Molecular and Dissociative Adsorption of Water on $(TiO_2)_n$ Clusters, n = 1 to 4

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Abstract

The low energy structures of the $(TiO_2)_n(H_2O)_m$ ($n \leq 4$, $m \leq 2n$) and $(TiO_2)_8(H_2O)_m$ ($m = 3,7,8$) clusters were predicted using a global geometry optimization approach, with a number of new lowest energy isomers being found. Water can molecularly or dissociatively adsorb on pure and hydrated TiO_2 clusters. Dissociative adsorption is the dominant reaction for the first two H_2O adsorption reactions for n = 1 2 and 4, and for the first three H_2O adsorption reactions for n = 3 and 8. As more H_2O's are added to the hydrated $(TiO_2)_n$ cluster, dissociative adsorption becomes less exothermic as all the Ti centers become 4-coordinate. Two types of bonds can be formed between the molecularly adsorbed water and TiO_2 clusters: a Lewis acid-base Ti–O(H_2) bond or an O•••H hydrogen bond. The coupled cluster CCSD(T) results show that at 0 K the H_2O adsorption energy at a 4-coordinate Ti center is ~ 15 kcal/mol for the Lewis acid-base molecular adsorption and ~ 7 kcal/mol for the H-bond molecular adsorption, in comparison to that of 8 to 10 kcal/mol for the dissociative adsorption. The cluster size and geometry independent dehydration reaction energy, E_D, for the general reaction 2 –TiOH → –TiOTi– + H_2O at 4-coordinate Ti centers was estimated from the aggregation reaction of n $Ti(OH)_4$ to form the monocyclic ring cluster $(TiO_3H_2)_n$ + n H_2O. E_D is estimated to be -8 kcal/mol, showing that intramolecular and intermolecular dehydration reactions are intrinsically thermodynamically allowed for the hydrated

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$(TiO_2)_n$ clusters with all of the Ti centers 4-coordinate, which can be hindered by cluster geometry changes caused by such processes. Bending force constants for the TiOTi and OTiO bonds are determined to be 7.4 and 56.0 kcal/(mol▪rad^2). Infrared vibrational spectra were calculated using density functional theory, and the new bands appearing upon water adsorption were assigned.

Keywords

Titanium dioxide; hydrolysis; transition metal oxide clusters; global geometry optimization; molecular adsorption; dissociative adsorption; H-bonding; Lewis acid-base interaction

Introduction

Titanium dioxide is widely utilized in different technologies, due to its unique photophysical and photochemical properties.[1] There is significant interest in TiO_2 because of its importance in the photolysis of water to produce hydrogen and oxygen [2] and photocatalytic water splitting reactions on TiO_2 and its nanoclusters has been extensively studied. The interaction of H_2O with a TiO_2 surface has been examined extensively. Henderson found that H_2O dissociation occurs at the defect sites of the TiO_2(110) surface.[3] Henrich and co-workers found that H_2O was molecularly adsorbed on both defective and near-perfect TiO_2 (rutile,100) surfaces at 160 K.[4] As the temperature increases above 200 K, a substantial amount of the molecularly adsorbed H_2O is removed, and OH groups form on the TiO_2 rutile 110 surface. Sato and White demonstrated that H_2 can be produced by UV-assisted water dissociation on a Pt-doped TiO_2 in the presence of CO (the water-gas shift reaction).[5] Schrauzer and co-workers used powdered samples of TiO_2 (rutile and anatase) and Fe-doped TiO_2 as the photocatalyst, and successfully generated O_2 and H_2 from H_2O vapor under UV radiation. [6] A recent study by Srivastava et al. showed that the photoelectrochemical performance of TiO_2 nanoclusters is enhanced as the size of the nanocluster is reduced, due in part to the increase of the surface area/volume ratio and an increase in the number of defect sites.[7]

Studies of small titanium oxide and titanium oxide/hydroxide clusters can provide a good starting point for understanding the reactivity of the clusters and potentially providing insights into the surface defects, which are important in water photolysis, as there is a similarity between the geometries of the small clusters and the local geometries of the surface defects. The active centers of a solid material can be divided into several types, corner, edge, surface, and bulk, based on the coordination numbers (CNs) with the CNs from low to high; the reactivity of the active centers are

highly correlated with their CNs. The structures of the small clusters, nanostructures, surfaces, and bulk materials can be distinguished by the ratio between the corner/edge/surface/bulk centers. Small clusters have a high percentage of active centers at the corner and edge positions. Nanostructures usually show high surface/bulk and medium edge/bulk ratios. Perfect surfaces only contain surface centers. Surface defects, such as steps and kinks, contain a considerable number of edge active centers and thus can display characteristics similar to those of small clusters and nanostructures.

The geometries and properties of small TiO_2 clusters have been extensively studied at different levels of theory.[8,9, 10, 11,12] The reaction mechanisms for the hydrolysis of small $(TiO_2)_n$ clusters, as well as the mechanisms for the O_2 and H_2 production reactions by the small titanium hydroxide clusters have been studied previously,[13,14] using density functional theory and coupled cluster CCSD(T) theory.[15,16,17,18] Yin and Bernstein studied H_2O oxidation by neutral Ti_2O_4 and Ti_2O_5 under visible light irradiation as well as with density functional theory.[19] Ignatyev and co-workers predicted the equilibrium structures for the $Ti(OH)_4$ dimer and trimer at the B3LYP/6-31+G(d) level, with titanium centers coordinated by more than 4 oxygens.[20] Berardo and coworkers predicted the low energy hydrated clusters for the TiO_2 monomer, dimer and trimer at the B3LYP/def2-TZVP level.[21]

The current work is focused on the prediction of the lowest energy $(TiO_2)_n(H_2O)_m$ ($n \leq 4$, $m \leq 2n$) structures and their properties based on a global minimum geometry search,[11] to obtain more details about the potential energy surfaces for the hydrolysis reactions, especially for complete hydrolysis of a given cluster. This extends our previous studies where complete hydrolysis was only reported for the monomer and partial hydrolysis for the dimer, trimer, and tetramer.[13] One of the our objectives is to determine stationary minima on the potential energy

surface for the $(TiO_2)_n$ hydrolysis reactions using a novel global geometry optimization technique, which is the prerequisite for predicting meaningful reaction paths. We compare the differences between the energetics of the dissociative adsorption and molecular adsorption of water to understand the interaction between H_2O and the active centers of titanium dioxide and titanium hydroxide clusters as well as to understand cluster decomposition. Although the majority of this work is about water adsorption reactions on the small $(TiO_2)_n$ clusters with n = 1–4, this work also shows initial global minima search results for the products of the water dissociative adsorption reactions on $(TiO_2)_8$, which are used to verify the conclusions made based on the calculations of the smaller clusters and provide insight into the structural and energetic evolution of the hydroxide clusters.

Computational Method

The initial structures for the global minima search of the $(TiO_2)_n(H_2O)_m$ clusters were generated using a novel Docking-HGA approach, which extends our tree growth-hybrid genetic algorithm–density functional theory (TG–HGA–DFT) method by incorporating a docking capability. Our Docking-HGA method enables the systematic study of adsorption reactions between metal oxides and adsorbates by progressively searching for global minimum structures for the adsorption products. In contrast, most of the current available genetic algorithm programs that perform global geometry searches can only handle much simpler structures such as binary clusters.

The initial $(TiO_2)_n(H_2O)$ clusters were constructed by docking a H_2O to $(TiO_2)_n$ clusters that were generated and optimized with our TG-HGA-DFT method.[11] The starting geometries of the $(TiO_2)_n(H_2O)_m$, m > 1, clusters for HGA were obtained by docking a H_2O to the Ti sites of the smaller $(TiO_2)_n(H_2O)_{m-1}$ clusters that had been optimized using HGA (Figure 1).[11, 22] In another

sense, the HGA-optimized clusters were subsequently docked with another H_2O. We elongated one of the OH bonds in the H_2O so that it can become either molecularly adsorbed or dissociatively adsorbed during the HGA. By repeating the docking and HGA steps, the low energy $(TiO_2)_n(H_2O)_m$ structures were obtained. The energy evaluation and geometry optimization procedures during the HGA steps were performed using the PM6[23] semi-empirical method in the MOPAC2012[24] program suite. The details of the HGA can be found in our previous work[11] as well as elsewhere.[22]

The resulting low energy structures generated by HGA were subsequently optimized using density functional theory (DFT)[25,26,27] with the B3LYP[28,29] functional and the DZVP2[30] basis set, as our previous work[13] showed that there is a good agreement between the B3LYP level and correlated molecular orbital theory at the coupled cluster CCSD(T) level for the energetics of the small titanium hydroxide clusters. The total energies of the lowest energy isomers for each $(TiO_2)_n(H_2O)_m$ cluster were then calculated using coupled cluster CCSD(T) theory, with the aug-cc-pVDZ(-pp) basis set for n = 1 to 3, and with cc-pVDZ(-pp) basis set for n = 4 (Calculations were also done with the cc-pVDZ(-pp) basis set for n = 1 – 3 to test the role of the augmented diffuse functions). [31,32,33,34,35]

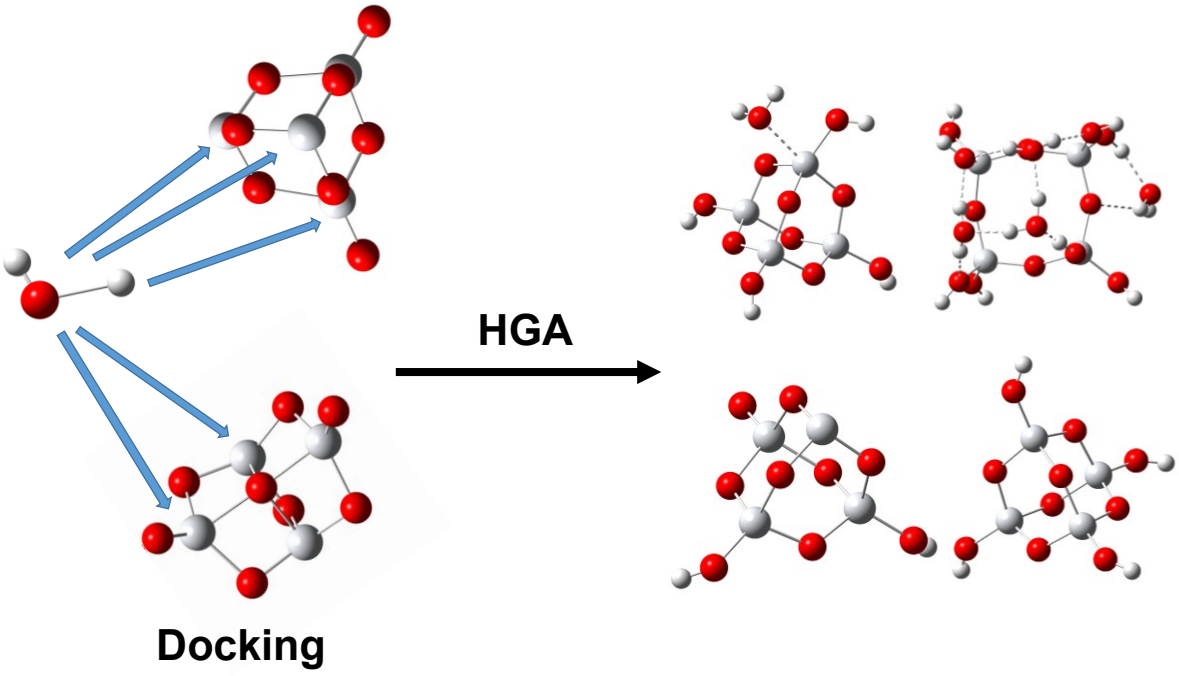


Figure 1. Graphical description for the molecular docking step of the molecular docking–hybrid genetic algorithm. Red (big): oxygen; Grey (big): Titanium; Grey (small): hydrogen.

All of the reported energies (and Gibbs free energies) have the zero point energy included. The vibrational properties, the zero point energy correction and the Gibbs free energy corrections were obtained from the second derivative calculations at the B3LYP/DZVP2 level. All of the DFT calculations were performed using the Gaussian 09 suite of programs.[36]The CCSD(T) calculations were performed with MOLPRO.[37]

Results and Discussion

The low energy products for the $(TiO_2)_n$ + m H_2O reactions, are labeled by "**n-mX**", where **X** = **a**, **b**, **c**, …, ordered by relative energies from low to high. The initial $(TiO_2)_n$ clusters, labeled as "n-0X", are taken from our previous work (see Figure S1 in the Supporting Information).[11] The enthalpies at 0 K ($\Delta H_0 = \Delta E_{electronic} + \Delta E_{ZPE}$) and Gibbs free energies at 298 K (ΔG_{298}) relative to the lowest energy isomers were calculated for the $(TiO_2)_n(H_2O)_m$ clusters at the CCSD(T)/cc-

pVDZ(-pp) level with Gibbs energy corrections at the B3LYP/DZVP2 level. The lowest energy isomers at 298 K are all the same as the lowest energy isomers at 0 K, as in general, increasing the temperature from 0 K to 298 K does not change the ordering of the stability of the hydrolysis reaction product isomers. The optimized geometries and relative energies for the lowest energy dissociative and molecular adsorption adducts of the $(TiO_2)_n$ reactions with water are shown in Figures 2 to 5 (see Figures S2 to S4 in the Supporting Information with more structures); the calculated enthalpies at 0 K and Gibbs free energies at 298 K for the H_2O dissociation energies of the adducts are in Table 1.

Monomer Geometries The addition of H_2O to the TiO_2 monomer results in a C_{2v} structure (**1-1a**) and a C_s structure (**1-1b**) as the lowest energy isomers (Figure 2). Structure **1-1b** is calculated to be 2.6 kcal/mol higher in energy than **1-1a** for ΔH_0 and ΔG_{298} at the CCSD(T)/cc-

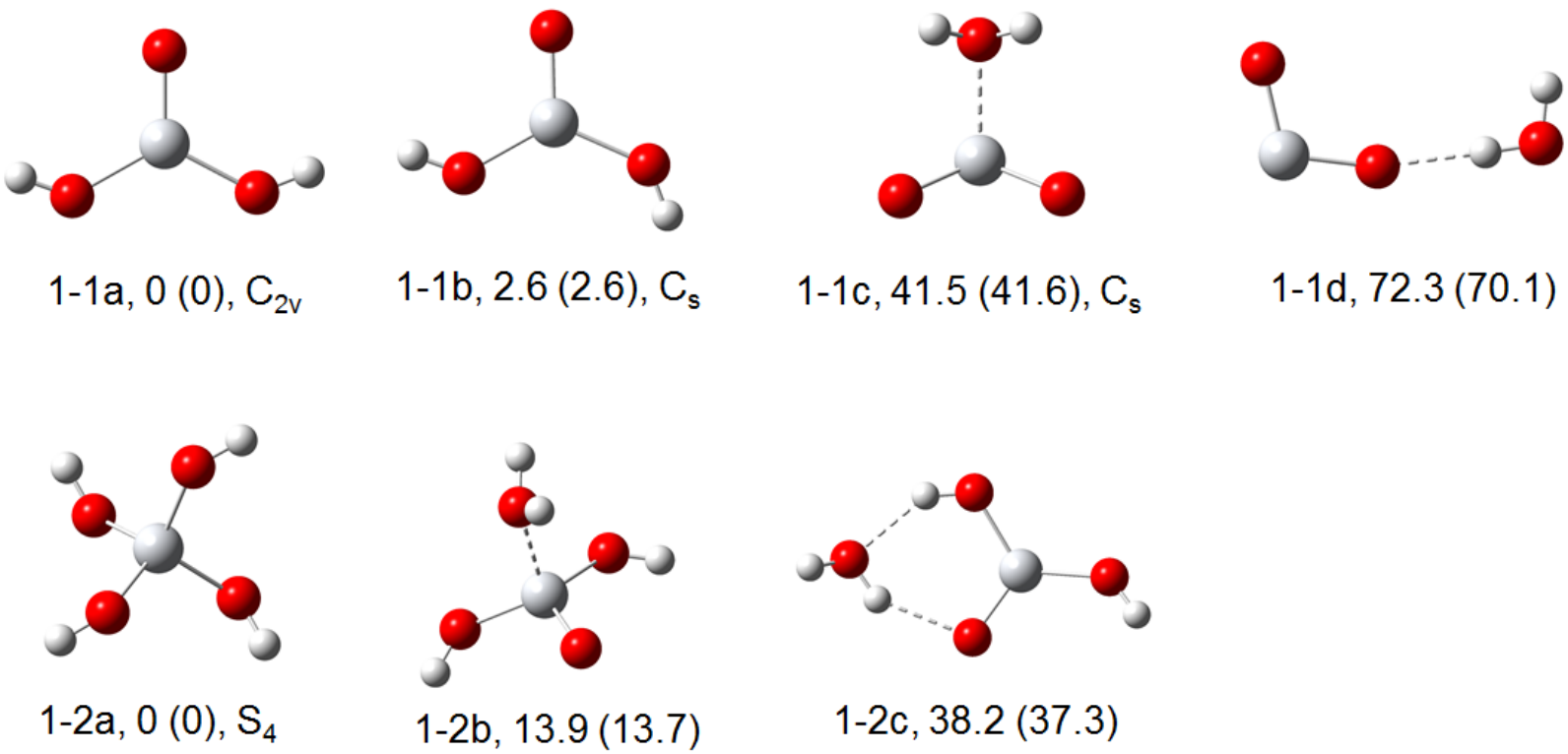


Figure 2. Geometries (denoted by "**1-mX**", X = a, b, c, etc.) and relative energies (in kcal/mol) at the CCSD(T)/cc-pVDZ(-pp) level for the low energy $(TiO_2)_1(H_2O)_m$ clusters. Relative energies at 0 K followed by relative Gibbs free energies at 298 K in parenthesis.

