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Interaction of TiO_2^- with water: Photoelectron spectroscopy and density functional calculations

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The interactions of titania with water molecules were studied via photoelectron spectroscopy and density functional calculations of $TiO(OH)_2^-$ and $Ti(OH)_4(H_2O)_n^-$ (n = 0–5) clusters which are corresponding to the $TiO_2(H_2O)^-$ and $TiO_2(H_2O)_{n+2}^-$ (n = 0–5) systems, respectively. Experimental observation and theoretical calculations confirmed that $TiO(OH)_2^-$ was produced when TiO_2^- interacts with one water molecule, and $Ti(OH)_4(H_2O)_n^-$ (n = 0–5) were produced successively when TiO_2^- interacts with two or more water molecules. The structures of $Ti(OH)_4(H_2O)_n^-$ with n = 4, 5 are slightly different from those of n = 1–3. The structures of $Ti(OH)_4(H_2O)_{1\text{-}3}^-$ can be viewed as the water molecules interacting with the $Ti(OH)_4^-$ core through hydrogen bonds; however, in $Ti(OH)_4(H_2O)_{4,5}^-$, one of the water molecules interacts directly with the Ti atom via its oxygen atom instead of a hydrogen bond and distorted the $Ti(OH)_4^-$ core. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4828815]

I. INTRODUCTION

Titanium dioxide, TiO_2, is one of the most intensively studied materials due to its wide range of technological and industrial applications.[1–4] TiO_2 is reactive with water but exhibits an outstanding resistance to corrosion in aqueous environments. The interaction between TiO_2 and water is of great interest for many areas of both fundamental and applied science, including photocatalysis, electrochemistry, active coatings, and corrosion.[5–7]

In the past several decades, extensive studies have been carried out to investigate reactions of water on titania surfaces,[8–21] and these studies have shown the importance of understanding water dissociation on TiO_2 surface. However, a clear picture of the water dissociation process is not achieved. Scanning tunneling microscopy (STM),[22–25] temperature programmed desorption (TPD),[26,27] X-ray photoelectron spectroscopy (XPS),[28] low-energy ion scattering spectroscopy (LEIS),[10] ultraviolet photoemission spectroscopy (UPS),[29] and near infra-red (NIR) measurement[30] were used to investigate the interactions of water with TiO_2 by many groups. Several STM investigations suggested that direct water dissociation at oxygen vacancies form an adjacent hydroxyl pair located on two neighboring bridge-bonded oxygen (BBO) sites.[23,24] TPD research[26,27] suggested that rutile-TiO_2(100) surface is more active for water dissociation than the TiO_2(110) surface, and H_2O molecules on reduced surfaces dissociatively adsorbed at 135 K to form two uncorrelated bridging OH species. The XPS[28] results of the interaction of water with surfaces of anatase-TiO_2(101) showed that the adsorbed water was predominantly bound to the surface in a molecular state. Near-infrared absorption spectroscopy[30] observed the combination bands of the fundamental vibration modes (symmetric stretching, bending, and asymmetric stretching) attributed to the H_2O molecules adsorbed on a TiO_2 surface. Additionally, the interactions of TiO_2 with water have also been studied via time-resolved two-photon photoemission (TR-2PP),[31] sum frequency generation (SFG) vibrational spectroscopy,[32] and density functional theory (DFT) method.[33,34]

Since atomic and molecular clusters can be regarded as models for understanding the fundamental mechanisms in condensed phases and on complex surfaces, numerous studies have been carried out to investigate the hydrated metal-oxide clusters and their corresponding isomers.[35–39] These studies suggested that metal oxides interacting with water can form hydrated metal-oxides or under water dissociation to produce the corresponding hydroxyl species. Recently, we have investigated the interaction of Co_nO^- with water and found that they prefer to exist in the form of $Co_n(OH)_2(H_2O)_n^-$.[40] In order to understand the interactions between titania and water, here we investigated $TiO(OH)_2^-$ and $Ti(OH)_4(H_2O)_n^-$ (n = 0–5) clusters employing photoelectron spectroscopy and density functional calculations.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Experimental

The experiments were conducted on a home-built apparatus consisting of a time-of-flight mass spectrometer and a magnetic-bottle photoelectron spectrometer, which has been described elsewhere.[41] In brief, the $TiO_3H_2^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) cluster anions were produced in a laser vaporization source, in which a rotating, translating Ti target was ablated with the second harmonic (532 nm) light pulses of a Nd:YAG laser, and helium gas with ~4 atm

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backing pressure seeded with water vapor was allowed to expand through a pulsed valve over the target. The residual oxygen on the target surface is enough for generating titanium dioxide. The reaction of titanium dioxide with water generated the resultant cluster anions. The clusters anions were mass-analyzed by the time-of-flight mass spectrometer. After mass-selection and deceleration, the $TiO_3H_2^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) clusters were photodetached with a second Nd:YAG laser. The electrons resulting from photodetachment were energy-analyzed by the magnetic-bottle photoelectron spectrometer. The photoelectron spectra were calibrated using the photoelectron spectrum of Cu^- taken at similar conditions. The resolution of the photoelectron spectrometer was approximately 40 meV for electrons with 1 eV kinetic energy.

B. Computational methods

The theoretical calculations were performed with density functional theory, using B3LYP[42–44] method and the 6-311+G(d,p) basis set. The geometries of all complexes were determined by optimizing the different initial structures at several multiplicities. Optimizations were performed without imposing symmetry constraints, and the calculated energies were corrected by the zero-point vibrational energies. Harmonic vibrational frequency calculations were performed to verify that the obtained structures are real local minima. All the calculations were conducted with the Gaussian 09 program package.[45]

III. RESULTS AND DISCUSSION

The photoelectron spectra of TiO_2^-, $TiO_3H_2^-$, and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) taken with 355 nm photons are presented in Figure 1. The photoelectron spectra of $TiO_3H_2^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) taken with 266 nm photons are shown in Figure S1 of the supplementary material.[46] The adiabatic detachment energies (ADEs) and vertical detachment energies (VDEs) measured from the photoelectron spectra are listed in Table I, where they are compared with the theoretical values from the DFT calculations. The VDEs were calculated as the energy difference between the electronic ground states of the neutrals and anions with the neutrals at the geometries of their corresponding anionic species. The ADEs were obtained as the energy differences between the neutrals and anions with the neutrals optimized to the nearest local minima.

