488267
O	-1.294413	0.000000	-0.488267
TI	0.000000	-1.325465	-0.252363
O	0.000000	-2.242876	1.182266
O	0.000000	2.242876	1.182266

Ti_2O_4 / $^3A_2$ (C_{3v})

TI	0.000000	0.000000	1.468482
O	0.000000	1.495693	0.384183
O	-1.295309	-0.747847	0.384183
O	1.295309	-0.747847	0.384183
TI	0.000000	0.000000	-0.945117
O	0.000000	0.000000	-2.591801

Ti_3O_6 / $^3A'$ (C_s ***a***)

TI	-0.245589	-0.521274	1.409677
O	1.144984	-0.193390	0.000000
O	-1.285467	-1.163977	0.000000
TI	-0.245589	-0.521274	-1.409677
O	0.114649	-1.506405	-2.759609
O	0.114649	-1.506405	2.759609
TI	0.637492	1.642568	0.000000
O	-0.245589	1.360061	1.570959
O	-0.245589	1.360061	-1.570959

Ti_3O_6 / ^3A (C_2)

TI	0.000000	0.000000	0.163190
O	-0.961495	1.347431	-0.698236
O	0.831156	1.370459	1.088651
O	-0.831156	-1.370459	1.088651
O	0.961495	-1.347431	-0.698236
TI	0.000000	2.708770	0.107643
TI	0.000000	-2.708770	0.107643
O	-0.990441	-3.647824	-0.910821
O	0.990441	3.647824	-0.910821

Ti_3O_6 / ^3A (C_1)

TI	0.062421	-0.050957	-0.070596
O	1.320160	-0.022179	1.267762
O	1.464269	-0.333767	-1.220742
O	-1.346161	-1.258005	-0.002528
O	-1.277248	1.240685	-0.313244
TI	2.759828	-0.295134	0.118606

TI	-2.642227	0.042547	-0.140799
O	-4.383231	0.189317	0.512120
O	3.727151	1.018695	0.011801

Ti_4O_8 / $^3A_2$ (C_{2v} ***a***)

TI	0.000000	1.996906	-0.654192
O	1.560844	1.772996	0.339352
O	0.000000	2.973302	-2.062967
O	0.000000	0.000000	2.184655
O	0.000000	0.000000	-0.715512
TI	1.318305	0.000000	0.890443
O	1.560844	-1.772996	0.339352
TI	0.000000	-1.996906	-0.654192
O	0.000000	-2.973302	-2.062967
O	-1.560844	1.772996	0.339352
TI	-1.318305	0.000000	0.890443
O	-1.560844	-1.772996	0.339352

Ti_4O_8 / ^3B_g (C_{2h} ***a***)

TI	0.893357	2.297089	0.000000
O	0.000000	1.852662	1.590571
O	2.136144	3.474849	0.000000
O	1.370151	0.341846	0.000000
O	-1.370151	-0.341846	0.000000
TI	0.000000	0.000000	1.322904
O	0.000000	-1.852662	1.590571
TI	-0.893357	-2.297089	0.000000
O	-2.136144	-3.474849	0.000000
O	0.000000	1.852662	-1.590571
TI	0.000000	0.000000	-1.322904
O	0.000000	-1.852662	-1.590571

Ti_4O_8 / $^3A_1$ (C_{2v} ***b***)

O	0.000000	0.000000	2.456004
TI	1.438934	0.000000	1.307555
TI	-1.438934	0.000000	1.307555
O	1.474432	1.457597	0.285658
O	1.474432	-1.457597	0.285658
O	-1.474432	1.457597	0.285658
O	-1.474432	-1.457597	0.285658
TI	0.000000	1.606840	-0.925176
TI	0.000000	-1.606840	-0.925176
O	0.000000	2.991461	-1.924836
O	0.000000	0.000000	-1.852050
O	0.000000	-2.991461	-1.924836

Table S19. Cartesian coordinates in Angstroms optimized at the CCSD(T)/aD level for the low-lying structures of the $(TiO_2)_n$ (n = 1, 2) clusters and their anions.