Table 1. Calculated reaction enthalpy at 0 K and Gibbs free energy at 298 K (in kcal/mol) for the H_2O dissociation reactions for low energy $(TiO_2)_n(H_2O)_m$ at the CCSD(T)/cc-pVDZ(-pp) level.

	ΔH(0) - H_2O	ΔG(298) - H_2O	ΔH(0) - m H_2O	ΔG(298) - m H_2O	n H_2O Dissoc[a]	n H_2O Lewis[a]	n H_2O H-bond[a]
1-1a	77.4	69.3	77.4	69.3	1		
1-1b	74.9	66.7	74.9	66.7	1		
1-1c	36.0	27.8	36.0	27.8		1	
1-1d	5.1	-0.8	5.1	-0.8			1
1-2a	46.3	36.6	123.7	105.9	2		
1-2b	32.3	22.9	109.8	92.2	1	1	
1-2c	8.1	-0.7	85.5	68.6	1		1
2-1a	61.2	52.1	61.2	52.1	1		
2-1b	59.4	50.3	59.4	50.3	1		
2-2a	63.8	55.8	124.9	107.9	2		
2-2d	12.7	5.6	73.9	57.8		2	
2-3a	17.3	6.7	142.3	114.7	2	1	
2-3b	12.4	3.6	137.4	111.5	3		
2-3c	7.5	0.0	132.4	107.9	2		1
2-4a	16.8	7.3	159.1	122.0	2	2	
2-4b	12.5	3.4	154.8	118.1	4		
2-4c	5.3	-0.1	147.6	114.6	3		1
3-1a	79.2	69.7	79.2	69.7	1		
3-1e	41.0	32.3	41.0	32.3		1	
3-2a	42.2	33.8	121.4	103.6	2		
3-3a	23.4	16.6	144.8	120.2	3		
3-3b	13.8	4.4	135.2	108.0	2	1	
3-3e	9.2	3.0	130.6	106.5	2		1
3-4a	16.2	4.6	161.0	124.7	3	1	
3-4b	14.8	4.2	159.5	124.4	3		1
3-4d	10.5	-2.4	155.3	117.7	4		
3-5a	14.5	1.8	175.5	129.8	3	2	

3-5b	14.2	3.0	175.2	130.5	3	1	1
3-5c	10.1	1.6	171.1	128.3	3		3
3-5g	3.0	-4.9	164.0	120.0	5		
3-6a	14.2	4.5	189.4	134.9	3	2	1
3-6b	13.4	3.6	188.6	134.1	3	3	
3-6c	12.6	0.4	187.8	130.9	6		
4-1a	67.3	58.0	67.3	58.0	1		
4-1f	35.6	26.7	35.6	26.7		1	
4-2a	72.4	64.4	139.7	122.5	2		
4-2e	1.8	-6.9	69.1	51.2		2	
4-3a	14.9	4.6	154.6	127.1	2	1	
4-3b	7.7	0.6	147.4	123.0	3		
4-4a	14.3	5.0	169.0	132.1	2	2	
4-4b	-0.1	-1.3	154.6	125.8	4		
4-4c	-0.7	-8.8	153.9	118.2	4		
4-5a	13.5	4.0	182.5	136.1	2	3	
4-5b	5.6	-0.4	174.6	131.7	4		1
4-5c	-0.9	-7.6	168.1	124.5	5		
4-6a	13.0	3.7	195.6	139.7	2	4	
4-6b	2.8	-2.6	185.3	133.5	4		2
4-6c	-5.9	-14.4	176.7	121.7	6		
4-7a	7.6	0.6	203.1	140.3	4		3
4-7b	-3.0	-10.2	192.6	129.5	6		1
4-8a	11.2	1.5	214.4	141.8	4		4
4-8b	0.5	-7.7	203.6	132.7	6		2

[a] "n H_2O" is the number of H_2O's of each adsorption type. "Disso" indicates dissociative adsorption, "Lewis" indicates Lewis acid-base molecular adsorption, and "H-bond" indicates H-bond molecular adsorption.

pVDZ(-pp) level. These structures correspond to dissociative adsorption. Structures **1-1c** (H_2O molecularly adsorbed on Ti of TiO_2 by a Lewis acid-base interaction) and **1-1d** (H_2O hydrogen bonded to O–TiO) are predicted to be much higher in energy than structure **1-1a**. The bond dissociation energy at 0 K (ΔH_0(BDE)) for the Lewis acid-base bond in **1-1c** is calculated to be 41 kcal/mol less than the adsorption energy and the H-bond ΔH_0(BDE) in **1-1d** is 31 kcal/mol smaller than the Lewis acid-base bond in **1-1c**. The lowest energy product for the complete hydrolysis of TiO_2 (addition of 2 H_2O) has an S_4 structure (**1-2a**) with the Ti tetrahedrally coordinated with 4 O's, in agreement with previous predictions.[12,13] Structure **1-2b** (H_2O adsorbed on Ti of **1-1a** by a Lewis acid-base interaction) and **1-2c** (H_2O hydrogen bonded to **1-1a**) are predicted to be 13.9 and 38.2 kcal/mol, respectively, higher in energy than the dissociative adsorption adduct, **1-2a** for ΔH_0. The second Lewis acid-base ΔH_0(BDE) is 32.3 as compared to the H_2O adsorption energy of 46.3 kcal/mol (ΔH_0) for the dissociative adsorption adduct **1-2a**. The molecular adsorption of H_2O on **1-1b** by H-bond interaction (to form **1-2c)** is exothermic by 8.1 kcal/mol for ΔH_0.The dominant reaction of the monomer with water is thus dissociative adsorption which leads to complete hydrolysis.

Dimer Geometries The $(TiO_2)_2$ reaction with 1 H_2O gives the dissociative adsorption adduct (**2-1a)** with two bridging O's and one terminal O as previously predicted (Figure 3).[13] Another dissociative adsorption adduct (**2-1b)** with 3 bridging O's is 1.8 kcal/mol higher in energy than **2-1a**. Transferring the H of a TiOH group in **2-1a** to a terminal O yields structure **2-1c (**Figure S2 in SI**)**, which is 4.4 kcal/mol higher in energy than **2-1a**. Structure **2-1c** was predicted to be the lowest energy isomer by Berardo and coworkers.[12] In structure **2-1c**, the Ti's have oxidation states of +3 and +5, respectively, as one Ti forms 3 Ti–O single bonds and the other Ti forms 3 Ti–O single bonds

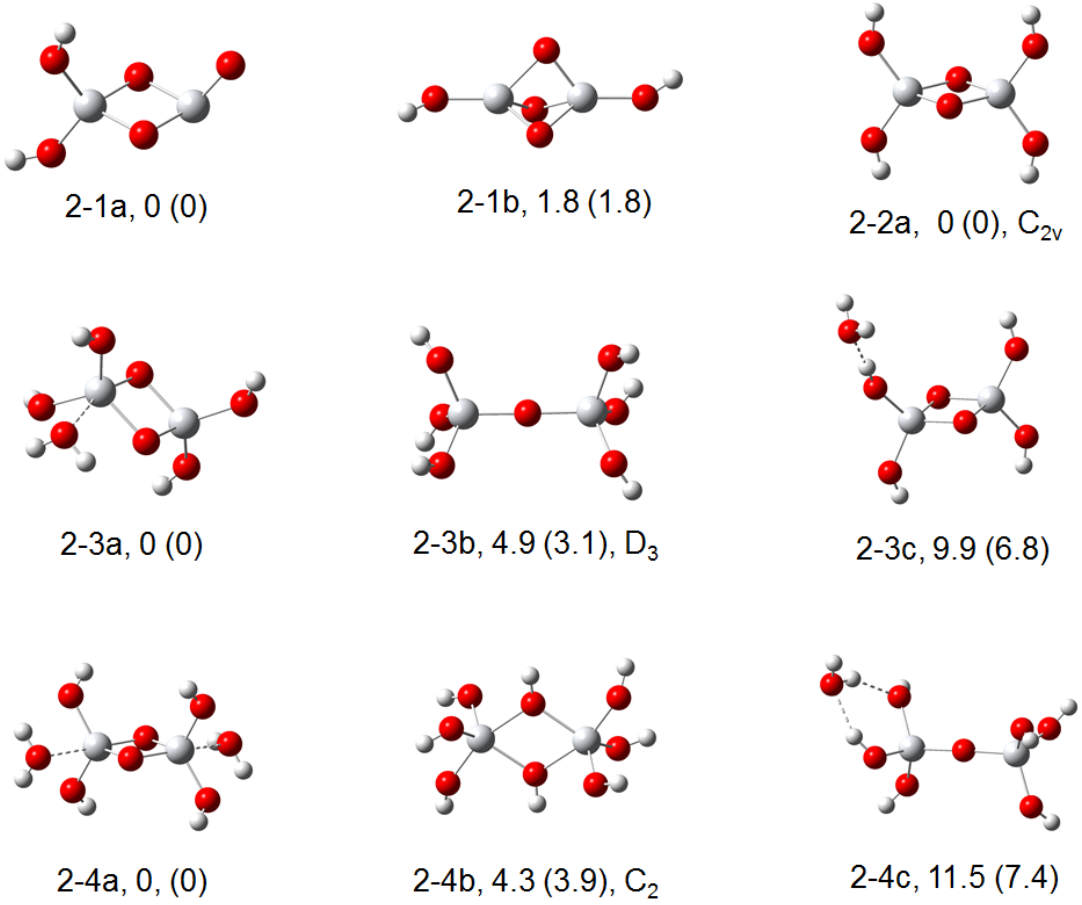


Figure 3. Geometries (denoted by "**2-mX**", X = a, b, c, etc.) and relative energies (in kcal/mol) at the CCSD(T)/cc-pVDZ(-pp) level for the low energy $(TiO_2)_2(H_2O)_m$ clusters. Relative energies at 0 K followed by relative Gibbs free energies at 298 K in parenthesis.

and 1 Ti=O double bond, and therefore is less stable than **2-1a** where both Ti centers have +4 oxidation states. Structure **2-1e** is a Lewis acid-base complex of $(TiO_2)_2$ and a molecular H_2O and is predicted to be 22.1 kcal/mol higher in energy than structure **2-1a** for ΔH_0.

The C_{2v} structure (**2-2a**) with 4 terminal OH's and 2 bridging O's is predicted to be the lowest energy dissociative adsorption adduct for the $(TiO_2)_2$ reaction with 2 H_2O's, in agreement with prior predictions.[13,21] Structure **2-2d,** in which $(TiO_2)_2$ forms 2 Lewis acid-base Ti-O bonds with 2 molecular H_2O's, is predicted to be 51.1 kcal/mol higher in energy than structure **2-2a**. The second Lewis acid-base bond energy is predicted to be ΔH_0(BDE) = 36.2 kcal/mol for **2-2d**. Like the $(TiO_2)_2$ reactions with 1 H_2O, the $(TiO_2)_2$ reactions with 2 H_2O also favor dissociative adsorption adduct.

The lowest energy isomer (**2-3a**) for $Ti_2O_7H_6$ is a Lewis acid-base complex comprised of **2-2a** and a molecular H_2O, where the Lewis acid-base ΔH_0(BDE) = 17.3 kcal/mol and ΔG_{298}(BDE) = 6.7 kcal/mol. Dissociative adsorption of a H_2O onto structure **2-2a** gives a higher energy adduct for the $(TiO_2)_2$ reaction with 3 H_2O's, a D_3 structure (**2-3b**) with three terminal OH's on each Ti. Structure **2-3b** is predicted to be 4.9 kcal/mol less stable than **2-3a** for ΔH_0. Structure **2-3c**, consists of **2-2a** and a H-bonded H_2O and is 9.9 kcal/mol higher in energy than **2-3a** for ΔH_0**.** The H-bond energy for **2-3c** is calculated to be 7.5 kcal/mol for ΔH_0(BDE) but ΔG_{298}(BDE) is 0 so the H-bond of **2-3c** will dissociate spontaneously at 298 K. The addition of the third water favors a Lewis-acid-base complex product, and the energy difference between it and the lowest energy dissociative adsorption product (**2-3b**) is ~ 5 kcal/mol for ΔH_0. Increasing the temperature to 298 K reduces the energy gap between the Lewis acid-base molecular adsorption adduct (**2-3a**) and the dissociative adsorption adduct (**2-3b**) by 2 kcal/mol. The Lewis acid-base interaction between the

molecular H_2O and the $Ti_2O_6H_4$ (**2-2a**) in **2-3a** is found to be stronger than the H-bond interaction in **2-3c**, as found for the monomer reactions.

Structure **2-4a** is predicted to be the lowest energy $Ti_2O_8H_8$ cluster. **2-4a** is essentially a complex of **2-2a** and two molecular H_2O's. Each molecular H_2O is bonded to a Ti of **2-2a** by a Lewis acid-base Ti-O bond. The total adsorption energy for the two molecular H_2O's in **2-4a** is calculated to be 34.1 kcal/mol for ΔH_0. The lowest energy dissociative adsorption adduct (**2-4b**) is essentially the cross-linked dimer of $Ti(OH)_4$ with two penta-coordinate Ti's. Structure **2-4b** is calculated to be second lowest in energy, 4.3 kcal/mol higher in energy than **2-4a** for ΔH_0. This is consistent with the previous prediction by Ignatyev and coworkers that structure **2-4b** is the lowest energy hydroxide with this stoichiometry.[20] The interatomic distances between the bridging O(H) and two Ti's are calculated to be 2.00 and 2.07 Å for **2-4b**, ~ 0.2 Å longer than the distances between Ti and terminal O(H)'s (~1.83 Å). The molecular adsorption product (**2-4c**), essentially structure **2-3b** forming two O•••H bonds with a H_2O, is 11.5 kcal/mol higher in energy than **2-4a** at for ΔH_0. The adsorption energy for the molecular H_2O in **2-4c** is calculated to be 10.1 kcal/mol for ΔH_0. Structure **2-4d**, 15.5 kcal/mol higher in energy than **2-4a** for ΔH_0, is a dimer complex of $Ti(OH)_4$ (**1-2a**) connected by two intermolecular Ti(OH)•••OTi bonds. The energies for the dissociation **of 2-4b** and the **2-4d** into 2 $Ti(OH)_4$ are calculated to be 27.6 and 16.4 kcal/mol for ΔH_0. The average Ti(OH) •••OTi bond energy is comparable to a typical H-bond between a hydrated TiO_2 complex and molecular H_2O. Structure **2-4e** can be formed by molecular adsorption of two H_2O's to structure **2-2a** by H-bond interactions, and is calculated to be 15.5 kcal/mol higher in energy than 2-4a for ΔH_0.