The optimized geometries of the typical low-lying isomers of $TiO_3H_2^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) are shown in Figures 2 and 3 and their corresponding neutral isomers are shown in Figures 4 and 5 with the most stable structures on the left.

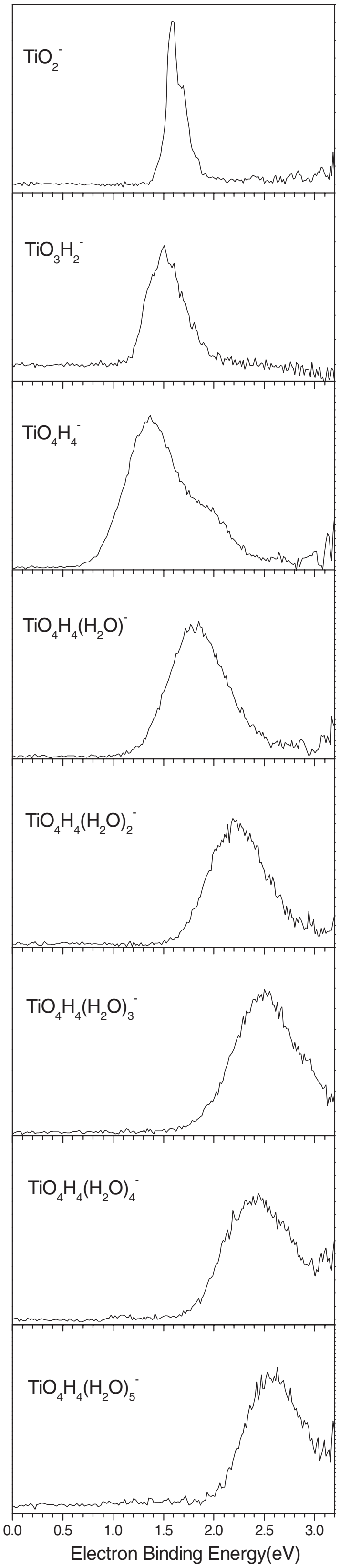

FIG. 1. Photoelectron spectra of TiO_2^-, $TiO_3H_2^-$, and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) taken with 355 nm photons.

A. Photoelectron spectra

As seen in Figure 1, the photoelectron spectrum of TiO_2^- taken with 355 nm photons is vibrationally resolved, the peak at 1.59 eV is designated as the VDE. The spectrum of $TiO_3H_2^-$ at 355 nm has only one unresolved broad feature centered at 1.51 eV, the electron binding energy (EBE) is slightly lower than that of TiO_2^-. This indicates that $TiO_3H_2^-$ cannot be simply considered as a hydrated TiO_2^- and its structure and electronic properties might be different from those of a hydrated TiO_2^-.

TABLE I. Relative energies, VDEs, and ADEs of the typical low-lying isomers of $TiO_3H_2^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) calculated at the B3LYP level of theory as well as the comparison with the experimental VDEs and ADEs. (The isomers labeled with bold are the most probable ones observed in the experiments.)

Isomer		Δ E (eV)	ADE (eV) Theo.	ADE (eV) Expt.	VDE (eV) Theo.	VDE (eV) Expt.
TiO_2^-	**0A**		1.59	1.59 ± 0.04	1.59	1.59 ± 0.04
$TiO_3H_2^-$	**1A**	0.00	1.31	1.15 ± 0.08	1.67	1.51 ± 0.08
	1B	0.11	1.21		1.72	
	1C	2.04	2.11		2.22	
$TiO_4H_4^-$	**2A**	0.00	0.58	0.77 ± 0.08	1.35	1.37 ± 0.08
	2B	0.60	1.73		2.24	
	2C	2.70	0.91		1.91	
$TiO_4H_4(H_2O)^-$	**3A**	0.00	0.97	1.23 ± 0.08	1.83	1.82 ± 0.08
	3B	0.76	1.09		2.67	
	3C	2.65	0.92		1.58	
$TiO_4H_4(H_2O)_2^-$	**4A**	0.00	1.03	1.62 ± 0.08	2.18	2.21 ± 0.08
	4B	0.00	1.16		2.25	
	4C	0.00	1.22		2.36	
	4D	0.78	1.03		3.10	
	4E	2.70	0.31		1.77	
$TiO_4H_4(H_2O)_3^-$	**5A**	0.00	1.63	1.91 ± 0.08	2.52	2.49 ± 0.08
	5B	0.06	1.37		2.63	
	5C	0.07	1.25		2.57	
	5D	0.80	1.01		3.37	
	5E	2.88	0.36		1.97	
$TiO_4H_4(H_2O)_4^-$	**6A**	0.00	1.36	1.84 ± 0.08	2.43	2.41 ± 0.08
	6B	0.00	1.85		2.91	
	6C	0.92	0.84		2.72	
	6D	2.26	0.54		1.76	
$TiO_4H_4(H_2O)_5^-$	**7A**	0.00	1.48	2.06 ± 0.08	2.68	2.57 ± 0.08
	7B	0.05	1.53		2.63	
	7C	0.06	1.95		3.27	
	7D	2.62	0.38		1.86	

$TiO_4H_4^-$ has a peak centered at 1.37 eV. This peak shifts to lower electron binding energy compared with that of $TiO_3H_2^-$, indicating that $TiO_4H_4^-$ is neither a solvated $TiO_3H_2^-$ nor a solvated TiO_2^-. Additionally, a hump at about 2.0 eV was observed in the spectrum of $TiO_4H_4^-$. This hump might be contributed by a different isomer. The photoelectron spectra of $TiO_4H_4(H_2O)_n^-$ (n = 1–3) are similar to that of $TiO_4H_4^-$ except that their photoelectron peaks shift toward higher EBE with increasing number of water molecules. The experimental VDEs of $TiO_4H_4(H_2O)_n^-$ for n = 0, 1, 2, and 3 are 1.37, 1.82, 2.21, and 2.49 eV, respectively. The similarities of the spectra of $TiO_4H_4^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 1–3) indicate that the addition of water molecules provides a simple solvation effect to $TiO_4H_4^-$. This will be verified by the following theoretical calculations.