TiO_2 / $^1A_1$ (C_{2v})

TI	0.00000000	0.00000000	-0.36992374
O	0.00000000	1.39377441	0.55351915
O	0.00000000	-1.39377441	0.55351915

Ti_2O_4 / ^1A_g (C_{2h})

TI	-1.30600500	-0.39956416	0.00000000
TI	1.30600500	0.39956416	0.00000000
O	0.00000000	0.00000000	1.27494183
O	0.00000000	0.00000000	-1.27494183
O	-2.62642358	0.59458923	0.00000000
O	2.62642358	-0.59458923	0.00000000

Ti_2O_4 / $^1A_1$ (C_{2v} ***a***)

TI	0.00000000	-1.36890337	-0.25414300
TI	0.00000000	1.36890337	-0.25414300
O	1.28210396	0.00000000	-0.29547815
O	-1.28210396	0.00000000	-0.29547815
O	0.00000000	-2.37236464	1.05602960
O	0.00000000	2.37236464	1.05602960

Ti_2O_4 / $^1A_1$ (C_{3v})

TI	0.00000000	0.00000000	0.98200929
TI	0.00000000	0.00000000	-1.44747461
O	0.00000000	0.00000000	2.63589673
O	1.45955225	0.00000000	-0.41431318
O	-0.72977612	1.26400933	-0.41431318
O	-0.72977612	-1.26400933	-0.41431318

TiO_2^- / $^2A_1$ (C_{2v})

TI	0.00000000	0.00000000	-0.36653086
O	0.00000000	1.43456898	0.54844237
O	0.00000000	-1.43456898	0.54844237

$Ti_2O_4^-$ / $^2A_1$ (C_{2v} ***a***)

TI	0.00000000	-1.34263323	-0.19613784
TI	0.00000000	1.34263323	-0.19613784
O	1.31785578	0.00000000	-0.02282573
O	-1.31785578	0.00000000	-0.02282573
O	0.00000000	-2.82644740	0.60979021
O	0.00000000	2.82644740	0.60979021

$Ti_2O_4^-$ / ^2A_g (C_{2h})

TI	-1.33606801	-0.20607600	0.00000000
TI	1.33606801	0.20607600	0.00000000
O	0.00000000	0.00000000	1.33115936
O	0.00000000	0.00000000	-1.33115936
O	-2.96534358	0.27786343	0.00000000
O	2.96534358	-0.27786343	0.00000000

$Ti_2O_4^- / {}^2A_1$ (C_{3v})

TI	0.00000000	0.00000000	0.94652790
TI	0.00000000	0.00000000	-1.45072187
O	0.00000000	0.00000000	2.63043398
O	1.47798640	0.00000000	-0.37385898
O	-0.73899320	1.27997377	-0.37385898
O	-0.73899320	-1.27997377	-0.37385898

Table S20. Cartesian coordinates in Angstroms optimized at the CCSD(T)/aT level for the low-lying structures of the $(TiO_2)_n$ (n = 1, 2) clusters and their anions.

TiO_2 / $^1A_1$ (C_{2v})

TI	0.00000000	0.00000000	-0.37131599
O	0.00000000	1.38438786	0.55560238
O	0.00000000	-1.38438786	0.55560238

Ti_2O_4 / ^1A_g (C_{2h})

TI	-1.30282991	-0.40318275	0.00000000
TI	1.30282991	0.40318275	0.00000000
O	0.00000000	0.00000000	1.26850644
O	0.00000000	0.00000000	-1.26850644
O	-2.60751220	0.60285623	0.00000000
O	2.60751220	-0.60285623	0.00000000

Ti_2O_4 / $^1A_1$ (C_{2v})

TI	0.00000000	-1.36724115	-0.25631798
TI	0.00000000	1.36724115	-0.25631798
O	1.27484255	0.00000000	-0.30483924
O	-1.27484255	0.00000000	-0.30483924
O	0.00000000	-2.33740055	1.07189956
O	0.00000000	2.33740055	1.07189956

Ti_2O_4 / $^1A_1$ (C_{3v})

TI	0.00000000	0.00000000	0.97937745
TI	0.00000000	0.00000000	-1.44408705
O	0.00000000	0.00000000	2.62799895
O	1.45435393	0.00000000	-0.41243445
O	-0.72717696	1.25950745	-0.41243445
O	-0.72717696	-1.25950745	-0.41243445

TiO_2^- / $^2A_1$ (C_{2v} ***a***)

TI	0.00000000	0.00000000	-0.36824860
O	0.00000000	1.42477310	0.55101263
O	0.00000000	-1.42477310	0.55101263

$Ti_2O_4^-$ / $^2A_1$ (C_{2v} ***a***)