Trimer Geometries The C_s structure (**3-1a**) with one terminal O and two terminal OH's is predicted to be lowest energy isomer for the $Ti_3O_7H_2$ clusters (Figure 4). The H_2O is dissociatively

adsorbed in **3-1a**, and the H_2O dissociation energy is predicted to be 79.2 kcal/mol for ΔH_0. Structure **3-1b (**Figure S3 in SI**)** with one terminal O, one bridging OH and one terminal OH resulting from transfer of a hydrogen in **3-1a** is 8.8 kcal/mol higher in energy for ΔH_0. Structure **3-1a** is 19.4 kcal/mol lower in energy than another dissociative adduct (**3-1c**) generated by the hydrolysis of a single Ti center in a cluster.[13] The lowest energy structures generated in the current study have the OH groups on different Ti atoms suggesting a quite different mechanism to forming this structure involving multiple hydrogen transfers. Structures **3-1d** and **3-1f**, produced by the hydrolysis of less stable $(TiO_2)_3$ isomers, are 31.3 and 47.0 kcal/mol higher in energy than **3-1a** for ΔH_0. The Lewis acid-base complexes, **3-1e** and **3-1g**, are 38.3 and 50.2 kcal/mol higher in energy than **3-1a**, with the Lewis acid-base interaction energies for ΔH_0 calculated to be 41.0 and 29.0 kcal/mol, respectively.

The dissociative adsorption of H_2O on structure **3-1a** produces structure **3-2a**, which is predicted to be the lowest energy isomer for the $Ti_3O_8H_4$ clusters, consistent with a previous study.[21] Structure **3-2b** is generated by the hydrolysis of structure **3-1d**, and is 10.0 kcal/mol less stable than **3-2a** for ΔH_0. The hydrolysis of structure **3-1f** leads to structure **3-2d**, which is predicted to be 32.4 kcal/mol higher in energy than **3-2a** for ΔH_0. A structure with an intramolecular O•••H bond (**3-2c**) is 18.6 kcal/mol higher in energy than **3-2a** for ΔH_0.

Structure **3-3a** in the shape of a 3-member monocyclic ring can be formed by the hydrolysis reaction of either **3-2a** or **3-2d**, and is predicted to be the lowest energy isomer for the $Ti_3O_9H_6$ clusters consistent with prior predictions.[12,13] Structure **3-3a** contains no molecular H_2O, and is thus a dissociative adsorption adduct for the $(TiO_2)_3$ reaction with 3 H_2O's. The reaction energy for the **3-3a** → **3-2a** + H_2O reaction is predicted to be 23.4 kcal/mol for ΔH_0. Structures

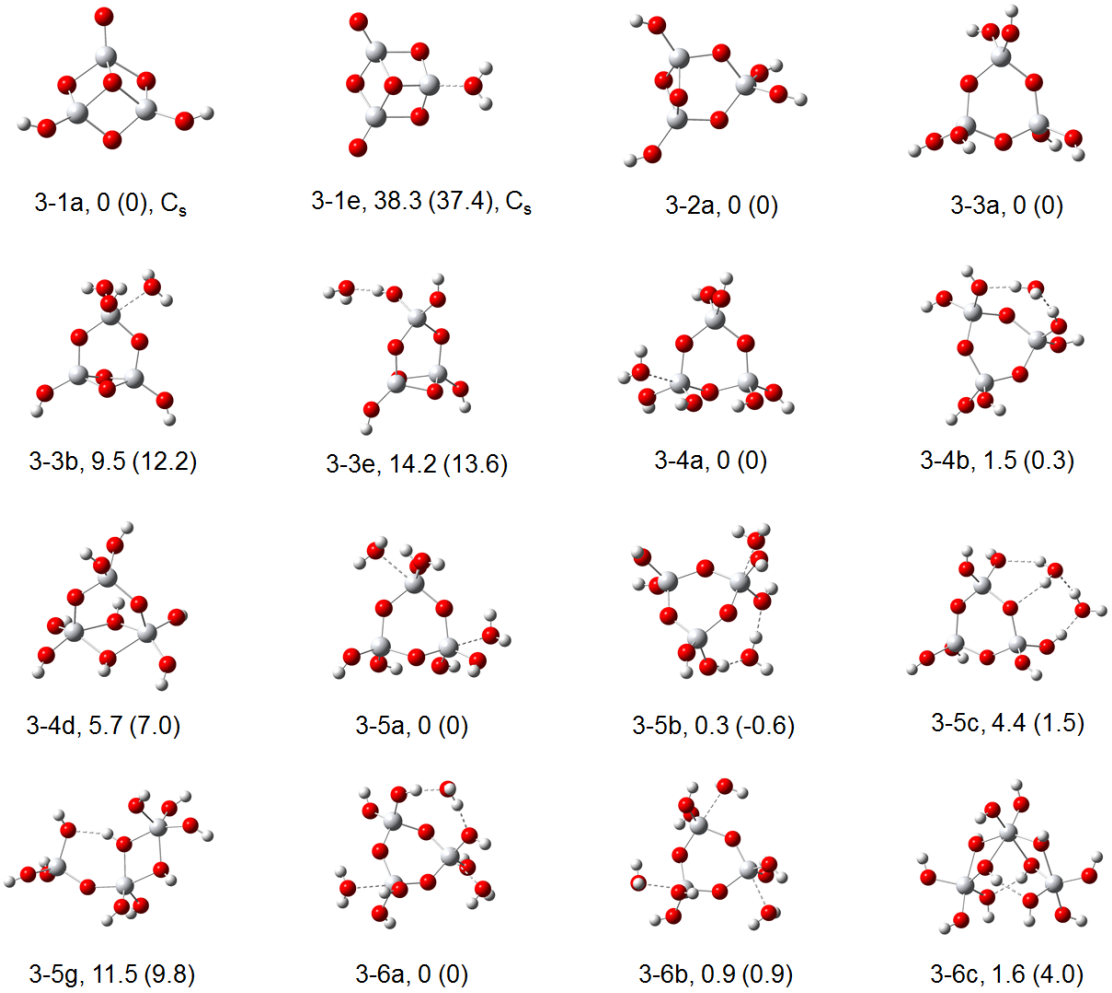


Figure 4. Geometries (denoted by "**3-mX**", X = a, b, c, etc.) and relative energies (in kcal/mol) at the CCSD(T)/cc-pVDZ(-pp) level for the low energy $(TiO_2)_3(H_2O)_m$ clusters. Relative energies at 0 K followed by relative Gibbs free energies at 298 K in parenthesis.

1-1a, **2-2a**, and **3-3a** can be viewed as members of a homologous series analogous to monocyclic cycloalkanes, for which the formula can be generalized to be $(TiO_3H_2)_n$. Each member of the $(TiO_3H_2)_n$ homologous series contains either a monocyclic ring or a terminal Ti=O. Structure **3-3b** is the molecular adsorption product of **3-2a** forming a Lewis acid-base Ti–O bond with a H_2O, and is predicted to be 9.5 kcal/mol higher in energy than **3-3a** for ΔH_0. The molecular adsorption energy for **3-3b** is calculated to be 13.8 kcal/mol for ΔH_0. The molecular adsorption product of **3-2a** with H-bonded H_2O, structure **3-3e**, is calculated to be 14.2 kcal/mol higher in energy than **3-3a** for ΔH_0, and the adsorption energy for the molecular H_2O is 9.2 kcal/mol for ΔH_0.

When a fourth H_2O is added to $(TiO_2)_3$, molecular adsorption is favored over dissociative adsorption. The two lowest energy products for the adsorption of 4 H_2O to $(TiO_2)_3$, **3-4a** and **3-4b**, are two complexes each comprised of a monocyclic ring (**3-3a**) and a molecular H_2O. The molecular H_2O is bonded to the monocyclic ring by a Lewis acid-base Ti-O bond in **3-4a**, with an adsorption energy of 16.2 kcal/mol for ΔH_0. The molecular H_2O can also form two H-bonds with the monocyclic ring to generate **3-4b** with the adsorption energy of 14.8 kcal/mol for ΔH_0. Structure **3-4b** is 1.5 kcal/mol higher in energy than **3-4a** for ΔH_0, and nearly isoenergetic to **3-4a** for ΔG_{298}. The Lewis acid-base complex (**3-4c**) between **3-2a** and two molecular H_2O's is 3.8 kcal/mol higher in energy than **3-4a** for ΔH_0. The total adsorption energy for the two molecular H_2O's is calculated to be 35.8 kcal/mol for ΔH_0. Structures **3-4d** and **3-4e** both contain 5-O penta-coordinate Ti centers, are predicted to be ~5 kcal/mol higher in energy than **3-4a**, and are found to be the lowest energy complete dissociative adsorption products for the $(TiO_2)_3$ hydrolysis reactions with 4 H_2O's. Structure **3-4f** is essentially a $(HO)_3Ti–O–Ti(OH)_2–O–Ti(OH)_3$ straight-chain

isomer which folds into a ring with two intra-molecular O•••H hydrogen bonds; it is 7.0 kcal/mol higher in energy than **3-4a** for ΔH_0.

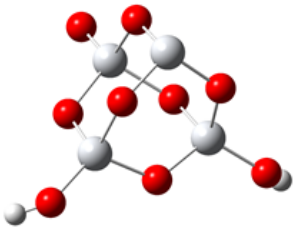
The lowest energy products (**3-5a, 3-5b and 3-5c**) for the reaction of $(TiO_2)_3$ with 5 H_2O's are found to be complexes that each contains a monocyclic ring (**3-3a**) and two molecular H_2O's. In **3-5a**, each molecular H_2O is bonded to a Ti by a Ti-O Lewis acid-base bond, and the total adsorption energy for the 2 molecular H_2O's is calculated to be 30.7 kcal/mol for ΔH_0. Structure **3-5b** contains a monocyclic ring (**3-3a**), a H-bonded H_2O, and a Lewis acid-base bonded H_2O and is calculated to be 0.3 kcal/mol higher in energy than **3-5a** for ΔH_0, and is found to be the lowest energy isomer in terms of ΔG_{298}. The total adsorption energy for the two molecular H_2O's in **3-5b** is calculated to be 30.4 kcal/mol for ΔH_0. Structure **3-5c** consists of **3-3a** and two H-bonded molecular H_2O's, and is predicted to be 4.4 kcal/mol higher in energy than **3-5a** for ΔH_0 in comparison to **3-5**a. The total adsorption energy for the two molecular H_2O's (that equals the sum of the bond energies of 3 H-bonds between H_2O and Ti complex and 1 H-bond between the 2 H_2O's) is calculated to be 26.3 kcal/mol for **3-5c** for ΔH_0. Structure **3-5d** is the molecular adsorption product of structure **3-2a** interacting with three molecular H_2O's (two Lewis acid-base bonded and one H-bonded), and is predicted to be > 5 kcal/mol higher in energy than the most energetically favored products. The lowest energy complete dissociative adsorption product, structure **3-5g**, with two penta-coordinate Ti centers, is predicted to be 11.5 kcal/mol higher in energy than **3-5a** for ΔH_0.

The lowest energy product (**3-6a**) for the $(TiO_2)_3$ reaction with 6 H_2O's is found to be a complex of **3-3a** with 3 molecular H_2O's. Two of the molecular H_2O's forms Lewis acid-base Ti-O bonds with **3-3a**, and one molecular H_2O forms two O•••H H-bonds with **3-3a**. The total adsorption energy for the 3 molecular H_2O's to form **3-6a** is calculated to be 44.7 kcal/mol for

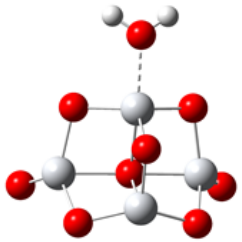
ΔH_0. The molecular adsorption product (**3-6b**) formed by **3-3a** with 3 Lewis acid-base bonded molecular H_2O's, is within 1 kcal/mol of **3-6a** in energy, with the total molecular adsorption energy calculated to be 43.8 kcal/mol for ΔH_0. Similar to the low energy molecular adsorption products of the $(TiO_2)_3$ with 5 H_2O's, the lowest energy Lewis acid-base molecular adsorption product and the lowest energy H-bonded molecular adsorption product are close in energy. This is mainly because the Lewis acid-base bond becomes weaker as more Ti centers are coordinated to more than 4 oxygen atoms. In addition, as the number of hydroxyl groups increases in the cluster, additional H_2O can potentially form more than 1 H-bond with a TiOH or a molecularly adsorbed H_2O, which makes molecular adsorption by H-bond interactions more favorable.

The structure with one hexa-coordinate and two penta-coordinate Ti centers (**3-6c**) is predicted to be the lowest energy complete dissociative adsorption product for the $(TiO_2)_3$ reactions with 6 H_2O's, and is 1.6 kcal/mol higher in energy than the most stable structure (**3-6a**) for ΔH_0. Structure **3-6c** was also predicted as the lowest energy hydroxide (dissociative adsorption adduct) previously by Ignatyev and coworkers.[20] Structure **3-6c** is essentially the trimer of $Ti(OH)_4$, where the three $Ti(OH)_4$ clusters are bonded with 4 Ti–O(H)–Ti bridge bonds and 2 intramolecular O•••H H-bonds. The average Ti-OH bond distance is ~ 2.15 Å. The $Ti(OH)_4$ trimer complexes with intermolecular H-bonds, **3-6h, 3-6i**, and **3-6j**, are predicted to be ~35 to 40 kcal/mol higher in energy for ΔH_0 than **3-6a**.