It is noteworthy that the VDE of $TiO_4H_4(H_2O)_4^-$ (2.41 eV) is slightly lower than that of $TiO_4H_4(H_2O)_3^-$, indicating that $TiO_4H_4(H_2O)_4^-$ cannot be simply considered as derived from a solvated $TiO_4H_4(H_2O)_3^-$. It is suspected that $TiO_4H_4(H_2O)_4^-$ should have a different electronic structure from the solvated $TiO_4H_4(H_2O)_3^-$. The photoelectron spectrum of $TiO_4H_4(H_2O)_5^-$ is similar to that of $TiO_4H_4(H_2O)_4^-$, except that its photoelectron peak shifts toward higher EBE, indicating that the addition of a water molecule to $TiO_4H_4(H_2O)_4^-$ is a simple solvation effect.

B. Theoretical calculations

1. $TiO_3H_2^-$ and TiO_3H_2

Three typical low-lying structures for $TiO_3H_2^-$ were identified by density functional calculations (Figure 2). Both isomers 1A and 1B are dihydroxide anions in the form of $TiO(OH)_2^-$. Isomer 1A is a C_s symmetry structure with two OH groups in trans positions and an oxygen atom interacting with the Ti atom to form a Ti-O bond. The calculated VDE of isomer 1A is ~1.67 eV, in agreement with the experimental VDE of 1.51 eV. Isomer 1B is a C_{2v} symmetry structure with the two OH groups in *cis* positions. It is higher than 1A by 0.11 eV. The calculated VDE of isomer 1B (1.72 eV) is also close to the experimental measurement. Our calculations show that the energy barrier between isomers 1A and 1B is about 0.14 eV. Isomer 1C is a hydrated metal-oxide species $TiO_2(H_2O)^-$ with an intact water molecule adsorbed on titania via two hydrogen bonds. It is higher than isomer 1A by ~2.04 eV in energy and much less stable than isomers 1A and 1B. It is unlikely for isomer 1C to be present in our experiments. Isomers 1A and 1B probably are the ones contributing to the photoelectron spectrum of $TiO_3H_2^-$ measured in our experiments. Thus, the first water molecule interacting with TiO_2^- prefers to form hydroxyl species $TiO(OH)_2^-$ instead of hydrated titanium-dioxide $TiO_2(H_2O)^-$. This reveals that the first water molecule interacting with TiO_2^- was dissociated to produce hydroxyl species. For the neutral TiO_3H_2, isomer 1A′ is an anchor structure with C_{2v} symmetry in the form of $TiO(OH)_2$. Isomer 1B′ is a hydrated metal-oxide species $TiO_2(H_2O)$ with C_s symmetry. Isomer 1B′ is much less stable and higher than isomer 1A′ by 2.83 eV in energy.

2. $TiO_4H_4^-$ and TiO_4H_4

For $TiO_4H_4^-$, we identified three typical low-lying isomers (Figure 2). Isomer 2A is the most stable structure in the form of $Ti(OH)_4^-$ with C_s symmetry and in ^2A state, in which the two water molecules interacting with TiO_2^- were dissociated to form hydroxyl species. The calculated VDE for isomer 2A is about 1.35 eV, in excellent agreement with the experimental VDE of 1.37 eV. Isomer 2B is in the form of $TiO(OH)_2(H_2O)^-$ with isomer 1A solvated by a water molecule. The calculated VDE of 2B is 2.24 eV. We speculate that isomer 2B contributes to the hump at ~2.0 eV in the spectrum of $TiO_4H_4^-$. Although isomer 2B is 0.6 eV less stable than isomer 2A, it is still possible for a small amount of isomer 2B to be present in the experiments because isomer 2B needs to overcome an energy barrier in order to undergo tautomerization to form isomer 2A. The similar tautomerization processes have been reported by Sambrano *et al.*[36] From above, we can see that isomer 2A is the dominate species in the experiments. Isomer 2C is a metal-oxide hydrated structure in the form of $TiO_2(H_2O)_2^-$ and is much higher than isomer 2A in energy, thus, its existence in the experiments can be ruled out. As for the neutral TiO_4H_4, isomer 2A′ is