TI	0.00000000	-1.33887354	-0.19986742
TI	0.00000000	1.33887354	-0.19986742
O	1.31123426	0.00000000	-0.01534508
O	-1.31123426	0.00000000	-0.01534508
O	0.00000000	-2.81177073	0.61347077
O	0.00000000	2.81177073	0.61347077

$Ti_2O_4^-$ / ^2A_g (C_{2h})

TI	-1.33153916	-0.22671042	0.00000000
TI	1.33153916	0.22671042	0.00000000
O	0.00000000	0.00000000	1.32128270
O	0.00000000	0.00000000	-1.32128270
O	-2.93879606	0.30740181	0.00000000
O	2.93879606	-0.30740181	0.00000000

$Ti_2O_4^- / {}^2A_1$ (C_{3v})

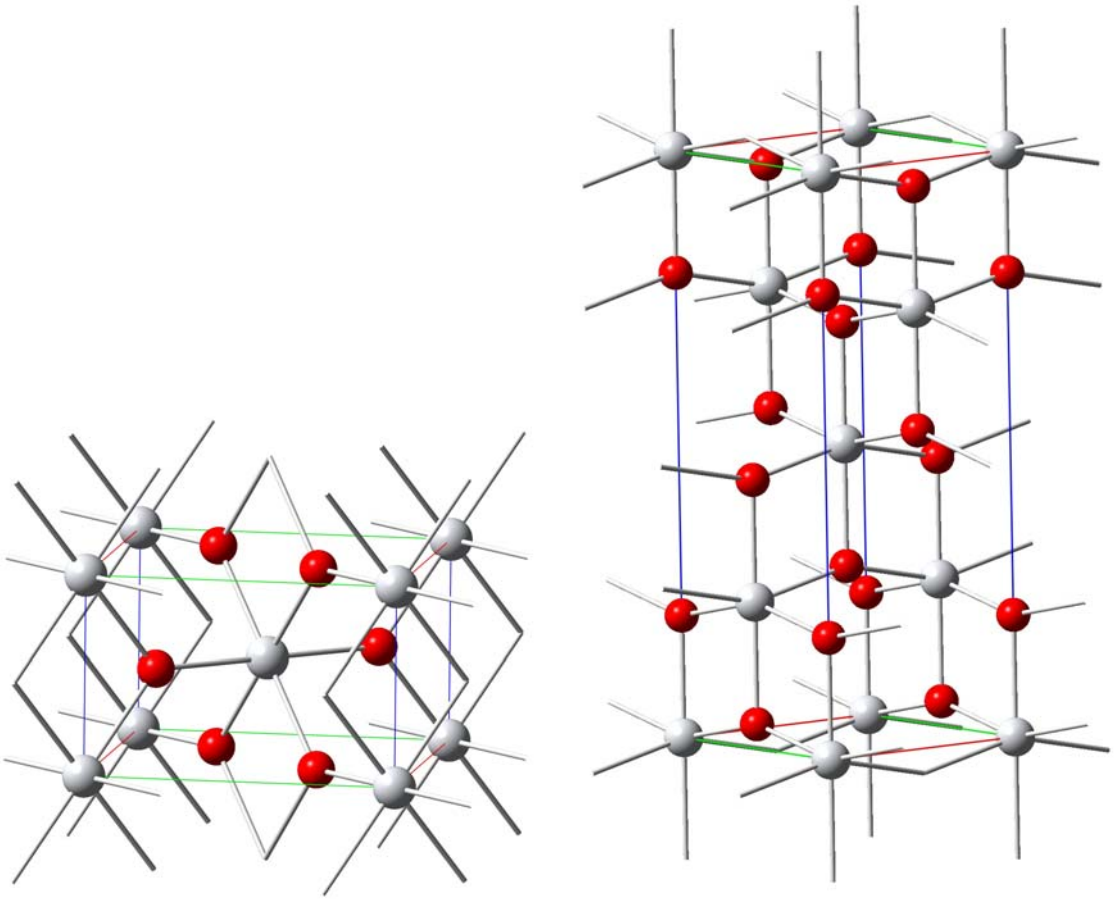
TI	0.00000000	0.00000000	0.94315708
TI	0.00000000	0.00000000	-1.44659195
O	0.00000000	0.00000000	2.62200127
O	1.47258646	0.00000000	-0.37180532
O	-0.73629323	1.27529728	-0.37180532
O	-0.73629323	-1.27529728	-0.37180532

Figure Captions.