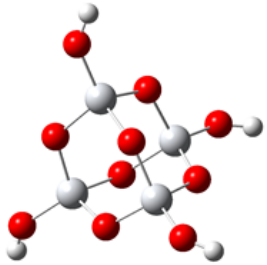
Tetramer Geometries Structure **4-1a** is predicted to be the lowest energy product for the $(TiO_2)_4$ + H_2O reactions (Figure 5), in which the 4 Ti's are positioned at the 4 vertices of a regular tetrahedron approximately. Dissociative adsorption of a second H_2O on **4-1a** generates the lowest energy isomer of the $Ti_4O_{10}H_4$ clusters (**4-2a),** again with approximately tetrahedral



4-1a, 0 (0)

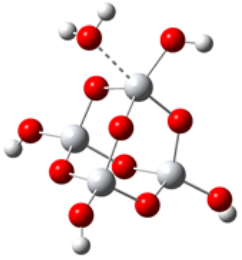


4-1f, 31.8 (31.4)

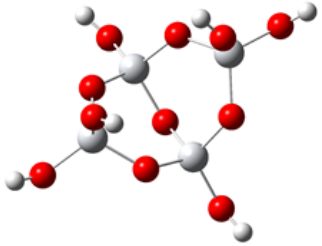


4-2a, 0 (0)

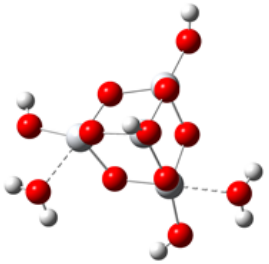
4-2e, 70.6 (71.3), C_{2v}



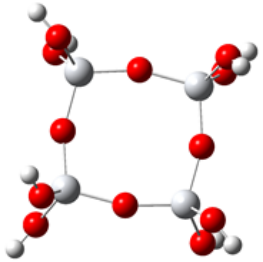
4-3a, 0 (0)



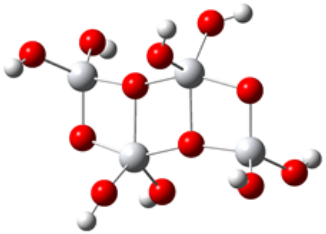
4-3b, 7.2 (4.0)



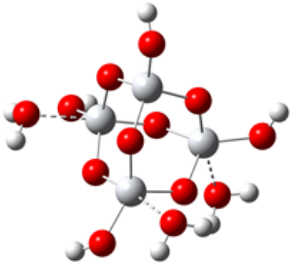
4-4a, 0 (0)



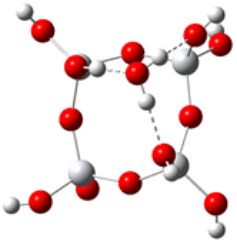
4-4b, 14.4 (6.3)



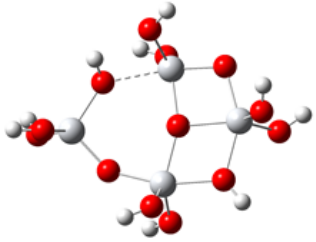
4-4c, 15.0 (13.9)



4-5a, 0 (0)



4-5b, 8.0 (4.4)



4-5c, 14.4 (11.5)

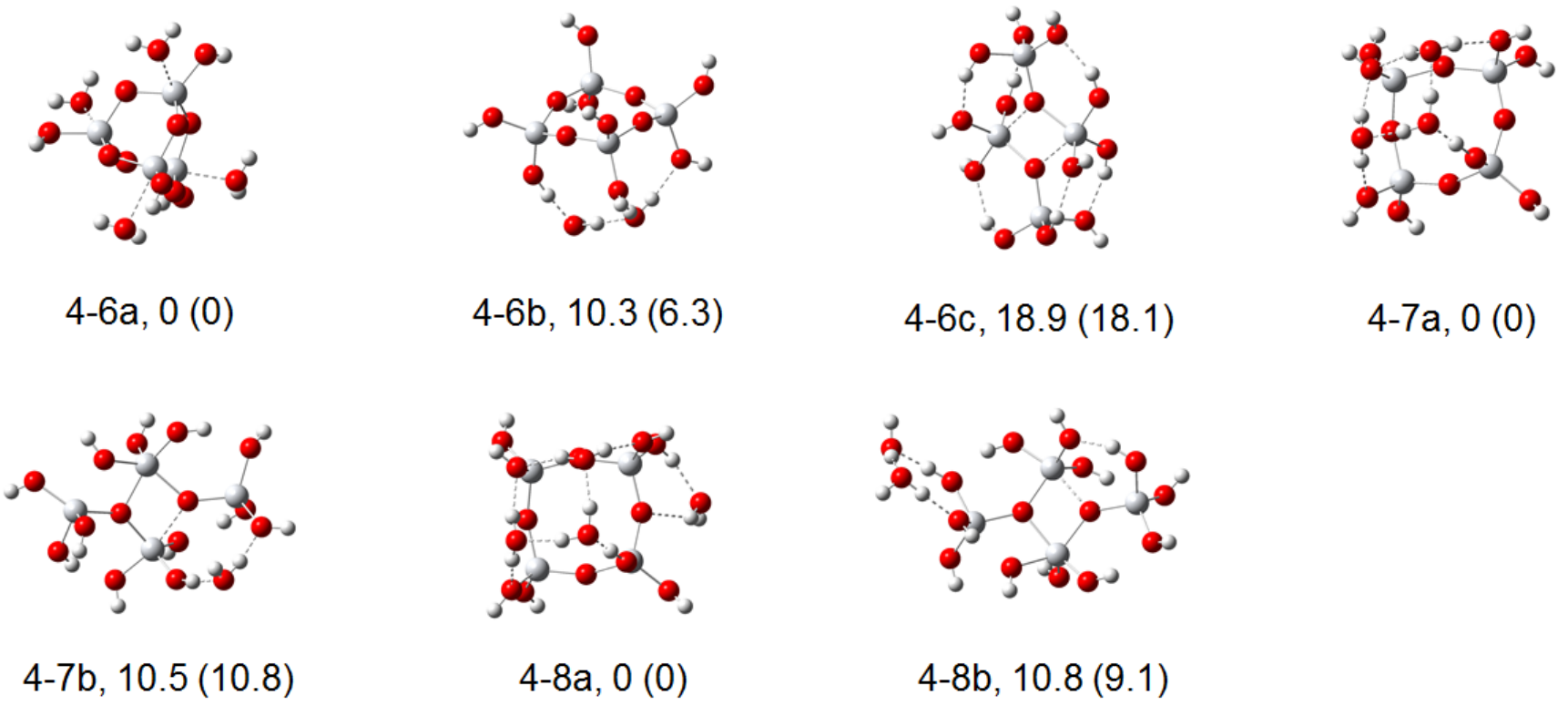


Figure 5. Geometries (denoted by "**4-mX**", X = a, b, c, etc.) and relative energies (in kcal/mol) at the CCSD(T)/cc-pVDZ(-pp) level for the low energy $(TiO_2)_4(H_2O)_m$ clusters. Relative energies at 0 K followed by relative Gibbs free energies at 298 K in parenthesis.

symmetry with one OH group per Ti. Structure **4-3a**, with a molecular H_2O bonded to **4-2a** via a Lewis acid-base Ti-O bond, is predicted to be the lowest energy product for the $(TiO_2)_4$ cluster reacting with 3 H_2O's. The adsorption energy for the H_2O adsorbed on **4-2a** to form Lewis acid-base complex **4-3a** is calculated to be 14.9 kcal/mol for ΔH_0. The lowest energy complete dissociative adsorption product for the $(TiO_2)_4$ reaction with 3 H_2O's, structure **4-3b**, in the shape of a fused bicyclic ring, is 7.2 kcal/mol higher in energy than **4-3a** for ΔH_0.

Structure **4-4a**, a complex of structure **4-2a** and two molecular H_2O's, is predicted to be the lowest energy $Ti_4O_{12}H_8$ cluster for ΔH_0 and for ΔG_{298}. Each of the two molecular H_2O's forms a Lewis acid-base Ti-O bond with **4-2a**, with a total molecular adsorption energy of 29.3 kcal/mol for ΔH_0. The lowest energy complete dissociative adsorption product for the addition of 4 H_2O to $(TiO_2)_4$ is predicted to be a 4-member monocyclic ring (**4-4b**) 14.4 kcal/mol higher in energy than **4-4a** for ΔH_0. The dissociative adsorption adduct **4-4c** with two penta-coordinate Ti centers is predicted to be 15.0 kcal/mol higher in energy than **4-4a** for ΔH_0. Two dissociative adsorption products (**4-4d** and **4-4e**, Figure S4 in SI) that each contain a 3-member monocyclic ring are predicted to be 19.6 and 22.3 kcal/mol higher in energy than **4-4a** for ΔH_0, respectively.

The lowest energy product (**4-5a**) for the reaction of $(TiO_2)_4$ with 5 H_2O's is a complex of **4-2a** with 3 molecular H_2O's, with 3 Lewis acid-base Ti-O bonds formed between the H_2O's and $Ti_4O_{10}H_4$ (**4-2a**). The total adsorption energy for the three molecular H_2O's is calculated to be 42.8 kcal/mol for ΔH_0. The molecular adsorption product that consists of a 4-member monocyclic ring (**4-4b**) with a molecular H_2O that forms 3 H-bonds with 3 OH's is 8.0 kcal/mol higher in energy than **4-5a** for ΔH_0. The adsorption energy of the H-bonded molecular H_2O is calculated to be 20.0 kcal/mol for ΔH_0. Structure **4-5d**, formed as a Lewis acid-base complex of **4-4b** with a molecular H_2O, is 15.0 kcal/mol less stable than **4-5a** for ΔH_0. The adsorption energy for the molecular H_2O

in **4-5d** is calculated to be 13.0 kcal/mol for ΔH_0. Structure **4-5c** with two penta-coordinate Ti centers is found to be the lowest energy complete dissociative adsorption product, and is predicted to be 13.5 kcal/mol higher in energy than **4-5a** for ΔH_0. The folded $(HO)_3Ti\text{-}(TiO_3H_2)_2\text{-}Ti(OH)_3$ isomer (**4-5e**) with all of the H_2O's dissociatively adsorbed, is 17.0 kcal/mol higher in energy than **4-5a** for ΔH_0. This structure is held together by bridging O(H)'s as well as by hydrogen bonds between OH groups.

The lowest energy product for the $(TiO_2)_4$ reaction with 6 H_2O's is a complex (**4-6a**) of **4-2a** with 4 molecular H_2O's, where the 4 H_2O's are molecularly adsorbed on **4-2a** by Lewis acid-base Ti-O bonds. The total adsorption energy for the 4 Lewis acid-base bonded molecular H_2O's in **4-6a** is calculated to be 55.8 kcal/mol for ΔH_0. Structure **4-6b** consists of a 4-member cyclic ring (**4-4b**) and a $(H_2O)_2$ cluster and is 10.3 kcal/mol higher in energy for ΔH_0 than **4-6a**. The total adsorption energy for the two H-bonded H_2O's in **4-6b** is calculated to be 30.7 kcal/mol for ΔH_0. The lowest energy complete dissociative adsorption product, **4-6c**, is a dimer of $(HO)_3Ti\text{-}O\text{-}Ti(OH)_3$ (**2-3a**) cross-linked by strong Lewis-acid base Ti-O bonds; it is 18.9 kcal/mol less stable than the lowest energy molecular adsorption product (**4-6a**) for ΔH_0.

The lowest energy products (**4-7a** and **4-8a**) for the reaction of $(T_iO_2)_4$ with 7 and 8 H_2O's are complexes of **4-4b** and molecular H_2O's. The total adsorption energy for the molecularly adsorbed H_2O's are 48.6 kcal/mol for ΔH_0 for **4-7a**, and 59.8 kcal/mol for ΔH_0 for **4-8a**. Structure **4-7a** has 7 H-bonds, therefore the average H-bond BDE is ~7 kcal/mol for ΔH_0. The hydrolysis reactions can result in a significant number of isoenergetic isomers, since the bond energies per H_2O for the Lewis acid-base $Ti\text{-}OH_2$ bonds, H-bonds between the Ti complex and H_2O's, and H-bonds for the H_2O clusters become comparable as the number of molecularly adsorbed H_2O's increases. An exhaustive search for such isoenergetic isomers is computationally intensive and

beyond the scope of the current work, so our predictions for the most stable molecular adsorption products are tentative for the addition of 7 and 8 H_2O's.

Structure **4-7a** is a complex of structure **4-4b** with a $(H_2O)_3$ cluster H-bonded to 4 hydroxyl groups on the Ti's. The O_{H2O}•••$H_{Ti(OH)}$ H-bond is found to be stronger than the $O_{Ti(OH)}$•••H_{H2O} and the O_{H2O}•••H_{H2O} H-bonds, as the Ti(OH) is partially deprotonated by H_2O in O_{H2O}•••$H_{Ti(OH)}$, suggested by the shorter O_{H2O}•••$H_{Ti(OH)}$ distance (1.41 Å) and longer $O_{Ti(OH)}$–$H_{Ti(OH)}$ distance (1.07 Å). Complete hydrolysis (dissociative adsorption) products with penta-coordinate Ti centers (**4-7b**, **4-7c**, and **4-7d**) are at least 10 kcal/mol less stable than **4-7a**.

Structure **4-8a** cluster can be generated by adding H-bonded H_2O to structure **4-7a**, or equivalently as **4-4b** H-bonding with a $(H_2O)_3$ and a molecular H_2O. The adsorption energy for the 8th H_2O added to **4-7a** is calculated to be 11.2 kcal/mol for ΔH_0, with the 8th H_2O forming a regular H-bond with a TiOH and a weaker H-bond with a bridging O. The hydrolysis products that contain 5-coordinate Ti centers are predicted to be at least 10 kcal/mol less stable than structure **4-8a**. Structure **4-8e** is a tetramer of $Ti(OH)_4$ (**1-2a**) with intermolecular hydrogen bonds between the monomers and is predicted to be 37.7 kcal/mol higher in energy at 0 K than **4-8a**.

Molecular and Dissociative Adsorption Energies H_2O adsorption energies, i.e. the calculated reaction enthalpy at 0 K and Gibbs free energy at 298 K for the single and total H_2O dissociation reactions for lowest energy $(TiO_2)_n(H_2O)_m$ at the CCSD(T)/cc-pVDZ(-pp) level are given in Table 1. At both 0 K and in terms of the free energy at 298 K, dissociative adsorption is the initial dominant reaction process with molecular adsorption dominating as more H_2O molecules are added to the TiO_2 clusters.

For the first and second H_2O's added to the TiO_2 monomer, adsorption energy for the second is slightly more than half of the first. The adsorption energy decreases for the second H_2O

because the reaction of the first H_2O with the 2-coordinate Ti is more exothermic than the reaction of the second H_2O with the 3-coordinate Ti. The adsorption energy for molecular H_2O in the monomer adsorption product **1-1c** where H_2O forms Lewis acid-base Ti–O bond with a 2-coordinate Ti center is half the dissociative adsorption value. This value decreases slightly for **1-2b**, where the H_2O is bonded to a 3-coordinate Ti. The H_2O adsorption energy for molecular adsorption product (**1-3c**) is calculated to be ~8 kcal/mol at 0 K, indicating that H-bonds are significantly weaker than the Lewis acid-base Ti-OH_2 bonds for the monomer clusters with the under-coordinated Ti center. At 298 K, the monomer cluster reactions to form the molecular adsorption products (**1-1d** and **1-2c**) with a H-bonded molecular H_2O are calculated to be endergonic as the negative of the $T\Delta S$ correction per H-bond at 298 K is slightly higher than BDE(H-bond).

Dissociative adsorption also dominates the reaction of dimer cluster with the first two H_2O's. The single adsorption energies for the first and second H_2O's that are dissociatively adsorbed on the dimmer are ~60 kcal/mol at 0 K with ΔG_{298} = ~50 kcal/mol. In contrast to the monomer reactions, the predicted adsorption energies for the first and second H_2O's adsorbed on the dimmer are comparable, as both reactions are essentially the reaction between H_2O and one of the two identical 3-coordinate Ti centers in the $(TiO_2)_2$ (**2-0a** in Figure S1 of SI). The typical Lewis acid-base interaction between H_2O and a 3-coordinate Ti center (in **2-1e** and **2-2d**) is ~ 37 kcal/mol for ΔH_0, which is ~5 kcal/mol greater than the adsorption energy for the Lewis acid-base bonded H_2O in the monomer reaction product (**1-2b**). For the third dissociatively adsorbed H_2O, the adsorption energy is much lower than that of the first and second dissociatively adsorbed H_2O's, as the reaction is now between H_2O and a 4-coordinate Ti center. At this point, molecular adsorption leading to the Lewis acid-base complex (**2-3a**) is now ~ 5 kcal/mol more exothermic

than dissociative adsorption for ΔH_0, and is ~ 3 kcal/mol more endergonic for ΔG_{298}. For the reaction of $(TiO_2)_2(H_2O)_3$ with the fourth H_2O, the molecular adsorption product (**2-4a**) with the fourth H_2O bonded to Ti by a Lewis acid-base interaction is the most energetically favored product for both ΔH_0 and ΔG_{298}. The adsorption energy for H_2O to form a Lewis acid-base bond with a 4-coordinate Ti is found to be ~ 17 kcal/mol for the dimer reactions for ΔH_0.