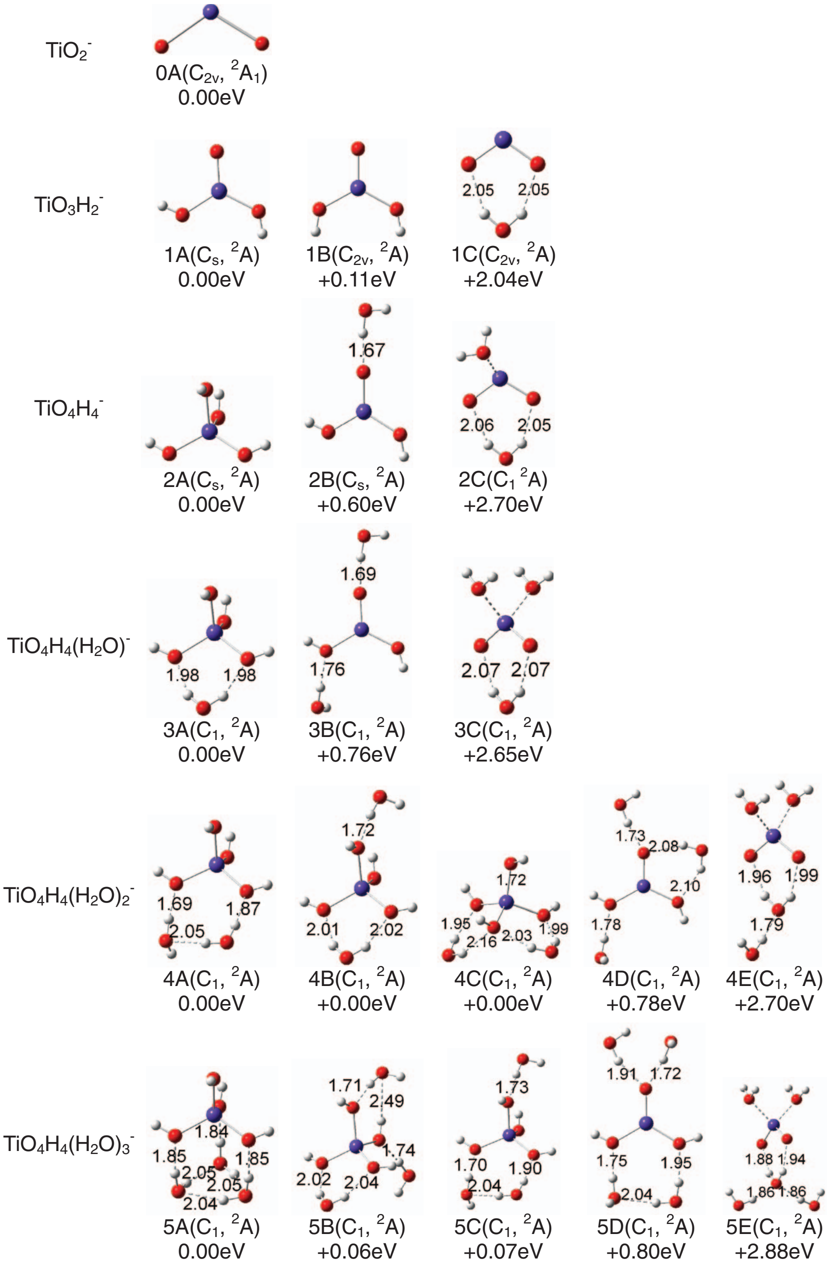

FIG. 2. Optimized geometries of the typical low-lying isomers of TiO_2^-, $TiO_3H_2^-$, and $TiO_4H_4(H_2O)_n^-$ (n = 0–3) clusters. The unit of the bond lengths is angstrom.

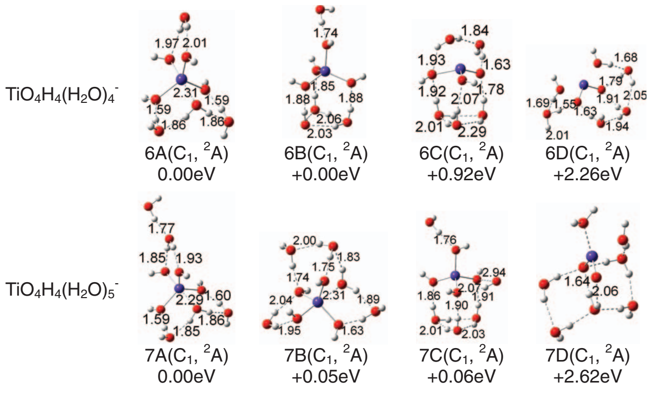

FIG. 3. Optimized geometries of the typical low-lying isomers of $TiO_4H_4(H_2O)_n^-$ (n = 4–5) clusters. The unit of the bond lengths is angstrom.

the most stable structure in the form of $Ti(OH)_4$. Isomers 2B′ $TiO(OH)_2(H_2O)$ and 2C′ $TiO_2(H_2O)_2$ are much less stable than isomer 2A′.

3. $TiO_4H_4(H_2O)^-$ and $TiO_4H_4(H_2O)$

For $TiO_4H_4(H_2O)^-$, the most stable structure is isomer 3A in the form of $Ti(OH)_4(H_2O)^-$, which is derived from the solvated isomer 2A. Isomer 3B is evolved from isomer 2B, in the form of $TiO(OH)_2(H_2O)_2^-$. Isomer 3C is a structure of hydrated titanium-dioxide with TiO_2^- solvated by three water molecules. Isomers 3B and 3C are higher than isomer 3A in energy by 0.76 and 2.65 eV, respectively. Therefore, isomers 3B and 3C cannot exist in our experiments. The calculated