Figure S1. Structures of the rutile (a) and anatase (b) phases of bulk TiO_2.

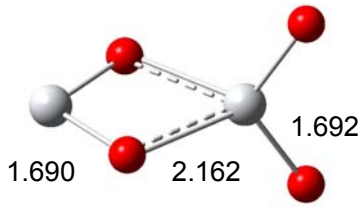
Figure S2. Additional high energy structures of $(TiO_2)_n^-$ (n = 2−4). The bond lengths (Å) and relative energies (kcal/mol) shown are calculated at the B3LYP/aD level.

Figure S1.

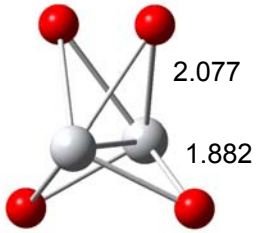


(a) (b)

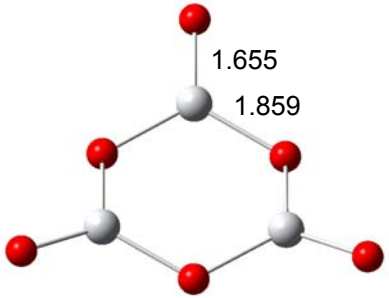
Figure S2.



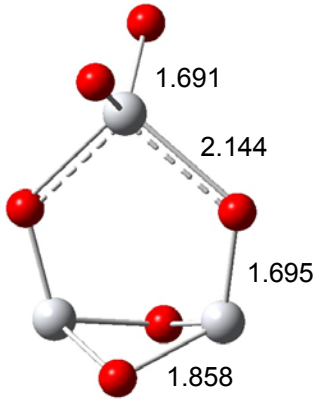
$Ti_2O_4^-$, $^2A_1$ (C_{2v} *b*), 28.6



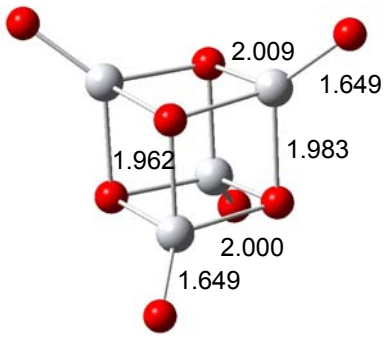
$Ti_2O_4^-$, $^2B_1$ (C_{2v} *c*), 135.5



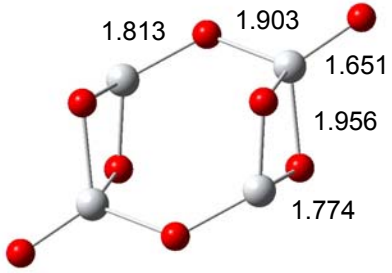
$Ti_3O_6^-$, $^2A_1$ (C_{3v}), 33.6



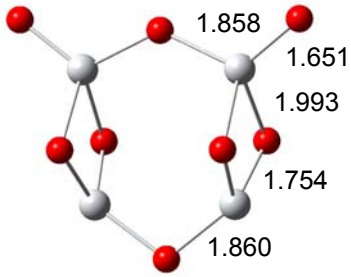
$Ti_3O_6^-$, $^2A_1$ (C_{2v}), 69.7



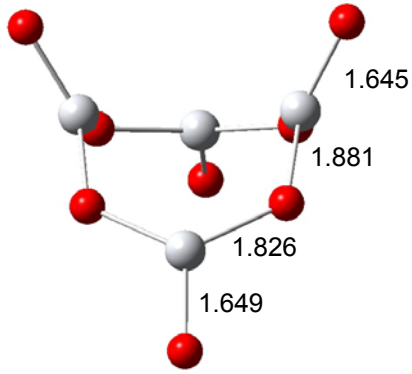
$Ti_4O_8^-$, $^2A_1$ (D_{2d}), 15.1



$Ti_4O_8^-$, ^2A_g (C_{2h} *b*), 17.8



$Ti_4O_8^-$, $^2A_1$ (C_{2v} *c*), 20.3



$Ti_4O_8^-$, $^2A_1$ (C_{2v} *d*), 59.4