For the trimer, dissociative adsorption is thermodynamically favored for the addition of up to three H_2O molecules. There is only one 3-coordinate Ti in $(TiO_2)_3$. The first H_2O reacts with the 3-coodinate Ti center, and the product **3-1a** has all 3 Ti's coordinated by 4 O's. The central O of **3-1a** is coordinated to all three Ti's. The second and third H_2O's both react with a 4-coodinate Ti center, but there is no 5-coordinate Ti formed in the products, as one of the 4 original Ti-O bonds is broken during the reaction. The second H_2O reaction is more exothermic than the third H_2O reaction, because the second H_2O reaction eliminates the less stable 3-coordinate O in the reactant. Addition of the fourth and fifth H_2O's to the trimer yields molecular adsorption products that are essentially complexes of **3-3a** with molecular H_2O's, where each molecular H_2O is bonded to a 4-coordinate Ti via a Lewis acid-base Ti-O bond. The bond energy for such Lewis acid-base Ti-O bonds is calculated to be ~ 14 kcal/mol for ΔH_0, ~ 3 kcal/mol smaller than that for the dimer reactions. The molecular adsorption products with H_2O's H-bonded to the cluster are essentially isoenergetic with the Lewis acid-base molecular adsorption adducts for the trimer hydrolysis reaction with 4 and 5 H_2O's. The lowest complete dissociative adsorption products are less favored by over 5 kcal/mol for ΔH_0. As additional water molecules are added, the new H_2O can form multiple H-bonds with hydroxyl groups of the cluster or the molecular adsorbed H_2O's. We found that the bond energy for a Lewis acid-base Ti-O bond between H_2O and a 4-coordinate Ti center is approximately twice that of a H•••O H-bond. A H_2O can be molecularly adsorbed, and form just

one Lewis acid-base Ti-O bond or up to three O•••H H-bonds with TiOH or the molecularly adsorbed H_2O. The former is limited by the number of Ti sites in the cluster and the latter is limited by the number and positions of hydroxyl groups. For addition of the sixth H_2O, the Lewis acid-base and the H-bond adsorption products are favored, and the adsorption energy is comparable to those for the the fourth and fifth molecular H_2O's. The complete dissociative adsorption product (**3-6c**) for the sixth H_2O reaction is only 2 kcal/mol higher in energy than the lowest energy molecular adsorption products, due to the intramolecular interactions.

Dissociative adsorption dominates the $(TiO_2)_4$ reactions with the first and second H_2O's. The adsorption energy for the first dissociatively adsorbed H_2O is smaller than that for the second H_2O, because **4-1a** is not directly connected to the lowest energy $(TiO_2)_4$ cluster (see Supporting Information), but to a $(TiO_2)_4$ isomer that is ~12 kcal/mol higher in energy at the CCSD(T)/cc-pVDZ(-pp) level. Molecular adsorption becomes the dominant reaction as more than 2 H_2O's are added to the hydrated TiO_2 tetramer cluster. The adsorption energy for a molecularly adsorbed H_2O that forms a Lewis acid-base Ti–O bond with the hydrated TiO_2 tetramer cluster is 13 to 15 kcal/mol for ΔH_0.

The energetic ordering of isomer clusters remains the same for ΔH_0 and ΔG_{298}, in general, indicating that entropy corrections are comparable for the different product isomers. For the hydrolysis (dissociative adsorption) reactions, the entropy correction to the Gibbs free energy is mainly due to the molar equivalent difference between the reactants and products, rather than bond breaking and forming. The $T\Delta S$ correction is found to be approximately -10 kcal/mol for the dissociative adsorption reaction for the hydrated $(TiO_2)_n$ clusters with one H_2O at 298 K, and the same value is predicted for the molecular adsorption reaction to form product with a Lewis acid-base Ti-O(H_2) bond. This $T\Delta S$ correction is mainly due to the loss of the translational component

of the H_2O water molecule. The TΔS correction for molecular adsorption reactions to form products with one H-bonded H_2O, is approximately -5 kcal/mol at 298 K, due to additional contributions from the low frequency modes of the loosely bonded molecular H_2O. When H_2O forms more than two H-bonds with Ti(OH) or molecularly adsorbed H_2O, it is no longer loosely bonded, and therefore the TΔS correction for such molecular adsorption reaction at 298 K becomes comparable to the TΔS correction (-10 kcal/mol) for the dissociative adsorption. Our prediction that molecular adsorption is less exergonic at 298 K than at 0 K is consistent with the experimental study of Hendrich and coworkers where molecularly adsorbed H_2O's were desorbed as temperature increases.[4]

The hydrolysis limit for the $(TiO_2)_n$ cluster is largely related to the number of "unsaturated" Ti's in the cluster. "Unsaturated" Ti's are Ti's with CNs less than 4, or 4-coordinate Ti's with an unstable coordination geometry. The maximum numbers of dissociatively adsorbed H_2O's are 2, 2, 3, and 2 for TiO_2, $(TiO_2)_2$, $(TiO_2)_3$, and $(TiO_2)_4$ at 0 K, respectively. All of the $(TiO_2)_n$, n = 1 to 4, have "unsaturated" Ti's before the dissociative adsorption of the second H_2O. For $(TiO_2)_3(H_2O)_2$, although all of the Ti's are 4-coordinate, two of its Ti centers are "unsaturated", as they are bridged by 2 bridging O's, resulting in angle strain due to the ∠OTiO displacement. The adsorption energy for the $(TiO_2)_n$ and the hydrated $(TiO_2)_n$ decreases as the Ti CN's in the reactant increases, from 60-80 kcal/mol at CN = 2 and 3 to ~10 kcal/mol at CN = 4. The Lewis acid-base bond energy decreases from ~ 30–40 kcal/mol for CN(Ti) = 2 and 3 to ~ 15 kcal/mol for CN(Ti) = 4. The H_2O molecular reaction to form a Lewis acid-base type bond is found to be more energetically favorable than the dissociative adsorption reaction for CN(Ti) = 4. An important question is how many H_2O's can be dissociatively adsorbed by a larger $(TiO_2)_n$ cluster (or nanocluster). The "unsaturated" Ti's only exist on the surface (especially on the edge or at the corner) of a much larger $(TiO_2)_n$ cluster

or nanocluster. Therefore, only a few H_2O's can be dissociatively adsorbed, whereas the majority of the adsorbed H_2O's will be molecularly adsorbed as structures with more bulk character become dominant.

Low Energy Hydrolysis products for $(TiO_2)_8$ Although the number of "unsaturated" Ti's centers is the major factor for determining the hydrolysis limit of $(TiO_2)_n$ clusters, the intramolecular weak interaction can sometimes play an important role, which can potentially lead to the hydrolysis product with more dissociatively adsorbed H_2O's than usual. To explore this possibility, we studied H_2O hydrolysis reactions of the larger $(TiO_2)_8$ cluster. The geometries of the $(TiO_2)_8$ and its low energy hydrolysis products are shown in Figure 6. The minimum amount of H_2O required to hydrolyze $(TiO_2)_8$ to form dissociative adsorption products with all Ti's "saturated" is found to be 3. The total adsorption energy of the first 3 dissociatively adsorbed H_2O's is calculated to be 162 kcal/mol for ΔH_0 at the B3LYP/DZVP2 level. Adding 4 more H_2O's to $(TiO_2)_8(H_2O)_3$ generates structure **8-7a**, essentially a complex in which **4-3b** and **4-4b** are stacked with intermolecular Lewis acid-base interactions. The total H_2O adsorption energy for the 7 H_2O's is calculated to be 175 kcal/mol for ΔH_0 for **8-7a**, while the adsorption energy for the last 4 H_2O's that are dissociatively adsorbed on 4-coordinate Ti's is calculated to be 13 kcal/mol for ΔH_0. The lowest energy dissociative adsorption product (**8-8a**) for the $(TiO_2)_8 + 8H_2O$ reaction is found to be a stacked dimer complex of **4-4b**, and the total adsorption energy is calculated to be 188 kcal/mol for ΔH_0. The combined adsorption energy for the last 5 H_2O is calculated to be only 26 kcal/mol for ΔH_0, so after the adsorption of first three H_2O's that eliminate the "unsaturated" Ti centers in $(TiO_2)_8$, the adsorption energy for each additional dissociatively adsorbed H_2O is ~ 4 to 5 kcal/mol, which is lower than the adsorption energy of the molecular H_2O that forms either Lewis acid-base bond or H-bond with 4-coordinate Ti. Even though structures **8-7a** and **8-8a** have

considerable amounts of intramolecular weak interactions, the complexation energies are only 19 and 22 kcal/mol, respectively. This is because of geometry distortion due to the formation of the intramolecular weak interactions that lower the stabilities of such structures. In summary, intramolecular weak interactions can stabilize the hydrolysis product, but whether Ti's are "saturated" is still the dominant factor in determining the hydrolysis limit.

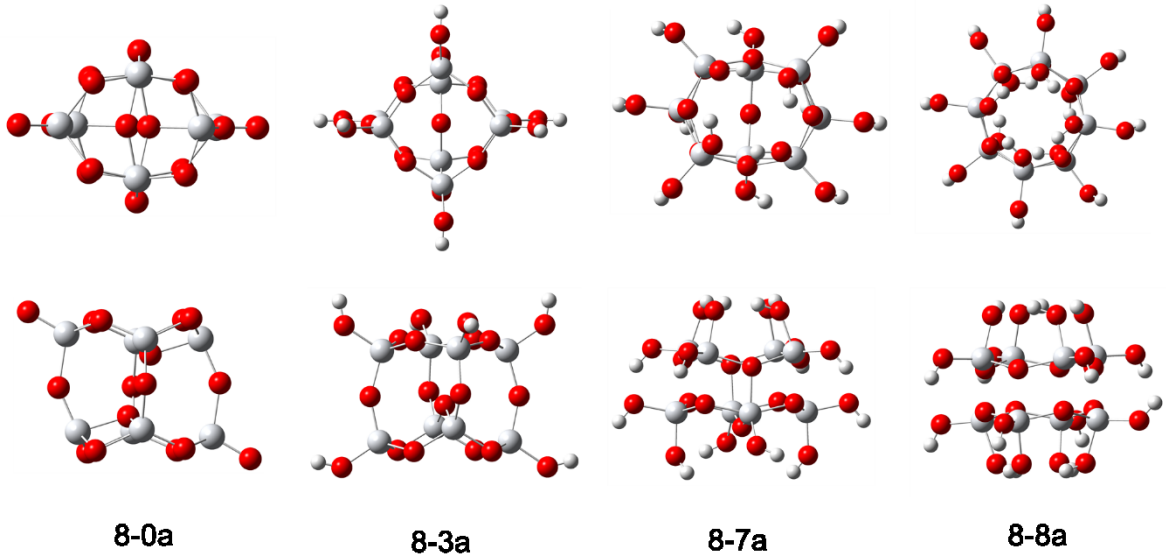


Figure 6. Geometries of $(TiO_2)_8$ and low energy hydrolysis products for the $(TiO_2)_8$ + m H_2O reactions.

Analysis of the Hydrolysis and Dehydration Reaction Energies The molecular adsorption of H_2O on the $(TiO_2)_n$ cluster can lead to hydrolysis of the $(TiO_2)_n$ cluster. Hydrolysis occurs when the dissociative adsorption energy is greater than the molecular adsorption energy, so the key to predict whether hydrolysis can occur is to compare the dissociative and molecular adsorption energies. Dissociative adsorption will lead to changes in the geometry of $(TiO_2)_n$ (or hydrated $(TO_2)_n$), especially bond angles. The geometry of $(TiO_2)_n$ is less affected by molecular adsorption

with Lewis acid-base interaction and even less affected by molecular adsorption by H-bonding. The adsorption energies for the molecularly adsorbed H_2O that forms Lewis acid-base bond and/or H-bond with the adsorbent are already known based on our calculations. In order to provide further insight into the energetics, we need to decompose the dissociate adsorption energy into the "pure" adsorption energy and the bond angle energy corrections. We can also analyze the dehydration energy, as the dehydration reaction is the reverse process of hydrolysis (dissociative adsorption of water). The "pure" dehydration reaction for a hydrated $(TiO_2)_n$ cluster can be expressed as equation (1):

$$2\ \text{–Ti(OH)} \rightarrow\ \text{–TiOTi–} + H_2O \qquad (1)$$

where the energy of reaction (1), E_D, is that for the dehydration reaction of two spatially available TiOH groups. E_D is only dependent on the electron configuration of the Ti centers. For the same type of Ti centers, such as 4-coordinate Ti centers, E_D is approximately considered to be constant. For a dehydration reaction, E_D is usually only part of the actually reaction energy, as the reaction energy is affected by the geometry changes, such as distortion of the bond angles and formation of the intramolecular weak interactions. Therefore, we selected a series of intermolecular dehydration reactions, for which the geometry changes can be expressed as simple mathematical functions of a controllable variable (such as the number of the leaving H_2O's), in order to separate E_D and the bond angle energy corrections from the actual dehydration energy. Our approach uses equation (2) to estimate E_D for the clusters with all of the Ti centers 4-coordinate

$$E_D = \langle E_{ring}(n)\rangle - \langle E_{ring\text{-}strain}(n)\rangle - \langle E_{H\text{-}bond}(n)\rangle \qquad (2)$$

Our goal is to eliminate the final two terms so that $E_D = \langle E_{ring}(n)\rangle$. The first term $\langle E_{ring}(n)\rangle$ can be calculated from the normalized energy for the intermolecular dehydration reactions of $Ti(OH)_4$ for clusters of different sizes as shown in reaction (3):

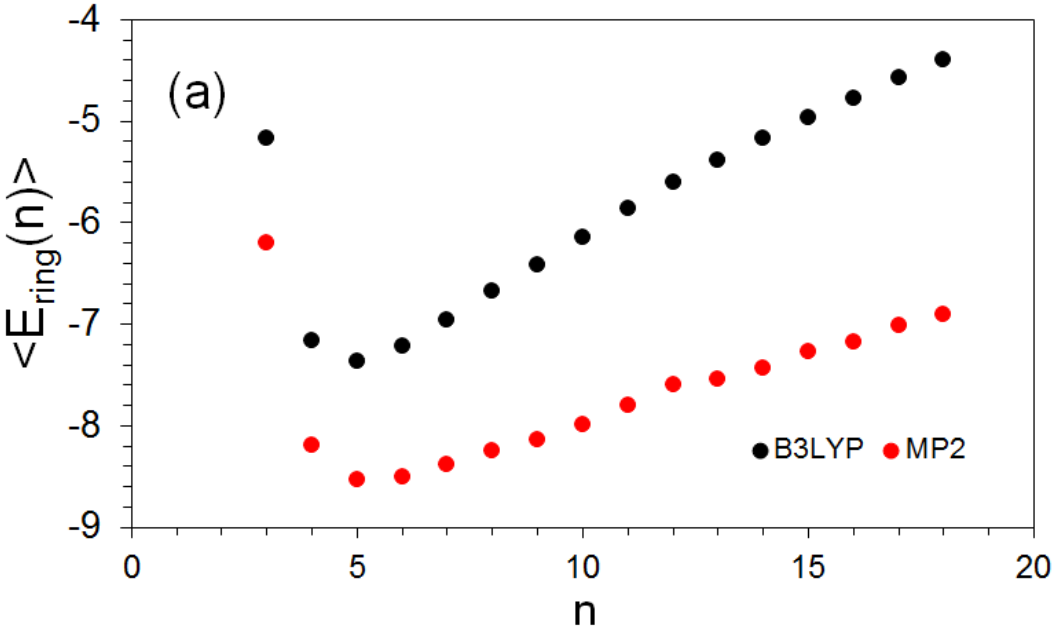
$$n\ Ti(OH)_4 \rightarrow (TiO_3H_2)_n + n\ H_2O \quad (3)$$