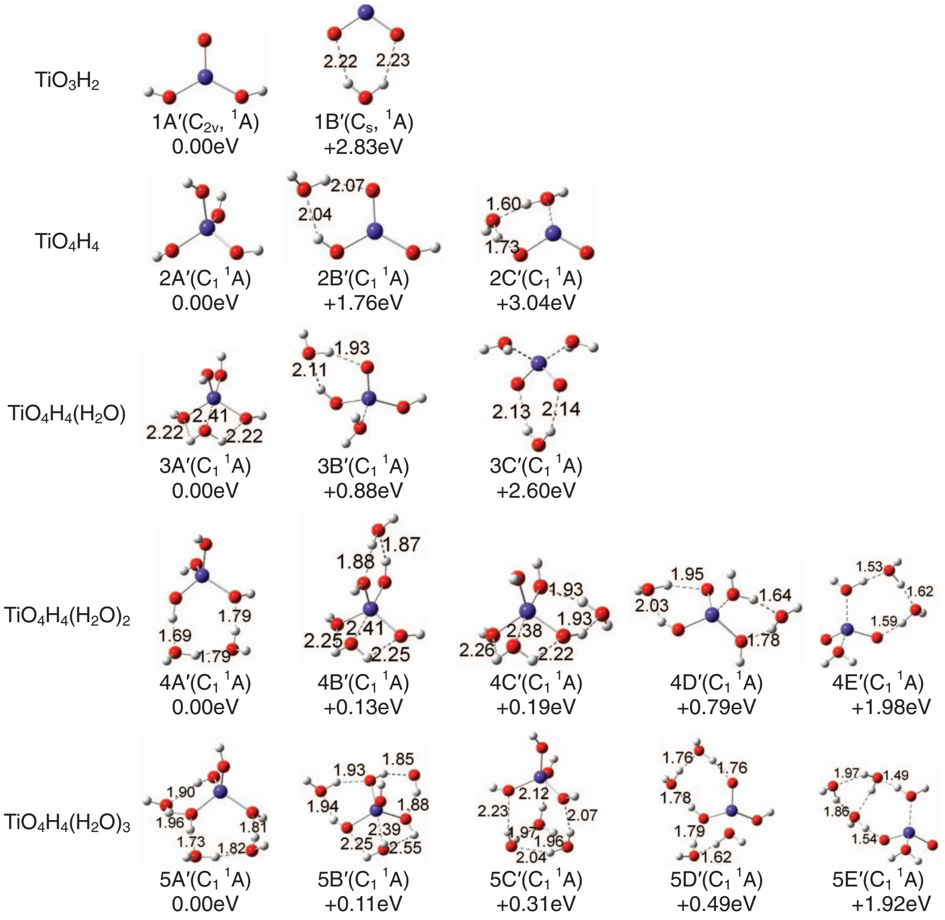

FIG. 4. Optimized geometries of the typical low-lying isomers of TiO_3H_2 and $TiO_4H_4(H_2O)_n$ (n = 0–3) clusters. The unit of the bond lengths is angstrom.

VDE value of isomer 3A is about 1.83 eV, in excellent agreement with the experimental value of 1.82 eV. Thus, we suggest that the spectrum of $TiO_4H_4(H_2O)^-$ in our experiments is contributed by isomer 3A ($Ti(OH)_4(H_2O)^-$). It is noteworthy that the hump observed in the spectrum of $TiO_4H_4^-$ disappears in the spectrum of $TiO_4H_4(H_2O)^-$. We speculate that the reason for this is that the energy barrier between isomer 3A and isomer 3B is substantially decreased by the additional water similar to that reported by Sambrano *et al.*,[36] thus, isomer 3B can easily transform to isomer 3A. The most stable neutral structure of $TiO_4H_4(H_2O)$ is isomer 3A′ in the form of $Ti(OH)_4(H_2O)$. Isomers 3B′ and 3C′ are much less stable than isomer 3A′.

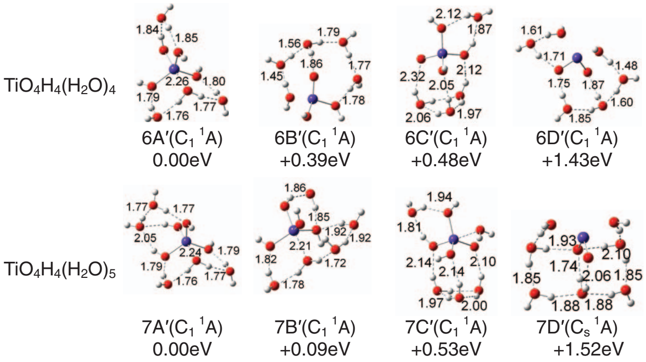

FIG. 5. Optimized geometries of the typical low-lying isomers of $TiO_4H_4(H_2O)_n$ (n = 4–5) clusters. The unit of the bond lengths is angstrom.

4. $TiO_4H_4(H_2O)_2^-$ and $TiO_4H_4(H_2O)_2$

For $TiO_4H_4(H_2O)_2^-$, isomers 4A, 4B, and 4C are all in the form of $Ti(OH)_4(H_2O)_2^-$ and they are almost degenerate in energy. Isomer 4A corresponds to a structure that two water molecules each form a hydrogen bond with the $Ti(OH)_4^-$ unit, in which the water-water interaction is also observed. Isomer 4B is derived from 3A and the additional water molecule forms a hydrogen bond with $Ti(OH)_4^-$ unit. In isomer 4C, two water molecules each form two hydrogen bonds with $Ti(OH)_4^-$. Isomer 4D in the form of $TiO(OH)_2(H_2O)_3^-$ is derived from 3B. Isomer 4E in the form of $TiO_2(H_2O)_4^-$ is a hydrated metal-oxide. Both isomers 4D and 4E are much less stable than 4A, therefore they cannot exist in our experiments. The VDEs of isomers 4A, 4B, and 4C are 2.18, 2.25, and 2.36 eV, respectively. They are all in excellent agreement with the experimental VDE value of $TiO_4H_4(H_2O)_2^-$. Therefore, we believe that 4A, 4B, and 4C coexist in the experimental photoelectron spectrum of $TiO_4H_4(H_2O)_2^-$. As for the neutral $TiO_4H_4(H_2O)_2$, 4A′ $Ti(OH)_4(H_2O)_2$ is the most stable structure. $Ti(OH)_4$ unit of 4A′ is distorted and different from that of anion isomer 4A.

5. $TiO_4H_4(H_2O)_3^-$ and $TiO_4H_4(H_2O)_3$

For $TiO_4H_4(H_2O)_3^-$, we identified five minima that are the consequence of the balance between water-water and ion-water interactions. From Figure 2, we can see that isomers 5A, 5B, and 5C are all in the form of $Ti(OH)_4(H_2O)_3^-$ and they are nearly degenerate in energy. Isomer 5A adopts a three-water ring motif, with each water molecule acting as both a donor and an acceptor to its neighbor and the other hydrogen atoms of the three water molecules each form a hydrogen bond by interacting with the oxygen atoms of the $Ti(OH)_4^-$ unit, respectively. The next two isomers 5B and 5C, both of them have a different water network from isomer 5A. Isomer 5B has no water-water hydrogen bond and isomer 5C has one interwater hydrogen bond with one water molecule as the donor and the other as the acceptor. Isomers 5D and 5E correspond to structures of $TiO(OH)_2(H_2O)_4^-$ and $TiO_2(H_2O)_5^-$ and they are higher than the most stable structure in energy by 0.80 and 2.88 eV, respectively. The calculated VDEs of isomers 5A, 5B, and 5C are 2.52, 2.63, and 2.57 eV, respectively, in excellent agreement with the experimental VDE (2.49 eV). Therefore, the broadening of the experimental peak of $TiO_4H_4(H_2O)_3^-$ can be rationalized in terms of the isomers 5A, 5B, and 5C configurations. The calculated VDEs of isomers 5D and 5E, 3.37 and 1.97 eV, respectively, show much deviations from the experimental value. Both of them can be ruled out in our experiments. For the neutral $TiO_4H_4(H_2O)_3$ in our calculations, the global minimum isomer 5A′ is in the form of $Ti(OH)_4(H_2O)_3$, in which one water molecule forms two hydrogen bonds with the $Ti(OH)_4$ unit while the other two water molecules each form one hydrogen bond with $Ti(OH)_4$.

6. $TiO_4H_4(H_2O)_4^-$ and $TiO_4H_4(H_2O)_4$

The first two isomers of $TiO_4H_4(H_2O)_4^-$ are nearly degenerate in energy. In isomer 6A, the number of water molecules increased to four, the outside water molecules forms hydrogen bonds with OH groups, increased one of the dihedral angles of O-Ti-O-O in $Ti(OH)_4^-$ to 162°, and weakened the interactions between the OH and Ti atom. This makes one water molecule have enough space to interact directly with Ti atom via its oxygen atom. It is noteworthy that the $Ti(OH)_4^-$ unit was largely distorted and the Ti atom is 5-coordinated here. Thus, isomer 6A cannot be considered as simple addition of a water molecule to $Ti(OH)_4(H_2O)_3^-$. This can explain why the spectrum peak of $TiO_4H_4(H_2O)_4^-$ shifts to low EBE compared to that of $Ti(OH)_4(H_2O)_3^-$ in our experiments. The calculated VDE of isomer 6A is about 2.43 eV, in excellent agreement with the experimental value 2.41 eV. Therefore, we suggest that isomer 6A is dominating in the experiments. Isomer 6B can be viewed as derived from the solvated isomer 5A, and the additional water molecule forms one hydrogen bond with the $Ti(OH)_4^-$ unit. The theoretical VDE (2.91 eV) of 6B overlaps with the broad photoelectron peak in the range of 1.8–3.2 eV. We suggest that 6B may contribute to the higher binding energy side of the photoelectron spectral peak. Isomer 6C is in the form of $TiO(OH)_2(H_2O)_5^-$ and is 0.92 eV higher than the most stable isomer 6A. Isomer 6D is a hydrated metal-oxide structure and much higher than 6A in energy. Therefore, the existence of isomers 6C and 6D in our experiments probably can be ruled out. For the neutral $TiO_4H_4(H_2O)_4$, the most stable structure 6A′ is similar to anionic structure 6A.

7. $TiO_4H_4(H_2O)_5^-$ and $TiO_4H_4(H_2O)_5$

For $TiO_4H_4(H_2O)_5^-$, we identified four low-lying isomers. Isomer 7A can be considered as evolved from isomer 6A by attaching an additional water molecule to the one of the first shell waters. Isomer 7B is nearly degenerate with 7A in energy and also can be regarded as derived from isomer 6A, in which the additional water molecule interacts with the $Ti(OH)_4^-$ unit and the neighboring water via one H atom and oxygen atom, respectively. Isomer 7C is higher than 7A by 0.06 eV, and can be viewed as 6B solvated by an additional water molecule. Isomer 7D is a structure corresponding to hydrated metal-oxide and much higher than the most stable isomer 7A. The calculated VDEs of isomers 7A and 7B are 2.68 and 2.63 eV, respectively, in excellent agreement with the experimental measurements. The VDE of 7C is calculated to be 3.27 eV, may contributed to the higher binding energy side of the photoelectron spectral peak. The calculated VDE of 7D is 1.86 eV, much lower than the VDE of our experiments. Isomer 7D is much less stable than isomer 7A. Thus, the existence of isomer 7D can be ruled out in our experiments. As for the neutral $TiO_4H_4(H_2O)_5$, the most stable structure 7A′ is derived from 6A′ and the additional water molecule forms one hydrogen bond with the neighboring water as well as two hydrogen bonds with the $Ti(OH)_4$ unit.