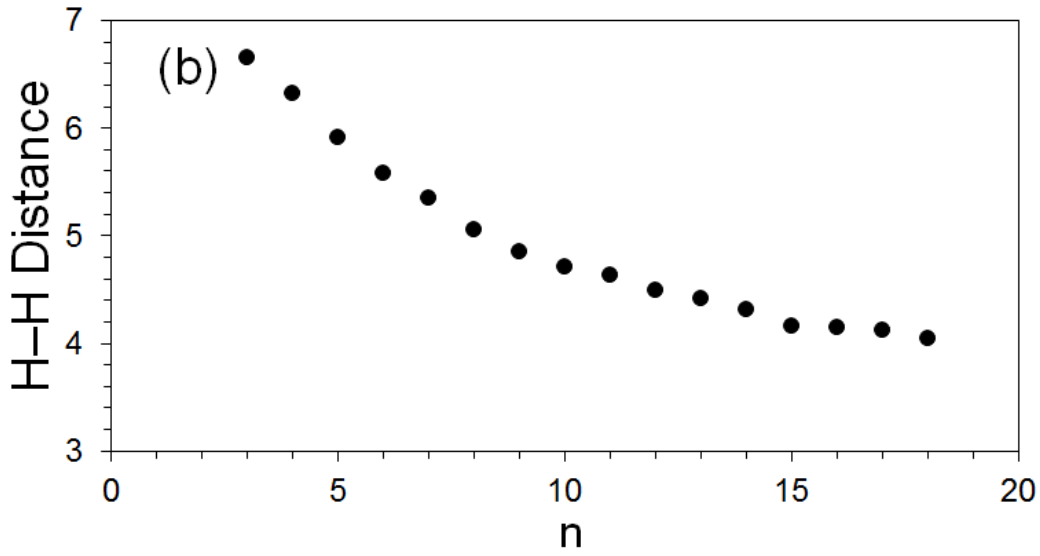
where $(TiO_3H_2)_n$ is a monocyclic ring in which each Ti is bonded to 2 terminal OH's and 2 bridging O's (**2-2a**, **3-3a**, **4-4b**, etc). The normalized reaction energy for (3) is given by equation (4) for a given value of n:

$$<E_{ring}(n)> = E((TiO_3H_2)_n)/n + E(H_2O) - E(Ti(OH)_4) \quad (4)$$

The second term in equation (2) is the ring strain energy $<E_{ring\text{-}strain}(n)>$ and it mainly depends on the bond angles ∠Ti-O-Ti and ∠O-Ti-O in the ring. The third term in the equation (2) is the intramolecular H-bond interaction energy between the side chains of the $(TiO_3H_2)_n$ monocyclic ring $<E_{H\text{-}bond}(n)>$ and will increase as n increases, as the distance between the terminal H's of the two adjacent side chains gets closer (Figure 7). To minimize $<E_{H\text{-}bond}(n)>$, we want to minimize the H-bond interactions between the side chains as much as possible and to limit the variation of the ∠Ti-O-Ti and ∠O-Ti-O angles, we re-optimized the $(TiO_3H_2)_n$ structures in D_{nh} symmetry (Figure S5), forcing all of the Ti's and the bridging O's to remain in the horizontal mirror plane, and forcing each TiOH side chains to remain on a plane normal to the ring plane. Note that these symmetry enforced structures are mostly not energy minima, but help in the estimation of E_D.

The $<E_{ring}(n)>$ values for n = 3 – 18 are given in the Supporting Information (Table S2). We found that B3LYP predicts an upper bound for the reaction exothermicity for reaction (3) whereas MP2 predicts a lower bound, so we use the average of the B3LYP and MP2 values to estimate $<E_{ring}(n)>$. The minimum in the plot of $<E_{ring}(n)>$ vs n is found for n =5 (Figure 7). The minimum at n =5 correlates with the evolution of ∠TiOTi in the ring plane. In $(TiO_3H_2)_5$,


(a)
<E_ring(n)>
-4
-5
-6
-7
-8
-9
0
5
10
15
20
n
B3LYP
MP2


(b)
H–H Distance
7
6
5
4
3
0
5
10
15
20
n

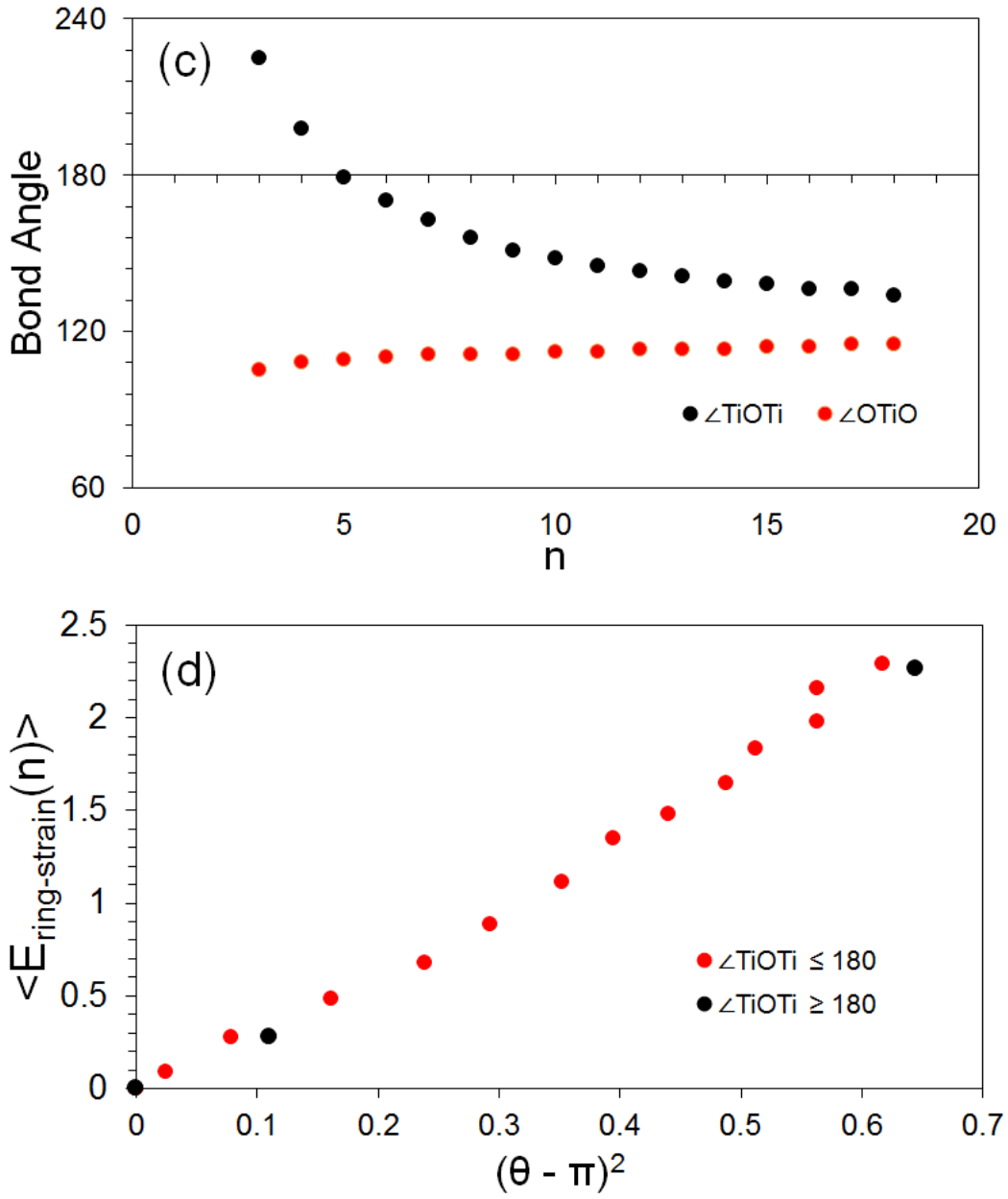


Figure 7. (a) Normalized dissociation energies (in kcal/mol per Ti) at 0 K for $(TiO_3H_2)_n$ rings in D_{nh} symmetry for n = 3-18 at the B3LYP/DZVP2 and MP2/cc-pVDZ(-pp) levels. (b) Distance (in Å) between terminal H's of the adjacent side chains for $(TiO_3H_2)_n$, n = 3-18. (c) ∠TiOTi and ∠OTiO evolution for $(TiO_3H_2)_n$, n = 3–18. (d) The normalized ring strain energy (in kcal/mol per Ti) as a function of the square of ∠TiOTi displacement (from π in rad), with energy values taken from the average of the B3LYP and MP2 values.

∠TiOTi is found to be 179˚, close to the optimal ∠TiOTi of 180˚ found in the unstrained straight chain $(HO)_3Ti–O–Ti(OH)_3$. Thus with the other two terms now zero in equation (2), $E_D = <E_{ring}(5)>$ = -8 kcal/mol. This value is in line with the calculated reaction energy of c.a. -10 kcal/mol for reaction (5)

$$2\ Ti(OH)_4 \rightarrow (HO)_3TiOTi(OH)_3 + H_2O \qquad (5)$$

at the CCSD(T)/cc-pVDZ(-pp) level; the average of the B3LYP and MP2 energies also agrees with the CCSD(T) value. The plot of ring ∠OTiO vs n is approximately linear (Figure 7), showing less local flexibility than the ring ∠TiOTi. The ∠OTiO for all of the $(TiO_3H_2)_n$ monocyclic rings with D_{nh} symmetry are close to the ∠OTiO around a perfectly 4-coordinate Ti center, 109.5˚, indicating that the steric effects from ∠OTiO angles are negligible for the $(TiO_3H_2)_n$ monocyclic rings with D_{nh} symmetry. The negative value of E_D shows that for a hydrated $(TiO_2)_n$ cluster with all Ti's 4-coordinate, the dehydration reaction of the TiOH groups is thermodynamically allowed, if the total bond angle energy correction is small or negative, which leads to the intramolecular dehydration reaction from the cluster and intermolecular dehydration that can enable the aggregation reaction between clusters. To stabilize a hydrated $(TiO_2)_n$ cluster, the dehydration energy (composed of E_D and bond angle energy corrections) needs to be overcome by either the interaction of the water to be lost with the cluster or by external interactions such as solvation. The free energy value for E_D at 298 K should be ~10 kcal/mol more negative than E_D(0 K) due to the translational component of the TΔS contributed by the leaving H_2O.

Since we have limited the intramolecular weak interaction in $(TiO_3H_2)_n$ ring by using the D_{nh} structures, the normalized ring strain energy is given by equation (6):

$$<E_{ring\text{-}strain}(n)> = <E_{ring}(n)> – E_D \qquad (6)$$

The ring strain energy is found to be a linear function of the square of the ∠TiOTi bond angle displacement from the equilibrium position (180˚), as shown in Figure 7c. Based on the linear fit of the normalized ring strain energy as a function of $(\angle TiOTi - \pi)^2$ the ∠TiOTi distortion energy can be expressed as equation (7a):

$$E_{\angle TiOTi} = \frac{1}{2} k_{\angle TiOTi} * (\angle TiOTi - \pi)^2 \quad (7a)$$

where $E_{\angle TiOTi}$ is in kcal/mol, ∠TiOTi in rad, and $k_{\angle TiOTi}$ is the bending force constant which is fit to be 7.4 kcal/(mol▪rad^2) ; or expressed as equation (7b) if degree (˚) is the angle unit:

$$E_{\angle TiOTi} = \frac{1}{2} k_{\angle TiOTi} * (\angle TiOTi - 180)^2 \quad (7b)$$

where $k_{\angle TiOTi}$ is fit to be 0.00225 kcal/(mol•degree^2).

The bending force constant for ∠OTiO is more difficult to obtain as several ∠OTiO angles on the same Ti centers are correlated. An additional complication is that the bending force constant for ∠OTiO could be different for different Ti CNs. The ∠O–Ti–O bending force constant for the 4-coordinate Ti centers can be estimated by performing a potential energy surface scan over one of the ∠O–Ti–O angles of $Ti(OH)_4$. The details are given in the Supporting Information.

The ∠O–Ti–O bending constant, $k_{\angle OTiO}$, was predicted to be 56.0 kcal/(mol•rad^2) or 0.017 kcal/(mol•degree^2), as defined in the expression of ∠O–Ti–O bending energy ($E_{\angle OTiO}$):

$$E_{\angle OTiO} = \frac{1}{2} k_{\angle OTiO} * (\angle OTiO - 109.5)^2 \quad (8)$$

Equations (7a and b) and equation (8) allow us to estimate the steric contribution due to the distortion of ∠TiOTi and ∠OTiO, which covers the most of the steric effect for the hydrated $(TiO_2)_n$ clusters. Angle distortion favors dissociative adsorption reactions that release bond angle strain, especially for the hydrated TiO_2 clusters with Ti centers under-coordinated. In order for the dissociative adsorption reaction to occur, the dissociative adsorption reaction need be more exergonic (or exothermic at 0 K) than the molecular adsorption reaction. According to the energy

decomposition of the adsorption energy, the decrease of the steric energy contribution caused by the dissociative adsorption need be greater than the sum of E_D and the molecular adsorption energy, with the approximation that the bond angle change is negligible for the molecular adsorption; the sum of E_D and the molecular adsorption energy is approximately 23 kcal/mol (8 + 15) for the Lewis acid-base molecular adsorption products with 4-coordinate Ti centers, according to our calculation results.

Whether dissociative adsorption or molecular adsorption is the thermodynamically favored reaction path for the $(TiO_2)_n$ reactions with water can also be estimated by examining the sum of the bond energies of all of the bonds in the hydrolysis product. As an example, the molecular adsorption product **4-3a** has 4 Ti–OH, 12 TiO–Ti, 4 TiO–H, 2 HO–H and 1 Lewis acid-base Ti–OH_2 bonds; and the dissociative adsorption product **4-3b** has 6 Ti–OH, 10 TiO–Ti and 6 TiO–H bonds. Assuming the bond strengths of the same type of bonds in **4-3a** and **4-3b** are invariant, the energy difference between **4-3b** and **4-3a** can be written as:

$$E(\mathbf{4\text{-}3b}) - E(\mathbf{4\text{-}3a}) = -E_{Lewis} - E_D \quad (9)$$

where E_{Lewis} is the binding energy for the Lewis acid-base Ti-H_2O bond, and E_D is the dehydration energy since E_D can be written as equation (10) in its bond dissociation energy (BDE) form:

$$E_D = 2\,BDE(TiO–Ti) + 2\,BDE(HO–H) - 2\,BDE(Ti–OH) - 2\,BDE(TiO–H) \quad (10)$$

equation (9) only works when the total bond angle strains in both adducts are comparable. In order to make more accurate prediction for the energy difference between the molecular adsorption product (**4-3a**) and the dissociative adsorption product (**4-3b**), equation (9) needs to be corrected with the energy differences between the bond angle energy corrections of **4-3a** and **4-3b**:

$$E(\mathbf{4\text{-}3b}) - E(\mathbf{4\text{-}3a}) = \sum E_{angle}(\mathbf{4\text{-}3b}) - \sum E_{angle}(\mathbf{4\text{-}3a}) - E_{Lewis} - E_D \quad (11)$$

where $\sum E_{angle}$ is the total bond angle energy, a sum of the bond angle energy correction for each individual bond angle in the adsorption product, which can be evaluated using equations (7) and (8).

All of the Ti's are 4-coordinate for **4-3a** and **4-3b**, so E_{Lewis} and E_D can be estimated to be -15 and -8 kcal/mol. Structure **4-3b** is predicted to be 23 kcal/mol less stable than **4-3a** using equation (9), which differs by 15 kcal/mol from the direct calculation result. If we include the bond angle energy correction (8 kcal/mol in favor of dissociative adsorption) for Ti–O–Ti angles to the relative energy using equation (7), structure **4-3b** is predicted to be 15 kcal/mol higher in energy than **4-3a** using equation (11), as compared to the 7 kcal/mol from the direct calculation. With further inclusion of the bond angle energy correction (10 kcal/mol in favor of dissociative adsorption) of the O–Ti–O bonds using equation (8), the relative energy is corrected to be 5 kcal/mol, which is in excellent agreement with the direct calculation result. A substantial improvement is found in comparison to the estimated relative energy obtained with equation (9).Our approach to predict the relative stabilities for different H_2O adsorption adducts on $(TiO_2)_n$ using equation (11) is qualitative, yet it allows us to predict the energetically favorable adsorption reaction path without carrying out costly direct electronic structure calculation for a larger system.