In order to understand the nature of bonding of $TiO_3H_2^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 0–5), we have carried out the analysis of their molecular orbitals. From Figure 6, we can see that the highest occupied orbitals (HOMOs) of both isomers 1A and 1B of $TiO(OH)_2^-$ are mainly localized on Ti and three oxygen atoms. This indicates that the photoelectron spectrum feature of $TiO_3H_2^-$ in our experiments is mostly contributed by the electrons on Ti and three oxygen atoms. For $TiO_4H_4(H_2O)_n^-$ (n = 0–3), the results of HOMOs of their most probable isomers show that their respective $Ti(OH)_4^-$ units lose the majority of charges during the photodetachment processes and indicate that the VDEs of these cluster anions are due to electron detachment from their respective $Ti(OH)_4^-$ units. This can explain why the photoelectron spectra of $TiO_4H_4(H_2O)_n^-$ (n = 0–3) in the experiments are so similar except that their peaks shift toward higher EBE. For the most stable isomer of $TiO_4H_4(H_2O)_4^-$, we can see an interesting phenomenon that the HOMO localize on not only the $Ti(OH)_4^-$ unit but also the water molecule interacting with Ti atom via oxygen atom. This indicates that the photoelectron spectrum feature of $TiO_4H_4(H_2O)_4^-$ is mainly from the combined contributions of the electrons on the $Ti(OH)_4^-$ unit and that on the water interacting with Ti atom. This reveals that $TiO_4H_4(H_2O)_4^-$ cannot be simply considered as a solvated $TiO_4H_4(H_2O)_3^-$. The HOMOs of the most probable isomers of $Ti(OH)_4(H_2O)_5^-$ show similar properties as that of $Ti(OH)_4(H_2O)_4^-$. So the spectrum of $Ti(OH)_4(H_2O)_5^-$ is similar to that of $Ti(OH)_4(H_2O)_4^-$ as expected in the experiments.

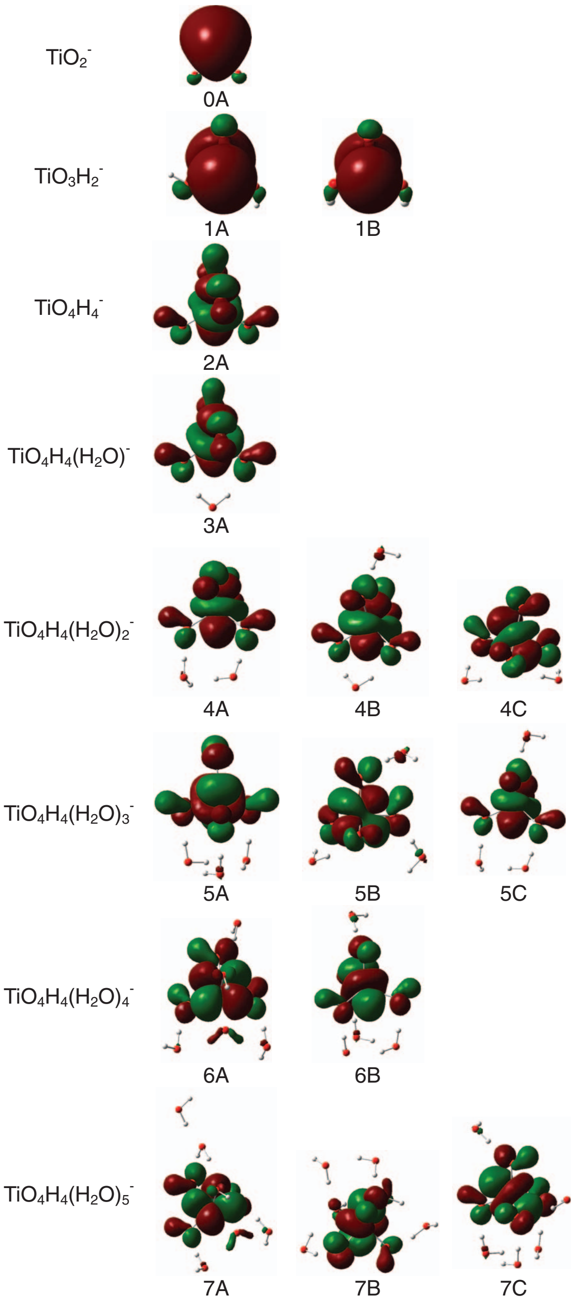

FIG. 6. The HOMOs of the typical low-lying isomers of TiO_2^-, $TiO_3H_2^-$, and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) clusters.

IV. CONCLUSIONS

$TiO_3H_2^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) cluster anions were investigated using photoelectron spectroscopy and density functional calculations. The possible structures of the $TiO_3H_2^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) clusters were determined by comparison of theoretical calculations with experimental measurements. Our studies show that $TiO(OH)_2^-$ was produced when TiO_2^- interacts with one water molecule, and $Ti(OH)_4^-$ were produced when TiO_2^- interacts with two water molecules. In $Ti(OH)_4(H_2O)_{1\text{-}3}^-$, the water molecules interact with the $Ti(OH)_4^-$ core through hydrogen bonds. On the other hand, the $Ti(OH)_4^-$ core in $Ti(OH)_4(H_2O)_{4,5}^-$ is distorted slightly because one of the water molecules interacts directly with the Ti atom via its oxygen atom instead of a hydrogen bond. Analysis of molecular orbitals shows that the negative charge of $TiO_3H_2^-$ mainly localizes on the Ti and three oxygen atoms. For $TiO_4H_4(H_2O)_n^-$ (n = 0–3), the negative charge mainly localizes on the $Ti(OH)_4^-$ units. As for $TiO_4H_4(H_2O)_n^-$ (n = 4, 5), the negative charge localizes not only on the $Ti(OH)_4^-$ unit but also on the water molecule interacting directly with the Ti atom.