Cluster Condensation (Aggregation) Reaction Energies The calculated reaction enthalpies at 0 K and Gibbs free energies at 298 K for the condensation reactions with or without elimination of H_2O at the B3LYP/DZVP2 level are shown in Table 2, Table 3 and Table S3 in the Supporting Information. Whether an aggregation reaction is exothermic or endothermic largely depends on whether the Ti's are 4-coordinate in the reactants and products. Most of the aggregation reactions with the reactants being hydroxide clusters (with no molecularly adsorbed H_2O's) with 4-coordinate Ti's

Table 2. Calculated reaction enthalpy at 0 K and Gibbs free energy at 298 K (in kcal/mol) for the cluster condensation (aggregation) reactions without water loss for the titanium hydroxide clusters at the B3LYP/CCSD(T)/cc-pVDZ(-pp) level.

Reaction	ΔH(0K)	ΔG(298K)	Reaction	ΔH(0K)	ΔG(298K)
(**1-1a**) + (**2-1a**) → (**3-2a**)	-110.3	-96.6	(**1-1a**) + (**3-4a**) → (**4-5a**)	-75.6	-60.0
(**1-1a**) + (**2-2a**) → (**3-3a**)	-69.8	-57.3	(**1-2a**) + (**3-3a**) → (**4-5a**)	-45.6	-28.0
(**1-2a**) + (**2-1a**) → (**3-3a**)	-87.3	-76.6	2 (**1-1a**) + (**2-3a**) → (**4-5a**)	-144.3	-115.1
3 (**1-1a**) → (**3-3a**)	-160.1	-135.2	2 (**1-2a**) + (**2-1a**) → (**4-5a**)	-133.0	-104.6
(**1-1a**) + (**2-3a**) → (**3-4a**)	-68.7	-55.2	3 (**1-1a**) + (**1-2a**) → (**4-5a**)	-205.7	-163.2
(**1-2a**) + (**2-2a**) → (**3-4a**)	-39.8	-25.3	(**2-1a**) + (**2-4a**) → (**4-5a**)	-101.1	-85.8
2 (**1-1a**) + (**1-2a**) → (**3-4a**)	-130.1	-103.2	(**2-2a**) + (**2-3a**) → (**4-5a**)	-54.1	-37.3
(**1-1a**) + 2 (**1-2a**) → (**3-5a**)	-98.3	-71.7	(**1-1a**) + (**3-5a**) → (**4-6a**)	-74.2	-58.6
(**1-1a**) + (**2-4a**) → (**3-5a**)	-66.5	-53.0	(**1-2a**) + (**3-4a**) → (**4-6a**)	-42.4	-27.2
(**1-2a**) + (**2-3a**) → (**3-5a**)	-37.0	-23.7	2 (**1-1a**) + 2 (**1-2a**) → (**4-6a**)	-172.5	-130.3
(**1-2a**) + (**2-4a**) → (**3-6a**)	-34.1	-21.5	2 (**1-1a**) + (**2-4a**) → (**4-6a**)	-140.6	-111.6
3 (**1-2a**) → (**3-6a**)	-66.0	-40.3	2 (**1-2a**) + (**2-2a**) → (**4-6a**)	-82.3	-52.5
(**1-1a**) + (**3-1a**) → (**4-2a**)	-114.6	-101.4	(**2-2a**) + (**2-4a**) → (**4-6a**)	-50.4	-33.7
2 (**2-1a**) → (**4-2a**)	-156.2	-142.1	2 (**2-3a**) → (**4-6a**)	-49.8	-34.3
(**1-1a**) + (**3-2a**) → (**4-3a**)	-87.3	-72.2	(**1-1a**) + 3 (**1-2a**) → (**4-7a**)	-133.8	-94.3
(**1-2a**) + (**3-1a**) → (**4-3a**)	-83.3	-69.5	(**1-1a**) + (**3-6a**) → (**4-7a**)	-67.8	-54.0
2 (**1-1a**) + (**2-1a**) → (**4-3a**)	-197.6	-168.7	(**1-2a**) + (**3-5a**) → (**4-7a**)	-35.5	-22.6
(**2-1a**) + (**2-2a**) → (**4-3a**)	-107.4	-90.9	2 (**1-2a**) + (**2-3a**) → (**4-7a**)	-72.5	-46.3
(**1-1a**) + (**3-3a**) → (**4-4a**)	-78.3	-60.6	(**2-3a**) + (**2-4a**) → (**4-7a**)	-40.6	-27.5

(**1-2a**) + (**3-2a**) → (**4-4a**)	-55.4	-40.7	(**1-2a**) + (**3-6a**) → (**4-8a**)	-32.8	-19.0
2 (**1-1a**) + (**2-2a**) → (**4-4a**)	-148.2	-117.9	2 (**1-2a**) + (**2-4a**) → (**4-8a**)	-67.0	-40.5
4 (**1-1a**) → (**4-4a**)	-238.4	-195.8	4 (**1-2a**) → (**4-8a**)	-98.8	-59.2
(**2-1a**) + (**2-3a**) → (**4-4a**)	-104.3	-89.2	2 (**2-4a**) → (**4-8a**)	-35.1	-21.7
2 (**2-2a**) → (**4-4a**)	-57.9	-40.0			

Table 3. Calculated reaction enthalpy at 0 K and Gibbs free energy at 298 K (in kcal/mol) for the cluster condensation (aggregation) reactions with water loss for the titanium hydroxide clusters at the B3LYP/CCSD(T)/cc-pVDZ(-pp) level.

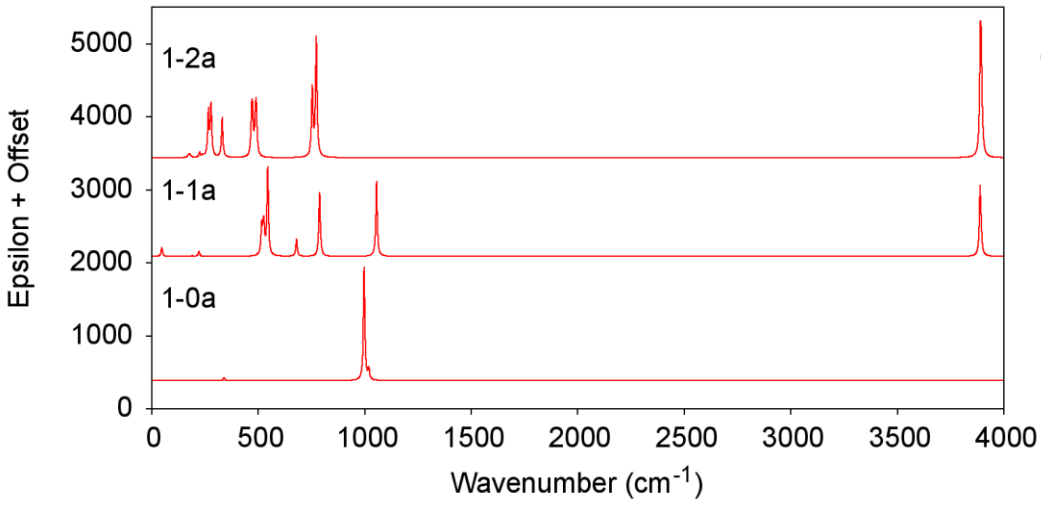
Reaction	ΔH(0K)	ΔG(298K)	Reaction	ΔH(0K)	ΔG(298K)
3 (**1-1a**) → (**3-1a**) + 2 H_2O	-94.6	-84.8	2 (**2-4a**) → (**4-2a**) + 6 H_2O	39.6	-2.6
3 (**1-2a**) → (**3-1a**) + 5 H_2O	44.2	24.8	4 (**1-1a**) → (**4-3a**) + 1 H_2O	-224.1	-190.8
3 (**1-1a**) → (**3-2a**) + 1 H_2O	-136.7	-118.6	4 (**1-2a**) → (**4-3a**) + 5 H_2O	-39.1	-44.7
3 (**1-2a**) → (**3-2a**) + 4 H_2O	2.0	-9.0	2 (**2-2a**) → (**4-3a**) + 1 H_2O	-43.6	-35.0
3 (**1-2a**) → (**3-3a**) + 3 H_2O	-21.3	-25.6	2 (**2-3a**) → (**4-3a**) + 3 H_2O	-8.8	-21.7
3 (**1-2a**) → (**3-4a**) + 2 H_2O	-37.6	-30.1	2 (**2-4a**) → (**4-3a**) + 5 H_2O	24.7	-7.2
3 (**1-2a**) → (**3-5a**) + 1 H_2O	-52.1	-35.2	4 (**1-2a**) → (**4-4a**) + 4 H_2O	-53.4	-49.7
4 (**1-1a**) → (**4-1a**) + 3 H_2O	-136.8	-121.8	2 (**2-3a**) → (**4-4a**) + 2 H_2O	-23.2	-26.7
4 (**1-2a**) → (**4-1a**) + 7 H_2O	48.2	24.3	2 (**2-4a**) → (**4-4a**) + 4 H_2O	10.4	-12.2
2 (**2-1a**) → (**4-1a**) + 1 H_2O	-83.8	-77.7	4 (**1-2a**) → (**4-5a**) + 3 H_2O	-67.0	-53.6
2 (**2-2a**) → (**4-1a**) + 3 H_2O	43.7	33.9	2 (**2-3a**) → (**4-5a**) + 1 H_2O	-36.7	-30.6
2 (**2-3a**) → (**4-1a**) + 5 H_2O	78.4	47.3	2 (**2-4a**) → (**4-5a**) + 3 H_2O	-3.2	-16.1
2 (**2-4a**) → (**4-1a**) + 7 H_2O	111.9	61.8	4 (**1-2a**) → (**4-6a**) + 2 H_2O	-80.0	-57.3
4 (**1-1a**) → (**4-2a**) + 2 H_2O	-209.1	-186.2	2 (**2-4a**) → (**4-6a**) + 2 H_2O	-16.3	-19.8
4 (**1-2a**) → (**4-2a**) + 6 H_2O	-24.2	-40.1	4 (**1-2a**) → (**4-7a**) + 1 H_2O	-87.6	-57.8
2 (**2-2a**) → (**4-2a**) + 2 H_2O	-28.7	-30.4	2 (**2-4a**) → (**4-7a**) + 1 H_2O	-23.8	-20.3
2 (**2-3a**) → (**4-2a**) + 4 H_2O	6.1	-17.1			

to form products with all 4-coordinate Ti's, is exothermic. If the reactant contains molecularly adsorbed water, the aggregation reaction can be endothermic, even if all the Ti's in the reactant and product are 4-coordinate. The Gibbs free energy correction for the aggregation reaction is basically due to the molecular equivalents change of the reaction, which lead to a net $T\Delta S_{translational}$ difference of ~ 10 kcal/mol per equivalent for the correction at 298 K. With only the entropy correction being considered, raising the reaction temperature will shift the equilibrium towards the direction in which the molecular equivalents increase. In another sense, aggregation reactions with leaving H_2O's are in general more exergonic at higher temperature. The aggregation reactions of the monocyclic rings have a negative ΔS, as the number of molar equivalents decreases, so increasing the temperature will decrease the exergonicity of the clustering aggregation reactions for the monocyclic ring clusters.

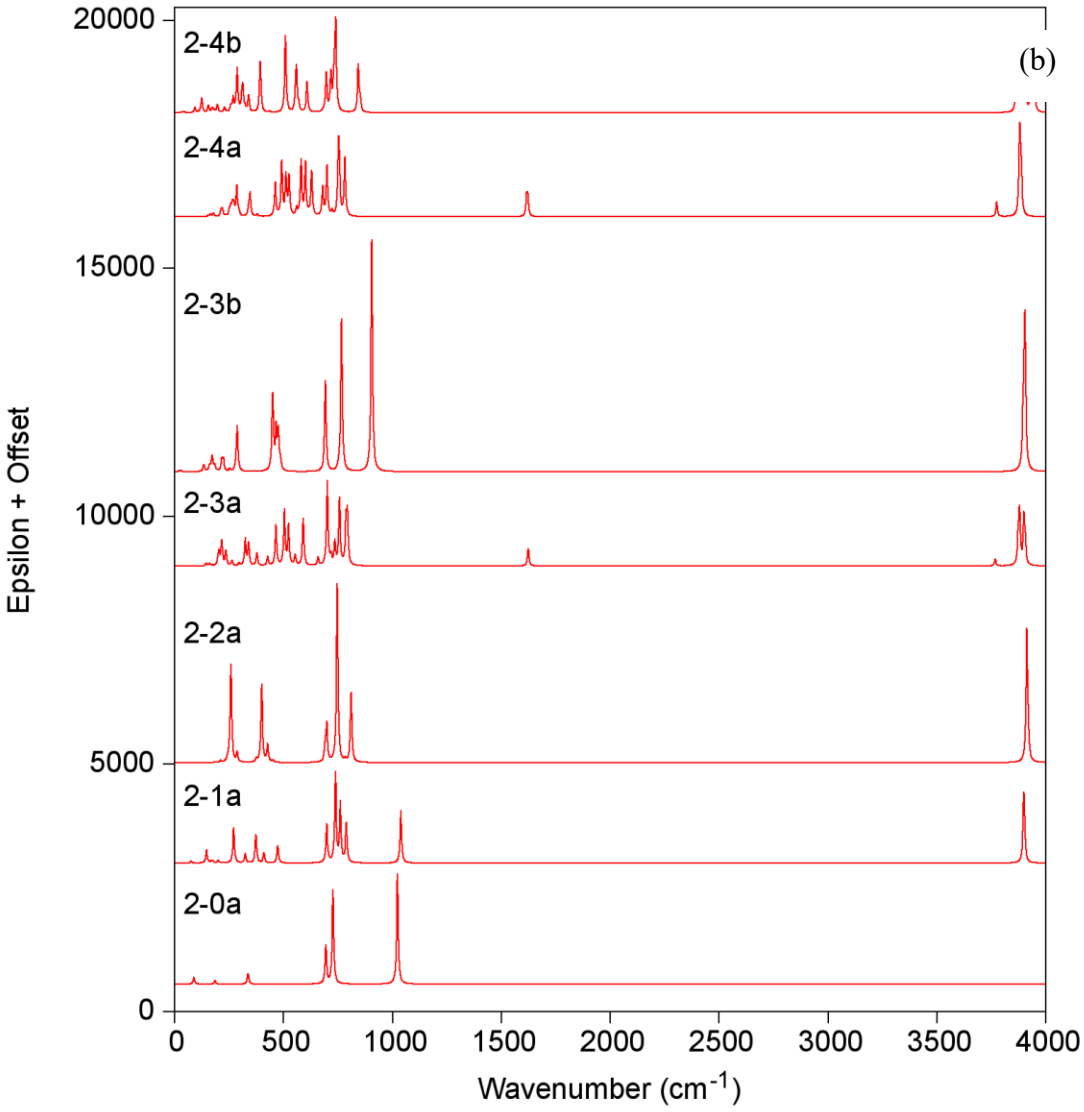
We have shown that the hydrolysis limit of $(TiO_2)_n$ is related to the number of Ti centers with CN less than 4 in the cluster. As n grows, ratio between such Ti centers and higher coordinated Ti centers will decrease.[11] The products for the hydrolysis reaction of a larger $(TiO_2)_n$ at the hydrolysis limit will have less dissociatively adsorbed H_2O's (than the total number of dissociatively adsorbed water in the reactants to form the large hydroxides), which infers H_2O loss in aggregation reaction to form such a structure. As a consequence, the aggregation reactions of products at the hydrolysis limit should be always exergonic, and increasing temperature will increase the exergonicity.

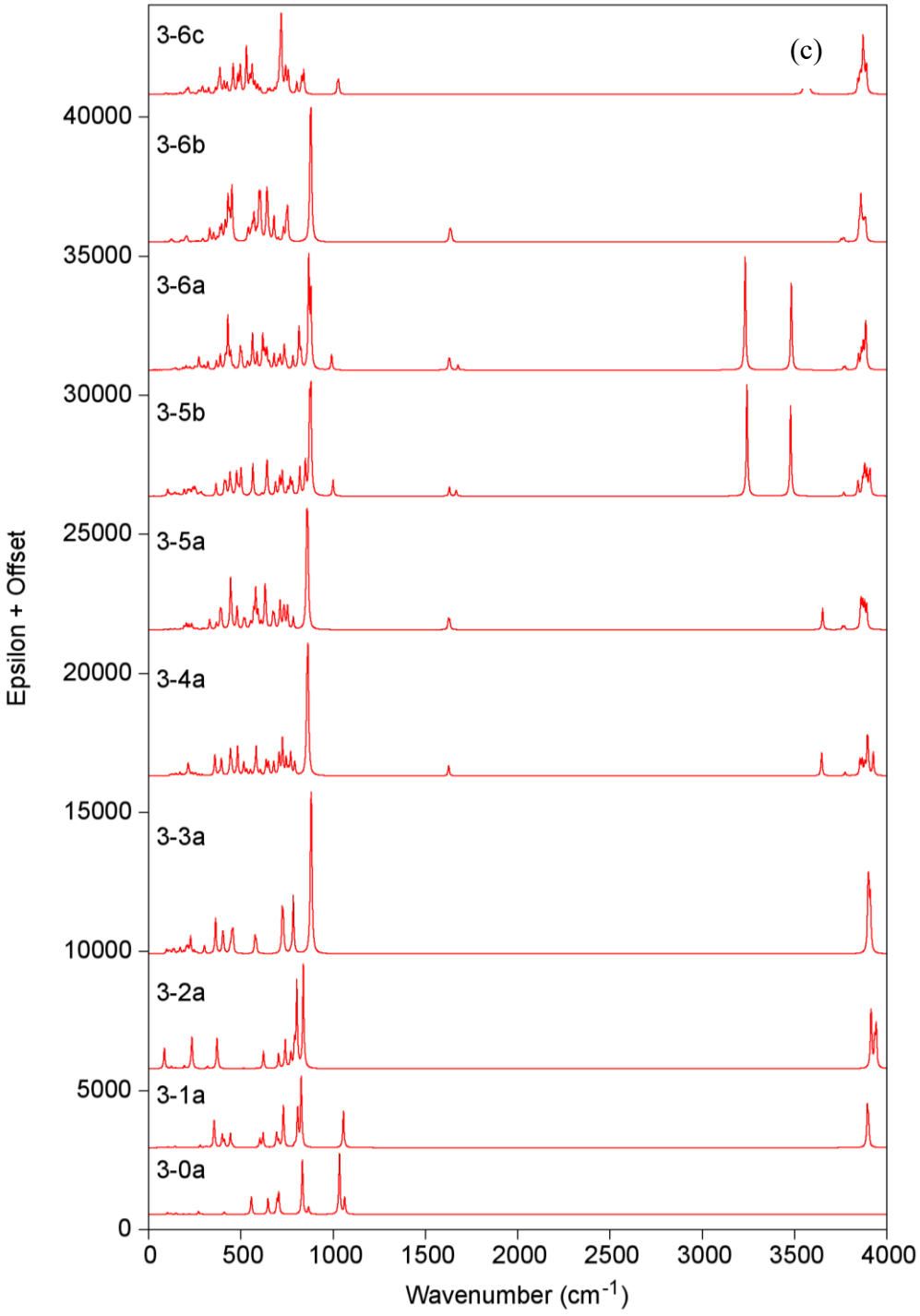
Vibrational frequencies The calculated infrared spectra for the lowest energy products of the $(TiO_2)_n$ + m H_2O reactions at the B3LYP/DZVP2 level are shown in Figure 8. The strong band at 997 cm^{-1} and the weak band at 1019 cm^{-1} in the TiO_2 monomer spectrum are the TiO_2 asymmetric

and symmetric stretching for the terminal oxygens. Addition of the first H_2O to TiO_2 blue shifts the two bands near 1000 cm^{-1} to a single strong band at 1055 cm^{-1}, a $Ti{=}O_{teminal}$



(a)


(b)
2-4b
2-4a
2-3b
2-3a
2-2a
2-1a
2-0a
Epsilon + Offset
Wavenumber (cm-1)
0
5000
10000
15000
20000
0
500
1000
1500
2000
2500
3000
3500
4000


(c)
3-6c
3-6b
3-6a
3-5b
3-5a
3-4a
3-3a
3-2a
3-1a
3-0a
Epsilon + Offset
0
5000
10000
15000
20000
25000
30000
35000
40000
0
500
1000
1500
2000
2500
3000
3500
4000
Wavenumber (cm-1)

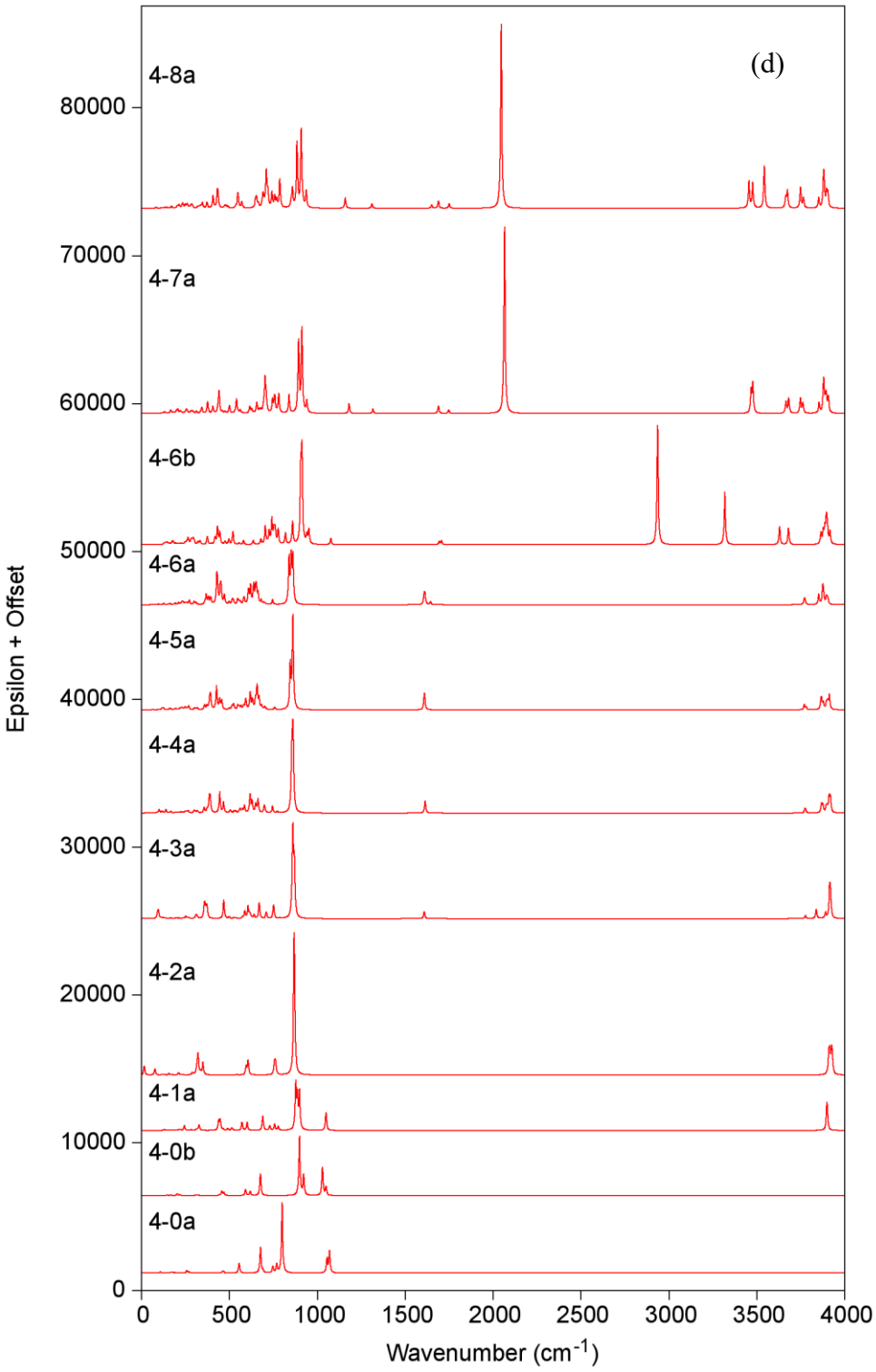


Figure 8. The calculated infrared spectra for the lowest energy products of the $(TiO_2)_n$ + m H_2O reactions for a) TiO_2, b) $(TiO_2)_2$, c) $(TiO_2)_3$, and d) $(TiO_2)_4$ at the B3LYP/DZVP2 level.

stretch. Several new bands appear in the infrared spectrum of $OTi(OH)_2$ (**1-1a**). The new bands near 3900 cm^{-1} are the (Ti)O–H stretching modes and the two new bands at 680 and 788 cm^{-1} are the Ti–O(H) stretching modes. The bands near 500 cm^{-1} are the Ti–O–H bends and the out-of-plane motions of the hydroxyl groups. The strong band near 1000 cm^{-1} disappears when two H_2O molecules are added to TiO_2, consistent with the fact that **1-2a** contains no terminal O's. The bands with frequencies lower than 500 cm^{-1} are the bending and out-of-plane wagging and twisting modes of structure **1-2a**, and the bands in the 600-800 cm^{-1} regions are the Ti–O(H) stretches.

The strong band near 1000 cm^{-1} in TiO_2 is increased for the $Ti{=}O_{teminal}$ stretches of $(TiO_2)_2$, and the two bands near 700 cm^{-1} are the stretching modes between the Ti's and the bridging O atoms. When H_2O's are dissociatively adsorbed (**2-1a** and **2-2a**), the new band near 3900 cm^{-1} is the OH stretch. The new bands below 500 cm^{-1} are the bending, wagging and twisting motions of the Ti–O–H groups, and the bands in the 600-800 cm^{-1} regions are assigned to the Ti–O(H) and Ti–O(Ti) stretches. The molecular adsorption reactions to form **2-3a** and **2-4a** give rises to two weak bands at approximately 1630 and 3870 cm^{-1}, which are the H–O–H bends and (H)O–H stretches of the Lewis acid-base bonded molecular H_2O. The Ti–O(H) stretches and Ti–O–H bends in **2-2a** split into finer structures as additional H_2O's are molecularly adsorbed by Lewis acid-base interactions to form **2-3a** and **2-4a**.

Similar assignments can be made for the reaction products of the addition of H_2O's to $(TiO_2)_3$ and $(TiO_2)_4$. The most intense bands in the 600-800 cm^{-1} regions can be assigned to the Ti–O(Ti) stretching modes. Weak peaks at ~ 1630 and 1670 cm^{-1} are assigned to the H–O–H bending modes of the molecularly adsorbed H_2O's, by Lewis acid-base interaction and by H-bond respectively. The weak bands near 3770 and 3880 cm-1 are assigned to the symmetric and asymmetric $O–H_2$ stretch of the Lewis acid-base bonded H_2O, whereas the strong bands in the

broad regions near 3200 and 3500 cm^{-1} are (Ti)O–H and (H)O–H stretches shifted by H-bonds, respectively. The more red shifted the ν(TiO–H) stretch, the stronger the hydrogen bond as the O-H bond is elongated and partially transferred to an adjacent O. The molecular adsorption conversion of **4-6b** to **4-7a** leads to a significant partial H transfer so that the TiO–H bond distance increases from 1.01 Å to 1.07 Å and the ν(TiO-H) stretch is red shifted from 2935 cm^{-1} to 2065 cm^{-1}.

Conclusions

The low energy structures of the $(TiO_2)_n(H_2O)_m$ ($n \leq 4$, $m \leq 2n$) clusters were predicted using a global geometry optimization approach combining molecular docking with a hybrid genetic algorithm. A number of new low energy isomers, including both dissociative and molecular adsorption adducts of water on $(TiO_2)_n$, were found. At 0 K, dissociative adsorption of H_2O dominates over molecular adsorption for the initial adsorption steps, whereas later steps are dominated by molecular adsorption. Dissociative adsorption of H_2O on Ti with CN(Ti) < 4 is much more exothermic than molecular adsorption of H_2O onto the same Ti center, whereas molecular adsorption of H_2O on Ti with CN(Ti) = 4 to form Lewis acid-base Ti-OH_2 bond is ~ 5 kcal/mol more exothermic than the dissociative adsorption reaction. The number of H_2O molecules required to eliminate all of the under-coordinated Ti centers and the 4-coordinated Ti centers with distorted geometry is the key for the hydrolysis limit, i.e. the maximum equivalents of H_2O that can be completely dissociatively adsorbed in favor of being molecularly adsorbed. The hydrolysis limits are predicted to be 2, 2, 3, 2, and 3 for $(TiO_2)_n$, n = 1, 2, 3, 4 and 8, respectively at 0 K. The Gibbs free energy for the hydrolysis reaction at 298 K is essentially the reaction enthalpy at 0 K corrected by the translational component of TΔS, which will reduce the exergonicity of the adsorption energy by 10 kcal/mol for dissociative adsorption and Lewis acid-base type molecular adsorption.

The TΔS correction for the molecular adsorption reactions to form one H-bond will only reduce the reaction exergonicity by 5 kcal/mol at 298 K, due to the additional vibrational TΔS contribution from low frequency modes of the loosely bonded H_2O. The size and geometry independent dehydration reaction energy for two Ti(OH) groups of the hydrated TiO_2 clusters were estimated to be -8 kcal/mol using a series of symmetry enforced $(TiO_3H_2)_n$ monocyclic ring structures. With the same approach, the bending force constants for the ∠TiOTi and ∠OTiO bonds are determined to be 7.4 and 56.0 kcal/(mol▪rad^2), respectively.

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Supporting Information Available Complete references for refs 36 and 37. Computational procedures to estimate the ∠O–Ti–O bending force constant, $k_{\angle OTiO}$. Optimized geometries for the low energy $(TiO_2)_n$ clusters, n = 1–4. Geometries and relative energies for the additional low energy $(TiO_2)_n(H_2O)_m$ clusters (n = 1–4, m ≤ 2n). Geometries for monocyclic $(TiO_3H_2)_5$ (in D_{5h}) and $(TiO_3H_2)_{10}$ (in D_{10h}) rings. Calculated reaction enthalpy at 0 K and Gibbs free energy at 298 K for the H_2O dissociation reactions for low energy $(TiO_2)_n(H_2O)_m$ at CCSD(T) level. Calculated Geometry parameters and energetics for the $(TiO_3H_2)_n$ monocyclic rings in D_{nh} symmetry. Calculated reaction enthalpy at 0 K and Gibbs free energy at 298 K for the additional cluster condensation (aggregation) reactions with water loss for the titanium hydroxide clusters at the

B3LYP level. Optimized Cartesian coordinates for the low energy $(TiO_2)_n(H_2O)_m$ (n = 1–4 and 8) clusters. Optimized Cartesian coordinates for the $(TiO_3H_2)_n$ (n=3–18) monocyclic ring clusters in D_{nh} symmetry. This material is available free of charge via the Internet at http://pubs.acs.org.

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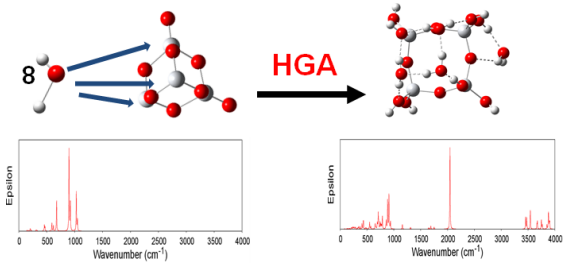
TOC Graphic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