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[1] B. O'Regan and M. Gratzel, Nature (London) **353**, 737 (1991).
[2] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, Chem. Rev. **95**, 69 (1995).
[3] W. G. Wamer, J.-J. Yin, and R. R. Wei, Free Radic Biol. Med. **23**, 851 (1997).
[4] E. J. Wolfrum, J. Huang, D. M. Blake, P.-C. Maness, Z. Huang, J. Fiest, and W. A. Jacoby, Environ. Sci. Technol. **36**, 3412 (2002).
[5] M. Gratzel, Nature (London) **414**, 338 (2001).
[6] T. Thompson and J. Yates, Top. Catal. **35**, 197 (2005).
[7] Z. Zhang, O. Bondarchuk, B. D. Kay, J. M. White, and Z. Dohnálek, J. Phys. Chem. B **110**, 21840 (2006).
[8] D. J. C. Yates, J. Phys. Chem. **65**, 746 (1961).
[9] G. Munuera, J. Catal. **18**, 19 (1970).
[10] J. M. Pan, B. L. Maschhoff, U. Diebold, and T. E. Madey, J. Vac. Sci. Technol. A **10**, 2470 (1992).
[11] S. Bourgeois, F. Jomard, and M. Perdereau, Surf. Sci. **279**, 349 (1992).
[12] T. Bredow and K. Jug, Surf. Sci. **327**, 398 (1995).
[13] A. Selloni, A. Vittadini, and M. Grätzel, Surf. Sci. **402–404**, 219 (1998).
[14] G. E. Brown, V. E. Henrich, W. H. Casey, D. L. Clark, C. Eggleston, A. Felmy, D. W. Goodman, M. Grätzel, G. Maciel, M. I. McCarthy, K. H. Nealson, D. A. Sverjensky, M. F. Toney, and J. M. Zachara, Chem. Rev. **99**, 77 (1999).
[15] T. Fujino, M. Katayama, K. Inudzuka, T. Okuno, K. Oura, and T. Hirao, Appl. Phys. Lett. **79**, 2716 (2001).
[16] M. A. Henderson, Surf. Sci. Rep. **46**, 1–308 (2002).
[17] T. Bezrodna, G. Puchkovska, V. Shymanovska, J. Baran, and H. Ratajczak, J. Mol. Struct. **700**, 175 (2004).
[18] K. Hashimoto, H. Irie, and A. Fujishima, Jpn. J. Appl. Phys., Part 1 **44**, 8269 (2005).
[19] Y. Namai and O. Matsuoka, J. Phys. Chem. B **109**, 23948 (2005).
[20] F. Allegretti, S. O'Brien, M. Polcik, D. I. Sayago, and D. P. Woodruff, Surf. Sci. **600**, 1487 (2006).
[21] J. Zhao, B. Li, K. D. Jordan, J. Yang, and H. Petek, Phys. Rev. B **73**, 195309 (2006).
[22] S. Suzuki, K.-i. Fukui, H. Onishi, and Y. Iwasawa, Phys. Rev. Lett. **84**, 2156 (2000).
[23] R. Schaub, P. Thostrup, N. Lopez, E. Lægsgaard, I. Stensgaard, J. K. Nørskov, and F. Besenbacher, Phys. Rev. Lett. **87**, 266104 (2001).
[24] S. Wendt, J. Matthiesen, R. Schaub, E. K. Vestergaard, E. Lægsgaard, F. Besenbacher, and B. Hammer, Phys. Rev. Lett. **96**, 066107 (2006).
[25] S. Wendt, R. Schaub, J. Matthiesen, E. K. Vestergaard, E. Wahlström, M. D. Rasmussen, P. Thostrup, L. M. Molina, E. Lægsgaard, I. Stensgaard, B. Hammer, and F. Besenbacher, Surf. Sci. **598**, 226 (2005).
[26] M. A. Henderson, Langmuir **12**, 5093 (1996).
[27] M. A. Henderson, Surf. Sci. **355**, 151 (1996).
[28] G. S. Herman, Z. Dohnálek, N. Ruzycki, and U. Diebold, J. Phys. Chem. B **107**, 2788 (2003).

[29] L. Q. Wang, K. F. Ferris, P. X. Skiba, A. N. Shultz, D. R. Baer, and M. H. Engelhard, Surf. Sci. **440**, 60 (1999).

[30] M. Takeuchi, G. Martra, S. Coluccia, and M. Anpo, J. Phys. Chem. B **109**, 7387 (2005).

[31] K. Onda, B. Li, J. Zhao, K. D. Jordan, J. Yang, and H. Petek, Science **308**, 1154 (2005).

[32] C.-y. Wang, H. Groenzin, and M. J. Shultz, J. Am. Chem. Soc. **127**, 9736 (2005).

[33] A. Vittadini, A. Selloni, F. P. Rotzinger, and M. Grätzel, Phys. Rev. Lett. **81**, 2954 (1998).

[34] P. J. D. Lindan and C. Zhang, Phys. Rev. B **72**, 075439 (2005).

[35] S. W. Sigsworth and A. W. Castleman, J. Am. Chem. Soc. **114**, 10471 (1992).

[36] J. R. Sambrano, J. Andrés, L. Gracia, V. S. Safont, and A. Beltrán, Chem. Phys. Lett. **384**, 56 (2004).

[37] J. R. Sambrano, L. Gracia, J. Andrés, S. Berski, and A. Beltrán, J. Phys. Chem. A **108**, 10850 (2004).

[38] D. Schröder, S. O. Souvi, and E. Alikhani, Chem. Phys. Lett. **470**, 162 (2009).

[39] H.-G. Xu, X.-N. Li, X.-Y. Kong, S.-G. He, and W.-J. Zheng, Phys. Chem. Chem. Phys. **15**, 17126 (2013).

[40] R. Z. Li, H. G. Xu, G. J. Cao, Y. C. Zhao, and W. J. Zheng, J. Chem. Phys. **135**, 134307 (2011).

[41] H.-G. Xu, Z.-G. Zhang, Y. Feng, J.-Y. Yuan, Y.-C. Zhao, and W.-J. Zheng, Chem. Phys. Lett. **487**, 204 (2010).

[42] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[43] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[44] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[45] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 09, Revision A.01, Gaussian, Inc., Wallingford, CT, 2009.

[46] See supplementary material at http://dx.doi.org/10.1063/1.4828815 for the photoelectron spectra of $TiO_3H_2^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 0–5) taken with 266 nm photons, as well as the Cartesian atomic coordinates of the typical low-lying isomers of $TiO_3H_2^-$ and $TiO_4H_4(H_2O)_n^-$ (n = 0–5).